Optimizing growth conditions for 2D MoS_2

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ABSTRACT

Growth of single and few layers of 2D molybdenum disulfide (MoS_2) through chemical vapor deposition shows sensitivity to a number of parameters. We demonstrate the effects of temperature, pressure, and reaction time by isolating individual variables. Subsequently, we compare growth mechanisms and relate these parameters to layer thickness. We also explore effects of the choice of seeding promoter on growth mode and material quality. Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) yields continuous MoS_2 film and perylene-3,4,9,10-tetracarboxylic potassium salt (PTAS) yield isolated, triangular MoS_2 flakes. Pressure and temperature are complementary in that increasing reaction temperature increases the size of isolated MoS_2 flakes while also increasing layer thickness. Increasing pressure inhibits vertical growth, thus achieving large, monolayer flakes by finding the right balance of temperature and pressure for growth. Holding the furnace temperature at 700^{o}C for 3 minutes at a pressure of 760 torr with a gas flow rate of 200 sccm consistently yields ~10μm 2D isolated MoS_2 flakes.

I. INTRODUCTION

Molybdenum disulfide (MoS_2) is a semiconductive material with potential applications in photovoltaics, small electronics, and splitting water for hydrogen gas production. Bulk MoS_2 is an indirect band gap material, but when a thickness of a single atomic layer is achieved it becomes a direct band gap material.[1] Chemical vapor deposition is a promising method for synthesizing MoS_2 thin films down to a single atomic layer. Vapor deposition presents some difficulties, however, because growth of single layer MoS_2 is sensitive to a number of parameters. This paper will examine the effects of temperature, reaction time, pressure, and choice of seeding promoter on growth mode and quality. Raman and photoluminescence spectroscopy were used to confirm sample species and thickness and atomic force microscopy was used to confirm sample thickness.

II. MATERIALS AND METHODS

A. Materials

Approximately 80 mg of sulfur (Sigma Aldrich 99.998%) placed outside of the heating zone of the tube furnace was used as the sulfur source. We discovered that fresh sulfur should be used in each run for best results. Ammonium heptamolybdate tetrahydrate (Sigma-Aldrich 99%) and molybdenum (VI) oxide (Sigma Aldrich 99.97%) placed either upstream from the growth substrate or directly beneath the growth substrate in a quartz boat were used as the molybdenum source. MoO_3 powder was chosen as the preferred precursor because of contamination issues caused when using AHM. 10-30 mg of MoO_3 powder was used depending on the substrate and its distance from the Mo source. Silicon with a thermal oxide layer ranging in thickness from 100-300 nm and quartz were used as growth substrates.

B. Substrate Preparation

The growths substrate were cleaned by sonication for 5 minutes in acetone, 5 minutes in methanol, and 5 minutes in DI water.[2] After sonication in DI water the substrate was rinsed in a stream of DI water to remove any residual particles. The substrate was then placed in UV ozone cleaner for 10 minutes to remove any hydrocarbons and achieve a hydrophilic surface. Various seeding promoters were applied to the substrate immediately after cleaning and the substrate was set-up in the tube furnace quickly to preserve the integrity of the growth surface. Silicon with a natural oxide layer did not produce significant growth when used with perylene-3,4,9,10-tetracarboxylic potassium salt (PTAS) as a seeding promoter because PTAS requires a very hydrophilic surface. Silicon with a 260 nm thermal oxide layer provided the best contrast for optical characterization. Catellanos-Gomez et al. found that a thermal oxide layer of either 55 nm or 220 nm provided the best contrast for observing MoS_2 monolayers.[3]

