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Los Angeles

Growth of MoS_2 Layers by

Two-Step Chemical Vapor Deposition

A thesis submitted in partial satisfaction

of the requirements for the degree Master of Science

in Materials Science and Engineering

by

An-Di Sheu

2015

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ABSTRACT OF THE THESIS

Growth of MoS_2 Layers by Two-Step Chemical Vapor Deposition

by

An-Di Sheu

Master of Science in Materials Science and Engineering

University of California, Los Angeles, 2015

Professor Suneel Kodambaka, Chair

Monolayer molybdenum disulfide (MoS_2), a two-dimensional (2D) crystal with a direct bandgap, is a promising candidate for nano electronic devices, energy storage, and photocatalysts. People are researching for large-area single-layer MoS_2 growth. In my work, I investigated the growth of monolayer MoS_2 on SiO_2/Si substrate by chemical vapor deposition (CVD). Using sulfur and molybdenum trioxide (MoO_3) as precursors to grow 2D MoS_2 in the tube furnace CVD system. As part of my thesis, I carried out several growth experiments while varying the deposition parameters. The as-grown samples are characterized using optical, scanning electron, and atomic force microscopes and Raman spectroscopy. I have also developed

a two-step approach to grow MoS_2 layers. This new approach has great potential to grow large-area single-layer MoS_2.

The thesis of An-Di Sheu is approved.

Yang Yang

Yu Huang

Suneel Kodambaka, Committee Chair

University of California, Los Angeles

2015

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Chapter 1: Introduction

1.1 Two-Dimensional Layered Materials

Since the discovery of graphene in 2004 [1], two-dimensional (2D) layered materials have drawn a lot of attention from materials scientists. With fascinating unusual properties, 2D layered materials could be used in field-effect transistors [2], photosensors [3], photovoltaics [4], ultracapacitors [5], composite materials [6], and photocatalysts [7]. 2D layered materials typically have strong in-plane bonds and weak van der Waals bonds between the layers. Interestingly, physical, chemical, and mechanical properties of these materials vary with the thickness. For instance, graphene is the strongest materials ever discovered with tensile strength of 130 gigapascals, compared to 0.4 gigapascals for A36 structural steel [8]. In contrast, graphite is very brittle due to its weak interlayer bonding. Graphene is also an excellent conductor of heat (heat conductivities: 2000 – 4000 W m^{-1} K^{-1}) and electricity (electronic mobility: 200,000 $cm^2 \cdot V^{-1}s^{-1}$) with ballistic transport [9]. However, the thermal and electronic conductivities of graphite are very anisotropic: phonons and electrons travel much more easily along the layer than across the layers. Despite all these attractive characteristics, the use of graphene in electronics has been limited because most of the electronic applications require a bandgap, which does not exist in graphene [10]. Researchers tried to introduce a bandgap in graphene by synthesizing graphene nano-ribbons but carrier mobility in the nano-ribbons is low [10]. This and other unsuccessful attempts to engineer its bandgap motivated researchers to focus on other 2D layered materials, which have bandgaps. Hexagonal

boron nitride (h-BN) and molybdenum disulfide (MoS_2) are two of the most studied 2D layered materials after graphene.

1.2 2D Transition-Metal Dichalcogenides

Transition-metal dichalcogenides (TMDCs) of the form MX_2 are produced by combining the transition-metals (M = Ti, Zr, Hf, V, Nb, Ta, Mo, W, Pt) with the chalcogens (X = S, Se, Te) in the form of MX_2 [7,11]. The transition-metal atoms are sandwiched between two layers of chalcogen atoms. Bulk TMDCs are multiple layers of TMDCs stacked together by van der Waals forces. One transition-metal atom is

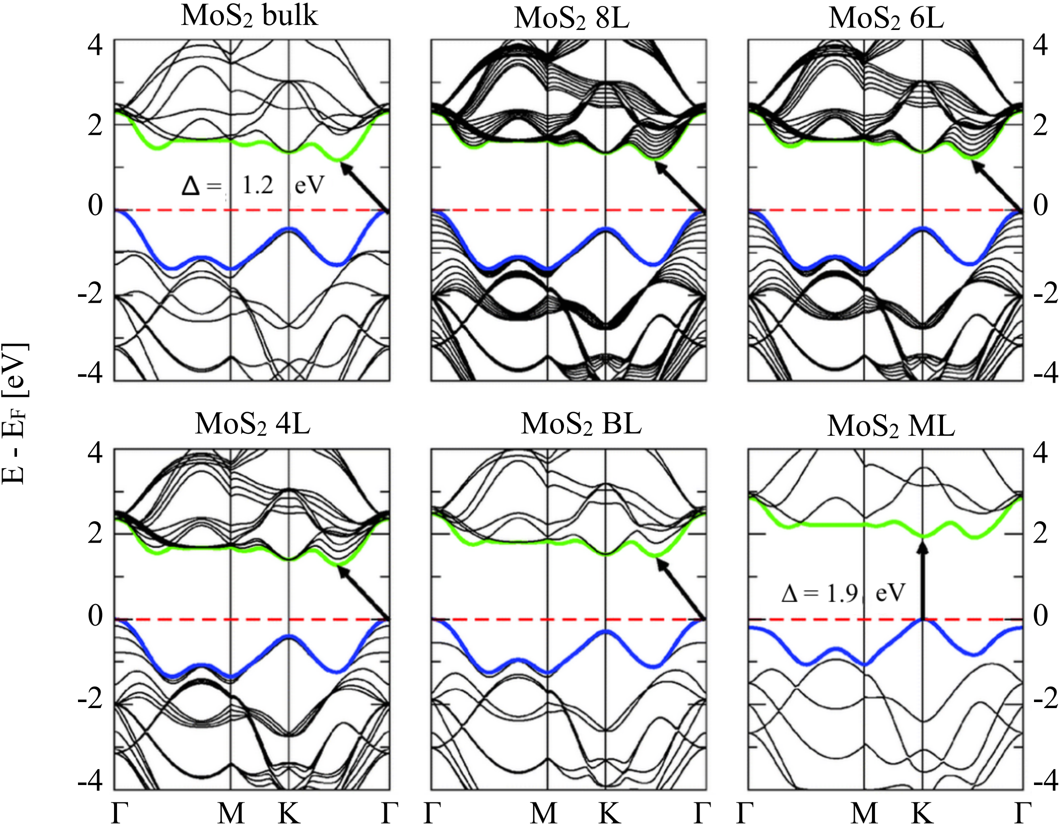


Figure 1. Calculated band structure of MoS_2. The bandgap of MoS_2 decreases with the increasing number of MoS_2 layer. The bandgap in bulk MoS_2 is indirect while the bandgap in monolayer MoS_2 is direct [12].

surrounded by six chalcogen atoms to form trigonal prismatic structure [11]. Among the TMDCs, MoS_2 and related alloys have been widely used as solid lubricant [13]. Similar to graphene, TMDCs also possess thickness-dependent properties [14,15]. In case of MoS_2, there is a change of bandgap from indirect to direct with decreasing number of layers [16], see figure 1. TMDCs composed of Mo or W are semiconductors and that is the reason why they are investigated more than other TMDCs. The lattice constants and bandgaps of Mo and W based dichalcogenides are listed in Table 1 [17-19], which shows that they are semiconductors. Other TMDCs such as $TiSe_2$ and NbS_2 are semimetals [11].

The Mo and W based TMDCs usually crystallize in three different structures: 2H, 3R, and 1T [20]. The difference in stacking between the layers for these structures are shown in figure 2. 2H is the most common and stable phase among these three. 1T is a metastable phase, which provides lower contact resistance and could be synthesized by lithium intercalation [21]. To date, the electronic properties of 3R phase remain largely unexplored. Both 1T and 3R phases can change to 2H structure through heating.

TMDC	MoS_2	$MoSe_2$	$MoTe_2$	WS_2	WSe_2	WTe_2
Lattice constant	3.11 Å	3.24 Å	3.46 Å	3.13 Å	3.25 Å	3.47 Å
Bandgap (bulk)	1.23 eV	1.09 eV	1.0 eV	1.35 eV	1.20 eV	0.8 eV
Bandgap (monolayer)	1.87 eV	1.62 eV	1.25 eV	1.98 eV	1.68 eV	1.24 eV

Table 1. Lattice constants and bandgaps of Mo and W based TMDCs [17-19]

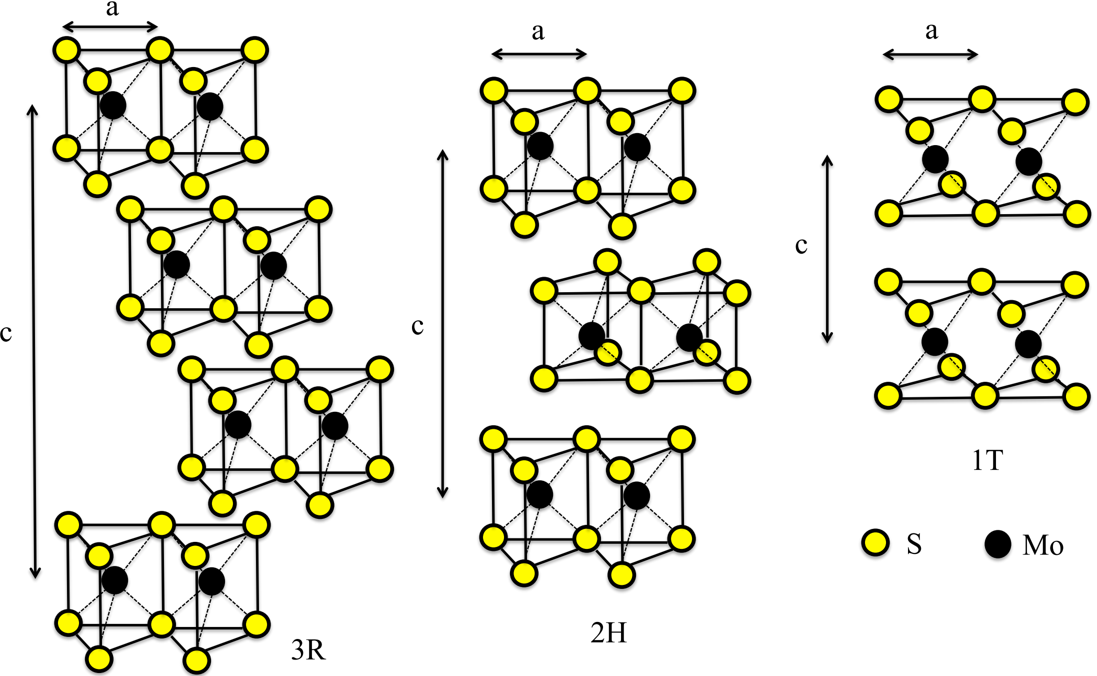


Figure 2. Three different kinds of stacking between layers resulting in different phases: 3R, 2H, and 1T. a and c are the in-plane and out-of-plane lattice constants, which for 2H-structured MoS_2 are 3.1 Å and 12.3 Å respectively.

1.3 Applications of Single Layer MoS_2

The 2D nature of monolayer MoS_2 leads to quantum confinement [22], high absorption coefficient [4], and efficient electron-hole pair generation [4] under photo-excitation. Due to the fact that TMDCs are vertically held together by van der Waals forces the lattice mismatch between the layers of different TMDCs is not a problem for the fabrication of vertical heterostructures. Also the lattice constants of the TMDCs (see Table 1) are very close. Therefore, it is possible to build vertical, lateral, and alloy heterostructures. Such TMDC heterostructures with dissimilar bandgaps have applications such as photocatalysts [23], photodetectors [24], and field-effect transistors [25].

Single layer MoS_2 has great potential in electronic devices because of its high on/off ratio (~10^8) [2]. Scientists have used single layer MoS_2 to fabricate ultra-thin field-effect transistors. Additionally, in contrast to graphene, monolayer MoS_2 has a direct bandgap of 1.8 eV, which is highly desirable for switching on and off. As mentioned earlier, the 2H and 1T phases in MoS_2 have different contact resistances. Scientists have utilized this resistance difference to build field-effect transistor [21]. The 1T phase is in contact with source and drain to provide better conductance and the 2H phase is in contact with gate to avoid leakage current.

Monolayer MoS_2 has also been used to fabricate photodetectors. Because monolayer MoS_2 is a direct bandgap semiconductor, it could be good for optoelectronic devices. The direct bandgap provides a high absorption coefficient and efficient electron-hole pair generation. The high photoresponsivity (880 AW^{-1}) is 10^3 times superior to the best graphene photodetector [3]. The ability to grow large-area MoS_2 layers can facilitate the development of flexible and high-sensitivity MoS_2 optoelectronic devices.

Monolayer MoS_2 is also a good photocatalyst for water splitting. TiO_2 nanocrystals grown in the presence of a layered MoS_2 hybrid are found to be high-performance photocatalysts for H_2 evolution [26]. Single-layer MoS_2 by itself was also reported as an efficient photocatalyst based on first-principles calculations [11,27]. There are three criteria to become a promising semiconductor for water splitting. First, the bandgap has to be larger than 1.6-1.7 eV to drive the kinetics of hydrogen evolution reaction. Second, the band edges must straddle the redox potentials of water. Last, the semiconductor should be insoluble in water. Fortunately, monolayer MoS_2 meets all the three criteria.

The highly flexible and transparent MoS_2 based field-effect transistor could also be used as biosensors for various biomarkers. It is able to detect cancer marker proteins [28] and pH variation [29]. The biosensor should meet criteria such as high detection speed, high sensitivity, low cost, and versatility. MoS_2 based FETs has higher on/off ratio (~10^8) than graphene based FETs and this is the main reason why MoS_2 based FETs are more suitable as biosensors.

Another promising application of MoS_2 is as anode in lithium ion batteries. The conventional lithium ion batteries utilize graphite as the anode. The theoretical capacity for graphite is low (372 mA h/g). Higher capacity materials such as Si (4200 mA h/g) and Sn (994 mA h/g) have poor cycling characteristic. However, they suffer from large volume changes when charging and discharging. The weak van der Waals bondings between MoS_2 layers allow Li^+ ions to diffuse in and out without a significant increase in volume expansion. The capacity of exfoliated MoS_2 could be maintained above 500 mA h/g after 50 cycles [30]. MoS_2 is also reported as an excellent supercapacitor. 2D layered MoS_2 based micro-supercapacitors with a high area capacitance of 8 mF cm^{-2} and good cycle performance are superior to graphene based micro-supercapacitors [31]. People have demonstrated a low-cost spray painting process and subsequent laser patterning to fabricate the MoS_2 micro-supercapacitors [31].

1.4 Synthesis of Single Layer MoS_2

Single Layer MoS_2 can be synthesized using a variety of methods. We can classify all the methods into two main categories, top-down and bottom-up approaches. Top-down methods typically involve mechanical, solution phase, or chemical exfoliation

of single and few layers from the bulk. Most commonly employed bottom-up approaches include chemical and physical vapor deposition (CVD and PVD) of MoS_2 layers.

1.4.1 Exfoliation

The first free standing graphene layers were obtained by mechanical exfoliation [1]. This method involves repeated peeling of individual graphene layers from highly oriented pyrolytic graphite with scotch tape. Since then mechanical exfoliation has been widely used for 2D layered material synthesis. 2D layers can also be produced in large amount by non-chemical, solution-phase exfoliation from their bulk counterparts [32]. This method is attractive for the deposition of 2D layered materials on a variety of substrates. Besides liquid exfoliation, people have tried exfoliation by chemical reactions involving the intercalant [33], thermal shock [34], and acid treatment [35]. However, these methods may not be ideal for the production of 2D layered materials for all the applications because the 2D layered materials produced by chemical exfoliation usually react with the solvent resulting in undesirable compositions and structures.

Until now, none of the above-mentioned top-down methods have been used for mass production because the yield rate and the reproducibility are low. In order to make 2D layered materials for commercial applications, we need to figure out ways other than exfoliation to synthesize large area 2D layered materials with desired composition and structure.

For the synthesis of MoS_2 layers, bottom-up approaches include deposition using solid, liquid, and vapor precursors. CVD usually involves precursors reacting with each other and the reaction product deposited on the substrate. PVD usually involves

generation and vapor phase transport of solid materials by heat, plasma, or pulsed laser and deposition of the condensate as a thin film on the substrate.

1.4.2 Chemical Vapor Deposition (CVD)

In this approach, a substrate is exposed to one or more volatile precursors, which react with each other and the reaction product is deposited on the substrate. The undesired byproducts are usually removed from reaction chamber by carrier gas using pumps. CVD systems could operate at various pressures, atmospheric pressure (or above), low vacuum (~10^{-3} Torr), or ultrahigh vacuum (10^{-6} ~ 10^{-8} Torr). MoS_2 thin films have been grown via CVD using a variety of Mo precursors, such as Mo film, $MoCl_5$, MoO_3, and solid S or H_2S gas. Thermal decomposition of single precursor such as $(NH_4)_2MoS_4$ has also been shown to yield MoS_2 layers..

1.4.3 CVD of MoS_2 using MoO_3 or $MoCl_5$ as the Precursor

In this approach, solid MoO_3 or $MoCl_5$ typically in the form of powders are vaporized and converted to MoS_2 by reacting with S vapor at high temperatures (> 800 °C). MoO_3 or $MoCl_5$ are placed at the hottest zone (T > 800 °C) of the furnace to vaporize them. Sulfur vapor is introduced into the system by heating sulfur powder and carrying the vapor with Ar flow. The precursors would react to produce MoS_2, which is subsequently deposited on the substrate [36].

1.4.4 CVD of MoS_2 using $(NH_4)_2MoS_4$ as the Precursor

Thermolysis of ammonium thiomolybdates [$(NH_4)_2MoS_4$] in a N_2 environment is known to result in the conversion of $(NH_4)_2MoS_4$ to MoS_3 at 120~360 °C [37]. The subsequent conversion of MoS_3 to MoS_2 requires a higher temperature (> 800 °C). It was also reported that the conversion of $(NH_4)_2MoS_4$ to MoS_2 in the presence of H_2 occurs at a lower temperature (425 °C) [38]. However, MoS_2 decomposes into Mo in

the H_2 environment at over 500 °C. A variation of this approach involves two steps. First, the substrate is dip-coated with $(NH_4)_2MoS_4$ in solution and the substrate is then heated in Ar/H_2 environment at 500 °C. To obtain better crystallinity, people annealed the sample in Ar/S atmosphere at 1000 °C or higher to form MoS_2 [38].

1.4.5 CVD of MoS_2 using Mo Metal and S Powder as the Precursors

MoS_2 layers have also been synthesized via sulfurization of Mo thin films. In this approach a thin film of Mo (1-5 nm thick) is first deposited on a substrate by evaporation or sputtering. The Mo films are then exposed to sulfur vapor at high temperature (750 °C) forming very thin MoS_2 layers [39].

1.4.6 Vapor Phase Deposition of MoS_2 via Thermal Evaporation

Direct thermal evaporation of MoS_2 has been shown to yield MoS_2 thin films. MoS_2 powder is first pressed into tablets and sintered for 20 min at 300 °C. The MoS_2 tablet is then placed in a closed box with pinholes. These pinholes could make the MoS_2 flow rate small enough to grow MoS_2 thin film. The reactive chamber is set at 500 °C with Ar as the carrier gas to bring MoS_2 vapor to the substrate [40].

1.4.7 Deposition of MoS_2 via Magnetron Sputtering

Magnetron sputtering was reported as a one-step process to synthesize monolayer MoS_2 at wafer scale. Initial base pressure is maintained at about 2.25×10^{-7} Torr to minimize impurities in the chamber. The Ar pressure is fixed at 4.5×10^{-4} Torr. MoS_2 films are grown at high temperature (> 700 °C) using Mo metal target sputtered in vaporized sulfur ambient. Sulfur is vaporized using heating tape. The sputtering power is maintained low to facilitate slow growth of MoS_2 thin films [41].

Each of the synthesis methods mentioned above have certain advantages and

disadvantages. For example, the MoS_2 sample grown using $(NH_4)_2MoS_4$ as the precursor involves many steps. First, $(NH_4)_2MoS_4$ converts to MoS_3 at 120~360 °C. Second, MoS_3 decomposes into MoS_2 at 800 °C. Last the MoS_2 sample requires further annealing at 1000 °C in an inert gas to improve its crystallinity [38]. Furthermore, $(NH_4)_2MoS_4$ is synthesized by dissolving $(NH_4)_6Mo_7O_{24}*4H_2O$ in ammonia solution (25%wt) and introducing H_2S to this solution [42]. To obtain highly crystalized MoS_2 with $(NH_4)_2MoS_4$ there are so many steps involved.

MoS_2 synthesized by e-beam evaporated Mo thin film and sulfurized in sulfur vapor at 750 °C is typically polycrystalline and the thickness of the film is not uniform. The grain size of MoS_2 synthesized by evaporated Mo is typically smaller (< 1 μm) than the counterpart synthesized by CVD using MoO_3 and sulfur as precursors. The smaller grain size imply more grain boundaries, which leads to more electron scattering within MoS_2.

The thinest MoS_2 thin film ever reported grown by thermal evaporation was quite thick (a few atomic layer to 10 nm thick) in comparison to other techniques. We can grow high quality MoS_2 thin films using $MoCl_5$ as a precursor but $MoCl_5$ is an aggressive oxidant and readily hydrolyzes to release HCl. HCl is a strong acid which could be dangerous. Among all the synthesis methods mentioned above, using MoO_3 powder and sulfur powder as the precursors has many advantages. MoO_3 has low melting point (T_M = 795 °C) and high vapor pressure (10^{-1} Torr at T = 703 °C) [43]. Using this method, monolayer single domain MoS_2 with very good electrical and photoelectric properties has been grown [40].

Researchers have synthesized MoS_2 layers at different temperatures (650 °C - 850

°C) [44,45], different pressures (low vacuum to over atmospheric pressures) [44,45] and on patterned and seeded substrates [46]. However, the growth mechanism is still not well-established. Only a few papers discuss the growth mechanism and the factors contributing to the growth of large-area single-layer MoS_2 in such conditions. Most of the literatures do not discuss the effect of growth parameters.

My thesis focused on the growth of MoS_2 and investigated the effect of parameters, including growth temperature, chamber pressure, precursor amount, and location of the substrate as a means to develop a better understanding of the MoS_2 layer growth mechanism.

Chapter 2: Experimental

2.1 2D Layered MoS_2 Growth

All of my growth experiments are carried out in a tube furnace. Figure 3 is a schematic of my CVD system. The temperatures of substrates and precursors, carrier gas flow rate, total pressure, and the amount of precursors could all be controlled independently in this system. The growth precursors and the samples are placed in a 1-inch diameter and 2.5 feet long quartz tube, which is surrounded by the furnace. One end of the tube is connected to a series of gas inlets through which gases such as argon (Ar), nitrogen (N_2), and oxygen (O_2) can be introduced into the system. The other end of the tube is connected to a mechanical pump. All of my MoS_2 synthesis experiments were carried out using Si(001) substrates covered with 300 nm thick SiO_2 (MTI Corporation©). The substrates were cleaned first with acetone and then with deionized water for 10 and 5 minutes, respectively. Then substrates were placed on top of a boat shaped aluminum oxide crucible (1 cm in diameter) as shown in the figure 3. A crucible containing MoO_3 powder (Alfa Aesar© 99.5%) was placed inside the aluminum oxide boat at the hottest zone (700 ~ 850 °C) of the tube and another

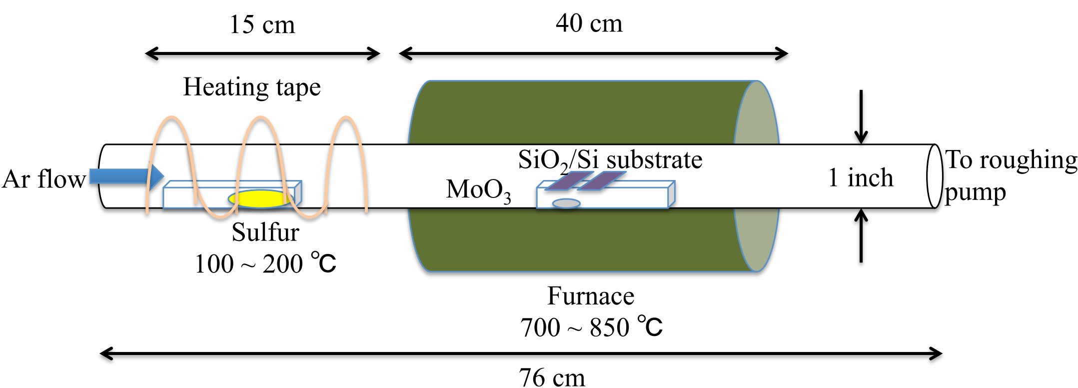


Figure 3. Schematic of tube furnace system.

crucible containing sulfur powder (Sigma-Aldrich© 99.9%) was placed at the upstream of the quartz tube. After both precursors and substrates were loaded into the tube, 50 ~ 200 sccm of Ar gas (Airgas© 99.995%), controlled by mass flow controller, was introduced into the tube to purge the system. Then the pump end of the tube was closed in order to maintain a high Ar pressure in the system. The base pressure before Ar purging is 0.03 Torr and after one hour Ar purging the pressure is around 100 Torr. One hour after pumping to 0.03 Torr, the furnace temperature is increased to simultaneously vaporize MoO_3 and heat the substrate. When the temperature of the MoO_3 reaches target temperature (700-800 °C), the sulfur powder is heated using the heating tape. Sulfur vapor is transferred to the center of the tube by Ar gas, where it reacts with MoO_3 to form MoS_2. The substrate temperature was set to 850 °C and the growth time is typically 10 to 15 minutes. After the growth, the outlet valve between the tube and the pump was opened to purge all the gases. The system was cooled to room temperature with continuous Ar flow (50 ~ 200 sccm) while the mechanical pump was running.

The Mo-S binary phase diagram [46] in figure 4 can help identify the deposition parameters favorable for the growth of MoS_2. From the phase diagram, it appears that stoichiometric, single-phase MoS_2 is best synthesized using S-rich conditions. The S to Mo ratio in my experiments is usually higher than 10 and the temperature is always higher than 700 °C. This growth condition is equivalent to the "MoS_2 + 1 atm gas" region. The need for this "1 atm gas" is supported by our experiments, where we grow MoS_2 at a higher pressure environment and will be discussed in Chapter 3.

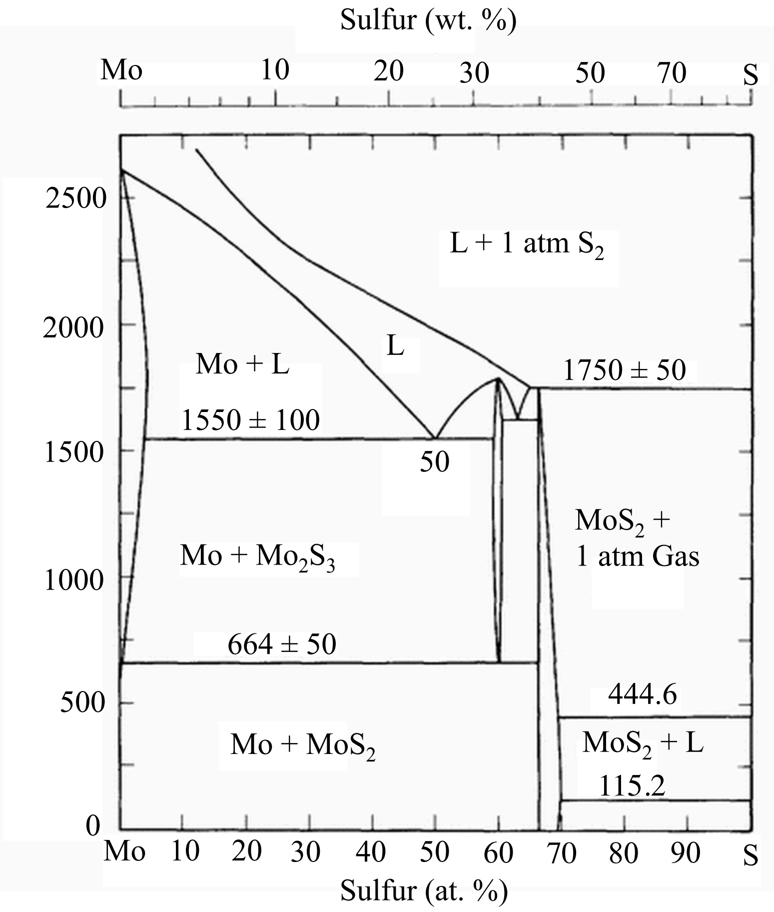


Figure 4. Mo-S binary phase diagram, from [47].

2.2 Sample Characterization

The as-grown MoS_2 samples were characterized using Raman spectroscopy (Renishaw InVia Raman Microscope) using laser wavelength λ = 785, 633 nm and a laser power of 1 mW, scanning electron microscopy (SEM)(FEI Nova nanoSEM 230), and atomic force microscopy (AFM)(Bruker Dimension FastScan Scanning Probe Microscope) in tapping mode.

