2D HYBRID NANOMATERIALS: CONTROLLABLE GROWTH OF MONOLAYER MOLYBDENUM DISULPHIDE

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Summary

The search for monolayer materials to substitute silicon in electronic devices has widened in the past decade. Despite the benefits of 2 dimensional graphene, it has no band gap and behaves as a semi-metal. Molybdenum disulphide is a promising material as it boasts a band gap of up to 1.9eV in a monolayer form. In this project, an inexpensive method of fabricating monolayer MoS₂ is designed and growths on various substrates for use in electronic devices will be attempted with this fabrication method. Grown MoS₂ on silicon substrate boasted a band gap of 1.88eV and monolayer triangles of up to $20\mu m$ while multilayer and possibly monolayer growths on HOPG and h-BN were achieved as well.

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List of Abbreviations

2D	Two Dimensional
AFM	Atomic Force Microscopy
Ar	Argon
CVD	Chemical Vapour Deposition
H-BN	Hexagonal Boron Nitride
HOPG	Highly Ordered/Oriented Pyrolytic Graphite
Mo	Molybdenum
MoO ₃	Molybdenum trioxide
MoS_2	Molybdenum Disulfide
MoSe ₂	Molybdenum Diselenide
POG	Peel-Off Graphite
PVD	Physical Vapour Deposition
SiO ₂ /Si	Silicon Dioxide on Silicon
S	Sulphur
SCCM	Standard Cubic Centimeters per Minute
TMDC	Transition Metal Dichalcogenide Crystal

1 Introduction

1.1 The search for 2D materials

The semiconductor industry has been comfortable with silicon for the last few decades. It is a semiconductor, meaning that it has a small band gap, that is tunable via doping with other elements. Conductivity through a semiconductor like silicon can also be easily switched on or off by magnetic or electric fields, changes in temperature, or even by mechanical deformation. This is ideal for the function of transistors or sensing devices. There are other elements and compounds which possess these qualities and are used in the semiconductor industry. However, silicon is the most popular due to its low cost from high abundance in our Earth's crust, and its relatively good temperature range, unlike the more sensitive Germanium.

Silicon and the other traditional semiconductors now face a daunting task. The ongoing demand for increasingly high power, small size electronic devices are forcing semiconductor devices to reach new limits in fabrication. The smallest commercially available transistors made by a large fabrication facility so far are 22nm and are expected to hit 14nm this year. As the transistors get smaller, more issues like short channel effects and defect densities become harder to hold back. A material with better electronic properties at smaller size scales is needed. Hence the search for 2D materials.

Graphene is a strong contender as a 2D device material. It has high electron mobility and room temperature, excellent optical transmittance and thermal conductivity. It is chemically inert and has a large Young's modulus¹. These are all qualities highly sought after in a semiconducting material. However, its lack of a band gap and semi-metal behaviour rules it

out as a semiconductor. Band gap engineering is required for graphene to have a band gap, however that also affects its desirable qualities in a not so desirable fashion.

The search for 2D materials has thus grown to encompass other materials which exhibit properties similar to that of graphene and traditional semiconductors. Transition metal dichalcogenides have layered structures similar to graphene, are inexpensive due to their abundance and have large band gaps³⁷. Another interesting 2D material is crystalline hexagonal boron nitride, which also has layers weakly held together by van der Waals forces. It however, has a very large band gap in the UV region and therefore has more insulating properties then TMDC, and has proven to be a superior substrate for graphene devices due to a lack of dangling bonds⁴⁰.

1.2 Motivation and Objectives

The focus of this project then, is to implement a relatively inexpensive method of controllable growth of monolayer TMDC, which may be feasibly used for device fabrication. The growth, if successful, will also be attempted on other substrates with 2D properties and likeliness to be utilised in the 2D semiconducting industry, such as h-BN and graphene. This could pave the way to flexible and transparent high performance electronics.

Molybdenum disulphide is chosen because of its desirable traits for use as a 2D semiconductor. MoS_2 and its pre-fabrication forms like MoO_3 are relatively inexpensive and abundant² compared to tungsten or selenium. It is also one of the more stable layered transition metal dichalcogens³. Its large direct band gap of 1.8eV will also make it useful in light detectors, emitters and solar cells⁹.

2 <u>Characteristics of Molybdenum Disulphide</u>

2.1 Bulk MoS₂

Bulk MoS₂ is a shiny black solid that has qualities very similar to those of graphite. It has a layered structure with layers which are weakly bound by van der Waals forces. Hence, it also acts as a very good solid lubricant. It is commonly found in a hexagonal 2H-MoS₂ stacking alignment, but it can also be found in a rhombohedral 3R-MoS₂ structure, which easily decomposes to its more stable hexagonal counterpart upon heating. It is relatively inexpensive and is easily formed by sulphurization of molybdenum trioxide or molybdenum metal directly. Other methods of growth will be expounded on in detail in chapter 5.

2.2 Monolayer MoS₂

Monolayer MoS_2 has vastly different properties as compared to its bulk counterpart, namely its band gap, crystal structure and electron mobility.

