Julian Lopez is a first-generation Latino student and OUS Scholar at Colgate University, a current junior, and will graduate in the spring of 2023. He is planning on obtaining a bachelor's degree in physics from Colgate University and participating in a Pre-Engineering program that will allow him to obtain a bachelor's degree in engineering at Washington University. Julian's future goal is to become a Mechanical Engineer and help his community through. The research for this paper was done through a Research Experience for Undergraduates (REU) program in association with the University of Memphis. Activities that Julian enjoys are playing volleyball, attending Physics Club, and leading the student population at his university through outdoor activities including mountain biking, ice-climbing, and kayaking.

Julian I Lopez

High-quality Few-layered MoS2 Thin Films through Plasma-enhanced CVD

Faculty Sponsor

Dr. Shawn Pollard

Abstract

As a 2D material, Molybdenum disulfide (MoS2) has been attracting attention due to its electrical, optical, mechanical, and possible magnetic properties that can be used in a wide variety of applications. However, precise control of monolayer thickness and high-quality growth is still a huge challenge with multiple methods. In this paper, we have successfully grown predominately few-layered MoS2 on nearly lattice-matching muscovite mica by using a plasma-enhanced low-pressure chemical vapor deposition (PELPCVD) method. The approach presented here synthesizes films in 15 minutes using sulfur powder (S) and molybdenum trioxide powders (MoO3) as precursors. Deposition utilizes a nonthermal plasma reactor and temperatures ranging from 500 °C to 600°C. Thin film growth characteristics and nucleation are studied as a function of argon flow rate, plasma, and temperature using SEM, AFM, XRD and Raman spectroscopy.

Introduction

Recently, ultrathin two-dimensional (2D) layered materials have captivated the nanoelectronic, spintronic, and valleytronic scene because of their availability to a wide variety of applications. The electrical, mechanical, optical, and magnetic characteristics of these materials are the epicenter of the attracted attention because of their dependence on overall structure and thickness [1]. This dependence on structure and thickness also constitutes them to be transition-metal dichalcogenides (TMDCs). With respect to structure, these atomically thin materials have adjacent layers that are subject to van der Waals (vdW) forces that hold them together [2].

Aligning with this research, molybdenum disulfide (MoS2) has extraordinary properties including a tunable bandgap, high tensile strength, thermal stability, and extreme flexibility that would make them the perfect candidate for devices such as photodetectors, solar cells, and light-emitting diodes [3]. The flexibility aspect of this material is mirrored with mica that not only has continuous flexibility itself but also has a lattice structure well-suited for the growth of few-layer MoS2 growth on the surface. Specifically, muscovite mica, which is used in this research, has a lattice constant in the (001) plane of 0.5199 nm. In comparison to MoS2, the lattice constant, a, is 0.3161 nm. The lattice constant of mica closely approximates $\sqrt{3}$ a, which equals to 0.5475 nm, with an approximate -5% lattice mismatch with MoS2 [4]. This means that an approximately 30-degree rotation of the MoS2 2 lattice leads to a commensurate structure with the mica substrate and promotes epitaxial growth. There are various other forms of mica that would provide a high-quality match; however, the cost outweighs the more favorable comparability which could limit their use in applications. For example, fluorophlogopite mica has a lattice constant of 0.5309 nm, a 2% better match than muscovite mica, but has a market price of 4-5 times higher. Apart from the previously mentioned devices, MoS2 on mica could also be used for technology where flexibility is key.

The electronic sphere continues to grow and the ultimate desire to create smaller, faster technology exponentially increases. This continual process of betterment is the primary rationale as to why these 2D materials are so important for the advancement of technology. The successful growth and creation of these materials with fascinating characteristics can lead to new generational multifunctional electronic and spintronic devices. A crucial progression in digital-analog applications is advancing the functional integration of electronics and logic circuits, which could easily be solved using ultrathin 2D materials [1].