2.2.1 Raman Spectroscopy

The phenomenon of Raman scattering is well-studied and it is beyond the scope of my thesis to present the details of this phenomenon and the measurement techniques. However, those interested in learning more about this topic may find more

information here [48,49] and elsewhere. Briefly, Raman spectroscopy provides information about molecular vibrations that can be used for sample identification. It is based on the inelastic scattering (Raman scattering) of monochromatic light such as laser. The laser beam scatters off mostly is unchanged in energy (Rayleigh scattering). Only a small fraction (1/10,000,000) of light loses or gains energy (Raman scattering) with the molecules of target materials. The CCD (charge coupled device) detectors are used for Raman spectroscopy because they are sensitive to light. They detect the frequency of light after scattering with the target materials. Each molecule has its own unique vibrational frequency. After the incoming light scattering with the molecules, the energy of light changes. The energy shift relates to the molecular vibrational

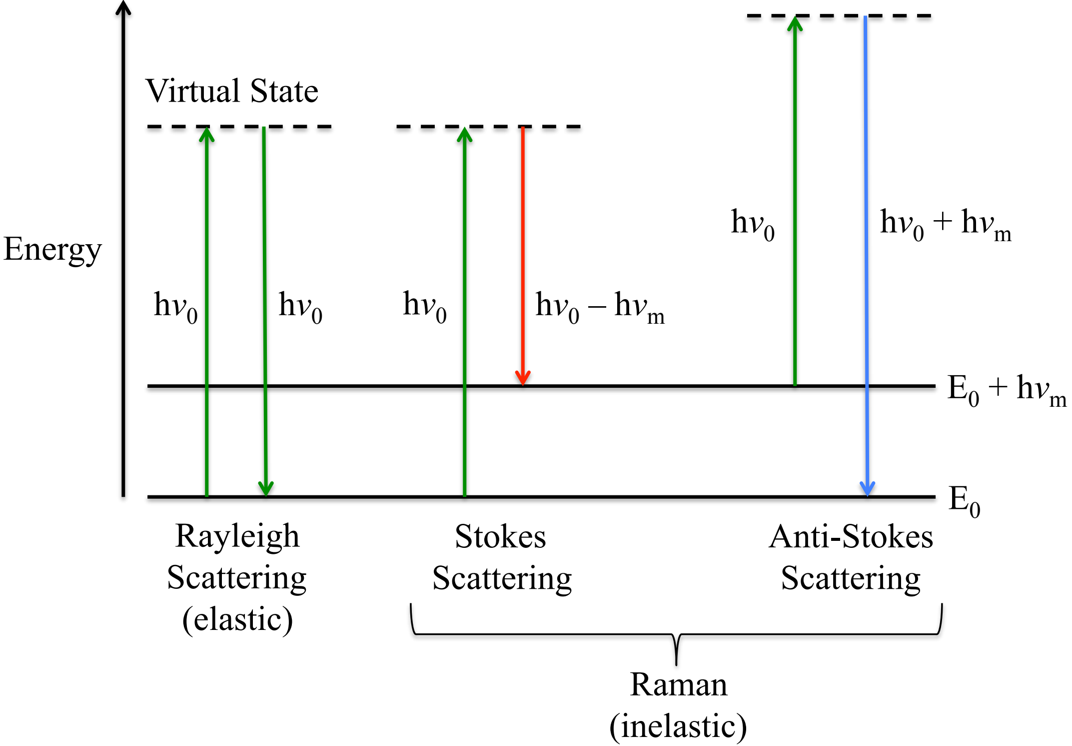


Figure 5. Energy-level diagram showing the energy change in Raman scattering and Rayleigh scattering. E_0: ground state; $h\nu_m$: energy difference after scattering; $h\nu_0$: energy of incident beam [50].

frequency. The sample may absorb energy in which case the emitted photon has a lower energy than the absorbed photon. The outcome is known as Stokes scattering. The sample could lose energy to the incoming photon and the emitted photon has a higher energy than the absorbed photon. This outcome is called anti-Stokes scattering. If the incoming photon does not gain/lose energy, i.e. when the photon is elastically scattered, the process is called Rayleigh scattering. The energy level diagram of Rayleigh, Stokes, and anti-Stokes scattering are shown in figure 5. Stokes scattering is a more common result compared to anti-Stokes scattering due to the fact that there are

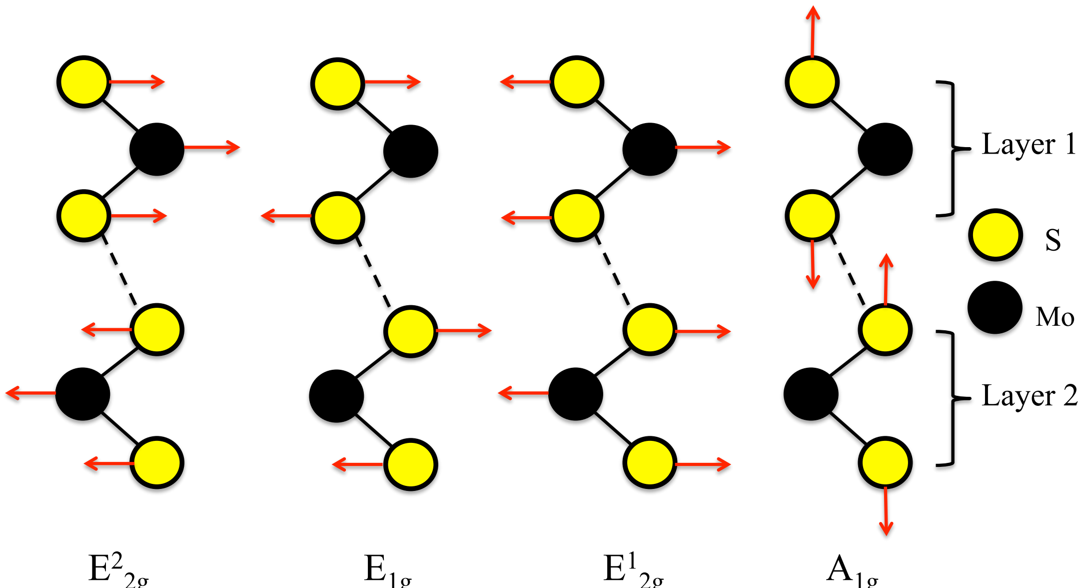


Figure 6. Four most common vibrational modes in MoS_2. The red arrows represent the atomic displacement during vibration. E^1_{2g} represents the in-plane vibration mode observed at around 383 cm^{-1} in Raman spectrum obtained using a laser λ = 633 nm. A_{1g} represents the interlayer vibration mode at around 409 cm^{-1} in Raman spectrum. E^2_{2g} cannot be detected because of the limited rejection of the Rayleigh scattered radiation. E_{1g} cannot be detected because of selection rules for our scattering geometry [51].

usually more molecules in the ground state at room temperature.

There are four Raman-active vibrational modes (E^2_{2g}, E_{1g}, E^1_{2g}, A_{1g}) in MoS_2 (figure 6). Using λ = 633 nm, I observed the E^1_{2g} and A_{1g} modes near 400 cm^{-1}. The other two modes (E_{1g}, E^2_{2g}) are hard to detect [51]. E^1_{2g} represents the in-plane vibrational mode, whereas A_{1g} is the interlayer vibrational mode and they are observed at around 383 cm^{-1} and 409 cm^{-1} respectively for bulk MoS_2. The positions of both the peaks are related to the thickness of MoS_2. For the given λ the distance between E^1_{2g} and A_{1g} decreases with decreasing thickness of MoS_2 [51]. This shift in the peak positions is attributed to thickness-dependent suppression of atomic vibrations by the interlayer van der Waals forces in MoS_2 [51]. As demonstrated in figure 7, different number of layers in MoS_2 corresponds to different E^1_{2g} and A_{1g} frequencies in Raman spectra [51]. The observed blue-shift (shifting to higher frequency) of A_{1g} peak with increasing layer number is consistent with the theoretical prediction [52]. Therefore, we can determine the number of layers in MoS_2 using Raman spectroscopy. An important factor to consider in characterization of MoS_2 using Raman spectroscopy, however, is the laser wavelength could influence the experiment results. MoS_2 is more sensitive to laser λ = 633 nm than 785 nm wavelength. We could barely detect single-layer MoS_2 with 785 nm laser but easily get the signal with 633 nm laser. This is due to the fact that the intensity of Raman scattering is proportional to the fourth power of source frequency. Hence, at the same laser energy, Raman signal obtained using λ = 633 nm is more intense than with the 785 nm.

In my thesis, I used Raman spectroscopy (λ = 633 nm) to confirm the existence of

MoS_2 and to determine the number of layers of MoS_2 thin film.

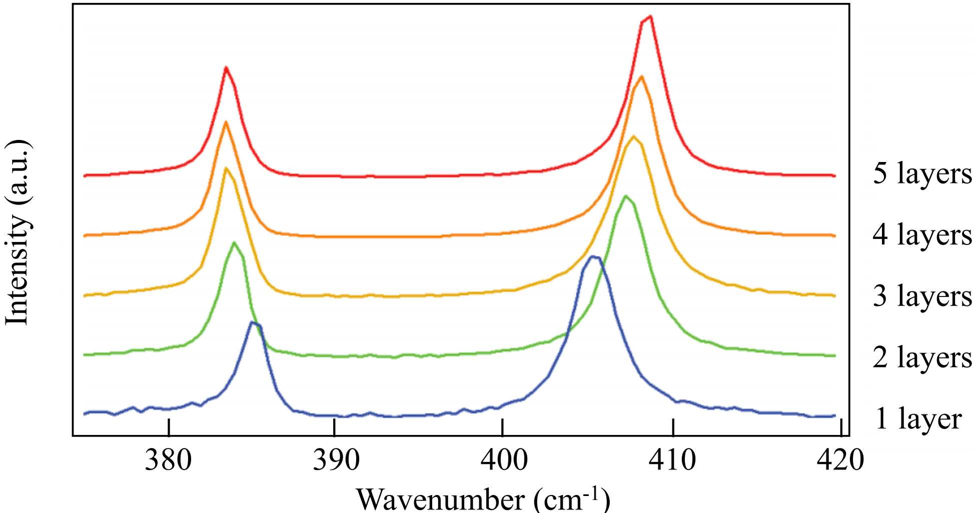


Figure 7. Raman spectra of MoS_2 in different number of layers. The peaks around 385 cm^{-1} and around 405 cm^{-1} correspond to the vibrational modes E^1_{2g} and A_{1g}, respectively. The distance between E^1_{2g} and A_{1g} increases as the number of layers increases [53].

2.2.2 Scanning Electron Microscopy

For a detailed description of operating principles and applications of scanning electron microscopy (SEM), please see [54]. Briefly, SEM utilizes a focused high energy (~ 0.2 to 30 kV) electron beam to scan the specimen and to generate a variety of signals at the surfaces of solid specimens. The different signals come from the different interactions between electrons and specimens. Secondary electrons, backscattered electrons, and characteristic X-rays are three of the most common signals used in the SEM for materials characterization. Secondary electrons are usually used for the determination of morphology and topography of the samples while backscattered electrons are valuable for illustrating compositional contrast in

multiphase samples. Characteristic X-rays are generated by the inelastic collision between incident electrons and electrons in samples providing the elemental composition of the samples. SEM is one of the best ways to visualize the topography at high resolution (~ 1 nm). As part of my thesis, I have used SEM to study the morphology and the distribution of MoS_2 triangles and films on SiO_2/Si substrates. I used the secondary electron mode to observe and characterize the triangles. I have determined the shapes of MoS_2 islands and also measured the size and density of the triangles. The size of the triangles in my experiments vary from 5 μm to 50 μm depending on the growth parameters. Energy-dispersive X-ray spectroscopy (EDS), commonly used to determine sample composition in the SEM, was not used in my experiments because the EDS peaks for Mo ($L\alpha$ = 2.29 keV) and S ($K\alpha$ = 2.31 keV) overlap making it difficult to quantify the Mo and S contents in the samples.

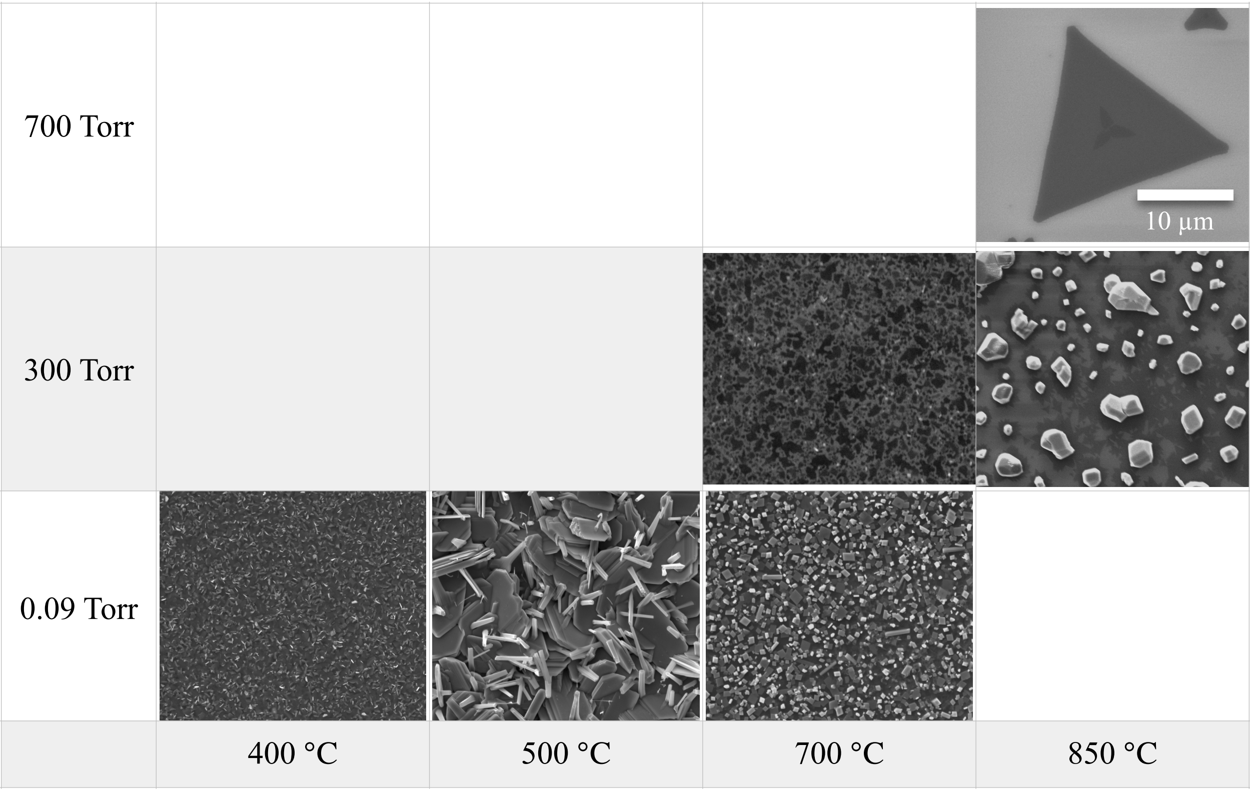
2.2.3 Atomic Force Microscopy

Atomic force microscopy (AFM) is a surface characterization technique used for high-resolution imaging of surfaces and measurement of surface topography. For a detailed description of AFM, its variants, and applications, please see [55]. The relevant surface topographical information is gathered by a mechanical probe "touching" the surface. The AFM consists of a cantilever with a very sharp tip used to scan the sample surface. When the tip is brought very close to the surface, there is a force between the tip and the surface resulting in deflection of the cantilever , which is used to determine the surface roughness. One of the main benefits of AFM, in contrast to a related surface characterization method, scanning tunneling microscopy (STM), is that it can be used to investigate electrically non-conductive materials. This feature facilitates characterization of our MoS_2 samples grown on SiO_2 substrates.