2.2.1 Band Gap

Monolayer MoS_2 has a large direct band gap of 1.8eV, much larger than its bulk form indirect band gap of $1.29eV^2$. This enables MoS_2 to have a tunable band gap based on the number of layers grown. In fact, MoS_2 may also have a tunable band gap by means of an external electric field, as shown by *A. RamasubRamaniam et al.* with calculations²³.



Figure 2-1 Band structure of bulk MoS_2 , where A and B show the direct gap transitions, as opposed to the indirect gap transition shown by L^2

2.2.2 Crystal Structure and Shape

Much of MoS_2 desired qualities may be due to its crystal structure in monolayer form. Its ability to be grown layer by layer is due to this sandwich structure that it possesses. An atomic plane of Mo atoms is found between two layers of S in a trigonal prismatic structure, as shown in Figure 2-2 below³.



Figure 2-2 Bilayer structure of MoS₂.³

Each molybdenum atom is bound to six sulphur atoms in this trigonal prismatic fashion while each sulphur atom is connected to three molybdenum atoms in a pyramidal structure. Since the sheets of sulphur atoms only have weak van der Waals forces between them, they are easily cleaved or separated from each other using a micromechanical cleavage technique⁵.

Monocrystalline MoS_2 takes on an interesting triangular shape when grown. It is usually observed to takes on either a Mo-zigzag edge or S-zigzag edge⁴. A bright field image of an Mo-zigzag edge MoS_2 triangle is shown in Figure 2-3.



Figure 2-3 Bright field image of an MoS₂ crystal.⁴

 MoS_2 is also relatively stiff and is resistant to breaking, allowing for potential use in flexible electronics⁸.

2.2.3 Electronic and Optical Properties

 MoS_2 devices have been shown to be able to transmit very high current densities close to 5 x 10^7 A/cm², even higher than that of copper⁶. This is shown below in Figure 2-4, which shows the maximum current attained in a monolayer MoS_2 device with channel length 500nm and width 2µm.



Figure 2-4 Time trace of drain current through a monolayer MoS₂ channel. The inset shows the time trace of the drain voltage.⁶

 MoS_2 also has a high on/off ratio 10^8 , which will be very beneficial in preventing power loss and leakages. In comparison to silicon, MoS_2 has similar electron mobility⁷.

 MoS_2 has strong fluorescence due to its direct band gap. Coupled with its aforementioned tunable band gap, this allows for MoS_2 to be used in optical sensing or emitting devices at different optical frequencies and wavelengths.

2.2.4 Mechanical Properties

 MoS_2 also has excellent mechanical properties to make it ideal for nanodevice manufacture. Bertolazzi et al. made a comparison of MoS_2 strength and elasticity with that of steel and found it to be comparable⁸. This group also mentions that MoS_2 has an elasticity which is comparable with polymer thin films like polyimide and polydimethylsiloxane used in flexible electronics currently, and can theoretically be integrated with them.

3 <u>Literature Review of Synthesis of Monolayer Molybdenum</u> <u>Disulphide</u>

There are numerous methods to grow or fabricate monolayer MoS_2 . Some of which have been very successful. In line with our aim to implement a controllable growth method, we have decided to focus on bottom-up approaches and leave out top-down approaches like mechanical exfoliation and lithium intercalation assisted exfoliation which have less control on the thickness of layers. Here, we go into a detailed study of these bottom-up methods, and how chemical vapour deposition was eventually chosen as the focus of this project.

There are several deposition techniques which occur in the liquid phase, where ionic reactants and precursors in aqueous form are used to produce monolayer MoS₂. Some of the categories include thermolysis, hydrothermal and electrochemical methods. Here, we will go through two of the more simple liquid phase methods.

3.1 Electrochemical Synthesis

Here, *Q. Li et al.* designed a two-step electrochemical/chemical synthesis of 2H-MoS₂. They did so by electrodepositing MoO₂ nanowires onto highly oriented pyrolytic graphite surfaces, before exposing them to hydrogen sulphide at high temperatures to reduce MoO₂ into its desired MoS₂ form.¹¹ This method involves the use of H₂S at high temperatures which is quite risky if it were to be adopted as an industrial process. H₂S in high quantities is highly poisonous and is a factor to consider in choosing an appropriately safe growth method.



3.2 Thermolysis of Ammonium Thiomolybdates

Figure 3-1 Two-step thermolysis of ammonium thiomolybdate.¹²

In this method developed by *K. Liu et al.*, ammonium thiomolybdate coated on an insulating substrate like SiO_2/Si is annealed twice to facilitate reduction to form MoS_2 trilayers. While this method appears reliable and simple, the high temperatures required and formation of multilayer MoS_2 is a concern.

As the intention is to fabricate monolayer MoS_2 with relatively lower temperatures and simpler pressure requirements, we will continue to seek out other more suitable methods.

3.3 Physical Vapour Deposition

There are also techniques which require vapour phase reactants and precursors, namely physical or chemical vapour deposition. Physical vapour deposition encompasses thermal or electron beam evaporation, pulsed layer deposition, sputtering, van der Waals and molecular beam epitaxy. Only thermal evaporation however, has been widely used due to its low equipment requirements and relatively simple set up. Here, we will go through some of the more feasible techniques considering the scope of the project.

