The Optimization of Thin Film Molybdenum Disulfide Synthesis

Michael Statt

Chemical and Biomolecular Engineering, Cornell University

NNIN REU Site: Institute for Electronics and Nanotechnology, Georgia Institute of Technology, Atlanta, GA

NNIN REU Principal Investigator: Prof. Eric Vogel, School of Materials Science and Engineering, Georgia Institute of Technology

NNIN REU Mentors: Philip Campbell and Dr. Alexey Tarasov, School of Materials Science and Engineering, Georgia Institute of Technology

Contact: mjs488@cornell.edu, eric.vogel@mse.gatech.edu, philip.campbell@gatech.edu, alexey.tarasov@mse.gatech.edu

Abstract and Introduction:

Two-dimensional materials have been a source of great interest and promise due to their interesting thickness-dependent properties. One class of these materials are transition metal dichalchogenides (TMDCs). TMDCs are layered materials with formula MX_2, where M is a transition metal (Mo, W, etc), and X is a chalcogen (S, Se, Te). TMDCs exhibit high mechanical strength and thickness-tunable band gaps that transition to direct band gaps in the monolayer limit for most TMDCs.

Molybdenum disulfide (MoS_2) is one example of a TMDC that has garnered significant interest recently due to its direct band gap at a monolayer thickness, high on/off ratios, and moderate mobilities. These properties make MoS_2 well-suited for applications such as 2D vertical heterostructure devices, thin film optoelectronics, and flexible, transparent electronics [1].

For TMDCs to be compatible with modern electronic fabrication processes, uniform, high quality, wafer-scale growths must be achieved. One straightforward approach to MoS_2 synthesis is the sulfurization of an evaporated thin film of molybdenum by annealing in a sulfur-containing environment at high temperatures. This method has been shown to create highly uniform, wafer-scale, trilayer MoS_2 films [2]. The resulting films, however, suffer from small grain sizes (~ 10 nm), which increase charge-carrier scattering, limit carrier mobility and reduce on/off ratios. This study investigated the effects of high temperature annealing on the crystallinity of MoS_2 films synthesized through sulfurization of thin molybdenum films.

High temperature annealing has been shown to cause lattice recrystallization and coarsening of the resultant grain structure [3]. Experimental results suggest that extended sulfur-rich and sulfur-deficient anneals are currently incompatible with high quality MoS_2 synthesis.

Experimental Methods:

Silicon wafers were thermally oxidized to form a 300 nm thick layer of SiO_2. A 1 nm layer of molybdenum was deposited on the SiO_2 using e-beam evaporation. The samples were then placed in a sulfurization furnace and pumped down to the chamber base pressure (~ 30 mTorr). The samples were annealed at 300°C for 30 minutes in an $Ar:H_2$ (4:1) atmosphere to remove atmospheric contaminants. In a separate vessel, a powder sulfur source was concurrently heated to 150°C to increase its vapor pressure. The sulfur vapor was injected into the chamber, which was backfilled with argon gas to a total pressure of approximately 5 Torr. The chamber was then heated to 1000°C and allowed to dwell at that temperature for times varying from five minutes to 12 hours to allow for sulfur to diffuse into the molybdenum layer and react to form MoS_2. This step will be referred to as the sulfur anneal step.

Next, the chamber was purged with argon gas at temperatures varying from 750°C-1000°C to remove any remaining sulfur gas. This process step required a minimum dwell time of 30 minutes to prevent sulfur precipitation on film surface and was extended up to 12 hours to thermally anneal the sample. This step will be referred to as the argon anneal step. The chamber was then cooled to room temperature under an argon flow.

XPS was used to characterize film stoichiometry and elemental composition. Raman spectroscopy was used to identify MoS_2 film uniformity and thickness through the appearance and separation of characteristic MoS_2 A_{1g} and E^1_{2g} peaks, which have been shown to be correlated with film thickness [4].

Results and Conclusions:

Sulfur anneal times longer than two hours yielded partially oxidized MoS_2 films, as indicated by the appearance of MoO_2 and MoO_3 peaks in the XPS spectra shown in Figure 1. These films also showed large areas with no characteristic MoS_2 Raman spectroscopy peaks. It was also found that small, ordered, circular regions of anomalous MoS_2 growth occurred in extended sulfur anneal time samples, as shown in Figure 2. These regions grew in size and density when sulfur anneal time was increased. Raman spectroscopy analysis of these regions indicated bulk thickness MoS_2 growth and atomic force microscopy (AFM) analysis showed that these regions were steps

approximately 10-30 nm above the rest of the film. It is currently unknown what caused these bulk thickness regions, but they limited the viability of extended sulfur anneals to increase grain size.

