Spectroscopic Ellipsometry for In Situ Monitoring of MoS_2 Growth at the Sub-Monolayer Limit

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The ability to monitor the growth rate of transition metal dichalcogenide (TMD) monolayer and few-layer films in situ is an area of great interest to achieve tight control of layer number and to gain insight into the fundamental mechanisms of film growth. Optical characterization techniques such as laser reflectivity are widely used for real time measurements of growth rate during thin film deposition by metalorganic chemical vapor deposition (MOCVD) but cannot be readily extended to the growth of 2D materials which require sensitivity in the sub-monolayer regime. Spectroscopic ellipsometry (SE), on the other hand, is widely used to measure the dielectric function and thickness of thin films and is a powerful in situ technique for atomic layer deposition providing information on film thickness per cycle and insight into the initial mechanisms of nucleation.

In this study, we investigate the use of SE as an in situ technique to monitor the growth of MoS_2 monolayer and few-layer films by MOCVD on c-plane sapphire substrates. The studies were carried out in a vertical cold wall MOCVD reactor equipped with a J.A. Woollam M2000XI ellipsometer with a spectral range of 210 – 1687 nm, integrated using purged optical ports on the reactor. Molybdenum hexacarbonyl ($Mo(CO)_6$) and hydrogen sulfide (H_2S) were used as precursors with H_2 as the carrier gas. Initial studies were carried out by keeping growth parameters constant at 100 Torr reactor pressure, 1050°C substrate temperature, $Mo(CO)_6$ flow rate of 8.6 x10^{-3} sccm, S/Mo ratio of ~46700 and varying growth time (5 – 40 min) to develop a series of samples with varying surface coverage. After each growth, SE was performed as a function of temperature during cooldown to room temperature under H_2S. Atomic force microscopy (AFM) and field emission scanning electron microscopy (FE-SEM) were used to measure the film coalescence and quantify monolayer and bilayer surface coverage. An optical model of the layer structure was developed assuming an interfacial layer between the film and substrate and using an effective medium approximation to consider partial film coverage where the effective medium is a variable combination of void and the MoS_2 film. The models were first used to fit the room temperature data to extract the dielectric function of MoS_2, which compared favorably to prior literature reports. The optical model was then used to predict the variation in the ellipsometric parameters (ψ and Δ) as a function of surface coverage demonstrating sensitivity in the sub-monolayer regime down to ~40% coverage. Additional studies are underway to determine the temperature dependence of the dielectric function in order to refine the models to accurately measure film coverage at growth temperature. The features of the ellipsometric curves soften at elevated temperatures compared to room temperature measurements and marked differences are observed when comparing samples of varying coverage, expounding the potential for SE to discern sub-monolayer coverages at growth temperatures. The optical models will then be applied to monitor MoS_2 film growth in situ, demonstrating the effectiveness of SE to allow precise control of film thickness and properties in real time through layer-by-layer tailoring of film deposition conditions.