

# Growing and Characterizing Monolayer Transition Metal Dichalcogenides (2D TMDs) Materials for PARADIM Users

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## **Abstract:**

Intense research into new atomically thin semiconducting materials has the electronics and semiconductor industries excited, however, the largescale monolayer growth of one of the earliest descendants of the class, transition metal dichalcogenide (TMD) films with spatial continuity and high electrical performance remains a challenge [1]. Metal-organic chemical vapor deposition (MOCVD) is a low temperature and versatile deposition process that is industrially scalable and proven to be a promising way to engineer film structure to produce high quality monolayer TMD films [2]. In our research, we grew monolayer molybdenum disulfide ( $\text{MoS}_2$ ) and tungsten disulfide ( $\text{WS}_2$ ) films on a 3-inch diameter silicon wafer, coated with a  $\text{SiO}_2$  layer, in the PARADIM facilities MOCVD lab, and refining the growth recipes to find the best parameters for high-quality uniform monolayer growth of the TMD films. Our initial goal was to optimize  $\text{MoS}_2$  and  $\text{WS}_2$  growth recipes to grow continuous monolayer polycrystalline films on a 3-inch silicon wafer, with 5-10 micron-sized grains, by manipulating the precursor materials and growth conditions on in-house built MOCVD reactors. We characterized our TMD films using Raman spectroscopy and scanning electron microscope (SEM) imaging to confirm a continuous monolayer film with the desired grain size. We optimized the growth recipes for monolayer  $\text{WS}_2$  films with > 4 micron-sized grains but with sparse continuity and monolayer  $\text{MoS}_2$  films with continuous ~ 2 micron-sized grains.

## **Summary of Research:**

Monolayer polycrystalline  $\text{MoS}_2$  and  $\text{WS}_2$  films were grown on 3-inch diameter silicon wafers, each in a designated MOCVD reactor system in the PARADIM facility. These two systems were clones of the systems built by Jiwoong Park at the University of Chicago. Our MOCVD reactors consisted mainly of a 4.3-inch diameter hot-wall quartz tube inside of a three-zone tube furnace with the inlet pipe connected to the precursor sources, with their flow rates individually controlled by respective mass flow controllers (MFCs).

A LabVIEW program was used to set temperatures for each zone in the tube furnace, control the flow rates of the precursors and the amount of time each parameter would run. Molybdenum hexacarbonyl (MHC) and tungsten hexacarbonyl (THC) were used as transition metal gas-phase precursors for the  $\text{MoS}_2$  and  $\text{WS}_2$  film growths, respectively, and diethyl sulfide (DES) was used as the chalcogen atom gas-phase precursors for both growths.

Argon and hydrogen gas ( $\text{H}_2$ ) were used as carrier gases for both growths.  $\text{H}_2$  is necessary to reduce DES and to remove carbonaceous species produced during MOCVD film growth processes [2].

Initially,  $\text{MoS}_2$  and  $\text{WS}_2$  films were grown on three small silicon wafer pieces with one piece placed within each zone of the tube furnace. A plate of NaCl was also placed within the tube furnace near the inlet, zone 3 of the tube furnace, as a desiccant to dehydrate the precursors entering the furnace [2]. The tube furnace was then pumped down to less than 100 mTorr. For our initial growth, we programed the MOCVD reactors with parameters from growth recipes used at the University of Chicago labs, to reproduce their growth of monolayer  $\text{MoS}_2$  and  $\text{WS}_2$  films with spatial continuity and 5-10 micron-sized grains. However, the reactors were not exact replicas of each other and the TMD recipes required tuning to produce the same high-quality films in our lab.

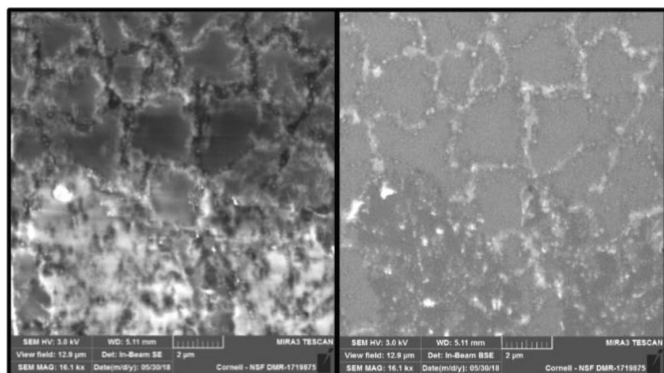


Figure 1: SEM characterization of MOCVD grown  $\text{MoS}_2$  film. a, SE image showing film continuity and  $> 2 \mu\text{m}$  grain size. b, BSE image of monolayer film.