C. Tube Furnace Set-Up

Synthesis was performed in a furnace with a quartz tube that measured 2 inches diameter and 4 feet in length. The sulfur precursor was placed approximately 38 centimeters upstream from the growth substrate and outside of the heating zone of the furnace. A heating belt was wrapped around the portion of the quartz tube containing the sulfur. The tube furnace contains three heating zones and zone 2 was used for MoS_2 synthesis. Creating space between the sulfur and the heat source of the furnace allowed for better temperature control of the sulfur, which is heated to 160^{o}C. It takes approximately 8 minutes for the heating belt to reach 160^{o}C, at which point the furnace is at a temperature of approximately 660^{o}C. The tube furnace is programmed to ramp up temperature at 20^{o}C/min until it reaches the desired temperature, then hold at that temperature for a specified amount of time before rapidly cooling (see Appendix A Figure A1). The quartz boat containing the molybdenum precursor and growth substrate was situated with the "front" end of the boat lined up with the upstream edge of zone 2 of the furnace (see Figure 1). Nitrogen was used as the carrier gas. The growth substrate was cut to lengths that allowed the it to rest in the top of the quartz boat approximately 0.5-1.5 cm above the MoO_3 powder (see figure 1). So far isolated flakes have only been produced when the growth substrate is placed directly above the Mo source.

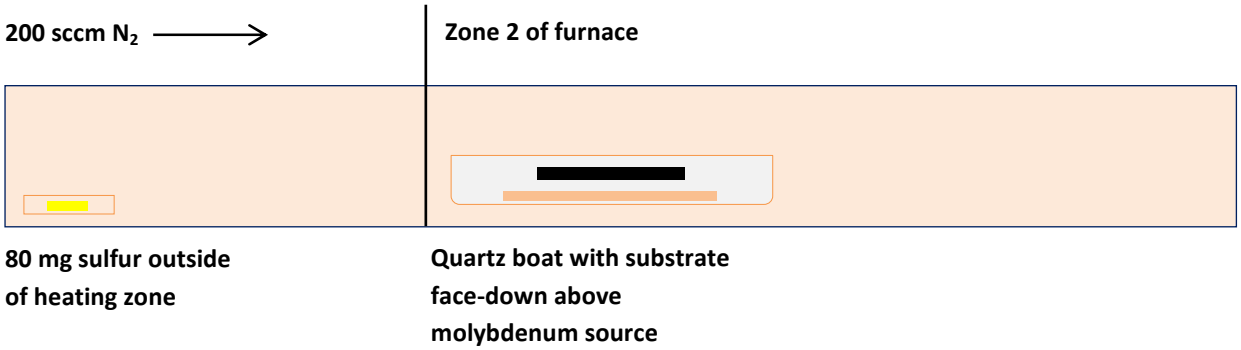

Figure 1. Tube furnace set-up.

D. Temperature, Pressure, and Reaction Time

Changing growth temperature within a 20°C range showed striking effects on isolated MoS_2 flakes. Below 670°C only particles with no distinct geometry were observed. As the temperature was raised to 690°C the growth area of isolated flakes increased, but variations were observed in the growth morphology and overall sample thickness increased with temperature. The temperature of the furnace fluctuated within a 7°C range during the hold time and tended to stay below the temperature set point. It should also be noted that the substrate was situated near the center of the tube, so the temperature at which growth occurred would have been lower than the maximum temperature of the furnace program. These experiments with temperature were performed with a gas flow rate of 200 sccm, pressure of 500 torr and 5 minute hold time. Increasing the pressure to 760 torr in later experiments allowed us to increase the growth temperature to 700°C which improved crystal size while minimizing vertical growth.