Using AFM, we can measure the thickness of the MoS_2 layer and estimate the number of layers within each MoS_2 triangle. Furthermore, we can compare the AFM data with Raman spectroscopy results to check if these two results agree with each other.

Chapter 3: Results and Discussion

In this chapter, I will present my results obtained from a series of growth experiments carried out at a function of deposition parameters. Table 2 shows representative scanning electron microscopy (SEM) images obtained from samples grown at various deposition parameters.



700 Torr				
300 Torr				
0.09 Torr				
	400 °C	500 °C	700 °C	850 °C

Table 2. Scanning electron microscopy (SEM) images obtained from SiO_2/Si samples after deposition of MoS_2 at different pressures and temperatures as listed in the table. The temperatures shown in the table are temperature of SiO_2/Si substrate during deposition. The magnification and the scale bar are the same for all the images.

3.1 Effect of Temperature

In order to determine the optimal condition for the growth of best-quality MoS_2 layers, I investigated, among other parameters, the effect of substrate to source distance. In my initial experiments to grow 2D layered MoS_2, the setup was different from the one I mentioned in Chapter 2. I did not place the substrates on top of the crucible. Instead, I placed them downstream with respect to the crucible making them 2 cm apart from each other. The setup is shown in figure 8. In this setup, the temperature of the substrate is lower than the temperature of the crucible containing MoO_3 precursor. I carried out several (400 °C and 500 °C) experiments with the substrate temperature < 700 °C but none of them showed Raman spectra characteristic of MoS_2. Typical SEM images obtained from such samples are shown in figure 9. Based upon these results, MoS_2 growth at low temperatures (< 700 °C) is not feasible. That is the reason why I changed my experiment setup for the following experiments. I placed the substrates right on top of the crucible, with the expectation that the growth temperature is approximately the same as the MoO_3 temperature.

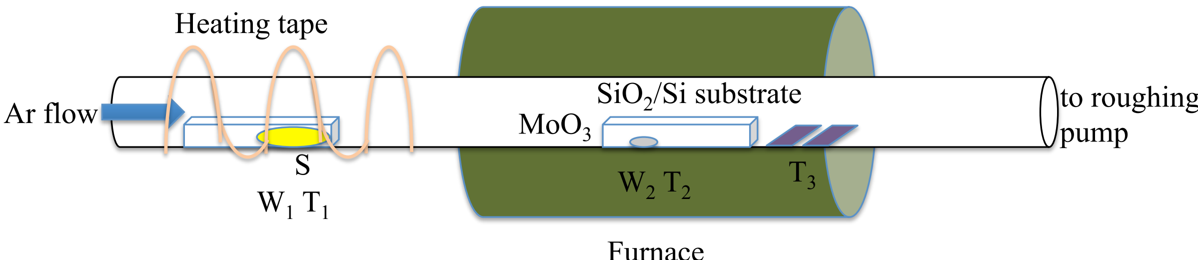


Figure 8. W_1 and T_1 are the weight and temperature, respectively of sulfur. W_2 and T_2 are the weight and temperature, respectively of MoO_3. T_3 is the temperature of SiO_2/Si substrate.

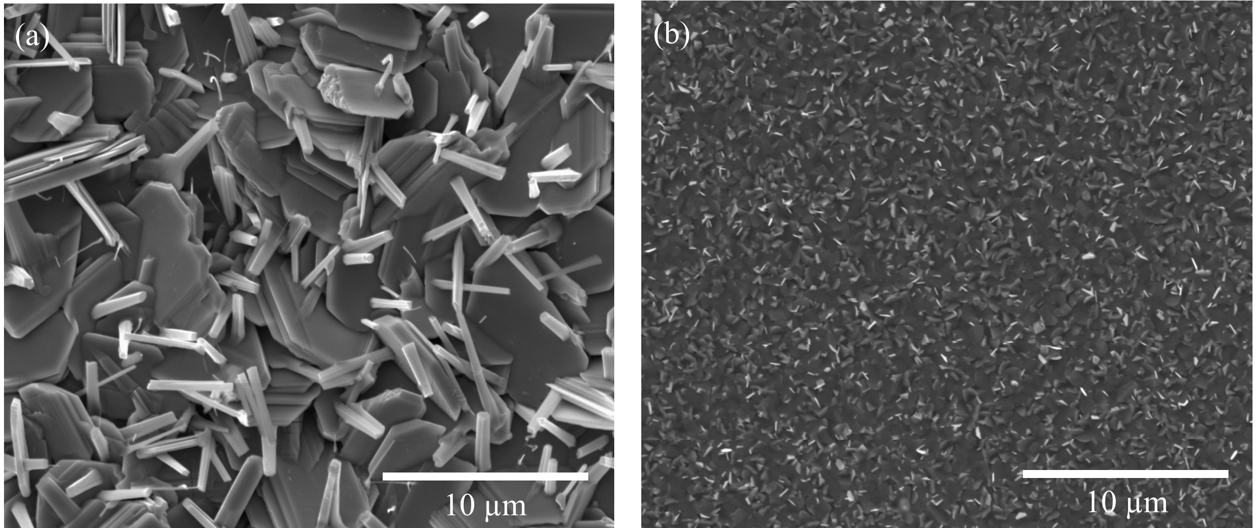


Figure 9. SEM images obtained from SiO_2/Si samples after deposition at temperatures T_3 = (a) 500 °C and (b) 400 °C. Both the depositions were carried out with the total pressure (Ar flowing) maintained at 0.09 Torr. W_1 = 80 mg, T_1 = 85-115 °C, W_2 = 40 mg, and T_2 = 700 °C.

3.2 Effect of Precursor Pressure and Flow Rate

All of my initial experiments were carried out using a constant Ar flow rate of 15 sccm at low pressure (0.09 Torr) using the CVD system reported in Chapter 2. I used 30 mg of MoO_3 in the center crucible and 80 mg of sulfur in the upstream crucible as the precursors. (The amount of precursors used in these low-pressure experiments are more than those used in the high-pressure (~ 1 atm) experiments. This is because the loss of precursors via vapor transport is higher when the chamber pressure is lower than when it is maintained at higher pressures.) It took approximately 18.5 minutes to heat the center crucible to 700 °C. After the center crucible reached 700 °C, I heat sulfur source with a heating tape. The sulfur temperature during

MoS_2 growth was not very stable. It was fluctuating between 85 °C and 115 °C. The temperature of center crucible was held at 700 °C for 15 mins after which both the furnace and heating tape were turned off. The results of these growth experiments are shown in figure 10.

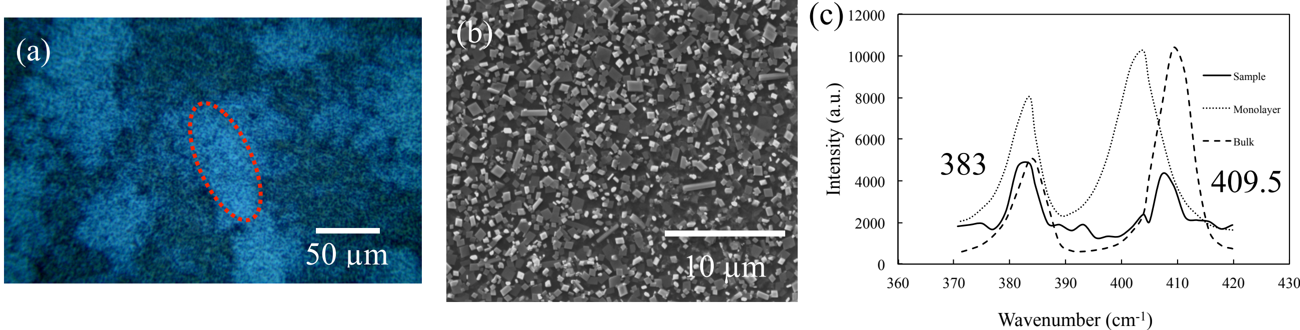


Figure 10. (a) Optical microscopy images, (b) SEM image, and (c) Raman spectrum obtained using a laser wavelength λ = 785 nm and power = 1 mW from a SiO_2/Si sample after deposition at 0.09 Torr. T_1 = 85-115 °C, W_1 = 80 mg, T_2 = 700 °C, and W_2 = 30 mg.

Figure 10(a) is a typical optical microscopy image obtained from the sample. The color variation visible in the image are due to the composition contrast. The brighter and the darker regions correspond to MoS_2 and non-MoS_2, respectively. An SEM image of the sample is shown in figure 10(b). We can see many cubic and cuboid structures in the SEM image. However, the presence of MoS_2 layers is not clear. Figure 10(c) shows the Raman spectrum obtained from the sample inside the red dotted oval in figure 10(a). The dashed and dotted lines in the plot correspond to bulk and monolayer MoS_2, respectively. The two stronger intensity Raman peaks observed at 383 cm^{-1} and 409.5 cm^{-1} indicate the presence of bulk-like MoS_2 on this sample. I have conducted other experiments with different precursor amount (20 mg MoO_3) and also with

sulfur heated when center crucible is at 600 °C or 650 °C. However, none of the samples yielded MoS_2 signal in Raman spectroscopy measurements. The reproducibility was not very good and I did not find any thin layered MoS_2 on the sample. I conclude that low pressure (0.09 Torr) is not ideal for 2D layered MoS_2 growth.

After a series of growth experiments at low pressure, I investigated the effect of increasing the total pressure in the CVD reactor on the growth morphologies. I ramped up the chamber pressure by closing the valve connected to the roughing pump and introducing Ar flow (10, 100, 150, 200 sccm) into the chamber for 30 or 60 mins before vaporizing the precursors. The growth pressure was set at 100, 300 or 700 Torr in different experiments. Since the vaporization of precursors in high pressure (> 100 Torr) environment is not as easy as in low pressure environment. It is because the loss of precursors via vapor transport is higher when the chamber pressure is lower than when it is maintained at higher pressures. The temperature (T_2) of center crucible was set at

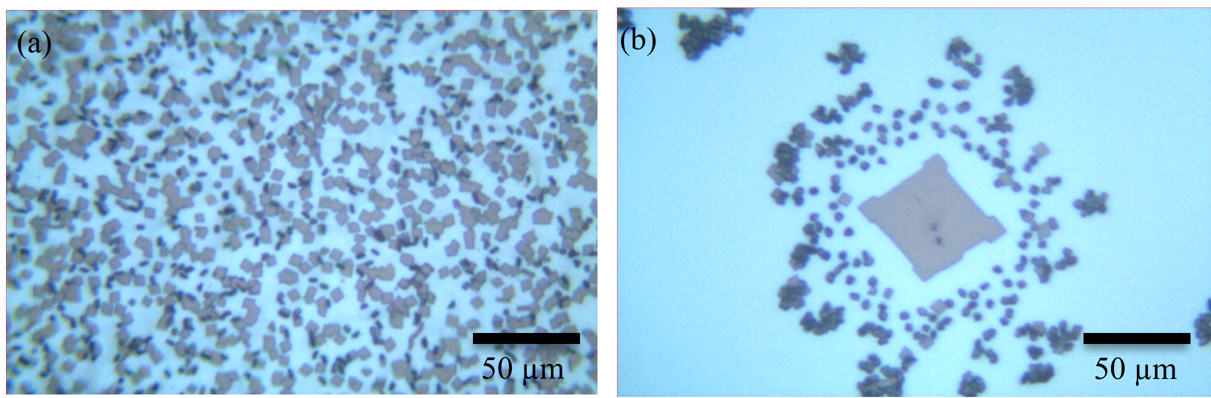


Figure 11. (a) and (b) are optical microscopy images obtained from a SiO_2/Si sample in different regions after deposition carried out using 100 Torr, T_1 = 110-140 °C, W_1 = 80 mg, T_2 = 750 °C, and W_2 = 20 mg.

750 °C or 850 °C and the temperature (T_1) of upstream crucible was set at 120 °C or 200 °C correspondingly. (T_1, T_2) = (120 °C, 750 °C) and (200 °C, 850 °C). The amount of sulfur was 80, 100, or 120 mg and the amount of MoO_3 was 20, 15, 10, or 8 mg in different experimental setups.

Figure 11 shows typical optical micrographs from the samples grown using 80 mg sulfur and 20 mg MoO_3 as precursors with the pressure at 100 Torr and T_2 = 750 °C. We can see light blue SiO_2 in the background and cubic non-MoS_2 structures from different regions of the sample. These samples did not show any MoS_2 signal. The first successful sample with triangle-shaped MoS_2 was obtained at 300 Torr with 100 sccm Ar flow rate at 850 °C. The optical micrograph, Raman spectrum, and SEM images acquired from this sample are shown in figures 12 and 13.