Most of the materials that are already being used as 2D semiconductors and other devices were produced with the mechanical exfoliation method. This method results in poor control of thickness and domain size, which leads to restrictions in fundamental characteristic examination [1]. The size and quality of the materials produced in this manner are a cause of concern for the applications that they may be used for. Regarding this issue, chemical vapor deposition (CVD) is the perfect substitution because it provides a controllable way to grow high-quality and large-area 2D materials [5]. Specifically, low-pressure CVD (LPCVD) produces a dramatic increase in uniform growth rate and reduces overall auto-doping, which is the introduction of volatile impurities into the epitaxial layer that originate from the substrate [6]. In addition to LPCVD, the introduction of a plasma-enhanced variation (PELPCVD) is used to decrease the required growth temperature and time period of these 2D few-layered materials. The use of PELPCVD has the advantage of a higher deposition rate, which stated before, decreases the growth time of these materials, thereby saving time and decreasing the amount of resources used and wasted.

Qingqing Ji, Yanfeng Zhang, Teng Gao, and others took in account some of the methods described above to research thin films of MoS2 in Epitaxial Monolayer MoS2 on Mica with Novel Photoluminescence [4]. With a procedure very similar to the one discussed in this paper, the researchers were able to grow monolayered MoS2. Two of the major differences between theirs and our methods is the use of fluorophlogopite mica in the paper mentioned above and the implementation of enhanced plasma in this paper. Ji et al. grew these monolayered MoS2 on mica through LPCVD with typical growth conditions being "pressure of 30 Pa, carrier gas flow rate of 50 sccm, growth temperature of 530 °C and growth time of 30-60 min" [4]. The result was full coverage of monolayer MoS2 on mica with distinct triangles that correspond to monolayer MoS2. This research team experienced full monolayer growth around the center of their substrate and sub monolayer growth as the edge was reached, i.e., distinct triangles. These results were very similar to the ones achieved in this paper. However, I was able to improve upon the methods described by including the implementation of plasma and the use of lower-cost mica.

To understand the influence of growth conditions on the quality and uniformity of MoS2 grown on Muscovite mica using PELPCVD, various parameters, i.e., growth temperature, carrier gas flow rate, and plasma power, were systematically modified and the quality of the grown films was evaluated utilizing a variety of materials characterization techniques. The purpose of this research is to understand the dependence of MoS2 growth on the given

parameters and the impact they have on the consistent geometric shape and size configurations grown on the surface that indicate high-quality growth, i.e., triangular, and hexagonal formations.

Methods

Experimental Section

The molybdenum disulfide (MoS2) thin films were synthesized via an PELPCVD process. The thin films grown within this experiment consisted of molybdenum trioxide powders (MoO3) (99.5% Sigma Aldrich) as the molybdenum source, and sulfur powders (S) (99.5% Alfa Aesar). To initiate the growing process, MoO3 and S powders were loaded into two separate alumina combustion boats positioned at the center of the left section of a dual-temperature-zone tube furnace and the edge of the hot zone upstream, respectively. A freshly cleaved piece of muscovite mica (Grade V2 Ted Pella Inc.) was loaded directly above the MoO3 boat face down. Before the film grows, the inside of the tube furnace would be put into a vacuum by turning on a pump downstream from the precursors. In addition, the tube furnace would be purged with nitrogen to replace impurities that could influence growth. Then, the temperature of the MoO3 was increased to a series of temperatures ranging from 500° C to 600° C while the sulfur was placed just outside of the hot zone at 180° - 200° C. The argon gas flowing downstream varied from 30 to 150 sccm and was maintained for 15 minutes of growth time with the plasma turned on at 100 W. There were some samples that did not have the implementation of the plasma to establish a baseline for comparison. Finally, the furnace was naturally cooled down to room temperature. Figure 1 shows a schematic of the process used in this work.

Characterization Section

The as-prepared MoS2 thin films were analyzed by SEM (Hitachi, S-4700) with a range of magnification from 10x to 20x, XRD (Bruker, D8 Advance), Raman spectroscopy (Thermo Scientific, DXR, excitation wavelength of 532 nm) with a collection time ranging from 1 to 5 minutes, and AFM (Nanosurf CoreAFM) under ambient conditions. The thin films were also coated with 1-2 nm of Gold (Au) to prevent major drifting in instruments mentioned above.