In a method used by *C. Gong et al.*, an MoS_2 powder source is placed in a quartz tube residing in a furnace, with the insulating substrate placed downstream where the temperature is around 650°C. The source is heated for 15-20min at about 900°C with Ar gas flowing at base pressure of 20mTorr.¹³ Such high temperature requirements for heating are definitely a

concern when it comes to designing a low cost process. The relatively low temperature of 600°C required for condensation on a substrate is also difficult to achieve in small furnace set ups where most of the furnace would be at one temperature or at an indeterminable range of high temperatures.

3.4 Chemical Vapour Deposition

CVD methods mainly comprise sulphurization of Mo reactants in various forms. Different Mo compounds may be used as precursors for CVD. One may use its metal form Mo, or oxide as MoO₃, or even MoCl₅. These may come in different physical forms, like a thin film metal deposited on a substrate, or even as nanorods. Now, we will take a look at specific aspects of the CVD growth process which are common amongst many groups attempting to fabricate monolayer MoS₂.

3.4.1 Seeding and Controlled Nucleation

Several groups employed seeding methods to encourage the nucleation and growth of MoS₂.

In a method employed by *Y. Lee et al.*, they used reduced graphene oxide (rGO), perylene-3,4,9,10-tetracarboxylic acid tetrapotassium salt (PTAS) and perylene-3,4,9,10tetracarboxylic dianhydride (PTCDA) to treat the substrate before the growth process¹⁴. For rGO, a GO solution is mixed with hydrazine and heated to cause the reduction, before a drop of rGO-hydrazine is spin coated onto the substrate. PTAS and PTCDA were also used in separate experiments to spin coat the substrate and successfully promote MoS_2 flake growth¹⁵.

One group chose to manipulate the substrate surface, to provide low energy locations for easier nucleation of MoS_2 . S. Najmaie et al. used lithography to pattern rectangular SiO_2

pillars to achieve a high density of nucleation and subsequently, the formation of large-area MoS_2 films¹⁶.

Another used the intermediate reduction product of MoO_3 to MoO_2 as nucleation structures. *X. Wang et al.* allowed MoO_2 rhomboidal microplates to form, before their surfaces were further annealed and reduced to MoS_2 with multiple layers depending on annealing time.

However, there were groups which focused on using clean substrates and not using any seeds whatsoever⁴.

3.4.2 Precursor, Reactant and Gas Flow

In terms of precursor and reactant, a majority of groups held to the use of high purity MoO_3 and sulphur powder respectively^{4,15-17}. However, there were groups which used different starting precursors.

Y. Shi et al., used ammonium thiomolybdate in vapour form as a precursor, and carried it to a graphene surface with a carrier gas before annealing to thernally decompose the precursor into epitaxial MoS_2 flakes on graphene¹⁹.

Y. Yu et al. used MoCl₅ powder and sulphur powder as precursor and reactant respectively. They grew high quality MoS₂ thin film at a high temperature of 850°C and a low pressure of 2 Torr, and varied the number of layers by changing the amount of precursor or the total pressure²⁰.

Y. Zhan et al. deposited Mo thin films onto SiO_2 substrates and sulphurized those directly with sulphur vapour²¹.

3.4.3 Temperature and Pressure

Groups that simply chose to use high purity MoO₃ and S powders had to use slightly higher temperatures of around 750°C to 950°C ^{4,15-17}. When seeding was involved or when the precursor used was in a less conventional form like Mo thin film or ammonium thiomolybdate, the growth process usually required a lower temperature of between 400°C to $750^{\circ}C^{15, 19, 21}$.

4 Methods of Characterisation

To analyse grown samples, a few tools were necessary to characterise them at a microscopic scale, since crystal compound growths of up to several micrometres in size were expected. The focus on streamlining the growth process and obtaining single layer growths suggested two useful means of characterising samples: Optical Microscopy and Raman Spectroscopy. Although the Atomic Force Microscopy (AFM) was initially used to characterise sample thickness, the study by *C. Lee et al.* deemed that Raman spectroscopy was accurate enough for determining layer thickness³.

4.1 Optical Microscopy

In this project, the focus was on designing an experimental method which could reliably fabricate monocrystalline MoS₂. Using optical microscopy was of the utmost importance as it reduced the analysis time required between each attempted growth. Single crystal MoS₂ is easy to optically identify from the triangular shapes grown of up to hundreds of micrometres in size⁴. Monolayers can also be quickly identified by the characteristic intensity difference between monolayer and multilayer MoS₂ as monolayers will have the least intensity and colour difference from the SiO₂/Si substrate³⁸. It is also noted that the monolayer single crystals may still possess bilayer or multilayer islands⁴. Overall, this simple tool with up to 50x or 100x magnification was sufficient for providing quick analysis of samples for signs of single triangular crystals of MoS₂ down to a few micrometres in size.

4.2 Raman Spectroscopy and Photoluminescence

For a more robust study of the composition and thickness of grown MoS_2 , Raman Spectroscopy and Photoluminescence data were used as well. In Raman spectroscopy, scattered photons with lower energy than their incident electron counterparts have undergone

Raman scattering. This energy difference is measured and plotted as a spectrum, where peaks reflect vibrational modes within a sample.

P. Tonndorf et al. Reports that MoS_2 has four active modes in its bulk 2H form, of which the E_{2g}^1 and A_{1g} modes usually reside at 383.5cm⁻¹ and 408.6cm⁻¹.²² These two peaks are expected to have a smaller frequency difference when MoS_2 is in monolayer form, then undergo shifts away from each other with increasing number of layers. This means that the E_{2g}^1 peak is expected to red shift while the A_{1g} peak is expected to blue shift.



Figure 4-1 Raman active and inactive modes of transition metal dichalcogens of the form MX₂, where M can be Mo, W while X can be Se, S.²²

This implies that the difference between the in-plane vibration mode E_{2g}^{1} and out-of-plane vibration mode A_{1g} exhibits an increasing separation, as layer thickness increases, as shown in Figure 4-2 below. This is expected for the A_{1g} mode because adding layers introduces more interactions between sulphur atoms in neighbouring layers, increasing the A_{1g} mode frequency. The E_{2g}^{1} mode on the other hand, has the self-interaction term of Mo atoms as a factor. This mode experiences a fall in frequency due to the stronger dielectric screening of the interlayer Coulomb interaction³⁴.

Monolayer MoS_2 is therefore expected to exhibit E^{1}_{2g} and A_{1g} modes at 384cm⁻¹ and 404cm⁻¹ respectively. Monolayer MoS_2 could also be characterised by checking the frequency difference between both these peaks. The difference is expected to be $20cm^{-1}$ for monolayers and $25cm^{-1}$ for bulk MoS_2 .^{34,35}



Figure 4-2 Raman peaks of MoS₂ at different layer thickness.³

Photoluminescence spectra may also be used to characterise monolayer MoS_2 . Multilayer MoS_2 would result in weak PL due to the indirect band gap, while a monolayer sample should exhibit direct band transitions around $660nm^{2,18,25}$.

All Raman spectroscopy done for this project was conducted with an excitation wavelength of 532nm and a grating of 1800g/mm or 600g/mm.

4.3 Atomic Force Microscopy

AFM is a method of characterisation which can give one high resolution scans of surface morphology of samples and also height profiles. It works by sensing deflections in a sharp probe at the end of a cantilever, as it is dragged or tapped across the surface. For samples grown for this project, the tapping mode was used to image samples, which was the less destructive mode of the contact modes.

5 <u>Chemical Vapour Deposition Theory</u>

Having chosen chemical vapour deposition as the means of fabricating monolayer MoS_2 , this chapter is devoted to the theory behind CVD.

5.1 Reaction Zones

During the deposition process, there are five reaction zones as shown in Figure 5-1 below, which play distinctly important roles.



Figure 5-1 Reaction zones during CVD.²⁶

Homogeneous nucleation occurs in Zone 1 as well as the main gas stream, whereas the heterogeneous reactions occur in Zone 2, the interface between the stagnant boundary layer and the coating. The reactions in these zones seem to affect the deposition rate and properties of the coating.²⁶

5.2 Physiochemical Steps

The process of CVD growth generally takes place in 6 steps. First, the reagents are transported in the main gas flow. Second, the reagents undergo gaseous phase reactions in the reaction zones to produce reaction intermediates and by-products. Third, the reactants are then transported to the surface of the substrate. Fourth, adsorption to the substrate surface then occurs. Fifth, nucleation, surface diffusion and more reactions take place on the surface.

Finally, the remaining volatile products are desorbed and transported away in the main gas flow.²⁷ These steps can be visualised in Figure 5-2 below.



Figure 5-2 Physiochemical steps of CVD.²⁷

5.3 Adhesion

Successful CVD requires that the grown coating is well adhered to the substrate surface. There are a multitude of factors which can affect this.²⁷

One such factor is stress. Deposition stress and mismatching thermal expansion coefficients during heating or cooling can affect the adhesive properties of a grown substance. To counter act this, the substrate should be left to cool naturally and slowly within the closed furnace after each experiment.

Another factor is homogeneous nucleation. This produces a powdery deposit across the substrate, and thin film growth cannot be obtained. The free energy of heterogeneous nucleation is expressed in Equation $5.1^{31,32}$ below.

$$\Delta G_{Hetero} = \Delta G_{Homo} f(\theta) \; ; \; f(\theta) = \frac{1}{2} - \frac{3}{4} \cos\theta + \frac{1}{4} \cos^3\theta \qquad 5.1$$

The contact angle θ represents the angle between the growing substance and the nucleation site. Since $f(\theta)$ varies from one to half to zero as θ changes from 180° to 90° to 0°, it is apparent that the free energy for heterogeneous nucleation also drops to zero as the contact angle decreases to zero, implying that wetting of the surface will increase heterogeneous nucleation. This is in line with the observations of seeding being beneficial to MoS₂ growth as seen in Chapter 3.³⁰

The formation of pores in the substrate or the coating may also facilitate the formation of boundaries or cracks in the growth. This can be reduced with simple substrate cleaning procedures.