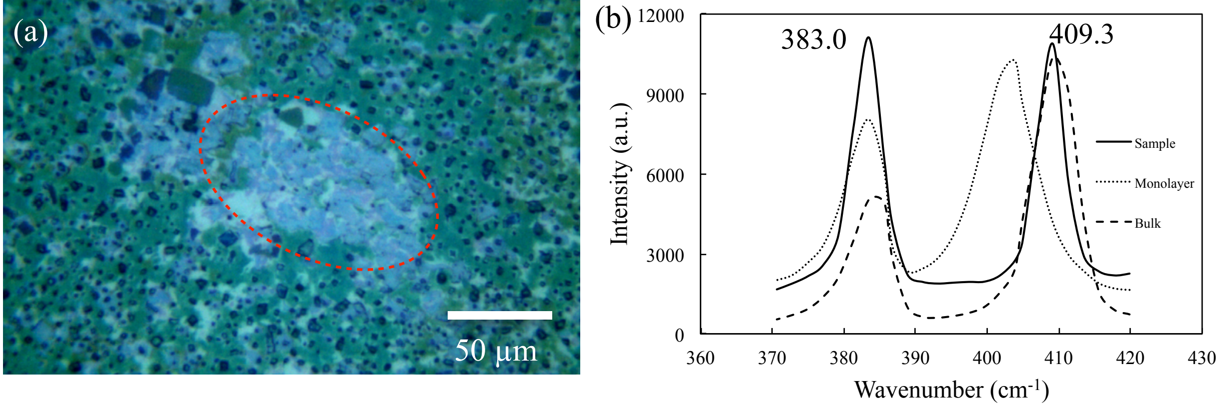


Figure 12. (a) Optical microscopy image and (b) Raman spectrum obtained from the elliptical region highlighted by a red dashed line in (a) corresponds to bulk MoS_2. SiO_2/Si sample after deposition carried out at 300 Torr, T_1 = 200 °C, W_1 = 80 mg, T_2 = 850 °C, and W_2 = 20 mg.

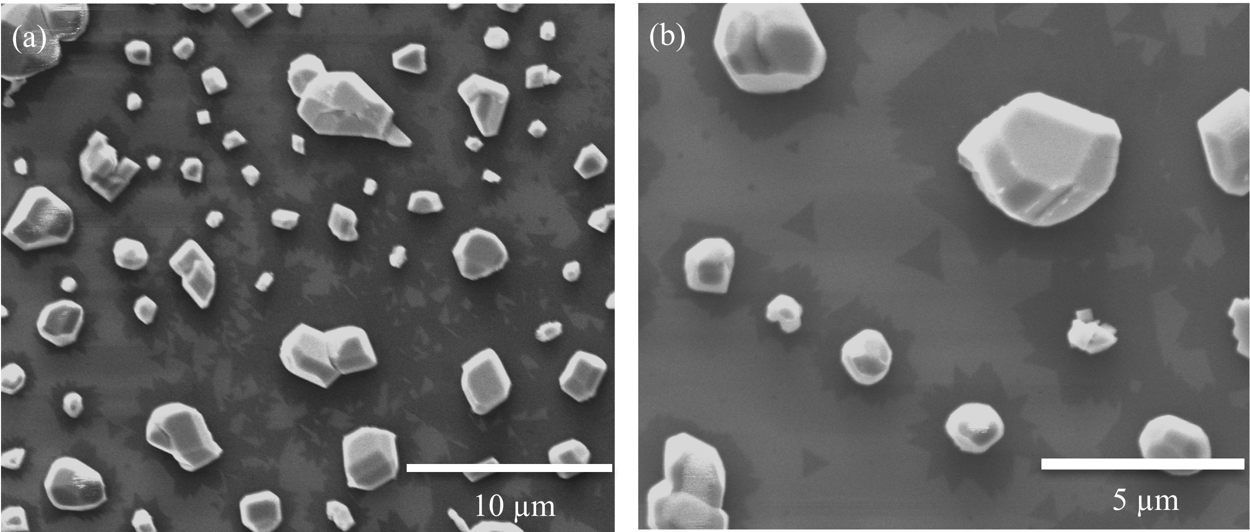


Figure 13. SEM images obtained from SiO_2/Si sample same as in figure 12. (a) and (b) are from different areas and at different magnification. Darker contrast triangles were first discovered around the 3D particles. The triangles are MoS_2 and 3D particles are probably unreacted MoO_3 or partially reduced $MoO_{3-x}S_x$.

Figures 13(a) and (b) are two representative SEM images obtained from the same sample shown in figure 12. As we can see in figure 13, there are many sub-micrometer scale darker contrast triangles around the brighter contrast particles. These 3D particles are probably unreacted MoO_3 or partially reduced molybdenum oxysulfide ($MoO_{3-x}S_x$) acting as seeds for MoS_2 triangle growth. In my experiments, I observed these triangular features primarily in those regions of the sample that are in contact with the crucible walls. There are also lots of non-MoS_2 structures at the center part of the sample as shown in figure 14. These initial experiments are promising and indicated that triangular-shaped MoS_2 islands form at these growth conditions. Moreover, the presence of large 3D islands suggest that there is excess MoO_3 precursor and only a portion of which is converted to MoS_2. In order to maximize MoS_2 island growth and eliminate

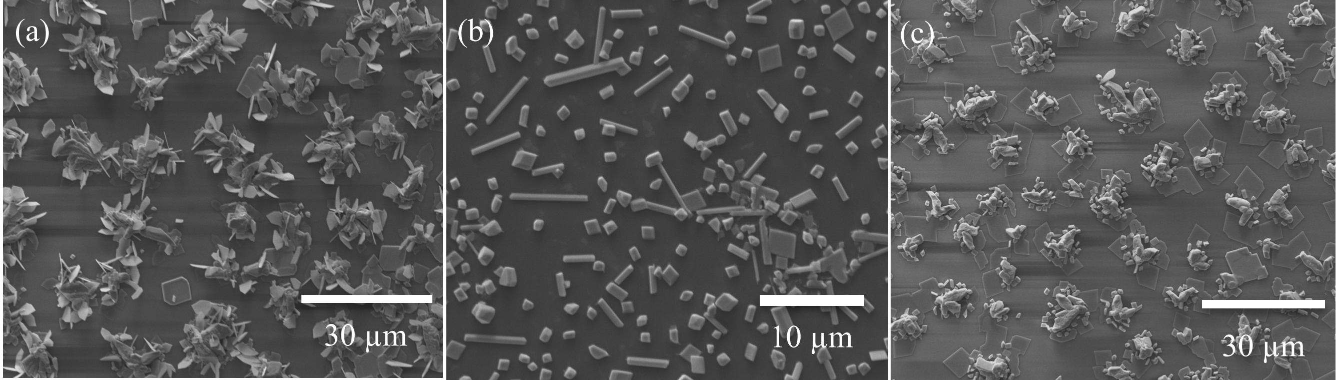


Figure 14. SEM images obtained from the center part of the same SiO_2/Si sample as in figures 12 and 13. (a), (b), and (c) were from different areas of center part of the sample. The larger 3D structures visible in all these images are likely to be MoO_3 or partially reduced $MoO_{3-x}S_x$.

MoO_3 precursor from the sample, I have also experimented with reduced amounts of MoO_3 precursor. However, as I will discuss later in this Chapter, complete transformation of MoO_3 to MoS_2 has been challenging.

I have also used much higher pressure (700 Torr) for my experiments. I found that the resulting MoS_2 triangles are much bigger and denser compared to those grown at lower pressures. In my experiments, I observed triangular islands of sizes between 3 μm and 14 μm. Figures 15 and 16 show representative SEM images obtained from the SiO_2/Si samples grown using 700 Torr. On some of the triangles, there are 3D particles situated at their centers (see figure 15). These particles are relatively smaller than those observed in samples grown using lower pressure (see figure 13). Given that the particles appear centrosymmetric with respect to the triangular islands, I speculate that these particles act as "seeds" for the nucleation and growth of MoS_2 triangles. Moreover, there are “tails” at the vertices of the bigger triangles (side length ~

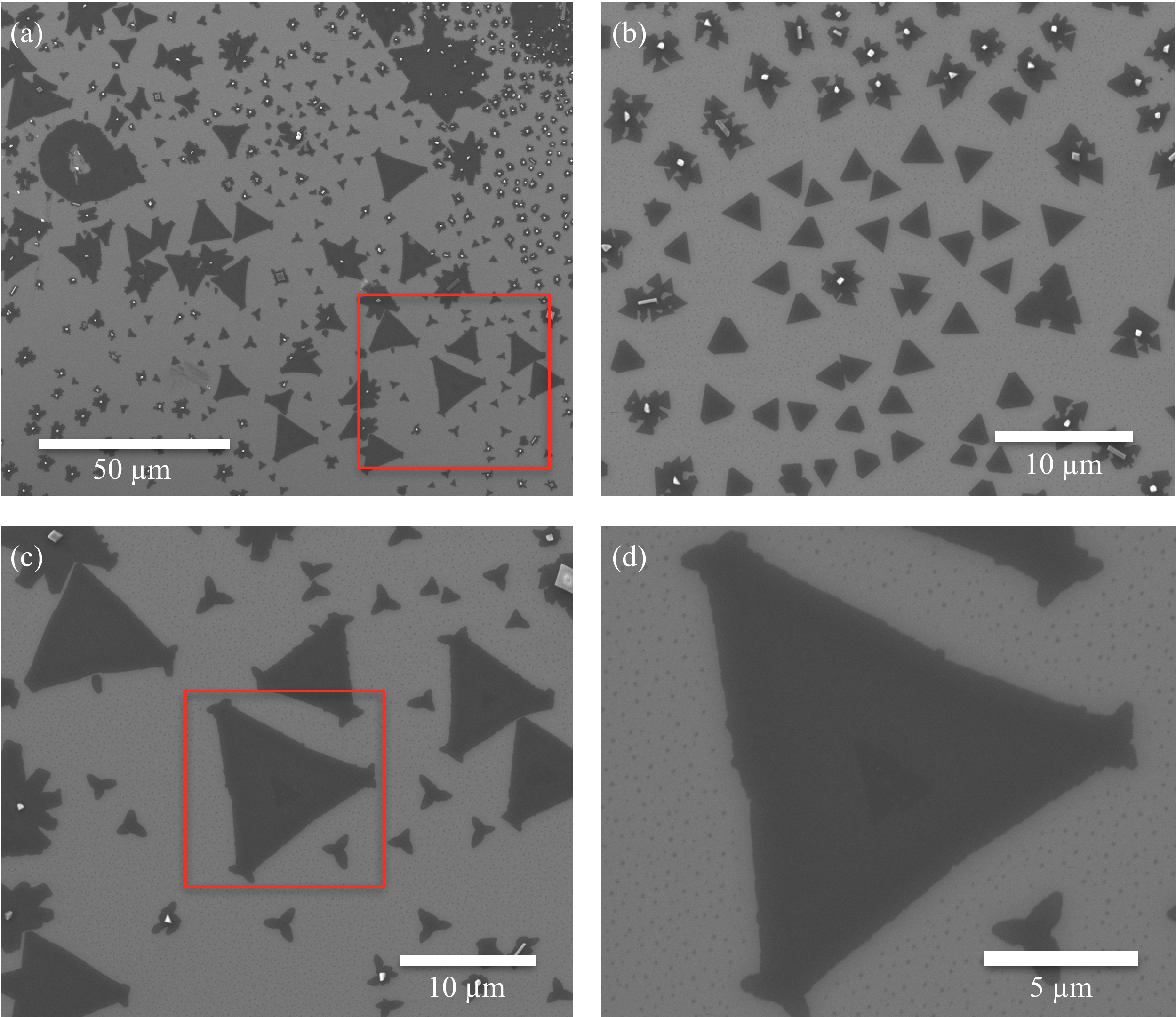


Figure 15. SEM images obtained from a SiO_2/Si sample after the deposition of MoS_2 with the pressure of 700 Torr, T_1 = 200 °C, W_1 = 100 mg, T_2 = 850 °C, and W_2 = 10 mg. (a) Overview of the different island morphologies. (b) Higher magnification images of smaller MoS_2 triangles. (c) and (d): higher magnification images of regions highlighted in (a) and (c), respectively.

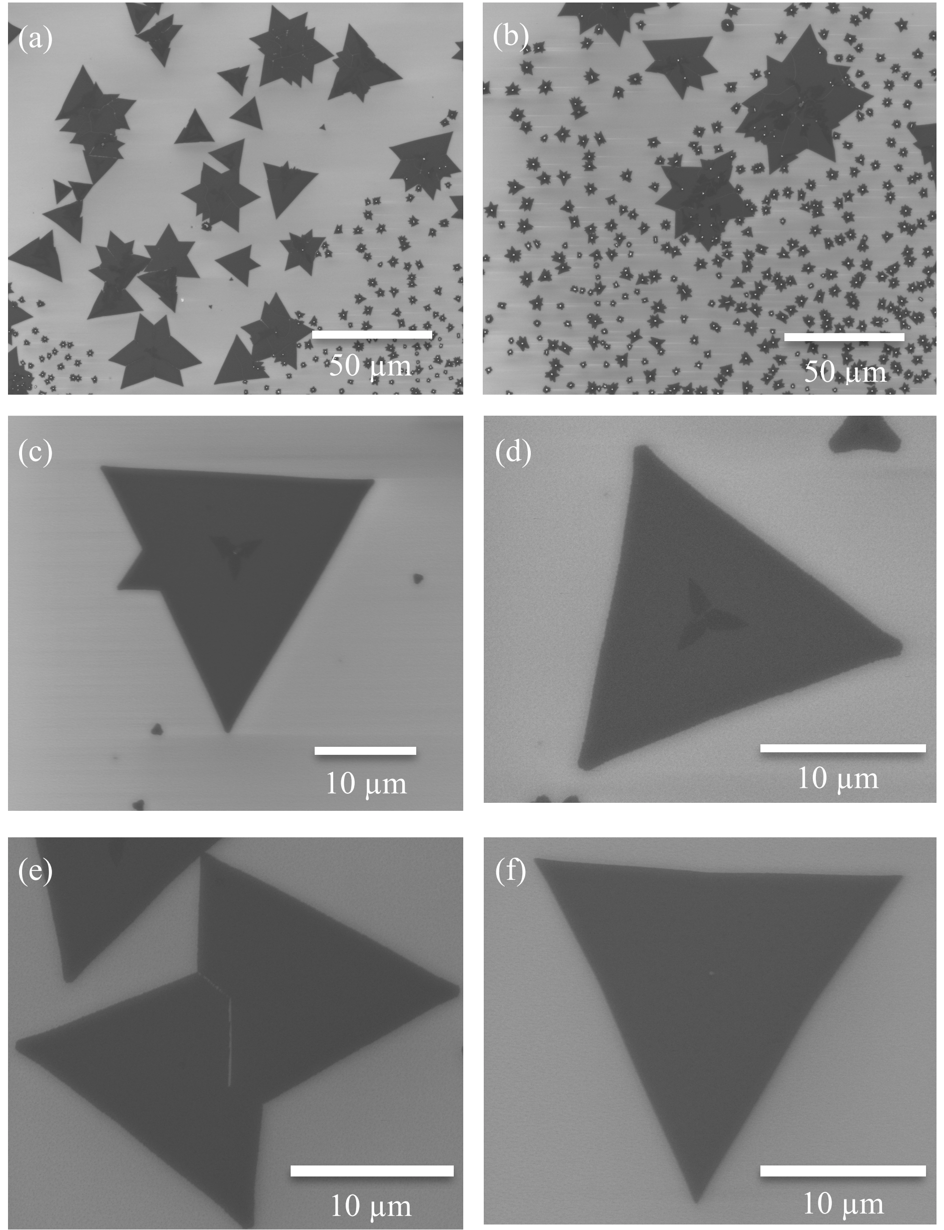


Figure 16. SEM images obtained from a SiO_2/Si sample after the deposition of MoS_2 with 700 Torr, T_1 = 200 °C, W_1 = 120 mg, T_2 = 850 °C, and W_2 = 8 mg. (a) and (b) Overview of the different island morphologies. (c) - (f) Higher magnification images of triangles with side length up to 25 μm. The star and other regular but non-triangular shapes visible in these images are due to the presence of multiple rotational domains within the islands.