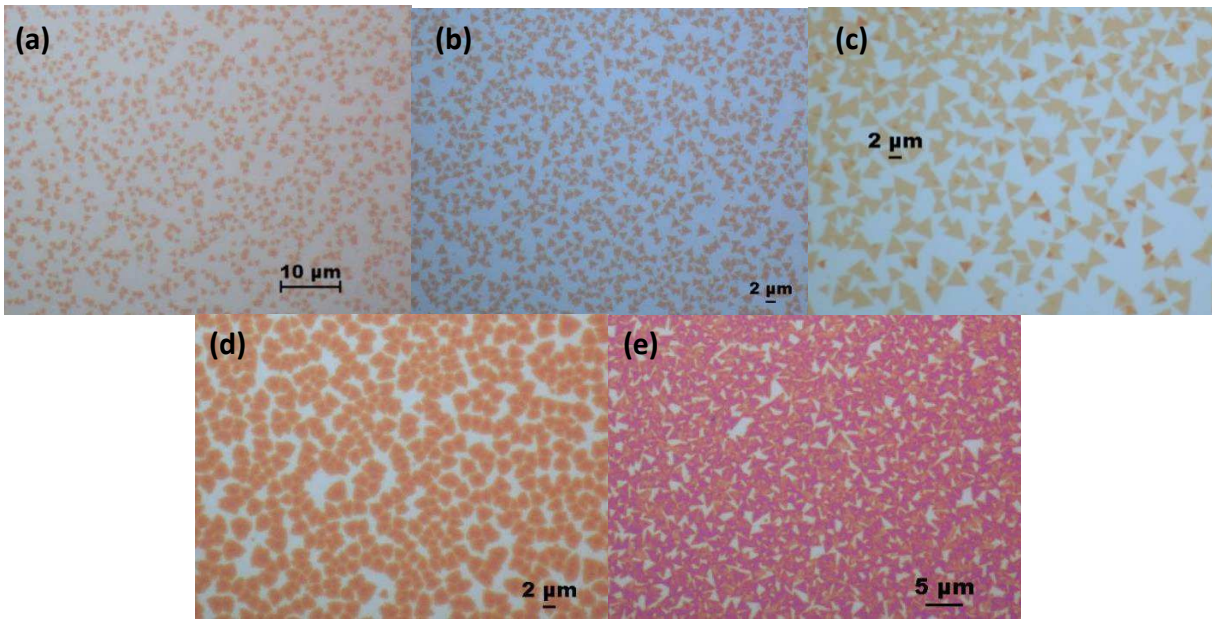

Figure 2. MoS_2 Isolated Flakes Synthesized at Various Temperatures at 200 sccm gas flow rate and 500 torr pressure. (a) 670° C. (b) 680° C. (c-e) Different areas of growth substrate at 690° C. (c) Monolayer flakes. (d) Rounded triangular flakes. (e) Overlapping asymmetrical triangles.

Lateral growth of isolated MoS_2 flakes increased with temperature to a point, but at a cost of increasing layer thickness. Increasing the pressure under which the reaction took place inhibited vertical growth with little costs to the size of isolated flakes. Pressure experiments were conducted with a 3 minute hold time at 700°C and 200 sccm gas flow rate. Pressures of 630 and 680 torr yielded large areas of continuous growth with stacked triangular layers. At 760 torr MoS_2 crystals were more discreet with 1-3 layer thickness.

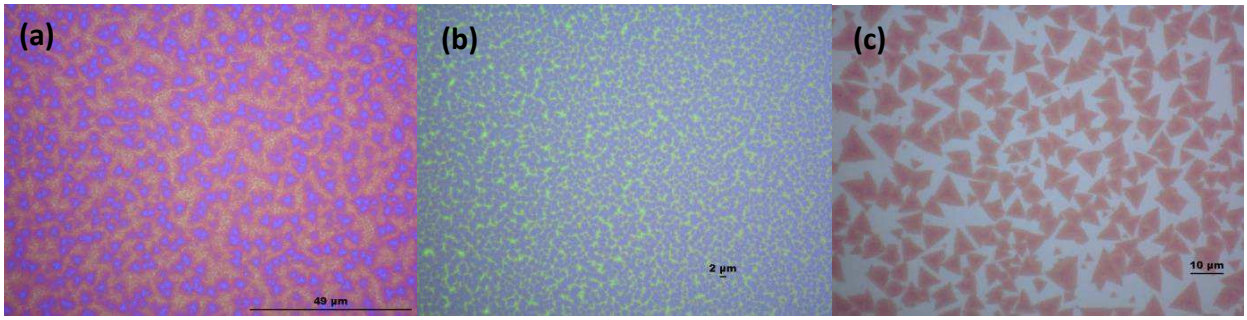

Figure 3. Optical images comparing pressure settings. (a) 630 torr. (b) 680 torr. (c) 760 torr.