When argon anneal temperatures were kept at 1000°C, argon anneal times longer than two hours yielded samples with little to no sulfur content, as indicated by XPS analysis, and no characteristic MoS_2 peaks in Raman analysis. When temperatures were reduced to 750°C, a two hour argon anneal resulted in MoS_2 peaks in Raman analysis, but peak separation indicated highly varying thickness across the sample (± 3 monolayers). This indicated that sulfur may be evaporating from the MoS_2 film due to a concentration gradient between the film and the sulfur-deficient atmosphere. Currently, this limitation makes extended argon anneals an unviable option for increasing crystallinity in MoS_2 films.

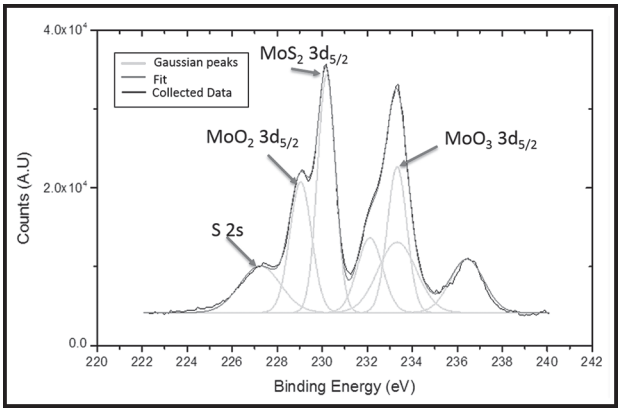

Figure 1: XPS spectra of sample annealed in sulfur-rich environment for 120 minutes.

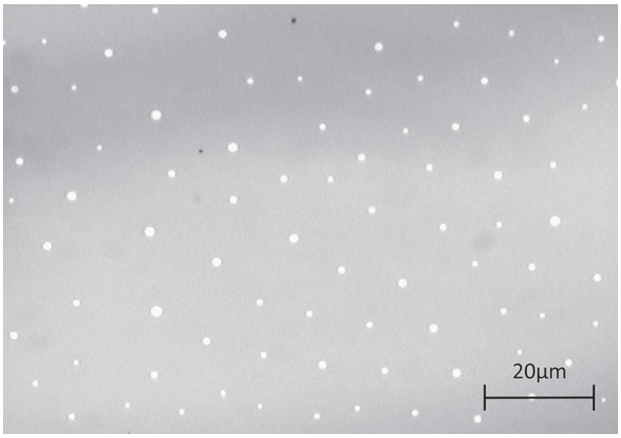

Figure 2: Optical micrograph shows bulk thickness spots on sample grown at 120 minute sulfur anneal time.

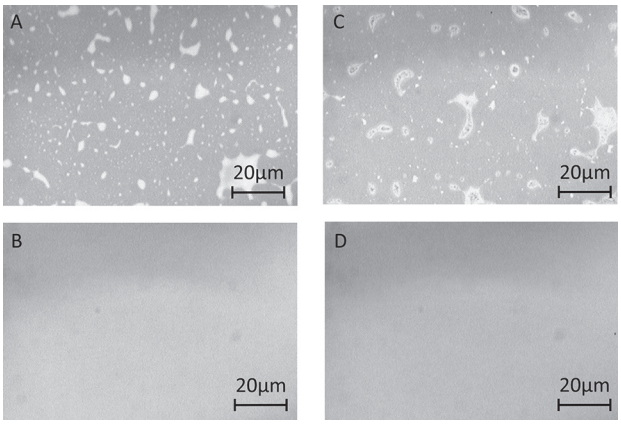

Figure 3: A and B are pre-sulfurization, C and D are post-sulfurization. A and C were cleaned with IPA and acetone, B and D were not.

During this investigation it was found that using organic solvents, isopropyl alcohol and acetone, to clean samples caused bulk thickness MoS_2 growth similar to that seen in extended sulfur anneal times. Figure 3 shows this through two samples grown concurrently: one cleaned with organic solvents and one cleaned only with a nitrogen gun. Bulk MoS_2 grew in regions where residue from organic solvents was present, while no MoS_2 grew in regions without residue. This indicates that organic surface contamination on the sample is altering the surface chemistry of the reaction.

Future Work:

These preliminary results indicate that high temperature anneals detrimentally affect MoS_2 film quality. In the future, conditions causing bulk thickness growth during long sulfur anneals must be quantified and mitigated to allow for uniform thickness growths. Transmission electron microscopy (TEM) and low energy electron diffraction (LEED) must be used to image MoS_2 grain structure.

Acknowledgements:

I would like to thank Professor Eric Vogel for this opportunity, the Vogel group for their mentorship; and Joyce Allen, Leslie O'Neill, and Dr. Nancy Healy for their coordination. This research was supported by the National Nanotechnology Infrastructure Network Research Experience for Undergraduates (NNIN REU) Program and NSF (Grant No. ECCS-0335765).

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