20 μm); and smaller islands (side length ~ 3 μm) are bounded by concave edges (see figures 15(c) and (d)). Higher magnification SEM images, such as the one in figure 15(d), reveal the presence of numerous smaller islands in the vicinity of larger triangles. Presumably, these are also MoS_2 islands. On the top of a few larger triangles, we have also observed smaller triangles, indicative of bilayer growth (see figures 15 and 16). In addition to regular equilateral triangular shapes, the images also reveal the presence of a variety of shapes, most of which appear to be aggregates of smaller triangles, such as the islands in figure 15(b) and star-shaped islands in figures 16(a) and (b). Such shapes are likely a consequence of rotational domains growing along the existing edges of a parent island. This process is probably best illustrated by the island in figure 16(c), in which a smaller triangle is attached along one of the edges of a larger (parent)

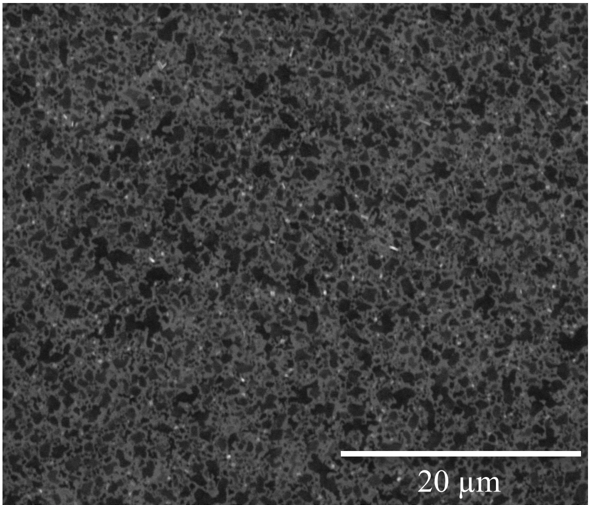


Figure 17. A typical SEM image obtained from SiO_2/Si sample after deposition under 300 Torr, T_1 = 200 °C, W_1 = 80 mg, T_2 = 700 °C, and W_2 = 15 mg.

triangle. Islands with shapes such as those seen in figure 16(e) could form as a result of two domains of different orientations growing into each other. I have also tried growing MoS_2 at lower temperature (700 °C) with the same pressure (300 Torr). Figure 17 is a typical SEM image obtained from a sample grown using 700 °C. The surface morphology of this sample is in distinct contrast to the triangular island morphologies observed on samples grown using higher-temperatures. Raman spectra (not shown) obtained from this sample did not indicate the presence of MoS_2. Based upon all the results presented so far, I conclude that 2D layers of MoS_2 are best grown using high pressures (> 100 Torr) and high temperatures (> 700 °C).

3.3 2D Layered MoS_2 Growth with Different Amounts of Precursors

I have also conducted a series of experiments to study how the amount of precursors influence sample morphology. As mentioned earlier, there are lots of undesired non-MoS_2 structures on the sample and all the MoS_2 triangles were found only at the edges of the sample that are in contact with the crucible walls. In order to maximize the the coverage rate of MoS_2 and eliminate (or minimize) remnant oxides and other non-MoS_2 structures, I experimented with different S/MoO_3 ratios. The rationale behind these experiments is that the fraction of MoS_2 vs. MoO_3 can be increased by increasing the S/MoO_3 ratio.

Figures 18(a-c) summarize the effect of increasing S/MoO_3 ratio on the growth morphologies. At lower S/MoO_3 ratio, there are lots of non-MoS_2 structures (3D cubes and rods) as seen in figure 18(a). With increasing S/MoO_3 ratio, the areal coverage of non-MoS_2 structures is found to be lower and more layered MoS_2 structures are observed (see figures 18(b) and (c)). These results are consistent with my prediction. However, I was not able to eliminate all the non-MoS_2

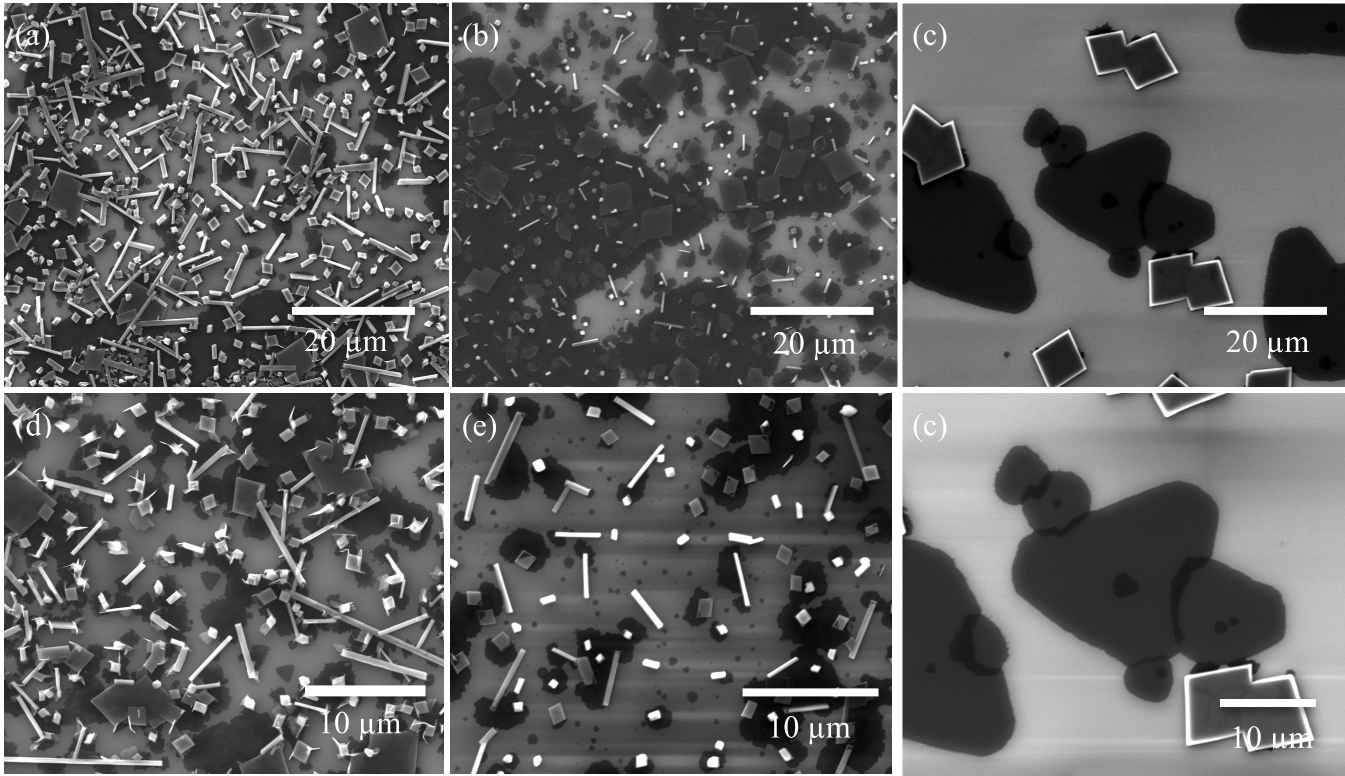
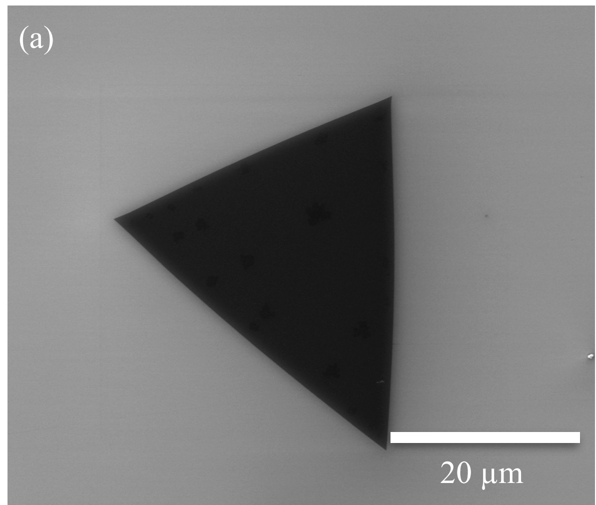


Figure 18. SEM images obtained from a SiO_2/Si sample after the deposition of MoS_2 using 700 Torr, T_1 = 200 °C, T_2 = 850 °C, with: (a) W_1 = 120 mg and W_2 = 8 mg, i.e. S/ MoO_3 = 120/8; (b) W_1 = 200 mg and W_2 = 10 mg (S/MoO_3 = 200/10); and (c) W_1 = 200 mg and W_2 = 5 mg (S/MoO_3 = 200/5). The top and bottom panels show lower and higher magnification images, respectively of the sample.

structures using this approach. Non-MoS_2 structures are observed despite using very small amounts of MoO_3, i.e. with high S/MoO_3 ratios (200/5) as in figures 18(c) and 19. Moreover, the MoS_2 triangles still are only found at the edges of the sample that are in contact with the crucible walls.



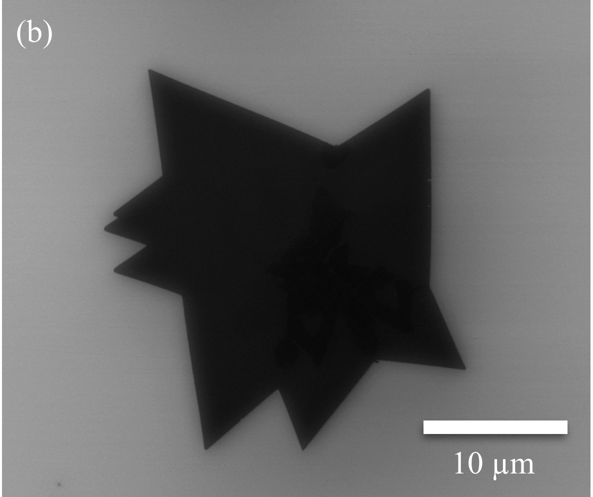


Figure 19. SEM images obtained from SiO_2/Si sample same as from figure 18.

(a) Triangles and (b) stars with side length of 30 μm were found at the edge of the sample.

3.4 Observation of Site-Specific Morphologies

In order to eliminate those non-MoS_2 structures, it is necessary to study the morphology throughout the sample. The thin layered MoS_2 triangles usually appear only in the regions that are in contact with the crucible walls. Thick (micrometer scale) MoS_2, and non-MoS_2 structures usually grow between the two crucible walls. Figures 20(a) to (h) are SEM images illustrating the effect of sample position with respect to the MoO_3 crucible on the resulting growth morphologies. From left to right, i.e. figures 20(a) to (d), the images show morphologies obtained outside the crucible, at the walls, inside the walls, and at the center of the sample. These images along with Raman spectra (not shown) help us better understand the growth kinetics of MoS_2. In my experiments, MoS_2 is barely observed and most abundant outside and inside the crucible, respectively. The desired layered MoS_2 islands are obtained along the edges of the samples that are in contact with the walls of the crucible. Based upon these observations, I

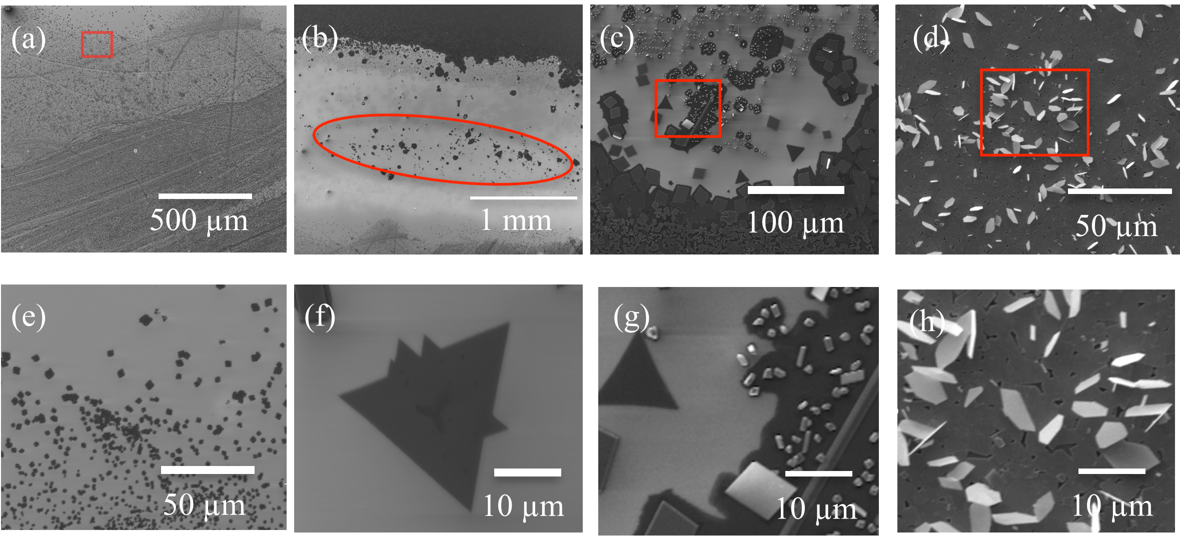


Figure 20. SEM images obtained from a SiO_2/Si sample after deposition using 300 Torr, T_1 = 200 °C, W_1 = 80 mg, T_2 = 850 °C, and W_2 = 4 mg. Images (a)-(d) are obtained from the sample at a region (a) farthest from the sample center and outside the walls of the crucible, (b) in contact with the walls, (c) near the inside edges of the walls, and (d) closer to the center of the sample. The top and bottom panels show lower and higher magnification images of the regions highlighted in the overview image and in the top panel images, respectively. (e)-(h) are magnified images from highlighted area in (a)-(e) respectively. (a) Not any MoS_2 observed in this region. (b) A strip of triangles are located along the line in contact with the crucible wall shown in the highlighted area. (c) 3D brighter contrast particles appear in this region. (d) Thick (micrometer scale) non-MoS_2 material covers the whole substrate with brighter contrast structures standing on top.

propose the following: MoS_2 layer formation requires appropriate fluxes of both MoO_3 and S. Outside the crucible, MoO_3 vapor flux is limited probably due to blocking by the crucible walls and hence there is little opportunity for MoO_3 to react with S and form MoS_2. As a consequence, growth of MoS_2 is suppressed in this region (see figure 20(a)). In contrast, the flux of MoO_3 vapor is highest at the center of the sample and this results in the deposition of a thick film of MoS_2 and partially sulfurized $MoOS_2$ (see figure 20(d)). Along the edges in contact with the crucible, it seems that the fluxes of MoO_3 and sulfur are most favorable for the growth of layered MoS_2, as visible in figure 20(b).

