Wafer-scale MoS$_2$ thin layers prepared by MoO$_3$ sulfurization†

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Atomic thin molybdenum disulfide (MoS$_2$) layers have attracted great interest due to their direct-gap property and potential applications in optoelectronics and energy harvesting. Meanwhile, they are extremely bendable, promising for applications in flexible electronics. However, the synthetic approach to obtain large-area MoS$_2$ atomic thin layers is still lacking. Here we report that wafer-scale MoS$_2$ thin layers can be obtained using MoO$_3$ thin films as a starting material followed by a two-step thermal process, reduction of MoO$_3$ at 500 °C in hydrogen and sulfurization at 1000 °C in the presence of sulfur. Spectroscopic, optical and electrical characterizations reveal that these films are polycrystalline and with semiconductor properties. The obtained MoS$_2$ films are uniform in thickness and easily transferable to arbitrary substrates, which make such films suitable for flexible electronics or optoelectronics.

1. Introduction

Graphene has attracted much attention due to its unique chemical structure, two-dimensionality and physical properties such as high carrier mobility and excellent sensitivity.$^1$ These properties make it a good candidate for high-frequency devices$^2$ and biosensor applications.$^3,4$ However, the gapless nature of graphene$^5$ slows its development in logic circuit applications. Other types of two-dimensional layered nanomaterials, transition-metal dichalcogenides, also show great potential in nanoelectronics and optical application.$^6–9$ In particular, atomically thin molybdenum disulfide (MoS$_2$) layers have drawn great interest because they exhibit many desirable physical properties. When the dimension of MoS$_2$ is reduced from a three-dimensional bulk form into a two-dimensional sheet, the band gap transforms from an indirect to a direct one.$^{10,11}$

Recently, exfoliated MoS$_2$ atomic thin layers have been fabricated into transistors which demonstrate excellent on/off current ratios and high carrier mobility, promising for low power electronics.$^{12}$ Several methods have been proposed to prepare MoS$_2$ atomic thin layers, including scotch tape assisted micromechanical exfoliation,$^{8–11,13}$ intercalation assisted exfoliation,$^{14–21}$ solution exfoliation,$^{5,16,17,22,23}$ physical vapor deposition,$^{24,25}$ hydrothermal synthesis,$^{26}$ electrochemical synthesis,$^{27,28}$ sulfurization of molybdenum oxides$^{29,30}$ and thermolysis of a precursor containing Mo and S atoms.$^{22}$ Most of these methods may produce good quality of MoS$_2$ layers but the lateral dimensions are in the range of several to several tens of micrometers, which are not suitable for use in large area electronics. Methods to synthesize highly uniform and large area MoS$_2$ thin films with ideal electrical performance is still limited since MoS$_2$ tends to form nanoparticles or nanotube structures during the synthesis.$^{31}$ Thus, wafer-scale synthesis of highly uniform thin MoS$_2$ films on insulating substrates is desirable. Zhan et al. have reported a method to obtain MoS$_2$ layers by direct sulfurization of Mo metal thin films,$^{32}$ where the obtained MoS$_2$ shows resistor-like behavior. In this contribution, we report that wafer-scale MoS$_2$ thin layers can be obtained by a two-step thermal process to convert a MoO$_3$ thin layer to a MoS$_2$ thin layer. Spectroscopic, optical and electrical characterizations reveal that these films are polycrystalline and with semiconductor behaviors. The MoS$_2$ films obtained are uniform in thickness and are easily transferable to arbitrary substrates, which make such films favorable for flexible electronics or optoelectronics.