5.4 Precursor and Growth Volatility

Since the precursors used in this experiment will be in solid form, their volatility is of natural importance. A good estimate of the temperature required to vaporise can be obtained by studies from other groups, and also from thermogravimetric analysis (TGA) data. TGA provides insight into how a material changes certain properties with temperature. In Figure 5-3 below for example, the graphs show how much mass of solid MoS₂ is loss or vaporized as temperature is increased.

One interesting point to be noted is that TGA data for the end product, MoS_2 , indicates more volatility in its nanoscale structures as compared to its bulk form.



Figure 5-3 TGA analysis of pure MoS2 and other mixed compounds (left)²⁹. TGA data of MoS₂ nanoparticles and other mixed compounds (right)²⁸.

The comparison in Figure 5-3 shows the expected TGA curve for bulk MoS₂ on the left with the 0% curve, while MoS₂ nanoparticles appear to begin evaporating at much lower temperatures of about 200°C as shown on the right. In one study by *Xin Lu et. al.*, MoS₂ underwent layer-by-layer thinning when thermally annealed³³. The group annealed samples at 650°C for one hour per cycle, which led to the loss of one layer per cycle. These are evidences that MoS₂ monolayers may still be relatively volatile even after surface adsorption and adhesion has occurred.

6 Experiment: CVD of Monolayer MoS₂

This chapter will expound on the experimental process undertaken in developing an inexpensive and reliable method of growing monolayer MoS₂.

6.1 Early Work

In our earlier work, without prior experience in growing this particular compound, we began by taking reference from the research group methods as reported in chapter 4 above^{4,15-17}. We decided to attempt CVD with the most popular precursor and reactant, MoO₃ and S powder respectively. MoO₃ was be placed on a SiO₂/Si substrate in a quartz tube, at the centre of a 30cm furnace where the heating is hottest. Substrates used in the beginning included CVD-Graphene(CVD-G), hexagonal Boron Nitride(h-BN) and Peel-Off Graphite(POG) to see if MoS₂ had any affinity for growth on these alternative substrates. S powder was placed in an aluminium foil container at 14cm upstream from the MoO₃ precursor. This S powder would be at the edge of the furnace where heating is less pronounced. Argon gas was passed through the quartz tube at all times during the experiment.



Figure 6-1Schematic of CVD Furnace with substrate placement during early work.

In our early work, we utilised only about 25mg of Sulphur powder and about 8mg of MoO₃ precursor. Initially, the furnace would be shifted off centre downstream, during the warming up phase, so as to prevent the sulphur and MoO₃ from vaporising prematurely. When the growth temperature of around 635°C was reached, the furnace would be shifted back upstream. The furnace would be displaced 1cm upstream off the usual placement for two

minutes to facilitate sulphur vaporisation at this early stage. It would then be shifted back after these two minutes, after the sulphur had visibly undergone phase change from solid to liquid or vapour. The vapour deposition would then be allowed for another 28 minutes at the growth temperature, to yield a total of 30 minutes at growth temperature. Ar gas at was flowed through the system at 20SCCM at all times. We conducted four experiments with these conditions but they only yielded nanoparticulate growth on the substrate surfaces or along the edges of graphene or BN structures.



Figure 6-2 Optical microscopy images of h-BN and Peel off-Graphene(POG) on with nanoparticulate growth on the left and right respectively.

Some atomic force microscopy and Raman spectroscopy was conducted to determine if the nanoparticles were indeed MoS_2 or not. They did not provide an easy to read signature on Raman spectroscopy, however the step height of about 5nm as seen in the imagery below, provides us little information on the composition of the nanoparticles.



Figure 6-3 AFM image and profile analysis of POG with nanoparticulate growth.

As seen in Figure 6-3, the nanoparticles along the edge of the mechanically exfoliated graphene appears to have a size of about 4nm. This is much larger than a monolayer of MoS_2 which is expected to only be as thick as $0.7nm^{36}$.

6.2 Intermediate Work

After our failed trials in the beginning, we realised that conditions for growth were far from ideal. Nanoparticle growths and relatively clean substrates indicated to us that MoS_2 seeds were simply not nucleating and its vapour density was not large enough for large crystal growth. This suggested that more precursor and reactant were required. The large particles of up to 4nm in size were also indicative of non-structured growth. This could be due to the low temperatures we were using, which could not provide enough energy for ordered crystal formation.

In this later stage of work, we therefore began to increase our sulphur reactant amounts up to 0.5g and our MoO₃ to 50mg. Temperatures for growth were raised to 700°C and above. Heating at this temperature was reduced to 20 minutes due to the observation of sulphur having mostly vaporized by then and to streamline energy efficiency. We also began to place

clean Si/SiO₂ substrates instead of substrates with existing structures, in lieu of our renewed focus in guaranteeing the right conditions for growth were attained. We began to place one such Si/SiO₂ substrate face down above the MoO₃ source. This could be done by utilising a ceramic boat to hold the source and substrates, and using the lips of the boat as an additional substrate support. This can be visualized in the diagram below.



