Growing and Designing 2D Transition Metal Dichalogenide (2D-TMDC) Materials for PARADIM Users

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Abstract:

Two-dimensional transition metal dichalcogenides (2D-TMDs) were grown using the metal-organic chemical vapor deposition (MOCVD) method. MoS_2 and WS_2 monolayers were grown with 100-200 nm and 2-4 μm grains respectively, and near-full coverage over a three-inch wafer. MoS_2, $MoSe_2$, WS_2, and WSe_2, were simulated using density functional theory (DFT) in bulk, bilayer and monolayer structures. Raman active modes were identified and compared with literature and experiment with differences under 10 cm^{-1}. Electronic band structures were calculated for MoS_2, $MoSe_2$, WS_2, and WSe_2 monolayers with band gaps of 1.8, 1.6, 1.8, 1.6 eV with indirect to direct band gap transitions observed between bulk and monolayers for all materials except WSe_2.

Research Summary:

2D-TMDs have unique properties that have applications in piezoelectronics, photovoltaics, valleytronics, modern electronics, and optoelectronics [1]. Study into these materials can further advance several devices such as solar cells and field effect transistors. The layers in bulk are held together by van der Waals forces and can be separated using the exfoliation method producing micron-scale samples [2]. MOCVD was used to grow 2D-TMDs such as MoS_2 and WS_2 on three-inch silicon wafers. The scalable growth of 2D-TMDs can produce samples to be studied by PARADIM users and advance the development of new devices.

MoS_2 and WS_2 were grown using MOCVD on a silicon substrate with a 250 nm coating of SiO_2. The starting parameters were provided by Dr. Jiwoong Park [1] and varied until near-uniform coverage and large grains were obtained. Figure 1 shows the parameters which yielded 100-200 nm grains for MoS_2, 2-4 μm grains for WS_2, and near-uniform coverage for both samples. SEM

	Ar Flow (sccm)	H_2 Flow (sccm)	Metal Source (sccm)	Chalcogen Source (sccm)	Temp Zone 1/2/3 (°C)	Time (hrs)
MoS_2	1000	1	5	0.4	650/650/550	3.5
WS_2	1000	1	8	0.3	650/650/550	6

Lattice Constants (Å)	a Ref[7]	a (calculated)	c Ref[7]	c (calculated)
MoS_2 (Ref[7],24000)	3.150	3.139	12.300	12.542
$MoSe_2$ (Ref[7],16948)	3.290	3.269	12.930	13.115
WS_2 (Ref[7],651387)	3.1530	3.146	12.323	12.656
WSe_2 (Ref[7],652170)	3.282	3.273	12.960	13.222

Figure 1: MOCVD growth parameters and lattice constants of bulk TMDs comparing DFT calculations with literature.

was used, on the Tescan Mira3 FESEM in the Cornell Center for Materials Research (CCMR), to determine degree of coverage and grain size, shown in Figure 2 for WS_2.

Raman spectroscopy was used to check chemical purity of the samples. Figure 3 shows a spectrum of WS_2, obtained using the Renishaw InVia Confocal Raman microscope in the CCMR, which agrees with literature [1] and DFT calculations within 10 cm^{-1} with peaks at 353 and 417 cm^{-1}.

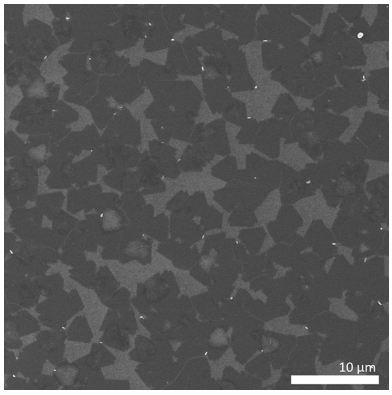

Figure 2: Secondary electron SEM of WS_2 showing near-full coverage of a silicon wafer with 2-4 µm grains.

spectrum of WS_2. The calculated modes are found at 354 and 416 cm^{-1}, which agree with literature and experiment within 10 cm^{-1} [1].

The electronic band structure was obtained by calculating the energy at each point in a 4 × 4 × 2 electronic momentum mesh and mapping out a path between symmetry points [8]. The band gaps of MoS_2, $MoSe_2$, and WSe_2 monolayers were 1.8, 1.6, and 1.6 eV, which agree with experimental values within 0.1eV. The calculation for a WS_2 monolayer is underestimated by approximately 0.3 eV with a band gap of 1.8 eV [2]. In MoS_2, $MoSe_2$, and WS_2 an indirect to direct band gap transition is observed between bulk and monolayer, but for WSe_2, the band gap remains indirect.

Properties of MoS_2, $MoSe_2$, WS_2, and WSe_2 were simulated using DFT within the framework of the VASP package [3,4], which uses a plane-wave basis set to describe the valence-electron wave function and charge density [5] and Perdew-Burke-Ernzerhof revised for solids (PBEsol) was used for the exchange-correlation functional and the projector augmented wave pseudopotentials [6].

Initial structures for bulk materials were found on the Inorganic Crystal Structure Database (ICSD) [7]. The electronic energy was converged with a tolerance of 10^{-6} eV, the forces on the atoms were calculated, the atomic positions adjusted, and this two-step cycle repeated until the forces converged with a tolerance of 10^{-4} eV/Å. The lattice constants of the bulk structures are summarized in Figure 1. Monolayers and bilayers were constructed by increasing the out-of-plane lattice constant from bulk to approximately 25 Å, keeping n layers in a unit cell, n = 1 for monolayers and n = 2 for bilayers.

The lattice parameters were held constant and the atomic positions were relaxed with an electronic momentum mesh of 8 × 8 × 2 for sulfides and 12 × 12 × 2 for selenides. Differences in bond lengths and angles were analyzed between bulk, bilayer, and monolayer which were less than 1 mÅ and 1°.

Vibrational modes were calculated using relaxed structures and a 4 × 4 × 2 electronic momentum mesh. Figure 3 shows the Raman active vibrational modes plotted on top of the experimentally obtained Raman

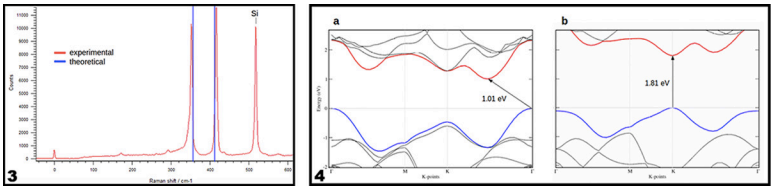

Figure 3, left: Raman spectra of WS_2 and Raman active vibrational modes calculated using DFT. Figure 4, right: Electronic band structure diagram of WS_2 in bulk, 4a, and a monolayer, 4b.

In summary, MoS_2 and WS_2 were grown with the MOCVD method and characterized by Raman spectroscopy and SEM. DFT was used to calculate lattice constants, vibrational modes, and electronic band structure. In the future, MoS_2 and WS_2 MOCVD parameters need to be adjusted to increase grain size and reduce bilayer growth, additionally, $MoSe_2$ and WSe_2 will be grown. More rigorous calculations could be performed by including spin-orbit coupling to get more accurate electronic band structures and phonon modes, potentially giving insight into the unexpected indirect band gap in WSe_2 monolayers.

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