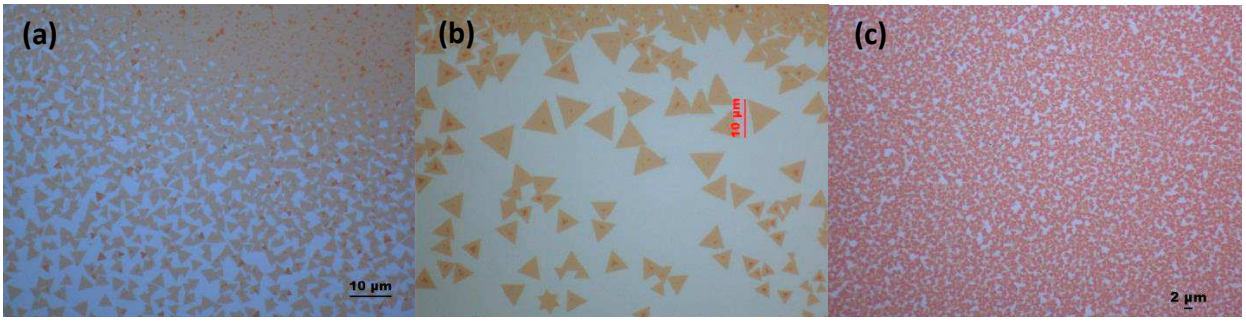

Figure 4. Optical images comparing maximum reaction temperature hold time. (a) 5 minutes. (b) 3 minutes. (c) 2 minutes.

E. Effects of Seeding Promoter

Two seeding promoters were employed to achieve single or few layer growth. Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) and perylene-3,4,9,10-tetracarboxylic potassium salt (PTAS) are both organic molecules that are believed to increase the surface adhesive force of MoS_2 so that layer growth is achieved.[4] The use of PTCDA as seeding promoter resulted in continuous sheets of MoS_2 with overlapping edges at the boundaries whereas PTAS seeding promoter was used to achieve growth in isolated flakes. Ling et al. also observed this difference in growth morphology when using PTCDA vs. PTAS as seeding promoters.[5] When PTAS was used as seeding promoter we were able to lift the MoS_2 off of the growth substrate using water but this was not the case with PTCDA. This may be due to the solubility of PTAS in water. The PTAS molecule seems to stay between the growth substrate and the MoS_2 as indicated by the presence of potassium in XPS measurements. When the MoS_2 is lifted from the surface with water and transferred to a clean substrate the potassium is removed along with other impurities (see Appendix A Figure A4).