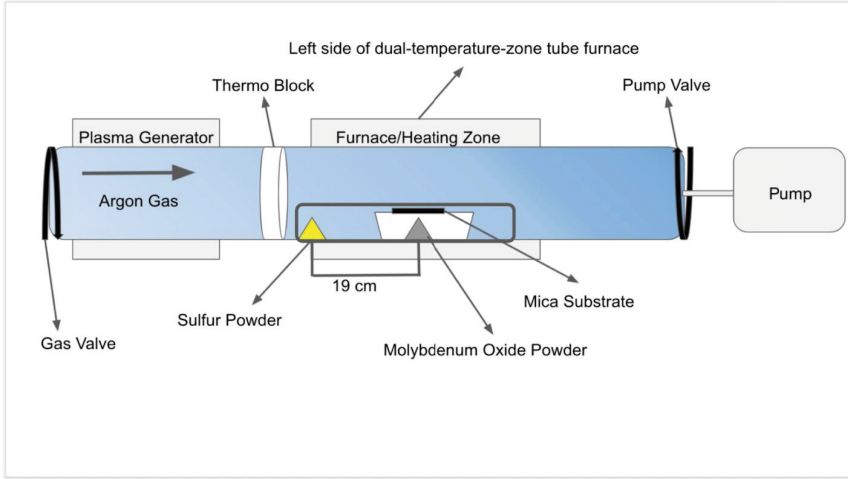


Figure 1. Schematic illustration of a CVD setup for the synthesis of ultrathin MoS2 flakes on mica on S powder and MoO3 powder as the co-evaporation sources.

Results and Discussion

van der Waal's Structure of Gexagonal MoS2

The typical process of creating Hexagonal MoS_2 through this form of CVD method is that MoO_3 is partially reduced by sulfur vapor, creating a volatile MoO_{3-x} series which is carried downstream by Ar carrier gas. It is then absorbed on mica, slowly diffuses on the surface, and reacts with sulfur to rearrange into MoS_2 layers [4].

$$S_2 + MoO_{3-x} \rightarrow MoS_2 + SO_2 \text{ [4]}$$

Figure 2 below illustrates the typical crystal structure of 2H-MoS2 through various frames of reference including a top view, a perspective view, and side views. MoS2's crystal structure consists of a hexagonal plane of S atoms on either side of a hexagonal plane of Mo atoms. These triple planes stack on top of each other, with weak van der Waal forces holding the Mo and S layers together, which is a commonality within TMDC's. These three planes form a monolayer of MoS2, which can be found in three different phases but mainly the 2H-MoS2 and 3R-MoS2 phases, where the "H" and the "R" indicate hexagonal and rhombohedral symmetry, respectively [7].

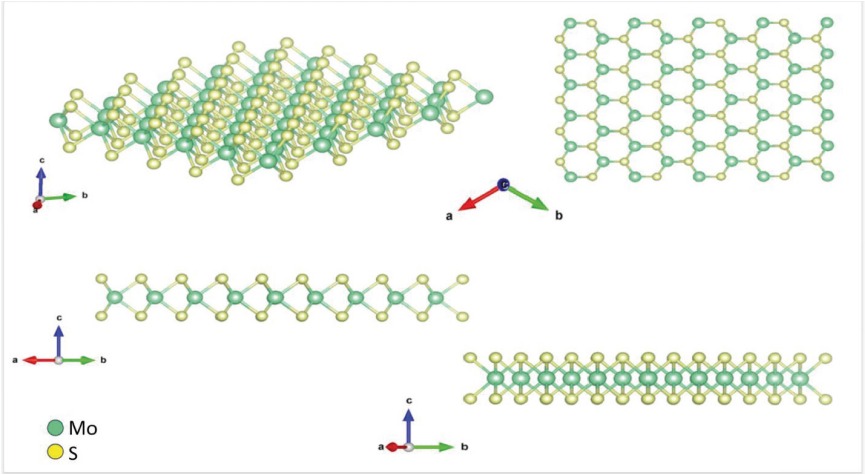


Figure 2. Structural models: perspective view, top view, and side views of the crystal structure of MoS_2.