3.5 Two-Step 2D Layered MoS_2 Growth

The mechanisms underlying the CVD of 2D MoS_2 layers are not yet well established. Very little is known concerning the diffusional and reaction processes occurring during the growth of MoS_2 from MoO_3. From my experimental results presented in the previous sections, it is clear that the growth of MoS_2 in my system depends on multiple parameters (relative fluxes of S and MoO_3, substrate temperature, operating pressure, etc.). Moreover, the flux of MoO_3 and substrate temperature are coupled because they both depend on the temperature of the alumina boat; increasing the substrate temperature will automatically lead to higher MoO_3 flux. As a means to independently control these two parameters and hence gain new insights into this MoO_3 --> MoS_2 transformation, I carried out two-step growth experiments as follows: first, I deposit a thin film of MoO_3; in the second step, sulfur is vapor transported to the MoO_3-covered surface to initiate MoS_2 growth. The details of these experiments are presented below.

First, I placed only the crucible with MoO_3 (5 mg) and SiO_2/Si substrate in the reactor with the

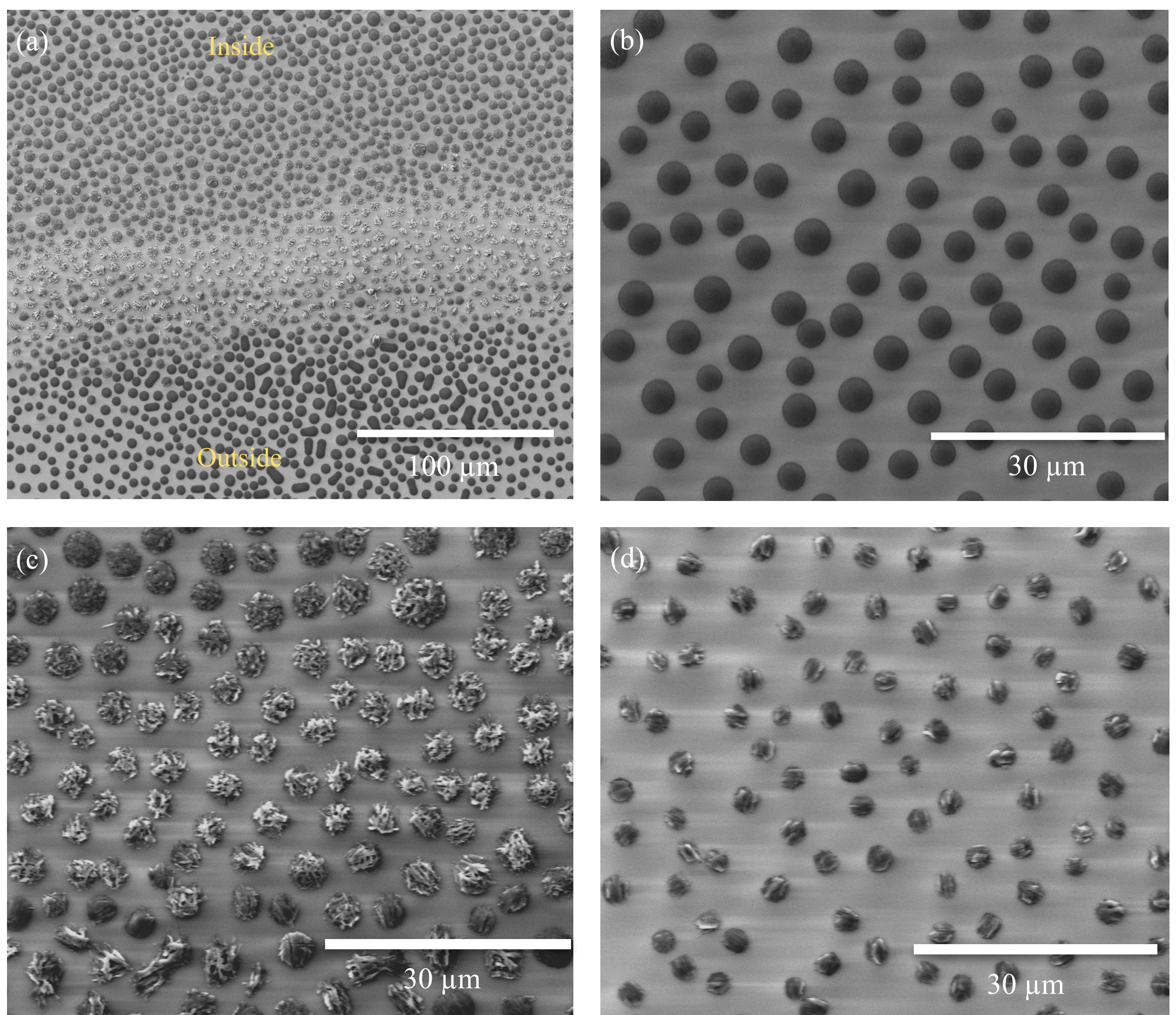


Figure 21. Typical SEM images obtained from a SiO_2/Si sample after deposition of 5 mg MoO_3 under 180 Torr at 850 °C. (a) Overview of the MoO3 deposited regions surrounding the crucible walls. (b-d) Morphologies and areal coverages of 3D MoO_3 mounds observed on the region of the sample is (b) outside the crucible, (c) along with edges in contact with the crucible, and (d) inside the crucible.

substrate positioned right on top of the crucible. I ramped up the pressure with 50 sccm Ar flow to 115 Torr over the course of an hour. Similar to my previous experiments, the temperature for

MoO_3 deposition was set at 850 °C. After staying at 850 °C under 180 Torr (Ar + MoO_3 vapor + sulfur vapor) for 10 mins, I switched off the furnace, purged the system of all remaining precursors, and let the system cool to room temperature in air. Surprisingly, the as-deposited MoO_3 was not in thin film form but the substrate surface was covered with 3D hemispherical mounds (~ 3 μm in diameter). Majority of the mounds appear smooth (see figure 21(b)) while others exhibit rough and/or spiky morphologies as seen in figures 21(c)-(d). It appears that the morphologies of these mounds depend on the position of the sample with respect to the crucible. Irrespective of their shape, all these mounds are evenly distributed on the substrate.

After the MoO_3 deposition and SEM analysis, I put the sample back in the reactor and exposed it to sulfur vapor at high temperatures. I placed 80 mg of sulfur in the upstream crucible and the substrate on top of another crucible at the hottest zone of the tube. The sulfurization was carried out at 850 °C under 200 Torr of Ar flowing at 200 sccm over a period of 10 mins These parameters are similar as those used to grow the sample shown in figure 20. The results of this two-step growth are very promising. I obtained highly dense arrays of MoS_2 triangles in the vicinity of the edges of the sample that are in contact with the crucible, as shown in figure 22. Figure 23 is a plot of the Raman spectra obtained from this region of this sample. By comparing the peak positions with those of monolayer, bilayer, and bulk MoS_2, I find that the triangles growing in the regions surrounding the crucible walls are monolayer and bilayer MoS_2. The areal coverage of MoS_2 triangles was higher than the coverages typically observed in my one-step growth experiments. I find that the number density of MoO_3 mounds is comparable to that of the MoS_2 triangles based upon which, I speculate that each of the MoO_3 mounds transforms into one MoS_2 triangle. Moreover, the non-MoS_2 structures, commonly observed in the one-step CVD

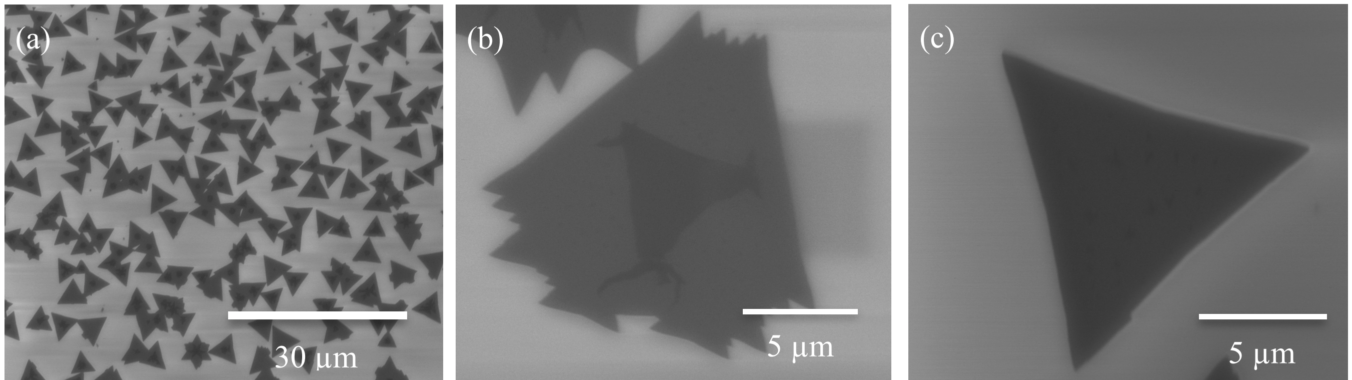


Figure 22. Representative SEM images obtained from a SiO_2/Si sample after sulfurization of MoO_3-covered substrate with 80 mg sulfur at 850 °C under 200 Torr. (a) Highly dense arrays of MoS_2 triangles distributed evenly along and around the edges that are in contact with the crucible walls. (b) and (c) Higher magnification images of few-layered MoS_2 islands with facetted edges.

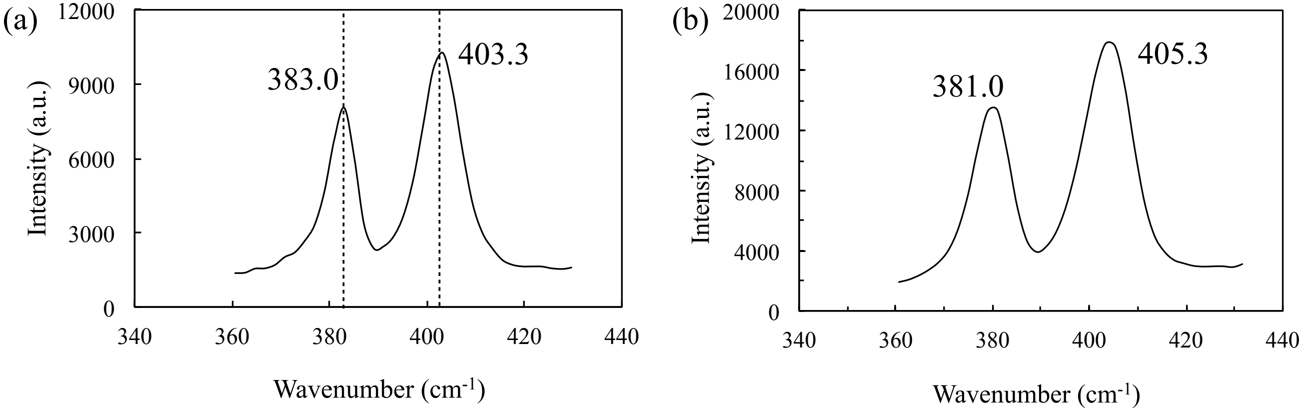


Figure 23. Raman spectra obtained from a SiO_2/Si sample same as from figure 22. (a) Monolayer MoS_2 triangle from the region in figure 22(c). The dotted lines represent the peak positions for monolayer MoS_2. (b) 2 monolayers MoS_2 triangle from the region in figure 22(b).

process, are virtually non-existent in this two-step growth approach. Away from the edges, near the center of the sample, I obtained thick MoS_2 (> 5 layers) islands (see figure 24). Figure 25(a) shows Raman spectra obtained from the regions near the center of the sample. The peak positions are comparable to those expected for bulk MoS_2, indicating that the layers are thick (> 5 layers). Raman spectra (see figure 25(b)) obtained from the regions inside the crucible reveal the formation of multi-layered MoS_2 (2~5 layers). This result is in striking contrast with the non-MoS_2 structures (and partially sulfurized features) that I typically observe at the center parts of the samples grown using one-step process. All of these results are very encouraging and the two-step approach seems to be a promising route to grow high-quality layered MoS_2 over large areas.

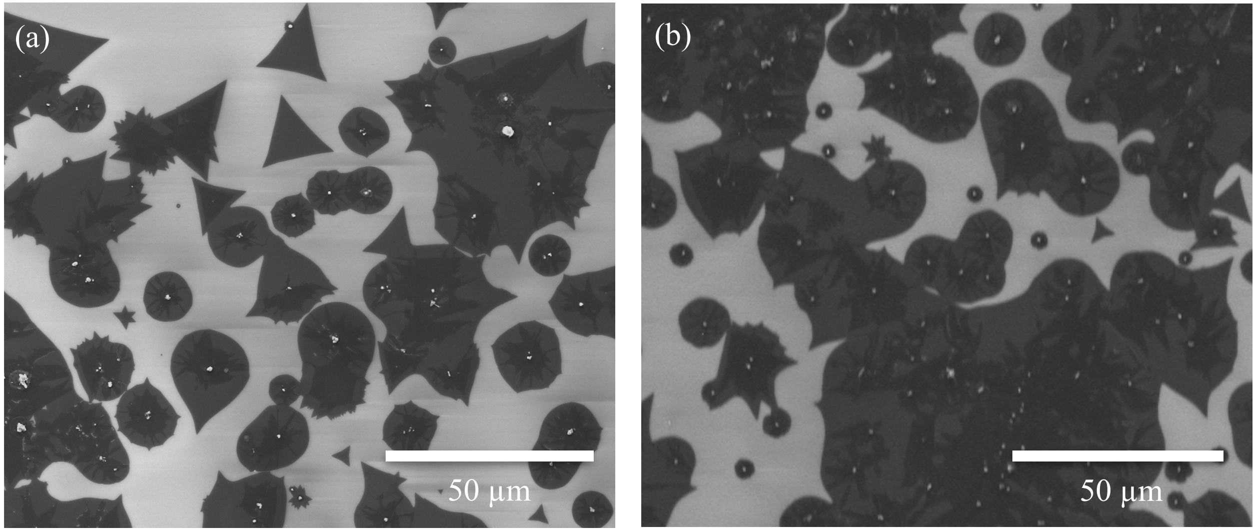


Figure 24. SEM images obtained from the same sample as in figure 22. (a) and (b) Morphologies of multi-layered MoS_2 islands obtained at regions (a) inside the crucible walls and (b) closer to the center of the crucible.