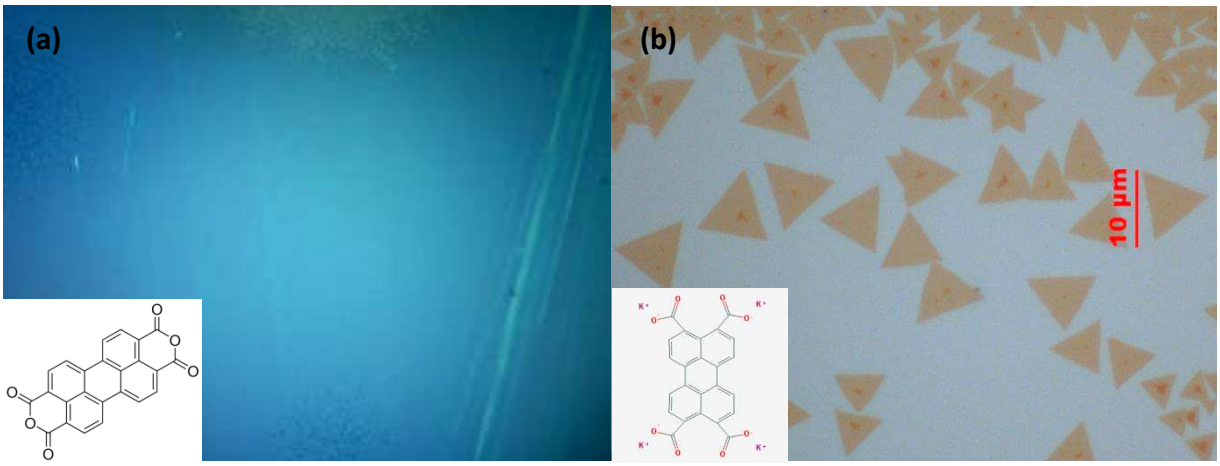

Figure 5. (a) Continuous film MoS_2 on Si with 300 nm thermal oxide layer using PTCDA as seeding promoter with PTCDA molecular shape inlaid. The bright lines are areas of layer overlap as confirmed by AFM. (b) Isolated triangular flakes on Si with 260 nm thermal oxide layer using PTAS as seeding promoter (color white balanced) with molecular structure of PTAS inset.

III. RESULTS & DISCUSSION

A. Raman and Photoluminescence Spectroscopy

The frequency difference between E_{2g}' and A_{1g} Raman modes shows layer dependence.[6] Raman characterization was performed with a 532 nm laser line on as-grown MoS_s on Si/SiO_x substrate with a 260 nm oxide layer. Raman peaks were located at 383 and 404 cm^{-1} with a 21 cm^{-1} frequency difference for what are likely monolayer triangular flakes. This difference grew to 23 cm^{-1} for multilayer triangular flakes and further increased to 26 cm^{-1} in areas of thick, continuous MoS_2 film where the growth morphology is dominated by particles. Photoluminescence measurements taken in the same area revealed a dramatic increase in emission intensity in the monolayer compared to two or more layers. Emission peaks were found at 1.83 eV (677 nm) on Si/SiO_x and 1.84 eV on quartz growth substrate. The choice of growth substrate will affect the position of the emission peak with a noted red shift for MoS_2 grown on silicon with an oxide layer.[7] Doping the MoS_2 to give it more P-type behavior blue shifted the emission peak by 57 meV (see Appendix A Figure A3).

