Growth and Characterization of 2D Transition Metal Dichalcogenides

Samuel Straney

2019 PARADIM REU Intern @ Cornell

Intern Affiliation: Nanoscale Engineering, SUNY Polytechnic Institute, Colleges of Nanoscale Science and Engineering

Program: 2019 Platform for the Accelerated Realization, Analysis, and Discovery of Interface Materials Research Experience for Undergraduates Program at Cornell University (PARADIM REU @ Cornell)

PARADIM REU Principal Investigator: Dr. Darrell Schlom, Materials Science and Engineering, Cornell University

PARADIM REU Mentor: Dr. Saien Xie, Materials Science and Engineering, Cornell University

Primary Source of PARADIM REU @ Cornell Funding: Support for PARADIM is provided under NSF Grant # DMR-1539918 as part of the Materials Innovation Platform Program

Contact: sstraney@sunypoly.edu, schlom@cornell.edu, sx68@cornell.edu

Website: http://cnf.cornell.edu/education/reu/2019

Primary PARADIM Tools Used: TESCAN Mira3 FESEM

Abstract:

Uniform monolayer growth of two-dimensional (2D) transition metal dichalcogenides (TMDs) over large areas offers the possibility for great advancements in the technologies of nanoelectronics, optoelectronics, and valleytronics. Chemically stable at three atoms thick, TMDs with direct bandgaps make both flexible and transparent devices more possible than before. This project's focus is to find suitable conditions for growth of monolayer molybdenum based TMDs over a three-inch wafer using metal organic chemical vapor deposition, (MOCVD). Changes in the growth chamber's flow rates, temperature, and internal arraignment are used to find reproduceable recipes for MoS_2 and $MoSe_2$ monolayer growth. TMD films are characterized using optical microscopy, scanning electron microscopy, and Raman spectroscopy to determine film thickness, coverage, and grain size. Molybdenum diselenide ($MoSe_2$) films have ~ 6 µm grain without multilayer growth. Molybdenum disulfide (MoS_2) films have grain sizes of ~ 5 µm, with uniformity on the inch scale with full wafer growths still being optimized.

Research Summary:

Growth tests were made using PARADIM's MOCVD reactors to optimize the recipe for a continuous polycrystalline, MoS_2 or $MoSe_2$, monolayer over an entire three-inch wafer. The MOCVD reactor consists of a 4.3-inch diameter quartz tube that rests in a three-zone tube furnace. Precursor gas flow rates to the MOCVD chamber were controlled through a LabVIEW program. Each precursor flowed through a separate mass flow controller (MFC) with argon and H_2 as the carrier gas. Molybdenum hexacarbonyl (MHC) is the transition metal source while diethyl sulfide (DES) and dimethyl selenium (DMSe) represent chalcogen sources. H_2 was required to decompose the chalcogen precursors and to remove carbonaceous species, generated during growth, from the chamber [1].

Samples were placed on two 3.5-inches by 6-inches glass plates that rested in the center of the chamber, both length wise and height wise. In the upstream direction from the sample plates rested two more glass plates one at 3.5-inches to a side and the other 2.88-inches to a side. The square plates were covered in salt, NaCl, to both desiccate the chamber and act as a catalyst for larger grain growth [1]. Growths were performed with several silicon chips both down the center of the chamber and along one edge to check for precursor uniformity both down the length of the

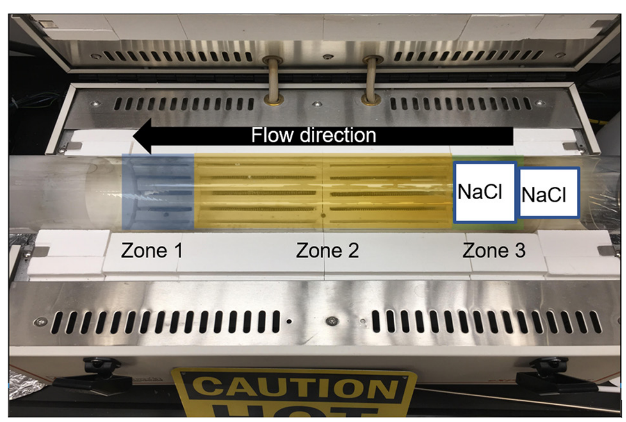

Figure 1: Overhead view of MOCVD reaction chamber with flow direction, furnace zones, and salt plate locations labeled.

chamber and from one wall to the other. An example of the MOCVD can be seen in Figure 1.