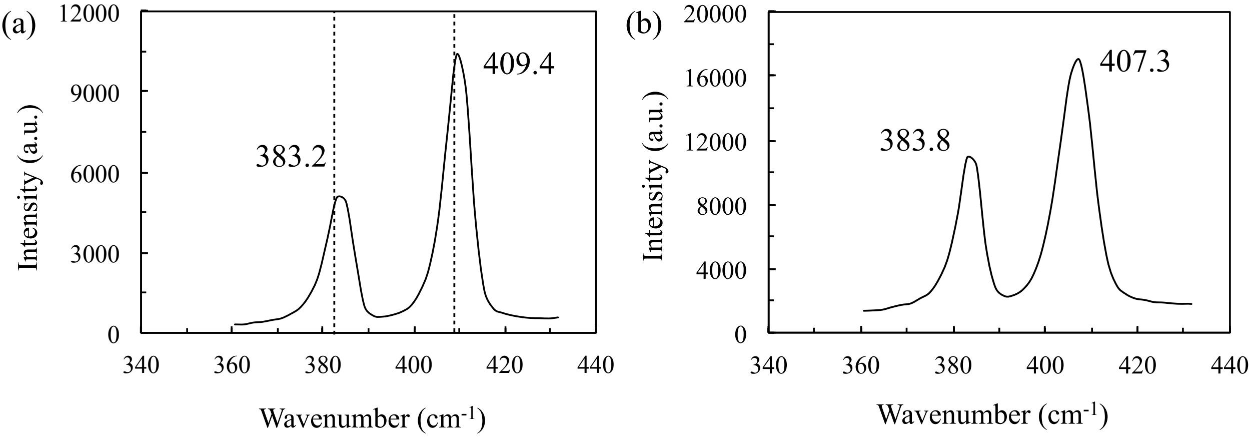


Figure 25. Raman spectra obtained from a SiO2/Si sample same as from figure 24. (a) Bulk MoS_2 from the region in figure 24(b). The dotted lines represent the peak positions for bulk MoS_2. (b) 4 monolayers MoS_2 from the region in figure 24(a).

In order to make sure that the observed MoS_2 triangles are indeed monolayers, I have also used AFM and determined the surface heights of the triangles. Figure 26 shows AFM images and surface height profiles obtained from a typical triangle-shaped MoS_2 island observed on a SiO_2/Si sample grown using the conditions presented in figure 22. Figure 26(a) shows the surface topography of the island with darker and brighter contrasts corresponding to lower and higher surface heights with respect to the background. At the center of this triangle, there is a smaller triangle rotated 180 degrees with respect to the bottom island. This particular island image was obtained from a sample that has been air exposed for over 120 days. The bright white features, ~3-5 nm tall (see figure 26(b)), decorating the step edges of the first and the second layers are likely to be surface oxides formed post-growth upon air exposure. I would like to point out that these are nanometer-scale islands, which were not visible in my SEM images shown earlier. Figure 26(c) and (d) shows surface height profiles of the first and the second layers obtained, respectively along the yellow and red lines shown in figure 26(a). I measure surface heights of 0.61 ± 0.07 nm and 0.74 ± 0.07 nm for the first and the second layers, respectively. In comparison, the expected interlayer spacing in MoS_2 is 0.65 nm. Given the large uncertainties (0.07 nm, whichever is larger) in AFM measurements, I conclude that this particular island is monolayer thick with a second layer situated on top of it. The AFM measurement provides further evidence that the larger MoS_2 triangles seen in SEM images are monolayer thick with smaller bilayers on top of a few of the islands.

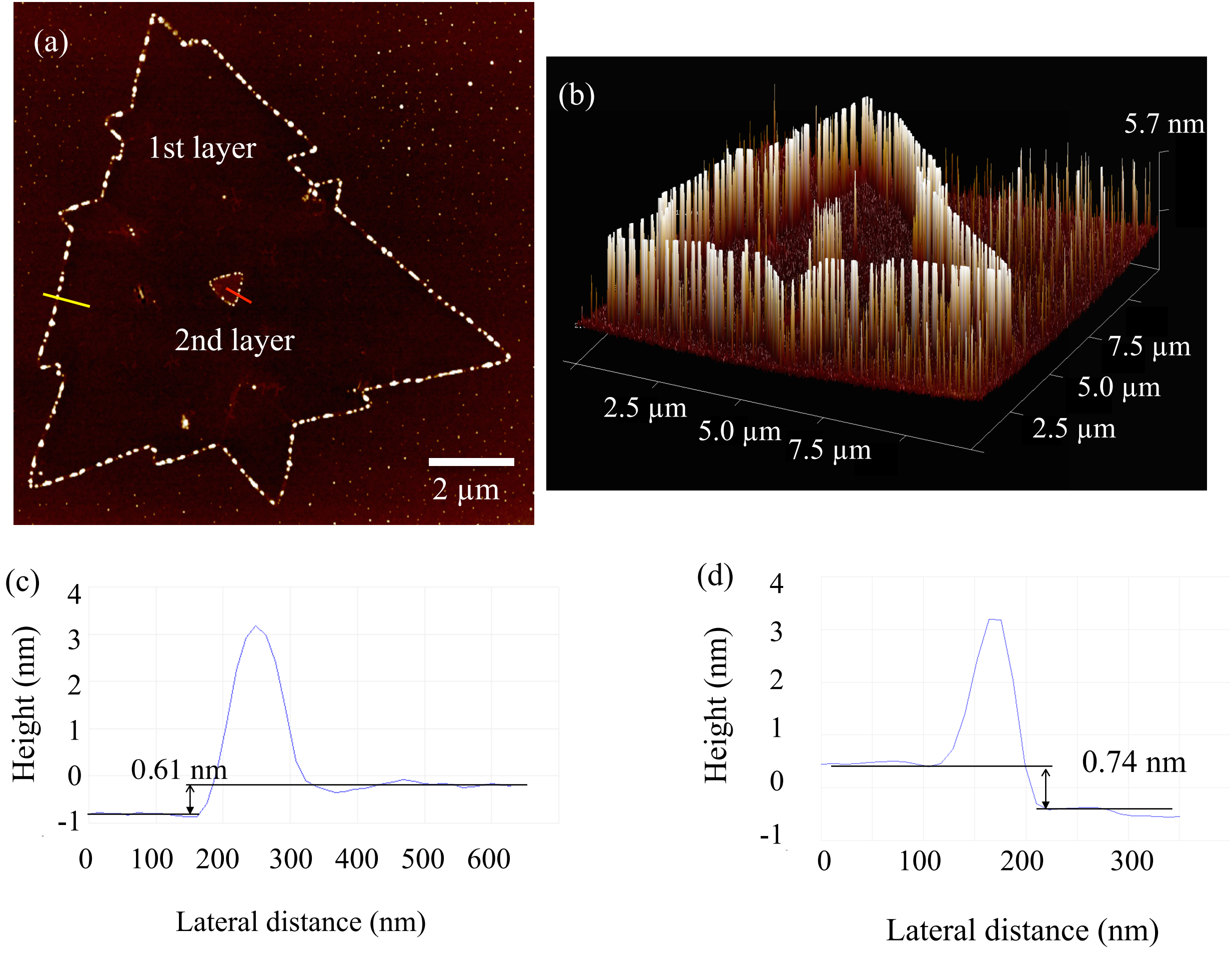


Figure 26. (a) Typical AFM image (12 x 12 µm^2) of a triangular MoS_2 island obtained from a sample shown in figure 22. The brighter and darker contrasts in the image are indicative of higher and lower surface heights. A smaller triangle is observed at the center of this island. (b) 3D perspective image of the island shown in (a). (c) and (d) Surface height profiles obtained along the yellow and red lines shown in (a).

3.6 Discussion

In the previous sections, I have presented a summary of my results obtained from a series of growth experiments carried out as a function of different deposition parameters. Through the low (0.09 Torr) and high pressures (> 300 Torr) experiments, I conclude that 2D layered MoS_2 grows better at higher pressure (> 300 Torr) in my CVD system. These results indicate that a low-pressure environment does not provide sufficient MoO_3 and/or S vapor fluxes required for the growth of MoS_2 layers. I attribute this result to the geometry of my CVD reactor, in which the residence times for the precursors is probably lower at lower pressures and limits the time available for condensation and reaction of the precursors on the growth substrate.

At a given pressure (for example, 300 Torr or higher), I found that higher temperatures (~ 850 °C) is desirable for the growth of layered MoS_2. At lower temperatures (700 °C), the oxide to sulfide transformation was not complete and the samples typically non-layered morphologies and partially sulfurized structures. I attribute these results to a combination of: 1) slower rates of MoO_3 --> MoS_2 conversion and 2) lower rate of MoO_3 desorption from the substrate surface at lower temperatures.

I have successfully demonstrated the growth of layered 2D MoS_2 islands using the one-step CVD process, where the precursors MoO_3 and S are simultaneously introduced, allowed to react, and form MoS_2. In my CVD reactor, I achieved the best results using high pressures (> 300 Torr), high temperatures (~ 850 °C), and high S/MoO_3 precursor ratios. However, I have not been able to completely eliminate the presence of non-MoS_2 (oxides and oxysulfides) on the surface. I attribute this result to limited control over the partial pressures of the precursors in my system. For example, as I mentioned earlier, the temperatures of the substrate and the MoO_3

source are controlled by the same heater and hence the MoO_3 vapor flux increases with increasing substrate temperature. In order to overcome this limitation, I developed a two-step CVD process, where I first deposit MoO_3 and then expose the sample to sulfur vapor. With only MoO_3 in the reactor in the first step, it is easier to control the thickness and uniformity of MoO_3 deposited on the sample, which in turn control the quality of MoS_2. This two-step growth method looks promising; however, there are still a few challenges. The coverage of MoS_2 is not uniform across the sample; monolayer and bilayer thick MoS_2 islands are obtained along the edges of the crucible while thicker films are found at the center of the sample. These thickness variations are likely due to the shape of the crucible which makes the precursors accumulate near the center part of sample. Additional experiments and detailed characterization of the sample before and after the growths of both MoO_3 and MoS_2 are necessary to determine the role of MoO_3 thickness on the final MoS_2 layer thickness and to determine the factors influencing the thickness uniformity across the sample.

Chapter 4: Conclusion

As mentioned in Chapter 1, monolayer MoS_2 and other two-dimensional layered dichalcogenides have lots of promising applications. All these applications require high quality (phase-pure, stoichiometric, defect-free, and preferably single-domain) monolayer MoS_2. In this work, I investigated the growth of monolayer MoS_2 on SiO_2/Si substrate by chemical vapor deposition. Using MoO_3 and sulfur as the precursors for the CVD of MoS_2 has many benefits as I mentioned in Chapter 2. As part of my thesis, I carried out several growth experiments while varying the deposition parameters such as reactor temperature, reactor pressure, and the starting amount of precursors. The as-grown samples are characterized using optical, scanning electron, and atomic force microscopies and Raman spectroscopy. The results are presented in Chapter 3.

In my experiments, I found that the optimal substrate temperature for the growth of the layered MoS_2 in my system is at 850 °C. At temperatures below 700 °C, I did not observe any MoS_2 growth. Additionally, the pressure in the reactor should be at least 300 Torr to grow monolayer MoS_2. Among all the experiments that I conducted at different temperatures using different amounts of precursors, I have routinely observed MoS_2 growth only at pressures > 300 Torr. Below this value, I obtained non-stoichiometric oxysulfides (MoO_xS_{2-x}). Based upon my studies, I conclude that higher pressure (300 - 700 Torr) is necessary for layered MoS_2 growth.

I have also developed a two-step approach to grow MoS_2 layers. The idea is to deposit MoO_3 of uniform thickness onto SiO_2/Si substrate first and ensure there is no excess MoO_3 in the reactor. Then, I introduce sulfur vapor into the reactor by evaporating the sulfur powder and sulfurize the MoO_3 into MoS_2. With this approach I can control the thickness of MoO_3 and hence MoS_2 film more precisely. Moreover, the sulfurization of MoO_3 into MoS_2 is more complete

based on my experiment results. I have been able to grow MoS_2 over the entire SiO_2/Si substrate. However, additional work is necessary to achieve thickness uniformity over the entire substrate.

The growth temperature in the two-step approach may not be as high as in conventional CVD (850 °C). And, in principle, one can use this two-step approach and grow large-area MoS_2 on SiO_2/Si substrate. However, the fraction of single layer MoS_2 on the substrate still requires improvement. However, additional studies are required to determine the optimal deposition parameters and to demonstrate the large-area growth of high-quality MoS_2 layers of desired thickness. In this regard, I have outlined a few possible future experiments with this new two-step approach. One of the critical factors affecting the MoS_2 layer quality (both thickness and thickness variation across the sample) is the MoO_3 layer thickness and uniformity. The temperature of the MoO_3 source and the substrate and the deposition time all influence the thickness of the MoO_3 thin film. In the second step, probably the important parameters that affect the composition and crystallinity of MoS_2 layers are the sulfur flux and the substrate temperature. I believe that it is possible to grow large-area monolayer MoS_2 in the near future by tuning the thickness of MoO_3 in the first step and the sulfurization temperature during the second step.

Other than growing large area monolayer MoS_2, we can also try to grow lateral and/or vertical heterostructures with different types of 2D layered materials such as graphene, $MoSe_2$, or WSe_2. The bandgap difference between these 2D materials offers the possibility to create devices with various functionalities. However, this is not a straight-forward task, for example, to grow MoS_2 on graphene. Chemical interactions between MoS_2 and graphene may need to be suppressed to avoid formation of any interfacial compounds. Growth of one chalcogenide over another, as in

$MoSe_2$ or WS_2 on top of MoS_2, may also be challenging due to intermixing across the interfaces. Growing transition-metal dichalcogenide alloys is another area of research interest. These layers have similar lattice constants (MoS_2: 3.11 Å, $MoSe_2$: 3.24 Å, WS_2: 3.13 Å); therefore, it is possible to grow substitutional alloys. The optical and electrical properties of these band-gap tunable TMDC alloys allow us to use in future device applications. In conclusion, the future is bright for these two-dimensional layered materials, especially the transition-metal dichalcogenides, which offer a great variety of properties. The recent advances in the development of new device architectures catered to take advantage of the two-dimensional geometries of these material can lead to potentially new applications.

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