2. Experimental section

2.1 Synthesis of thin-layer MoS$_2$

MoO$_3$ (molybdenum(vi) oxide) powder was purchased from Alfa Aesar (99.998%). MoO$_3$ thin films with desired thickness were thermally deposited on a c-face sapphire substrate at a rate of 0.5 Å s$^{-1}$ by a thermal evaporator, where the sapphire substrate was cleaned with a standard piranha solution prior to the
deposition of MoO$_3$. The MoO$_3$ film coated on a c-face sapphire substrate was placed in the cold zone of the quartz tube flowing with an Ar–H$_2$ mixture (flow rate = 4:1; 1 Torr). When the centre of the furnace reached 500 °C, the substrate was moved to the hot zone of the furnace for the first annealing. The chamber was kept at a low pressure (1 Torr) in an Ar–H$_2$ atmosphere (flow rate 4:1). After 1 h, the sample was moved to the cold zone and sulfur powder loaded in a ceramic boat was placed in the cold zone in the furnace. Then the samples together with the sulfur boat were moved to the centre of the furnace again for the second annealing after the hot zone reached 1000 °C. The substrate was heated to 1000 °C at a rate of 15 °C min$^{-1}$. The sample was kept at 1000 °C for 30 min using 70 scm Ar as carrier and protection gas (pressure: 600 Torr). After this, the heater of the furnace was turned off, and the sample was left in the chamber to cool down to room temperature.

2.2 Transfer of MoS$_2$ onto fresh SiO$_2$/Si or other substrates

To transfer as-grown MoS$_2$ onto fresh SiO$_2$ (300 nm)/Si substrates, the MoS$_2$ film was coated with a layer of poly(methyl methacrylate) (PMMA) (Micro Chem. 950K A4) by spin-coating (step 1: 500 rpm for 10 s; step 2: 3000 rpm for 60 s), followed by baking at 100 °C for 10 min. After that, the PMMA-capped MoS$_2$ was then put into a NaOH (2 M) solution at 100 °C for 30 min. The PMMA-supported MoS$_2$ film was then transferred to deionized (DI) water to remove the etchant and residues. A fresh SiO$_2$/Si substrate was then used to “fish out” the PMMA-capped MoS$_2$ film, followed by drying on a hot-plate (100 °C for 10 min). The PMMA was removed by acetone, isopropyl alcohol (IPA), followed by DI water and chloroform rinsing.

2.3 Characterization

The AFM images were taken in a Veeco Dimension-Icon system. The scanning rate was 0.976 Hz with 512 scanning lines. Raman spectra were collected in a NT-MDT confocal Raman microscopic system (exciting laser wavelength 473 nm and laser spot-size of ~0.5 μm). The Si peak at 520 cm$^{-1}$ was used as reference for wavenumber calibration in Raman characterization. Photoluminescence (PL) measurements were performed with excitation from a solid-state 473 nm laser with a power of 500 μW. The laser radiation was focused onto the MoS$_2$ sheets with a spot-size around 0.5 μm. The nanostructure of MoS$_2$ sheets was investigated in a JEOL-2010F TEM with accelerating voltage of 200 keV. Chemical configurations were determined by X-ray photoelectron spectroscopy (XPS, Phi V6000). XPS measurements were performed with an Mg-Kz X-ray source on the samples. The energy calibrations were made against the C 1s peak to eliminate the charging of the sample during analysis. The field-effect transistor device was fabricated by evaporating Au electrodes (80 nm thick) directly on top of the selected, regularly shaped graphene sheets using a copper grid (200 mesh, 20 μm spacing) as a hardmask. The typically obtained channel length between source and drain electrodes was around 20 μm. The electrical measurements were performed in ambient conditions using a Keithley semiconductor parameter analyzer, model 4200.

3. Results and discussion

A schematic illustration for the synthesis of thin MoS$_2$ layers is shown in Fig. 1a. A layer of MoO$_3$ (3.6 nm thick) was deposited on a clean c-face sapphire substrate by thermal evaporation with a deposition rate of 0.05 nm s$^{-1}$. The MoO$_3$-coated sapphire substrate was first reduced to MoO$_2$ or other reduced forms in a hydrogen/Ar environment at 500 °C for 1 h. The sample was then annealed in a sulfur-rich environment at 1000 °C for 30 min, where the chamber pressure was kept at 600 Torr and Ar was used as a dilute gas during the reaction. The approach is simple and scalable to wafer-scale fabrication. It is noteworthy to point out that we have attempted the one-step direct sulfurization of MoO$_3$ with sulfur at 1000 °C, where the obtained MoS$_2$ films exhibited semiconductor properties, but the electrical carrier mobility was at least one order of magnitude lower than that from the two-step thermal process. The chemical equations for the two-step reaction are proposed in eqn (1) and (2).