Identification of Gexagonal MoS2

X-ray diffraction (XRD) analysis was carried out to determine the overall crystal structure of the synthesized material on the mica substrate and validate that the growth was what I desired to create: MoS2. As shown in Figure 3, the two prominent peaks of (002) and (105) were indexed to the crystal plane of 2H-MoS2, confirming that the desired growth was completed. Of the various samples that were created and examined, the position of the scattering angles rarely varied from MoS2, but frequently showed signs of other peaks as well including some MoO3 growth. As I was able to better synthesize high-quality thin-layered MoS2, the signs of MoO3 decreased but still never disappeared. The larger repeated peaks that can be seen throughout the Figure 3 are typical peaks related to the substrate mica. These repeated peaks of mica and two prominent peaks of MoO3 are highlighted in Figure 4.

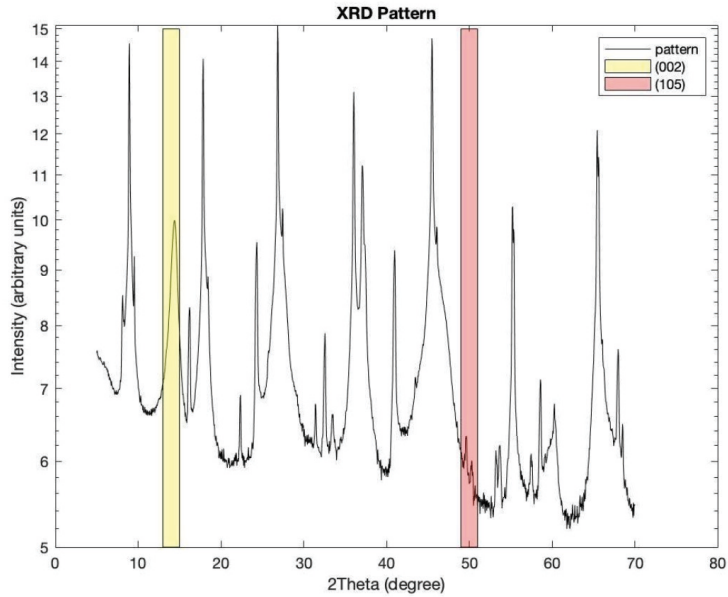


Figure 3. XRD pattern for MoS2 sample and highlighting of prominent diffraction peaks: (002) and (105).

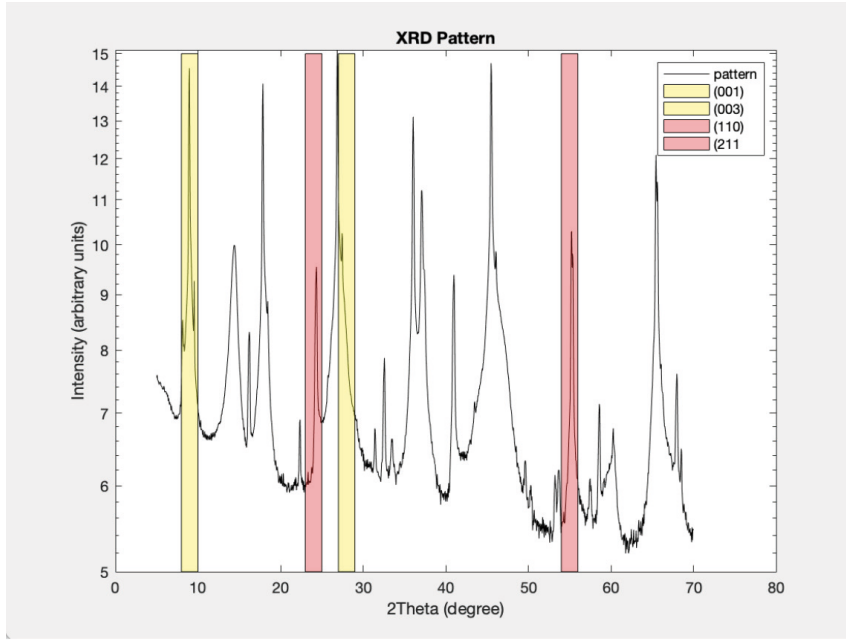
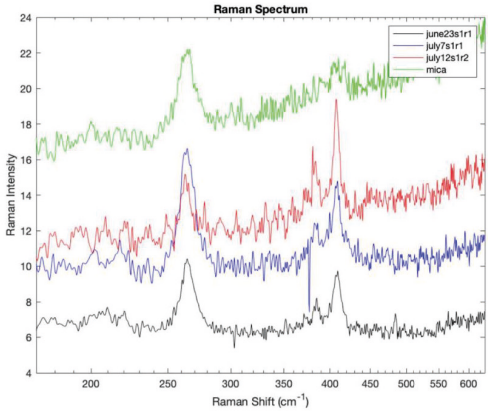