Figure 6-4 Schematic of set up henceforth. Now including a ceramic boat, facedown substrate and larger amounts of precursor and reactant. Substrates were named "a", "b" and so on from left to right, with the facedown substrate being "a".

We conducted five more experiments using these new conditions, one of which yielded something other than nanoparticle growth. This particular experiment used 50mg of sulphur and 10mg of MoO₃. The substrates were heated for 20 minutes at 750°C with Ar flow rate at 20SCCM.



Figure 6-5 Optical images of Si/ SiO_2 facedown substrate at 20x and 100x on the left and right respectively. Optical microscopy images revealed that rhomboidal structures had grown in high density on most of our substrates. The facedown substrate had lower density growths which were easier

to analyse and are displayed above in Figure 6-5. We suspected that these were MoO_2 microplates¹⁷ which had undergone incomplete reduction due to a lack of sulphur or other conditions.



Figure 6-6 Raman spectra of rhomboidal microplates. Inset shows 100x video image.

The Raman spectra of monoclinic MoO₂ is expected to have peaks at 203, 228, 345, 363, 461, 495, 571, 589 and 744cm⁻¹.²⁴ From our own analysis, it appears that the 203, 345, 571 and 744cm⁻¹ peaks are comparable with our own results, save for some blue shifting of our experimental peaks, which is likely due to systematic error between our own experiment and the literature. Seeing that these structures were indeed most likely MoO₂, we also took a look at their atomic thickness.



Figure 6-7 AFM image and profile analysis of MoO₂ microplates.

The microplates appeared to be up to 15nm thick, which agrees with the fact that MoO_2 takes on a monoclinic lattice in a distorted rutile structure²⁴, and cannot attain the monolayer thickness of MoS_2 cleaved layers.

Following this set of experiments, we obtained a new MoS₂ powder source and decided to attempt physical vapour deposition, due to its relative simplicity in the lack of any chemical reaction required. However, the growths were unsuccessful as our samples either came out clean, despite using high temperatures of up to 950°C and low pressures of 4torr. We abandoned the thought of PVD considering that the quartz tube may not hold under such frequently used high temperatures

At this juncture, we returned to CVD but with some new amendments. We realised that vaporization of the precursor MoO₃ was likely occurring too quickly and resulting in the dense nanoparticulate growth observed in some of our experiments. We came up with the idea of mixing MoO₃ with MoS₂ powder and using this mixture as the precursor during our experiment. The MoS₂ powder has a much higher melting point of 1165°C, and therefore could act as a stable buffer mass to reduce direct heating from the furnace. We first mixed MoO₃: MoS₂ in low ratios of 1:5, with 0.1g of MoO₃ and 0.5g of MoS₂. In lieu of our much

increased amount of precursor used, we decided to correspondingly raise the amount of sulphur used as well to 0.6g and above. A higher flow rate of 50SCCM was selected to account for the expected increase in vapour density of precursor and reactant.

In one particularly successful growth, we obtained 8μ m triangular growths on our facedown substrate as shown in Figure 6-8 below. 0.1g of MoO₃ were used with 0.5g MoS₂. We used 0.6g of sulphur and a flow of 50SCCM Ar gas. The growth was conducted at 800°C for 20 minutes.



Figure 6-8 Optical image (50x) of suspected MoS₂ on SiO₂/Si.

Raman spectroscopy was conducted on the sample to determine its composition. The results are shown below in Figure 6-9.





Figure 6-9 (a) Raman spectrum of MoS₂ on SiO₂/Si, at dot indicated in (b),(c). Grown on 4th Dec 2013. (b) Spectral data sum view of 365cm⁻¹ to 385cm⁻¹. (c) Spectral data sum view of 385cm⁻¹ to 420cm⁻¹.

The two prominent modes expected at 384cm⁻¹ and 404cm⁻¹ are found here but with a slight blue shift of 1% and 0.5% respectively. This could be due to the visible multilayer growth, most prominently displayed along the edges of the grown structures. The thicker growth along the edges can be seen from the optical image in Figure 6-8 and the spectral data sum images in Figure 6-9 which reflect an inhomogeneous surface topography. This multilayer growths would have a "hardening" effect or a blue shift on the peaks due to interlayer forces affecting the vibration modes being analysed. The growths are therefore considered to be MoS₂ but not clearly monolayer. By this stage, various growth conditions had been attempted. Some of the changes in these conditions are tabulated below in Table 1.

(a)

Stage	Temperature	MoO 3 Precursor (MoO3:MoS2)	Reactant (S)	Flow rate and Time
Early	615°C-635°C	8.8mg (1:0)	25mg-50mg	20SCCM, 30min
Intermediate	650°C-850°C	25mg-0.1g (1:1)	0.6g-1g	10SCCM-50SCCM, 20min
Late	775°C	0.1g-0.14g (2:1)	>1g	50SCCM, 20min

Table 1 Table of important growth conditions during each stage of project.

