Growing 2D Transition Metal Dichalcogenides

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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 (WS_2) and tungsten diselenide (WSe_2). 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 WS_2 with a grain size of ~ 10 μm, while the recipe for WSe_2 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 dichalcogenieds (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 piezoelectricitronics, valleytronics, photovoltaics, modern electronics and optoelectronics, and energy storage devices [1,2]. Uniform monolayer tungsten disulfide (WS_2) and tungsten diselenide (WSe_2) were grown on 1 × 1 cm SiO_2/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 hexacarbonly ($W(CO)_6$), 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 (H_2) 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 precursors, which is crucial for a uniform high-quality growth of TMDs. 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 H_2 weren't changed too much, DES and the position of the salt plates were changed the most frequent out of all parameters.

Table 1. Growth Parameters		
	WS2	WSe2
Growth time (hr)	3.5	3
$W(CO)_6$ flow rate (sccm)	20	20
Chalcogen flow rate (sccm)	1.2	1.5
Argon flow rate (sccm)	1200	1200
Hydrogen flow rate (sccm)	5	5
Temp zone 1 (°C)	650	650
Temp zone 2 (°C)	650	650
Temp zone 3 (°C)	500	500

Table 1: Growth parameters.

The effects of having a W/S ratio to high or too low results in having accumulations of W covering the SiO_2/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 WSe_2 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 WS_2 and current recipe for WSe_2.

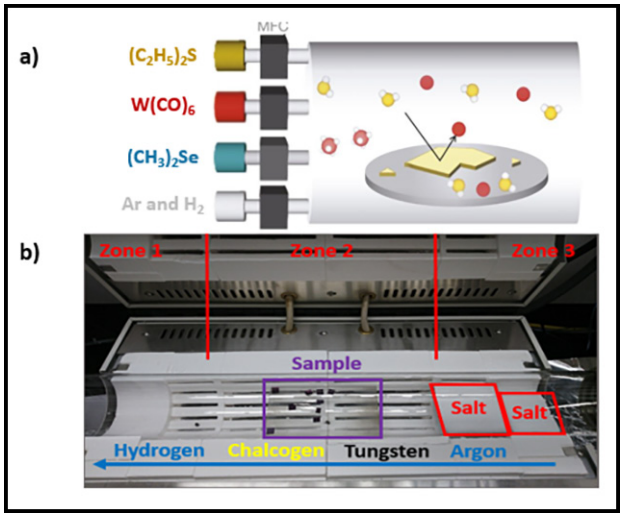

Figure 2: The results of our optimization gave grain sizes ranging from 6-10 μm with chips at the center edges of the sample plate giving 90% coverages of a uniform monolayer growth.

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% coverage of a uniform monolayer growth. The growth of multilayers was checked by the use of in-beam backscattered electrons and the change in contrast from the substrate. The optimized recipe is for edge placed chips, since center placed chips suffer from multilayer growth due to higher concentrations of precursors found in center of stream, and the recipe has shown to be reproducible for 1 × 1 cm chips.

Recipes for uniform monolayer WSe_2 are still under development. For 3-inch diameter wafers, the high concentration in the center of the stream can be resolved by a splitter placed on the main gas flow inlet, this will break the concentrations. Lastly, the samples will need to be tested for their electronic applications and physics by the PARADIM users.

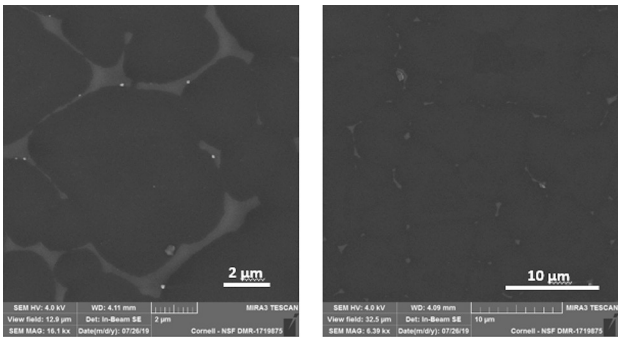

Figure 3: SEM images of optimized WS_2 sample showing high coverage and grain size.

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References:

[1] Kang, K.; Xie, S.; Huang, L.; Han, Y.; Huang, P. Y.; Mak, K. F.; Kim, C.-J.; Muller, D.; Park, J. High-mobility three-atom-thick semiconducting films with wafer-scale homogeneity, https://www.nature.com/articles/nature14417#search-menu (accessed Aug 5, 2019).

[2] Samadi, M.; Sarikhani, N.; Zirak, M.; Hua Zhang, H.-L. Z.; Moshfegh, A. Z. Group 6 transition metal dichalcogenide nanomaterials: synthesis, applications and future perspectives https://pubs.rsc.org/en/content/articlelanding/2018/nh/c7nh00137a#!divAbstract (accessed Aug 5, 2019).