\[
\text{MoO}_3(\text{s}) + H_2(\text{g}) \rightarrow \text{MoO}_2(\text{s}) + H_2O(\text{g}) \tag{1}
\]

\[
\text{MoO}_2(\text{s}) + 2S(\text{g}) \rightarrow \text{MoS}_2(\text{s}) + O_2(\text{g}) \tag{2}
\]

Fig. 1b shows a photograph for the MoS$_2$ thin layer grown on a 2 inch sapphire wafer, where the MoS$_2$ layer is continuous and uniformly flat across the wafer. The root-mean-square surface roughness measured by atomic force microscopy (AFM) is around 0.2 nm as shown in Fig. 1c. To estimate the thickness of the synthesized MoS$_2$ film, AFM was used to analyze the topography of an area with an occasionally found void as shown in Fig. 1d, where the cross-sectional height profiles for several randomly selected traces (indicated as white lines) show that the thickness of the MoS$_2$ layer ranges from 1.8 to 2.0 nm. The cross-sectional profile for one of the traces is shown in Fig. 1e. Additional AFM images are provided in Fig. S1 (ESI†).

Tunnelling electron microscopy (TEM) was used to further examine the layer number of the obtained wafer-scale MoS$_2$ thin films discussed in Fig. 1. The low-magnification TEM image in Fig. 2a shows the MoS$_2$ film on TEM grids and some wrinkles are evident on the edge of the film. These wrinkles were caused by the unavoidable film folding after the mechanical scratching during the TEM sample preparation. Three MoS$_2$ layers, where each layer is ~0.65 nm thick are identified at the wrinkled area in Fig. 2b, providing direct evidence that the synthesized films are trilayer MoS$_2$. The TEM images in Fig. 2c and d show the large-scale view for the MoS$_2$ film. The typical high-resolution TEM image for the MoS$_2$ layer is shown in Fig. 2e, where the periodic atom arrangements suggest that the MoS$_2$ layer is polycrystalline. The inset of Fig. 2e displays the selected area electron diffraction (SAED) pattern for the sample taken with an aperture size (~160 nm), and the points arranged in multiple hexagons also suggests that the MoS$_2$ layer stacking is polycrystalline. The TEM sample was transferred onto the TEM grid from a sapphire substrate by mechanical scratching and thus we can occasionally find monolayer MoS$_2$ on TEM grids. Fig. 2f shows the TEM and SAED pattern for the monolayer MoS$_2$ area, where the diffraction points (110) and (100) are indicated. Meanwhile, the lattice spacing of 0.27 and 0.16 nm corresponding to the (110) and (100) planes are indicated. These results
further corroborate that the MoS\textsubscript{2} grown by the method is crystalline.

Fig. 3a and b display detailed X-ray photoemission spectroscopy (XPS) scans for the Mo and S binding energies of the MoO\textsubscript{3} layer before and after sulfurization. The survey scans are provided in Fig. S2 (ESI†). The MoO\textsubscript{3} layer exhibits two characteristic peaks at 235.5 and 232.2 eV, attributed to the 3d\textsubscript{3/2} and 3d\textsubscript{5/2} binding energies for Mo\textsuperscript{6+}. After sulfurization, the Mo 3d peaks are observed at 232.5 and 229.3 eV, assigned to the doublet

Fig. 1  (a) Schematic illustration for the synthesis of MoS\textsubscript{2} layers by MoO\textsubscript{3} sulfurization. A layer of MoO\textsubscript{3} (~3.6 nm) was thermally evaporated on the sapphire substrate. The MoO\textsubscript{3} was then converted to a MoS\textsubscript{2} by a two-step thermal process. (b) MoS\textsubscript{2} layer grown on a sapphire wafer. (c and d) Surface topographic images obtained by AFM. (e) A selected cross-sectional height profile showing the thickness of the MoS\textsubscript{2} layer.

Fig. 2  (a and b) Low-magnification TEM images of the MoS\textsubscript{2} layers. The folded area at the edge clearly shows that the film is a MoS\textsubscript{2} trilayer and the distance between each layer is 0.65 nm. (c and d) TEM images show the large-area view of the film, where polycrystalline structures can be identified. (e) Typical high-resolution TEM image and SAED pattern for the trilayer MoS\textsubscript{2} film. (f) Selected high-resolution image and SAED pattern for the single-layer MoS\textsubscript{2}.

Fig. 3  X-Ray photoemission spectroscopy scans for (a) Mo and (b) S binding energies of the MoO\textsubscript{3} layer before and after sulfurization. (c) Raman and (d) photoluminescence spectra for the obtained MoS\textsubscript{2} trilayer after MoO\textsubscript{3} sulfurization.
Mo $d_{3/2}$ and Mo $d_{5/2}$ for Mo$^{4+}$. The stoichiometric ratio ($S : Mo$) estimated from the respective integrated peak area of XPS spectra is close to $\sim 2$. The result further confirms the formation of MoS$_2$. Fig. 3c and d show the Raman spectra and photoluminescence (PL) spectra for a MoS$_2$ trilayer, respectively. The excitation source is a laser with a wavelength of 473 nm. The Raman characteristic peaks at 303.8 and 356.8 cm$^{-1}$ correspond to the $A_{1g}$ and $E_{2g}$ modes, respectively. The PL spectrum in Fig. 3d shows two main emission peaks at 627 and 673 nm, consistent with other reports for MoS$_2$ thin sheets obtained from exfoliation methods. These emissions are the $A1$ and $B1$ direct excitonic transitions as reported elsewhere.\(^{10}\) Fig. S3 (ESI†) shows the absorption spectrum for the MoS$_2$ film where we also observe the $A1$ and $B1$ absorption peaks.

To access the homogeneity of the MoS$_2$ thin layers across the wafer, the MoS$_2$ film on a 2 inch sapphire wafer was divided into several areas, and numbers are labelled at the sites as in Fig. 4a. Raman spectra were taken at each numbered site. The energy difference between $A_{1g}$ and $E_{2g}$ Raman peaks ($\Delta$) has been found to relate to the number of MoS$_2$ layers.\(^{33}\) In Fig. 4b, we plot the statistical values as a function of numbered site (as indicated in Fig. 4a), where the variation of $\Delta$ is reasonably small (within 0.5 cm$^{-1}$) across the whole wafer. It is known that the peak width of the Raman peak is also sensitive to the crystalline quality of the MoS$_2$ layers.\(^{33}\) The full width at half maximum (FWHM) of the $E_{2g}$ peak as a function of numbered site is shown in Fig. 4b, where the variation also consistently suggests that the as-grown MoS$_2$ wafer layers exhibit good uniformity. In addition to the statistical measurements, we have also performed PL and Raman mappings for a 50 $\mu$m $\times$ 50 $\mu$m square area and the results shown in Fig. S4 and S5 (ESI†) demonstrate that the spectroscopic quality of MoS$_2$ film is very continuous, where many isolated MoS$_2$ domains are observed (Fig. S6, ESI†).

Table 1 summarizes the thickness and morphology for the obtained MoS$_2$ structures upon sulfurization starting with various MoO$_3$ thicknesses. Also, the MoS$_2$ layers synthesized on sapphire are of superior quality to those obtained on SiO$_2$/Si substrates, and the results presented in the text were all for films synthesized on sapphire substrates. We have also performed Raman and PL characterizations for MoS$_2$ layers obtained from thinner MoO$_3$ films and the results are summarized in Fig. S7 (ESI†). In general, the Raman wavenumber value increases and the PL peak position red shifts with the initial MoO$_3$ thickness, consistent with the reported trend for those obtained from exfoliated MoS$_2$ layers.

The as-grown wafer-scale MoS$_2$ film on sapphire can be transferred on to arbitrary substrates such as 300 nm SiO$_2$ on Si (SiO$_2$/Si) by the PMMA-assisted transfer method, a conventionally used method for graphene transfer.\(^{36}\) Fig. 5 illustrates the procedure to transfer an as-synthesized MoS$_2$ layer from a sapphire to a SiO$_2$/Si wafer.