6.3 Successful Work

After a few setbacks which hampered the reproducibility of the aforementioned growth, one experiment yielded a growth of triangular substances of about 20µm in size. The amount of MoO₃ used was 0.14g together with the MoS₂ of 0.07g to provide 0.21g of precursor. 1g of fresh sulphur powder was used in the aluminium boat, but this does not include the residual sulphur left in the quartz tube and dark polymeric sulphur left in the aluminium boat from previous growths. The furnace was shifted downstream by 5cm and warmed up to 775°C at 30°C/min, before shifting back upstream 5cm for a growth period of 20 minutes. Ar gas was passed through the system at 50SCCM up to this point. After the growth period, the furnace is switched off, shifted 2cm to prevent continued heating of the aluminium boat and the gas flow rate is turned down to 20SCCm for natural cooling.



Figure 6-10 Optical images of MoS₂ on SiO₂/Si "b" substrate at 10x and 50x on the left and right respectively.

Raman spectroscopy of one of the triangular structures revealed that it had two prominent peaks in close proximity to the expected E_{2g}^{1} and A_{1g} peaks at 384cm⁻¹ and 404cm⁻¹ respectively. The experimental Raman shifts of 384cm⁻¹ and 405.cm⁻¹ were only at most 0.2% from the literature values.



Figure 6-11(a) Raman spectrum of MoS₂ on SiO₂/Si, at dot indicated in (b),(c). (b) Spectral data sum view of 370cm⁻¹ to 390cm⁻¹. (c) Spectral data sum view of 390cm⁻¹ to 415cm⁻¹.

To further verify the few layer thickness of this grown sample, an analysis of the photoluminescence spectra was needed, as shown in Figure 6-12. A PL peak of 1.87eV is much higher than the MoS₂ bulk band gap of 1.29eV. This is highly indicative of the growth

being monolayer since a large band gap can also be used to characterise monolayer $MoS_2^{2,18,25}$.



Figure 6-12 PL spectra of MoS₂ sample.

6.3.1 Common Issues and Solutions

By this phase of work, a sleuth of commonly occurring issues had surfaced which would guide the direction of the project.

One simple issue was the quick vaporization of MoO_3 precursor, which was easily solved by using a mixture of MoS_2 and MoO_3 as mentioned earlier on.

One large issue was the uneven nucleation of MoS_2 across the whole SiO_2/Si substrate. As seen in Figure 6-8 above, MoS_2 was found to nucleate around large impurities or defects in the surface of the substrate. Evenly separated nucleation was not observed and thus very difficult to obtain. This problem would persist through all experiments and no simple solution was found aside from seeding which was explored by other groups.

Another would be the lack of sulphur vapour towards the end of the growth period. Some sulphur would quickly melt and vaporize within the first 10 minutes of heating while the rest

would remain as a dark solid within the aluminium boat, which is assumed to be a mixture of polymeric sulphur chains. The solution to this was threefold. We increased the amount of sulphur in the system by adding more reactant, by leaving the condensed and solidified sulphur in the quartz tube from the previous growth(any which did not affect the safe function of the CVD system), and by reusing the aluminium boat despite the accumulating dark coloured polymeric sulphur residue.

The last issue was due to a change in MoO₃ precursor used. A new batch of MoO₃ was purchased after the old batch ran out, and the colour of the precursor had changed distinctively from a light grey to a light green powder. The numerous experiments succeeding this new precursor had minimal growths on substrates and had set back the project substantially. This issue had no simple solution, save for experimenting with different temperatures and precursor ratios until the right conditions were met again.

6.4 Attempted Growth on Other Substrates

After successfully growing MoS_2 on SiO_2/Si , some attempts were made with the same conditions to grow MoS_2 on hexagonal boron nitride and exfoliated graphene.

6.4.1 Hexagonal Boron Nitride (h-BN)

The growths on h-BN however, were mostly unsuccessful. Only one sample appeared to have MoS₂ growing alongside h-BN. However the growth appeared to be contaminated and the usual triangular shapes indicative of crystal growth were not observed. Nevertheless, Raman spectroscopy performed on an area with apparently large film-like MoS₂ growth yielded a strong signal. The Raman peaks had a frequency difference of 23cm⁻¹, indicating that the growth was probably not monolayer but multilayer instead.



Figure 6-13 Optical image (50x) of MoS_2 on exfoliated Boron Nitride (top). Raman spectra of large film MoS_2 (bottom).

More information was gleaned from the optical images of the MoS_2 on this particular sample. The visible greenish blue was prevalent across the SiO_2/Si substrate and even took on what appears to be thick growth on some faces on exfoliated h-BN, as seen in Figure 6-13 above.

6.4.2 Peel-Off Graphite (POG)

Peel-off graphite (POG) samples were mechanically exfoliated Highly Oriented Pyrolytic Graphite(HOPG) on SiO₂/Si. Some POG samples did experience good crystalline MoS₂ growths. As seen in Figure 6-14.



Figure 6-14 Optical images (50x) of MoS₂ triangles and film on exfoliated graphene.

By observation, MoS₂ appears to have no bias to growing on or around multilayer graphene or bulk graphite. The Raman spectroscopy data collected was also promising.



Figure 6-15 Raman spectra of MoS₂ particle(left) and MoS₂ film(right).