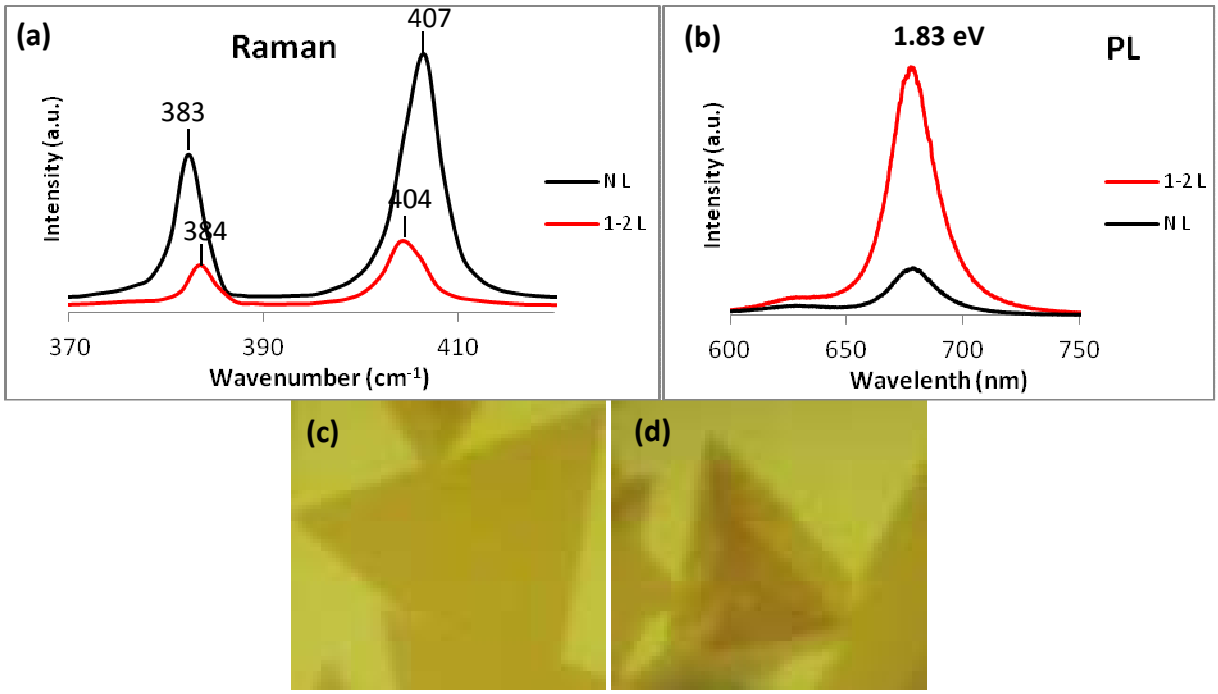

Figure 7. (a) Raman spectroscopy measurements using a 532 nm laser line. Separation between the E_{2g}' and A_{1g} peak frequencies show layer dependency. (b) Photoluminescence spectroscopy using 532 nm excitation frequency. Intensity shows layer dependency but peak emission frequency is largely independent of layer thickness. (c) Optical image of monolayer MoS_2. Measurements labeled as 1-2 L were taken near the center of this triangular flake. (d) Optical image of multilayer MoS_2. Measurements labeled N L were taken near the center of this triangular flake. Raman and PL measurements taken by Dr. Hanyu Zhang.

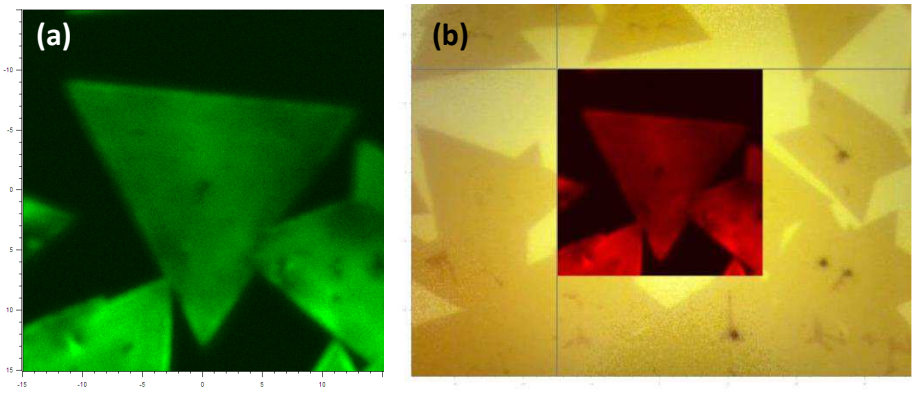

Figure 8. Photoluminescence mapping using 633 nm excitation frequency. (a) 670 nm emission. (b) 680 nm emission overlayed on optical image. PL images taken by Dr. Hanyu Zhang.

B. Atomic Force Microscopy

Layer thickness was provisionally established using atomic force microscopy (AFM). The expected thickness for each MoS_2 layer is 0.615 nm.[8] The silicon substrate had a roughness of around 3 nm, and the quartz had roughness of around 2 nm, so conclusively determining the height of the MoS_2 samples was not possible on these growth substrates. We were able to make some height estimations, however, and determined that the thinnest flakes were no more than two molecular layers in height.

