Growing 2D Transition Metal Dichalcogenides

Jarek Viera

2019 PARADIM REU Intern @ Cornell

Intern Affiliation: Chemistry, University of North Georgia

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, 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: jpvier2910@ung.edu, sx68@cornell.edu, schlom@cornell.edu
Website: http://cnf.cornell.edu/education/reu/2019

Abstract:

Monolayer transition metal dichalcogenides (TMDs) are three atom thick materials that are ideal candidates for electronic and optoelectronic devices such as photodetectors and light emitting diodes. TMDs are also unique for their electronic properties including the large excitonic effect, indirect-to direct bandgap transition, piezoelectricity, and valleytronics. Metal-organic chemical vapor deposition (MOCVD) is on the forefront in producing high-quality large scale TMDs. The focus of this project was to develop reproducible MOCVD recipes for uniform monolayer tungsten disulfide (WS₂) and tungsten diselenide (WSe₂). To achieve this goal, we optimized the growth conditions including growth temperature, flow rates of the precursors, and growth time. Optical microscopy (OM), scanning electron microscopy (SEM), and Raman spectroscopy were used to characterize the TMDs (e.g. grain size and formation of multilayers). Currently a reproducible recipe has been developed for synthesizing continuous films of monolayer WS₂ with a grain size of ~ 10 µm, while the recipe for WSe₂ is still under development.

Summary of Research:

Semiconductor electronics have transformed and revolutionized our lives in multiple aspects. As time moves on, we continue to optimize their quality. The growth of thin-film semiconductors, specifically transition metal dichalcogenides (TMDs), have boomed in recent years for overcoming traditional semiconductors (like silicon) limitations, mainly their “thickness”. These materials have unique properties like a large excitonic effect and indirect-to direct bandgap transition, combined with their thinness gives them potential applications in piezoelectricity, valleytronics, optoelectronics, and energy storage devices [1,2]. Uniform monolayer tungsten disulfide (WS₂) and tungsten diselenide (WSe₂) were grown on 1 × 1 cm SiO₂/Si substrates using metal-organic chemical vapor deposition (MOCVD). The synthesis occurs in a vacuum sealed quartz tube, which is placed inside of a three-zone furnace with inlet pipes that introduce the precursor gasses into the environment.

In the process tungsten hexacarbonyl (W(CO)₆), diethyl sulfide (DES), and dimethyl selenide (DMSe) were used as the transition metal, sulfur, and selenium precursors respectively. Argon (Ar) was used as a carrier gas and hydrogen (H₂) was used to for the decomposition of the chalcogen precursor, as well as to remove the carbon contaminations [1]. Salt plates are present inside of the quartz tubes to serve as desiccants and as a catalyst for the reaction [1 supplemental]. The three-zone temperature control allows the precise control of the decomposition of the chalcogen precursor, as well as to remove the carbon contaminations [1]. Characterization was done with optical microscopy (OM) and scanning electron microscopy (SEM). OM was used as a rough and quick method mainly measuring the grain size and checking coverage while SEM is more important as it’s used to go full into detail for grains and check the amount of layers grown using backscatter detectors, provided by TESCAN Mira3 SEM in the CCMR at Cornell University.
The original recipes were very broad with the focus of getting a general idea of conditions, optimization came later. This helped set up a frame of reference, while the flow rates for Ar, W(CO)₆ and H₂ weren’t changed too much, DES and the position of the salt plates were changed the most frequent out of all parameters.

<table>
<thead>
<tr>
<th>Table 1: Growth parameters.</th>
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<tr>
<td>Growth time (hr)</td>
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<td>Ar(CO)₆ flow rate (sccm)</td>
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<tr>
<td>Hydrogen flow rate (sccm)</td>
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<tr>
<td>Argon flow rate (sccm)</td>
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<td>Temp zone 1 (°C)</td>
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<td>Temp zone 2 (°C)</td>
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<td>Temp zone 3 (°C)</td>
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The effects of having a W/S ratio to high or too low results in having accumulations of W covering the SiO₂/Si chips, and if the salt plates are positioned too close to the samples grains of salt can end up on the chips. Once enough trials had been conducted, it was found that placing the salt plates at the edge of zone 3 and a ratio of 20/1.2 of W/S gave the best results. For WSe₂ the current samples have a 60% coverage, but suffer from high amounts of multilayer growth. The results in Table 1 show the optimized recipe for WS₂ and current recipe for WSe₂.

As seen in Figure 2, the results of our optimization gave grain sizes ranging from 6-10 µm with chips at the center edges of the sample plate giving 90% coverages of a uniform monolayer growth.

Acknowledgements:
I would like to express my gratitude to my mentor, Saien Xie, and my PI, Darrell Scholm, and REU coordinators and staff, especially Julie Nucci and Don Werder, for their continued support and coaching. Support for this PARADIM project was funded by the National Science Foundation’s grant, DMR-1539918 as part of the Materials Innovation Platform Program.

References: