Thickness Modulated MoS2 Grown by Chemical Vapor Deposition for Transparent and Flexible Electronic Devices

UTD AUTHOR(S): Gil Sik Lee

©2015 AIP Publishing, LLC

Two-dimensional (2D) materials have been a great interest as high-performance transparent and flexible electronics due to their high crystallinity in atomic thickness and their potential for variety applications in electronics and optoelectronics. The present study explored the wafer scale production of MoS2 nanosheets with layer thickness modulation from single to multi-layer by using two-step method of metal deposition and CVD process. The formation of high-quality and layer thickness-modulated MoS2 film was confirmed by Raman spectroscopy, AFM, HRTEM, and photoluminescence analysis. The layer thickness was identified by employing a simple method of optical contrast value. The image contrast in green (G) channel shows the best fit as contrast increases with layer thickness, which can be utilized in identifying the layer thickness of MoS2. The presence of critical thickness of Mo for complete sulphurization, which is due to the diffusion limit of MoS2 transformation, changes the linearity of structural, electrical, and optical properties of MoS2. High optical transparency of >90%, electrical mobility of ~12.24 cm2 V−1 s−1, and Ion/off of ~105 characterized within the critical thickness make the MoS2 film suitable for transparent and flexible electronics as compared to conventional amorphous silicon (a-Si) or organic films. The layer thickness modulated large scale MoS2 growth method in conjunction with the layer thickness identification by the nondestructive optical contrast will definitely trigger development of scalable 2D MoS2 films for transparent and flexible electronics.

© 2015 AIP Publishing LLC [http://dx.doi.org/10.1063/1.4905476]
thickness of MoS₂, we employed a simple and nondestructive method utilizing a camera image of MoS₂ films deposited on glass substrates. Our method is better than the previously reported white light contrast spectroscopy where continual white light source, spectrometer, and expensive charged coupled device (CCD) detectors are required. Furthermore, the high field effect mobility in large-scale MoS₂ film in addition to its high optical transmittance (~95%) and Ion/off ratio will make it suitable candidate for future transparent and flexible optoelectronic devices.

Large area growth and thickness modulated MoS₂ films were synthesized by using the two-step synthesis method. First step involves the sputter deposition of Mo films on (100)-oriented doped Si substrates with 300 nm thick SiO₂ top layer. A high purity (99.99%) Mo target was sputtered at different deposition times, such as 4 (L₁), 10 (L₂), 30 (L₃), 60 (L₄), and 180 (L₅) s to control the Mo film thickness. Second step involves the subsequent vapor phase sulfurization of Mo films in a low pressure chemical vapor deposition (LPCVD) system at 600°C, 5 Torr by using argon as a carrier gas to convey sulfur vapor species to the downstream Mo films. Thickness measurement of Mo and MoS₂ films was performed by an AFM (Parks NX-10) system and TECNAI F20 S-Twin (FEI Co, The Netherland) Transmission Electron Microscope (TEM). Raman spectra of MoS₂ thin films were collected in Almega XR Raman spectrometer equipped with an Olympus BX51 microscope. The electrical measurements were performed at room temperature by using an Agilent B2912A precision source/measure unit connected to a probe station. Room temperature photoluminescence (PL) and visible spectroscopy were employed to characterize the quality and optical transmittance of MoS₂ films.

Fig. 1(a) shows the Raman spectra corresponding to samples L₁–L₅ measured at 532 nm excitation laser line to assess the presence and quality of the MoS₂ films. Raman peaks for the E₁²g and A₁g vibration modes could be seen in all the samples. A peak frequency difference (Δk) of 19.7 cm⁻¹ between two characteristic Raman modes E₁²g (385.5 cm⁻¹) and A₁g (405.2 cm⁻¹) in sample L₁ indicates the presence of single-layer MoS₂. A gradual increase in Δk from 19.7 cm⁻¹ (sample L₁) to 27 cm⁻¹ (sample L₅) represents an increase in the number of MoS₂ layers from single to bulk-like nature. Raman peak broadening is also observed (Fig. 1(a)) when thickness is increased from SL MoS₂ (sample L₁) to bulk MoS₂ (sample L₅). The increment of lateral inhomogeneity present over the film with increasing film thickness is the major cause of the Raman peak broadening. In order to assess the semiconducting phase and optical quality of SL MoS₂, we carry out PL spectroscopy on sample L₁ as shown in the inset of Fig. 1(a). The peak at photoluminescence energy of ~1.89 eV at K point in the visible region confirms the presence of single-layer MoS₂. However, two additional peaks in PL spectra with smaller energies below the bandgap could be attributed to the presence of trap levels between conduction and valence band arising from imperfections of MoS₂ lattice. The number of MoS₂ layers present in the MoS₂ samples was also determined by AFM height profile measurement as shown in Fig. 1(b). The thickness of MoS₂ as estimated by AFM height profiles was found to be 0.72, 3.01, 5.40, 7.16, and 12.69 nm for L₁, L₂, L₃, L₄, and L₅, respectively. Fig. 1(c) shows the photograph of MoS₂ nanosheet transferred on the flexible polyethylene terephthalate (PET) substrate confirming its feasibility in flexible and transparent electronic device applications.

We observed that Mo films were fully sulfurized into MoS₂ only up to a critical thickness in our CVD process. The extent of sulfurization in Mo films was performed by a simple calculation based on the lattice parameters of Mo (bcc) and MoS₂ (hcp) materials. Theoretically, when Mo films are completely sulfurized, lattice constant (~3.147 Å) of Mo crystal is changed into MoS₂ lattice constant (~3.147 Å). As shown in the inset of Fig. 2(a), the expected thickness change during Mo to MoS₂ transformation can be estimated by

\[ T_{Mo} \times 3.91 = T_{MoS_2} \]  

where \( T_{Mo} \) and \( T_{MoS_2} \) are the thicknesses of Mo and MoS₂ films, respectively. Fig. 2(a) compares the theoretically (Eq. (1)) and experimentally measured (AFM) thickness of MoS₂ films corresponding to samples L₁–L₅. It is evident from the figure that up to sample L₃, the MoS₂ thicknesses are in agreement with the theoretical calculations demonstrating that the Mo films are completely transformed into MoS₂. However, a significant deviation is observed for samples L₄ and L₅. It could be explained that during sulfurization, sulfur vapor diffusion is the rate-limiting process. Hence, the sulfur atom could not react with Mo molecules beyond a certain thickness of MoS₂ film at given temperature and time. Therefore, the thicknesses for L₄ and L₅ were lower than the calculated values. Figs. 2(b)–2(d) show the cross-sectional HRTEM images for samples L₁, L₂, L₃, and L₅, respectively. The thickness of MoS₂ film for sample L₁, as determined by HRTEM, was ~0.69 nm, which is in agreement with our AFM results. The inset of Fig. 2(b) clearly shows the formation of SL MoS₂. The HRTEM image of sample L₂ shows the formation of 3–4 layers of MoS₂. It is
localized trap states at the interface of Si/SiO₂ substrate and conductance which could be attributed to the presence of mic scale. (b) UV-vis optical transmittance spectra of MoS₂ films corresponding to samples (b) L1, (c) L2, and (d) L4.

worth noting that the cross-sectional HRTEM image of sample L₄ shows the presence of two different materials (different contrasts in Fig. 2(d)) with a wavy type layered structure of MoS₂ on top-section while a thin interfacial structure on the bottom-section. It seems that the interfacial structure is not fully sulfurized and affects its electrical and optical properties. A similar image was observed in case of sample L₅.

The electrical properties of MoS₂ films were determined by characterizing MoS₂-field effect transistor (FET) devices using 50 nm thick Au as source and drain electrodes, 300 nm thick SiO₂ served as dielectric layer, and doped silicon as the back gate. Electrical measurements on sample L₁ showed a very high resistance without an indication of FET behavior or gate biasing effect. It could be attributed to the large spatial constraints imposed by the substrates for very thin layers of MoS₂ and/or grain discontinuity across the film. The electrical characterization (Iₑ-Vₑ curve) of MoS₂ thin film corresponding to samples L₂ and L₃ (Fig. 3(a)) exhibits p-type conductance which could be attributed to the presence of localized trap states at the interface of Si/SiO₂ substrate and MoS₂ film. The inset of Fig. 3(a) shows the Iₑ-Vₑ curves of L₂ on L₃ on logarithmic scale. The field effect mobility is calculated using formula: μ = (L/WC₀)ΔG/ΔVₑ,³³ where G = Iavadoc/VD₅ is the conductance, L = 10 μm is the length, and 30 μm is the width of the MoS₂ channel. ΔG/ΔVₑ = (1/VD₅)(ΔIavadoc/ΔVₑ) is determined from the slope of a linear-fit of the data ranging from Vₑ = +15 V to Vₑ = −15 V. C₀ = ε₀ε₁d is the capacitance per unit area, where the thickness of the SiO₂ layer d = 300 nm, the free-space permittivity ε₀ = 8.854 × 10⁻¹² F m⁻¹, and the relative permittivity of Si ε₁ = 3.9. The average value of field effect mobility (μ) and current on/off (Iₑ/on/off) ratio for sample L₁, as determined from Fig. 3(a), is 12.24 ± 0.741 cm² V⁻¹ s⁻¹ and 1.57 × 10⁶, respectively. It is important to note that the measured mobility in our sample is higher than the previous reports of exfoliated single-crystal MoS₂ and CVD grown MoS₂, and it is comparable with the mobility of amorphous silicon (α-Si) and organic materials. For sample L₃, the values for μ and Iₑ/on/off are 0.44 ± 0.062 cm² V⁻¹ s⁻¹ and 5.7 × 10⁴, respectively. However, samples L₄ and L₅ show a conducting nature of MoS₂ films with very low resistance (≈10¹⁰ Ω), which could be attributed to the presence of un-transformed interfacial layer at the bottom of film. The spectral transmission for the MoS₂ films with different thicknesses, samples L₁–L₅, was also measured over the wavelength range of 300–800 nm (Fig. 3(b)). An average optical transmittance value up to 95% was observed in the single layer MoS₂ film and the value was decreased with increasing film thickness. The very low transmittance from L₄ and L₅ MoS₂ film is attributed to the presence of the interfacial layer as explained above. The high optical transmittance with high field effect mobility and Iₑ/on/off ratio in sample L₂ makes it suitable for optoelectronic devices.

To identify the number of layers in thickness-modulated CVD grown MoS₂, we introduced a method of using the contrast of a photographic image, which is a simple and non-destructive characterization method. Fig. 4(a) shows a typical camera image of the MoS₂ films (L₁–L₅) on glass. The photographic image (Fig. 4(a)) was decomposed into its red (R), green (G), and blue (B) channels shown in Figs. 4(b)–4(d) by using scientific python, which allows to determine the contrast of each channel. The contrast of MoS₂ films on glass/paper can be calculated using the following equation:³⁴

\[
C = \frac{I_{0} - I}{I_{0}},
\]

where I₀ and I are the reflected light intensities from the air-glass (substrate) interface and air-MoS₂ interface, respectively. Our definition of contrast (Eq. (2)) is modified slightly to instantiate a definition for the contrast of each separate channel (R, G, and B)

\[
C_{RGB} = \frac{I_{0,RGB} - I_{RGB}}{I_{0,RGB}},
\]

where I₀,RGB and I.RGB are the channel intensities of either red, green, or blue channel from light that interacts with substrate and MoS₂, respectively. The calculated results by using Eq. (3) for all three channels, R, G, and B, across the
substituting the green configuration of Eq. (3) into Eq. (4), and solving for \( x \)

\[
C_G = \frac{I_{0,RGB} - I_G}{I_{0,RGB}} + 0.0259, \quad \text{(5)}
\]

with this Eq. (5), the MoS\(_2\) thickness can be predicted by simply knowing the \( I_{0,G} \) and \( I_G \) values, which can be easily determined from any color image by using its green channel.

We found that the image contrast in green (G) channel shows the best fit as contrast increases with layer thickness, which can be utilized for identifying the layer thickness simply by taking an optical image of MoS\(_2\). Fig. 4(f) shows the three dimensional contrast image of the green channel of samples L\(_1\)–L\(_5\) calculated by Eq. (5). Contrast differences for the MoS\(_2\) samples with different thicknesses can clearly be seen in this figure.

We report the synthesis of layer-thickness modulated MoS\(_2\) film from multilayers to single layer and its optical and electrical properties towards its application in transparent and flexible electronics. The formation of high quality and layer thickness modulated MoS\(_2\) film was confirmed by Raman spectroscopy, AFM, HRTEM, and PL analysis. The characterized high optical transparency of \( >90\% \), electrical mobility of \( \sim 12.24 \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \), and \( I_{\text{on/off}} \) of \( \sim 10^6 \) of the large scale MoS\(_2\) film are suitable for transparent and flexible electronics as compared to conventional amorphous silicon (a-Si) or organic films. We observed the presence of critical thickness of MoS\(_2\) over which Mo film was not fully sulfurized due to its diffusion limit in phase transformation. A simple layer thickness identification method based on calculated contrast values in green channel is very well matched with the experimental data confirming its utilization in layer-thickness identification in CVD grown MoS\(_2\) film. The layer-thickness modulated MoS\(_2\) growth in conjunction with the layer-thickness identification method will definitely trigger development of scalable 2D MoS\(_2\) films for transparent and flexible electronics.

This work was supported by a start-up fund from University of North Texas. J. S. acknowledges a partial support from the I-GRO program, University of North Texas.

![Image of MoS\(_2\) films with different number of layers (L\(_1\)–L\(_5\)).](image)

**FIG. 4.** (a) Photographic camera image of MoS\(_2\) films with different number of layers (L\(_1\)–L\(_5\)). The (b) red (c) green, and (d) blue channel images of the original camera image, obtained using matplotlib module for scientific python. The rectangles in 4(c) show examples of domains where \( L \) and \( I \) were taken to calculate the contrast. (e) Contrast values of MoS\(_2\) films for R, G, and B channels as a function of thickness. (f) Three-dimensional contrast image of the green channel of samples L\(_1\)–L\(_5\) calculated by Eq. (5), demonstrating the variation of MoS\(_2\) thickness.

five thicknesses are shown in Fig. 4(e). These contrast values were calculated by taking the statistical mean of \( I_{0,RGB} \) and \( I_{RGB} \) across rectangular domains from the substrate and each MoS\(_2\) film to account for variations (see Fig. 4(c)) for an example of the rectangular domains. This data is plotted as a function of MoS\(_2\) thickness (measured from AFM) so that a linear regression (solid lines) can be fit to the experimental data. The linear regression then provides the link between contrast and expected thickness. It is clear from Fig. 4(e) that blue channel has the largest range with the worst linear fit of \( R^2 = 0.7237 \). The green channel has the best linear fit of \( R^2 = 0.996 \) making it the most accurate channel for thickness identification. The corresponding linear regression of the green channel is

\[
C_G = 0.06894x - 0.0259, \quad \text{(4)}
\]

where \( C_G \) is the contrast of the green channel and \( x \) is the MoS\(_2\) thickness. This yields the critical link between the layer thickness of the MoS\(_2\) layer, \( x \), and the contrast of the green channel, \( C_G \). Thus, an explicit relationship between \( x \) and the green intensities, \( I_G \) and \( I_{0,G} \), can be acquired by solving the green configuration of Eq. (3) into Eq. (4), and solving for \( x \):

\[
C_G = \frac{I_{0,G} - I_G}{I_{0,G}} + 0.0259, \quad \text{(5)}
\]

with this Eq. (5), the MoS\(_2\) thickness can be predicted by simply knowing the \( I_{0,G} \) and \( I_G \) values, which can be easily determined from any color image by using its green channel.

We found that the image contrast in green (G) channel shows the best fit as contrast increases with layer thickness, which can be utilized for identifying the layer thickness simply by taking an optical image of MoS\(_2\). Fig. 4(f) shows the three dimensional contrast image of the green channel of samples L\(_1\)–L\(_5\) calculated by Eq. (5). Contrast differences for the MoS\(_2\) samples with different thicknesses can clearly be seen in this figure.

We report the synthesis of layer-thickness modulated MoS\(_2\) film from multilayers to single layer and its optical and electrical properties towards its application in transparent and flexible electronics. The formation of high quality and layer thickness modulated MoS\(_2\) film was confirmed by Raman spectroscopy, AFM, HRTEM, and PL analysis. The characterized high optical transparency of \( >90\% \), electrical mobility of \( \sim 12.24 \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \), and \( I_{\text{on/off}} \) of \( \sim 10^6 \) of the large scale MoS\(_2\) film are suitable for transparent and flexible electronics as compared to conventional amorphous silicon (a-Si) or organic films. We observed the presence of critical thickness of MoS\(_2\) over which Mo film was not fully sulfurized due to its diffusion limit in phase transformation. A simple layer thickness identification method based on calculated contrast values in green channel is very well matched with the experimental data confirming its utilization in layer-thickness identification in CVD grown MoS\(_2\) film. The layer-thickness modulated MoS\(_2\) growth in conjunction with the layer-thickness identification method will definitely trigger development of scalable 2D MoS\(_2\) films for transparent and flexible electronics.

This work was supported by a start-up fund from University of North Texas. J. S. acknowledges a partial support from the I-GRO program, University of North Texas.

---

31 W. O. Winer, Wear 10, 422 (1967).