The Raman spectrum for standalone MoS_2 triangles had significantly smaller amplitudes of response as compared to the spectrum for MoS_2 film. The A_{1g} peak for MoS_2 film was found to have 1.72 times the CCD count of the same peak for MoS_2 particles according to data. This is consistent with expectations as the possibly multilayer film is expected to yield a stronger signal in Raman compared to its monolayer counterpart. The frequency difference is also larger in the film, 23cm^{-1} vs 22cm^{-1} in the standalone triangles, which is once again expected as the thinner MoS₂ samples are expected to have a smaller frequency difference.



Figure 6-16 Photoluminescence spectra of MoS2 on POG substrate. Inset shows 100x video image with orange dot indicating sample spot.

The photoluminescence spectra for the MoS_2 was also encouraging. A peak at 675nm or 1.84eV was indicative of the fact that monolayer MoS_2 had indeed grown on this sample.

Optical images for MoS_2 growth on these POG substrates showed MoS_2 growing on certain faces of peeled-off graphite and multilayer graphene(dark blue shapes), as shown in Figure 6-14. The obvious blue-green colouration is probably a sign of thick MoS_2 growth on some parts of the graphite, while other portions may have the monolayer growth seen from the Raman spectroscopy.

6.5 Discussions

One major point of error in this experiment would have to concern the high temperatures used during growth. Temperatures expressed were based on the value on the furnace display, as shown in the appendix below. The temperature in the furnace was hardly uniform and barely accurate, as early tests using a temperature probe proved that the hottest temperature reached at the centre of the furnace was usually at least 100°C below the displayed value. The temperature would also taper off by at least 200°C towards the edges of the furnace. This systematically large discrepancy from displayed temperature might be an issue if other groups with different setups wish to replicate the experiment. The temperature testing could not be conducted while the system was sealed, with gas flowing. Therefore the predicted shift of temperatures downstream by convection, was also not tested or detected.

Another source of error may stem from the grain boundaries of MoS₂ as mentioned by *van der Zande et al.* The grain boundaries have S or Mo terminations which result in differing electron densities and effective doping of the boundaries. This could affect photoluminescence data or Raman modes near the grain boundaries of MoS₂ crystals. The grain boundaries themselves may also affect the band gap, and may lift off the SiO₂/Si substrate surface to affect photoluminescence data. Despite precautions taken to take data only at areas away from the grain boundaries, the photoluminescence peak values in particular may be affected by a systematic error of 26meV upshift⁴.

7 Conclusion

The objectives of this project were to design and implement a simple and inexpensive method of growing monolayer MoS_2 on SiO_2/Si and on alternative substrates for device applications.

A chemical vapour deposition method was developed within the means of equipment available to grow monolayer MoS_2 . The conditions for successful growth were researched and experimentally fine tuned to achieve reproducible growth of fairly large monolayer MoS_2 crystals of up to 20µm. A 0.21g precursor mix of MoO_3 and MoS_2 powder mixed in a ratio of 2:1 respectively was used, with more than 1g of sulphur. The sample was grown at 775°C for 20minutes with 50SCCM of Ar gas flow and atmospheric pressure.

This method was applied to other substrates like h-BN and exfoliated graphene and bulk graphite which have the potential to be used in electronic devices. Monolayer growth on the SiO_2/Si surface was confirmed while visual observation of optical imagery indicates that at least film-like or multilayer MoS_2 had grown on these alternative substrate surfaces.

7.1 Future Work

Although MoS_2 has been heavily studied these last few years, a method for consistent and reproducible growth is still far off, as experienced during the course of this thesis. The recently released study by *X*. *Ling et al*³⁰., highlights the steps in the right direction as MoS_2 growth moves towards more even nucleation and lower temperatures required. Growths on alternative substrates however, are still relatively understudied. Although there is research on constructing Graphene-MoS₂ heterostructures as photodetectors³⁹, more can be done to explore the potential of MoS_2 heterostructures. Monolayer crystalline MoS_2 growth on h-BN in particular should be further explored, as h-BN has been shown to be a superior 2D substrate⁴⁰. The research could then progress to transferring graphene onto these MoS_2 -BN heterostructures to form a 2D version of the tradition MOS transistor. Graphene would act as the metal electrode, while MoS_2 and h-BN would act as the semiconductor and insulator respectively. This work could pave the way to 2D transistors becoming realizable.

Appendix

1) CVD Setup



- 2) Wafer Cleaning and Quartz Tube cleaning
 - a) Rinse wafers in acetone in sonicator for 5 minutes. Repeat but with isopropyl alcohol for another 5 minutes.
 - b) Remove and blow dry with Nitrogen gas.
 - c) Clean quartz tube with paper towels and acetone, before cleaning with isopropyl alcohol.
- 3) Pre-growth preparation
 - a) Seal all valves and switch on vacuum pump. Allow flow of Ar gas at 20SCCM for 5 minutes.
- 4) Additional optical images from some growths
 - a) 4/02/13 (MoS₂ on SiO2/Si)



b) 17/02/13(MoS₂ on POG)



c) 19/02/13 (MoS₂ on BN)





d) 19/02/13 (MoS₂ on POG)



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