Figure 4. Same sample of MoS2 but highlighting the XRD pattern of MoO3 (red) and muscovite mica (yellow)

In addition to the use of XRD, Raman spectroscopy was also utilized to characterize the synthesized material. The ~384.0 cm-1 peak corresponding to the in-plane E2g mode and the peak at ~408.0 cm-1 in line with the out-of-plane A1g mode that characterizes MoS2 can clearly be seen in the Raman spectral mapping in Figure 5. As I was able to better synthesize high-quality MoS2, the Raman intensities associated with these two peaks increased. In addition to the location of these two peaks, the frequency difference of ~24 cm-1 between the E2g and A1g modes is also consistent with a two-dimensional MoS2 thin film [8]. A Raman spectral mapping of mica was also included within the graph to contrast the MoS2 shift from the mica shift within the examined sample.



Growth Conditions of samples

1. June23s1r1
   a. 650°C, 50 SCCM, Sulfur (60 mg) & MoO3 (5 mg)
2. July7s1r1
   a. 550°C, 30 SCCM, Sulfur (120 mg) & MoO3 (5 mg)
3. July12s1r2
   a. 525°C, 30 SCCM Sulfur (120 mg) & MoO3 (5 mg)

Figure 5. Raman spectra of MoS2 thin films and Raman spectrum of mica substrate.

Atomic Resolution Study of Hexagonal MoS2

The scanning electron microscope (SEM) was implemented to produce images and examine the surface topography and composition of the synthesized MoS2 on mica substrates. To verify that the growth of MoS2 was high-quality, I searched for epitaxial and uniform growth of triangular and hexagonal geometric shapes. Within the search for these geometric shapes, I was able to identify three different areas that constitute the samples, i.e., Thick Region, Center Region, and Thin Region. The Thick Region was directly above the MoO3 precursor and comprised numerous layers of thick MoS2 that were in various shapes such as nanosheets and tubes. Within this region it was difficult to clearly identify the individual shapes, and as a result, this region was not considered further in this study. The Center Region varied from the various series of temperatures that were conducted.

Some samples were very similar to the Thick Region, while others had clear geometric shapes. Geometric shapes were consistently found in the Thin Region. However, these shapes decreased in size as the edge reached. Figure 6 shows representative images of the various regions.

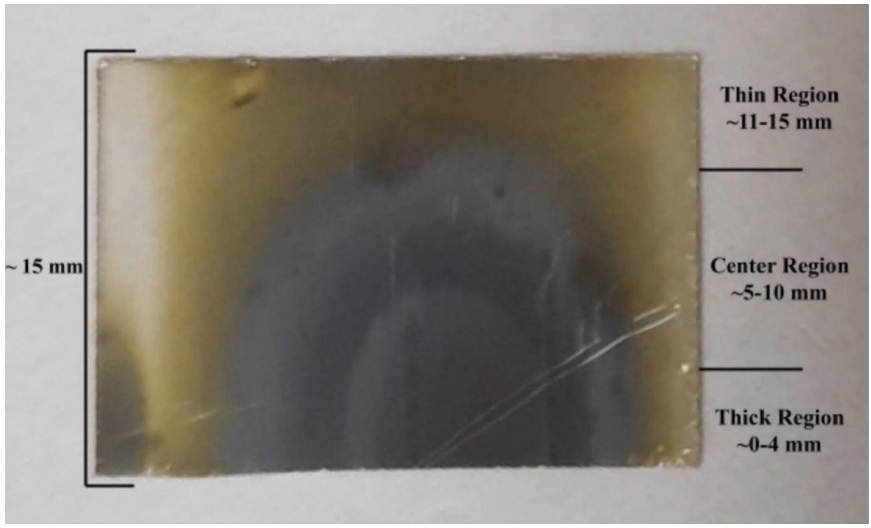


Figure 6. Illustration showing the three separate regions and their ranges within a sample that exhibit different growths.mica substrate.