The TESCAN Mira3 field emission scanning electron microscope (FESEM) was used to image sample films grain size and topology. Growth parameters that yielded films with poor grain size or coverage and/or multilayer TMD growth were adjusted using precedents from literature or observed in previous growth trials [1]. Growth parameters that were adjusted were temperature, flow rates, salt plate placements, and growth times.

Results:

Starting growth parameters for MoS_2 were taken from Mr. Don Werder, with limited changes before full wafer growths were attempted. Starting from the same parameters as MoS_2, $MoSe_2$ films achieved full monolayer coverage without full wafer uniformity. Salt plate placement at position 0 cm is on the upstream edge between zone 3 and zone 2 of the furnace while position -1 cm is 1 cm towards the inlet to the reaction chamber. Optimized films of both MoS_2 and $MoSe_2$ can be seen in Figure 2 and Figure 3 respectively.

Both films boast grain sizes above 5 µm with limited multilayer growth. Grain shape for the MoS_2 growth is mostly triangular suggesting a molybdenum deficient growth, while the optimal growth shown for$MoSe_2$ has hexagonal grains with a more balanced precursor ratio [2]. Optimized growth parameters for MoS_2 and $MoSe_2$ are displayed in Figure 4.

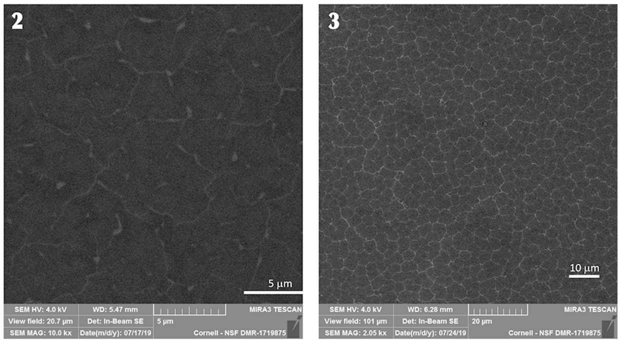

Figure 2, left: Optimized MoS_2 monolayer growth imaged with the TESCAN Mira3. Figure 3, right: Optimized $MoSe_2$ monolayer growth imaged with the TESCAN Mira3.

Table 1: Optimized MoS_2 and $MoSe_2$ recipes

	MoS_2	$MoSe_2$
Zone 1 temperature (°C)	650	600
Zone 2 temperature (°C)	650	600
Zone 3 temperature (°C)	550	500
H_2 flow rate (sccm)	1	5
Ar flow rate (sccm)	800	1000
Chalcogen flow rate (sccm)	0.3	0.3
Molybdenum flow rate (sccm)	6	4
Growth time (hrs)	3.75	4
Salt placement (cm)	0	-1

Figure 4: Table of optimized MoS_2 and $MoSe_2$ growth recipes.

Conclusions and Future Work:

Areas of monolayer growth with limited multilayer growth have been achieved for both MoS_2 and $MoSe_2$, however larger homogeneous areas of growth need to be achieved for 3-inch trials to be successful. To help create larger areas of continuous monolayer growth within the chamber, precursor distribution needs to be even over a larger area. Wafers may be lifted slightly on the downstream side to help create a lesser gradient in precursors along its surface. To help with a gradient in precursors in the reaction chamber's cross section a wider inlet geometry may be used. Further tests on both the electrical and optical properties of the films grown need to be made to better determine their quality.

Acknowledgements:

First, I would like to thank my PI and mentor, Dr. Saien Xie. For their help both inside and outside lab I would like to thank Dr. Julie Nucci, Dr. Darrell Schlom, and Mr. Don Werder during these past ten weeks.

Special thanks to Jarek Viera who was working on a parallel project to my own and was always a great help both with growths and keeping spirits high. PARADIM is funded by the NSF through Grant # DMR-1539918 as part of the Materials Innovation Platform Program.

References:

[1] Kang, K., Xie, S., Huang, L., Han, Y., Huang, P. Y., Mak, K. F., Park, J. High-mobility three-atom-thick semiconducting films with wafer-scale homogeneity. Retrieved from https://www.nature.com/articles/nature14417 (2015, April 30).

[2] Jung, Yeonjoon; Ji, Eunji; Capasso, Andrea; Lee, Gwan-Hyoung. Recent Progresses in the Growth of Two-dimensional Transition Metal Dichalcogenides. Journal of the Korean Ceramic Society. 56. 10.4191/kcers.2019.56.1.12 (2019).

[3] Chhowalla, M., Shin, H. S., Eda, G., Li, L., Loh, K. P., and Zhang, H. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. Nature Chemistry, 5(4), 263-275. doi:10.1038/nchem.1589 (2013).