To evaluate the electrical performance of the MoS$_2$ thin layers, we fabricated bottom-gate transistors by evaporating Ti/Au electrodes directly on top of the MoS$_2$ layers on SiO$_2$/Si. Fig. 6a shows the typical output characteristics (drain current $I_d$ vs. drain voltage $V_d$) of the MoS$_2$ device while Fig. 6b shows the typical transfer curves ($I_d$ vs. gate voltage $V_g$) of the device. It is noted that the FET shows typical n-type behavior, consistent with other reports.\(^{12,30,33}\) The field-effect mobility of electrons was extracted based on the slope $\Delta I_d/\Delta V_g$ fitted to the linear regime of the transfer curves using the equation $\mu = (L/W)C_{ox}(\Delta V_g/\Delta V_f)$, where $L$ and $W$ are the channel length and width and $C_{ox}$ is the gate capacitance.\(^{37}\) It is observed that the on/off current ratio for the MoS$_2$ device is around $10^5$ and the field-effect electron mobility of the device is about 0.8 cm$^2$ V$^{-1}$ s$^{-1}$.

<table>
<thead>
<tr>
<th>Thickness of MoO$_3$</th>
<th>Thickness of the obtained MoS$_2$</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8 nm</td>
<td>1.52 nm (2 layers)</td>
<td>Isolated domains</td>
</tr>
<tr>
<td>1.5–2.2 nm</td>
<td>1.5–2.2 nm (2–3 layers)</td>
<td>Isolated domains</td>
</tr>
<tr>
<td>3.6 nm</td>
<td>1.8–2.0 nm (3 layers)</td>
<td>Continuous</td>
</tr>
</tbody>
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![Fig. 4](image_url) (a) The numbers in the photo indicate the sites for Raman statistical measurements. (b) The statistical $\Delta$ values and the full-width at half-maximum (FWHM) of the $E_{2g}$ peak plotted as a function of numbered site.

![Fig. 5](image_url) Pictures showing the procedure to transfer as-synthesized MoS$_2$ layer from a sapphire to a SiO$_2$/Si wafer.

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**Table 1: Effect of MoO$_3$ thickness on the morphology of resulting MoS$_2$**
In conclusion, we have proposed a simple method to synthesize MoS$_2$ thin layers in wafer-scale by a two-step thermal process on evaporated MoO$_3$ layers in the presence of sulfur. Various spectroscopic and microscopy methods including Raman, PL, XPS and TEM establish the crystallinity and compositions of MoS$_2$ thin layers. The obtained MoS$_2$ thin layers are uniform in thickness and easily transferable onto arbitrary substrates. A field effect transistor fabricated with MoS$_2$ thin layers in a bottom gate geometry shows n-type behaviour with on/off current ratio $\sim 10^2$, and the field-effect electron mobility of the device is about 0.8 cm$^2$ V$^{-1}$ s$^{-1}$, comparable with the FET prepared by mechanically exfoliated MoS$_2$. This approach paves the large-scale route to the synthesis of MoS$_2$ films for future flexible electronics or optoelectronics.

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References


Fig. 6 (a) Output characteristics (drain current $I_D$ vs. drain voltage $V_D$) and (b) transfer curves ($I_D$ vs. gate voltage $V_G$) for the bottom-gate transistor based on the MoS$_2$ trilayer.

4. Conclusions

In conclusion, we have proposed a simple method to synthesize MoS$_2$ thin layers in wafer-scale by a two-step thermal process on evaporated MoO$_3$ layers in the presence of sulfur. Various spectroscopic and microscopy methods including Raman, PL, XPS and TEM establish the crystallinity and compositions of MoS$_2$ thin layers. The obtained MoS$_2$ thin layers are uniform in thickness and easily transferable onto arbitrary substrates. A field effect transistor fabricated with MoS$_2$ thin layers in a bottom gate geometry shows n-type behaviour with on/off current ratio $\sim 10^2$, and the field-effect electron mobility of the device is about 0.8 cm$^2$ V$^{-1}$ s$^{-1}$, comparable with the FET prepared by mechanically exfoliated MoS$_2$. This approach paves the large-scale route to the synthesis of MoS$_2$ films for future flexible electronics or optoelectronics.