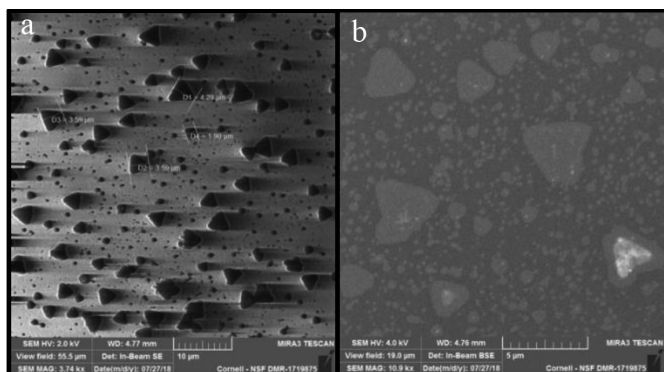


Figure 2: SEM characterization of MOCVD grown  $\text{WS}_2$  film. a, SE image showing film topology,  $> 4 \mu\text{m}$  grain size. b, BSE image of monolayer grains.

Using the Tescan Mira3 FESEM, in the CCMR facility at Cornell University, we then looked at the topology of our grown TMD films (Figures 1 and 2). If we had sub-micron sized grains, we used the CCMR Renishaw InVia Confocal Raman microscope to characterize the molecular composition of our grown TMD films based on measured Raman spectra (Figure 3) before adjusting our growth parameters. If the SEM images showed us grains greater than a micron but with poor continuity we adjusted our growth parameters based on precedents from the Chicago lab, recent literature, as well as trends we observed from previous runs. We then started a new growth changing one of the films growth parameters; growth time, precursor and carrier gas flow rates, or zone temperature. When we achieved a TMD growth with 5-10 micron-sized grains and adequate continuity, we ran the same recipe on a 3-inch diameter silicon wafer for PARADIM users.

## Results and Conclusions:

Our optimized growth recipes for MOCVD grown monolayer TMD films are summarized in Figure 3. Our recipe for  $\text{WS}_2$  produced  $> 4$  micron-sized monolayer grains but with sparse grain continuity. The growth recipe for  $\text{MoS}_2$  produced a continuous monolayer film with

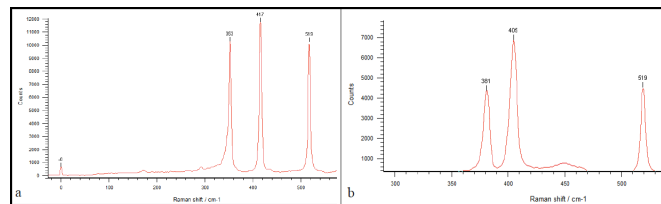


Figure 3: Raman spectrum for PARADIM lab grown TMD films. a, b, molecular identification of  $\text{WS}_2$  (a) and  $\text{MoS}_2$  (b) films.

Table 1: Optimized  $\text{MoS}_2$  and  $\text{WS}_2$  growth parameters

	$\text{MoS}_2$	$\text{WS}_2$
Growth time (hrs)	3	6
Transition metal precursor flow rate (sccm)	5	8
Chalcogen precursor flow rate (sccm)	0.4	0.3
Argon flow rate (sccm)	1000	1000
Hydrogen gas flow rate (sccm)	1	1
Furnace temperature: zone 1 ( $^{\circ}\text{C}$ )	650	650
Furnace temperature: zone 2 ( $^{\circ}\text{C}$ )	650	650
Furnace temperature: zone 3 ( $^{\circ}\text{C}$ )	550	550

Figure 4: Optimized growth recipes for monolayer  $\text{MoS}_2$  and  $\text{WS}_2$  film growth.

$\sim 2$  micron-sized grains (Figure 2). With our optimized parameters, we have the recipe to grow monolayer  $\text{MoS}_2$  and  $\text{WS}_2$  films for PARADIM users.

## Future Work:

The recipes for monolayer  $\text{MoS}_2$  and  $\text{WS}_2$  films will continue to be refined, as well as the growth recipes for other monolayer TMD films including molybdenum diselenide ( $\text{MoSe}_2$ ) and tungsten diselenide ( $\text{WSe}_2$ ) to synthesize nanosheets with grain boundaries  $< 200$  nm in width and grains  $> 5 \mu\text{m}$  in diameter. The optimized parameters will then be used to grow monolayer TMDs on oxides in the MBE-ARPES-MOCVD system being developed at the PARADIM facility to study TMD heterostructures and new physics and applications at the interfaces of 2D TMD and oxide materials.

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## References:

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- [2] Kibum Kang. High-mobility three-atom-thick semiconducting films with wafer-scale homogeneity. *Nature*, 520, 656-660 (2015).