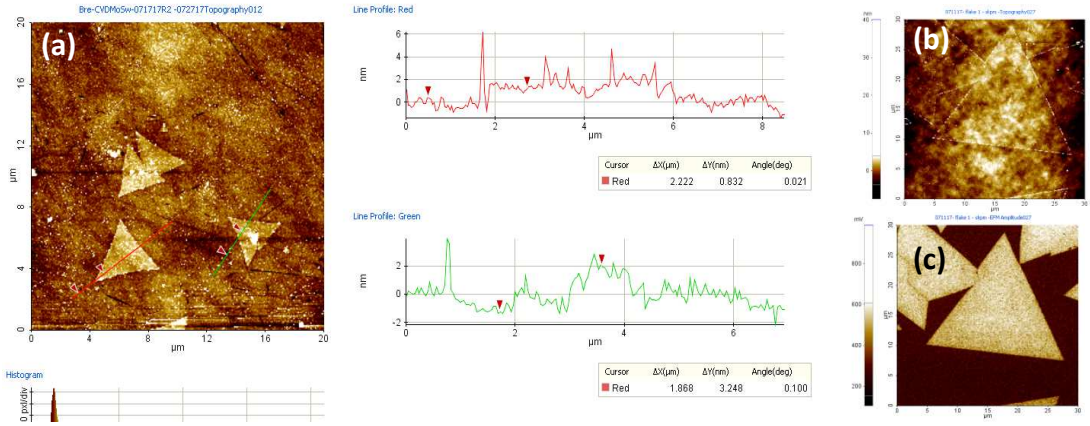

Figure 9. (a) AFM topography measurements of 1-4 layer flakes. (b) AFM topography. (c) Electric force microscopy amplitude.

IV. CONCLUSION & FUTURE RESEARCH

Temperature, reaction time, pressure, seeding promoter type and concentration all affect the size and quality of MoS_2 thin films and isolated flakes. Furthermore, these variables are *inter*-dependent. Temperature, flow rate, and pressure often needed to be adjusted when one of these variables was changed. Our best results were obtained at a temperature of 700^o C, a pressure of 760 torr, a N_2 flow rate of 200 sccm, and a 3 minute hold time at the highest furnace temperature. Raman spectroscopy, photoluminescence, and atomic force microscopy confirm that the material produced is single to few layers of 2D MoS_2. When the gas flow rate was adjusted higher or lower than 200 sccm the sample quality was diminished due to an increase in growth height. This variable was not fully explored, however, and other groups have successfully grown single layer MoS_2 at lower gas flow rates. Another area of further research is in the concentration of the seeding promoter. Isolated flakes were successfully produced by depositing a concentrated strip of promoter (100mM for PTAS) at the upstream edge of the growth substrates and allowing the carrier gas to distribute the promoter and create a concentration gradient. The result was a band of isolated flakes just downstream of the promoter that gradually morphed into particles as the distance from the promoter increased. This suggests that the promoter concentrations that allow for monolayer growth are very narrow and that there is some promoter concentration that could be evenly distributed across the growth substrate to achieve a larger area of isolated, monolayer flakes. Attempts to find a promoter concentration that yields good quality growth when distributed over the entire growth substrate have so far yielded

particle growth with significant MoO_3 contamination. We also successfully achieved solution phase lift-off of the as-grown 2D MoS_2 films, which enables the transfer of this material to any other substrate without destruction.

V. ACKNOWLEDGEMENTS

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VI. APPENDICES

Appendix A:

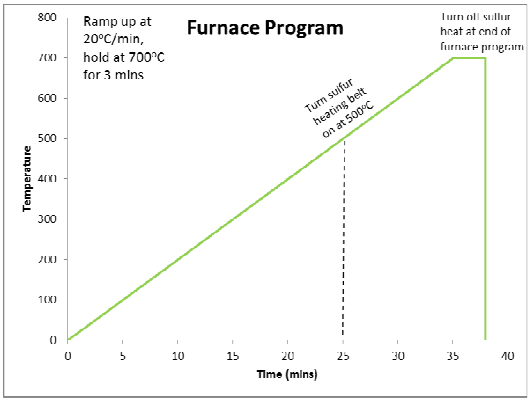

Figure A1. CVD furnace program.

Figure A2. MoS_2 flakes on quartz substrate. Conditions of 700^{o}C for 3 minutes, 760 torr pressure, and 200 sccm gas flow rate were successfully used to grow single and few layer crystals on substrates other than Si/SiO_x.

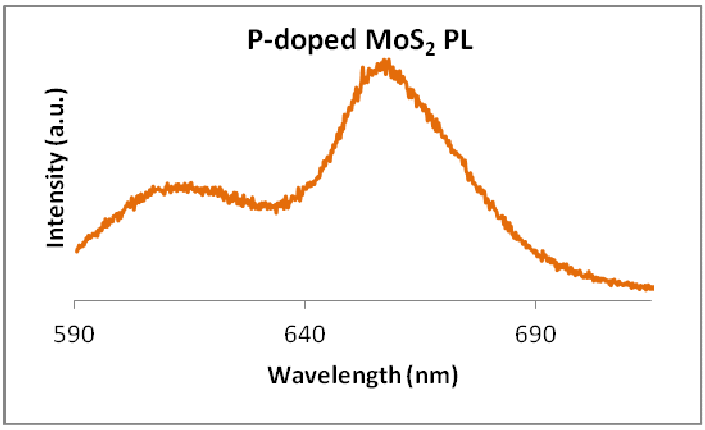

Figure A3. Doping the MoS_2 to give it more P-type behavior shifted the emission peak to 1.89 eV (657 nm), which is a 57 meV blue shift from the emission of as-grown MoS_2 on Si/SiO_x substrate.

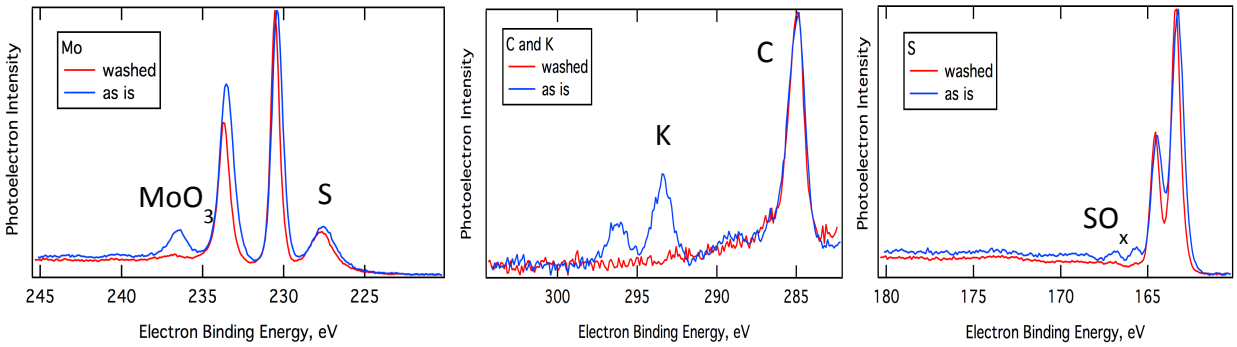

Figure A4. XPS data comparing as-grown MoS_2 using PTAS as seeding promoter with MoS_2 film lifted off of growth substrate with water and transferred to clean substrate. XPS data collected by Elisa Miller.

x170725		C	S	K	Mo		S:Mo	S:C
_1	as is	28.75	38.9	3.04	29.31		2.06	1.35
					18.89	MoS2		
_4	washed	20.15	47.95	0	31.90			
					22.37	MoS2	2.14	2.38

Table A1. As-is sample compared with water transferred sample element relative percentages.

VII. REFERENCES

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