After gathering images and data from the various series ranging from 500º to 600º and 30 to 150 sccm, I was able to determine the relationship between edge length, temperature, and the use of plasma. The edge length of MoS2 has an inverse proportion to the growth temperature, and gradually decreases with the increase of growth temperature. Figure 7 clearly shows that the longer edge lengths are associated with lower temperature and decrease in size as the temperature increases to 600º. In addition, it can clearly be seen in Figure 6 that the use of plasma significantly increases the edge length growth. The green, red, and blue plots are MoS2 samples that were synthesized with the use of plasma. The black plot is a MoS2 sample that was synthesized without the use of plasma. The 500º series grown utilizing plasma have an approximate magnitude of five times larger than those that did not.

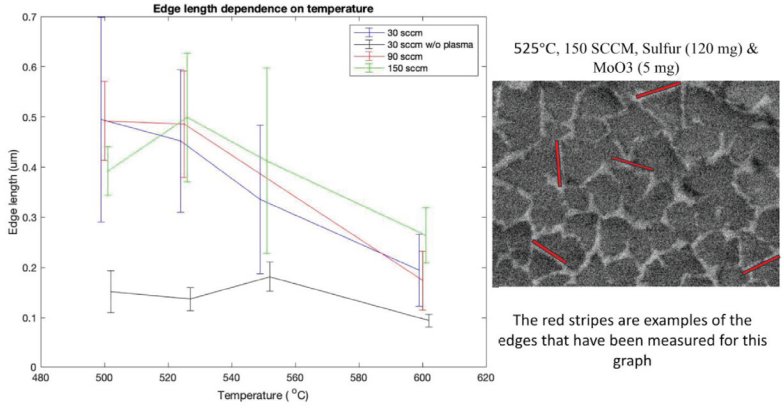


Figure 7. Edge length dependence on temperature and flow rate with standard deviation error bars. Examples of edge length measurements

To illustrate the dependence of high-quality growth on temperature, I held a constant flow rate and varied temperature in Figure 8. As seen in the previous figure, the edge length of these geometric shapes decreases as temperature increases. The 500°C image shows bigger semi-triangular shapes with a low density in the frame. As I increase to 550°C, the size of the geometric shapes decreases, and the density of them increase within the frame. The 600°C image does not have a dramatic decrease in size, but it does contain a huge variety of multilayered growth. While it may have some larger geometric shapes, however, the average size in this frame is smaller than the previous two.

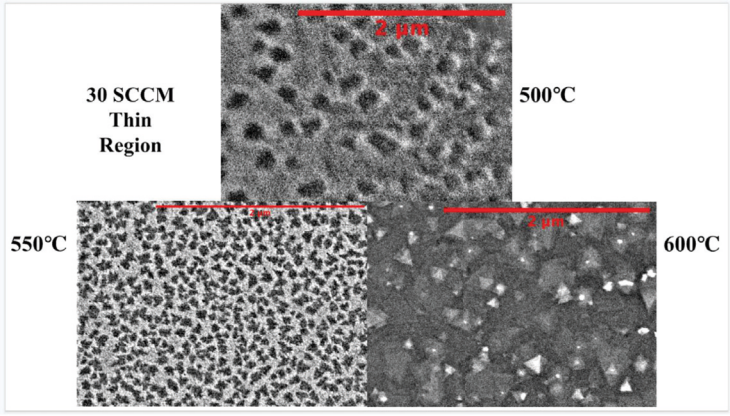


Figure 8 Illustration that presents the thin region of samples grown at ranging temperatures and held at a constant flow rate.

In similarity with growth being dependent on temperature, it is also dependent on the distance from the precursor. As stated before, I noticed that there was a discontinuity of growth within an individual sample. Each sample could be split into three different regions: thick, center and thin. To try and find a relationship between distance from precursor and epitaxial high-quality growth, I imaged the structures found in each region, as shown in Figure 9, at different flow rates but at a constant temperature. Although no clear relationship between the conditions is present, I found a decrease of the thick growth in the Thick Region as the flow rate increased, indicating a more uniform growth process. The triangular structures found within the Thin Region were consistent and almost independent of flow rate, but the center varied too much to find a correlation. In relation to finding geometric shapes that indicate high-quality growth, it seems as if 90 sccm is the more favorable of the three different flow rates.

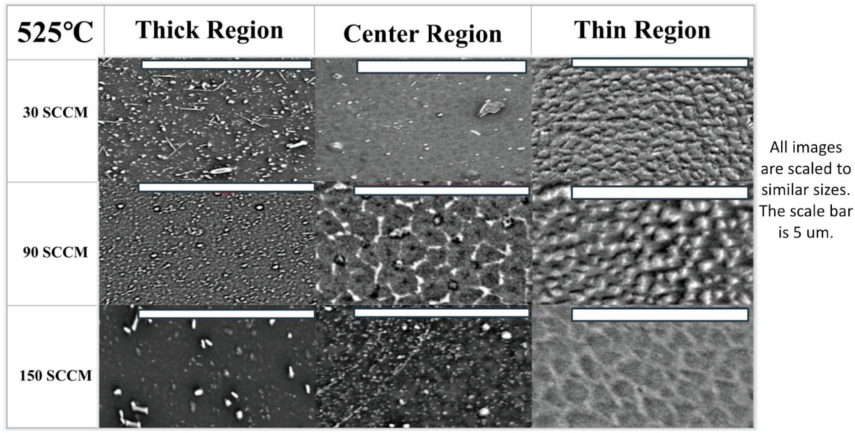


Figure 9. Illustration that presents the three different regions within a sample that were grown at 525° C with various flow rates.

In addition to the use of the SEM, the atomic force microscope (AFM) helped us produce images and examine the surface topography and composition of the synthesized MoS2. Figure 10 is a 5um x 5um AFM image that helped indicate around and sub-nm growth. Growth below a few nanometers is consistent with monolayer growth but can also be associated with few-layer growth. Due to instrument limitations, I was unable to confirm single layer growth.

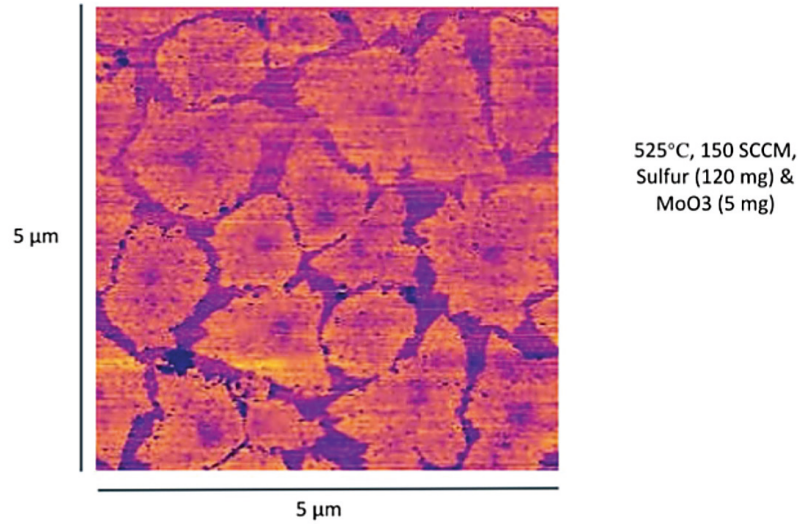


Figure 10. AFM image that shows triangular geometric shapes that indicate high-quality growth

Conclusion

In conclusion, I was able to synthesize high-quality few-layered MoS2 at various conditions. This study has found evidence of high-quality growth in both of my series relating to temperature and flow rate. The temperature series were 500° C, 525° C, 550° C, and 600° C, while the flow rate series was 30 sccm, 90 sccm, and 150 sccm. Through this extensive research, it can be inferred that MoS2 growth is highly sensitive to both temperature and flow rate and that the presence of an argon plasma significantly increased the size of triangular MoS2 domains. The maximum size measured within the samples was approximately 1.69 um. The use of the AFM also helped indicate there was growth below a few nanometers. However, due to instrument limitations, single-layer growth could not be confirmed.

In the future, the space confined method, or more colloquially known as the sandwich method, will most likely be employed. The space confined method was used near the end of this research and also be desirable to determine the lower temperature limit which still yields high-quality growth. Concerning applications, this work may pave the way towards growth of MoS2 on cheap, available flexible substrates, making it a candidate for flexible optoelectronics, LEDs, Photodetectors, Solar Cells, Sensors, and Wearable devices.

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