Growth of wafer-scale MoS\(_2\) monolayer by magnetron sputtering

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The two-dimensional layer of molybdenum disulfide (MoS\(_2\)) exhibits promising prospects in the applications of optoelectronics and valleytronics. Herein, we report a successful new process for synthesizing wafer-scale MoS\(_2\) atomic layers on diverse substrates via magnetron sputtering. Spectroscopic and microscopic results reveal that these synthesized MoS\(_2\) layers are highly homogeneous and crystallized; moreover, uniform monolayers at wafer scale can be achieved. Raman and photoluminescence spectroscopy indicate comparable optical qualities of these as-grown MoS\(_2\) with other methods. The transistors composed of the MoS\(_2\) film exhibit p-type performance with an on/off current ratio of \(\sim 10^3\) and hole mobility of up to \(\sim 12.2\) cm\(^2\) V\(^{-1}\) s\(^{-1}\). The strategy reported herein paves new ways towards the large scale growth of various two-dimensional semiconductors with the feasibility of controllable doping to realize desired p- or n-type devices.
control of thickness, purity and uniformity is still a challenge. For practical application, a scalable and controlled synthesis technique is required. Therefore, alternative approaches, either complementary or advanced, are highly desired.

To date, the majority of the synthesized MoS$_2$ films based on the abovementioned methods are n-type doped.$^{13,28,30}$ Very recently, it has been reported that p-type-doped MoS$_2$ can be realized by efficient plasma treatment.$^{31}$ Moreover, the formation of MoS$_2$ p-n junction devices was exhibited by using electric double-layer gating.$^{32,33}$ To meet the digital logic application demands, the research for an intrinsically p-type TMD monolayer has become necessary. However, the large-scale device applications still rely on the breakthrough in the growth of large-sized, control-doping thin layers.

In this work, we report a one-step process that can grow good quality monolayers or few-layer MoS$_2$ films at wafer scale on various substrates using magnetron sputtering. The detailed growth procedure is given in the ESI.$^\dagger$ As is well known, the magnetron sputtering technique is capable of large scale massive production, which is compatible with current industrial processes with low cost and easy controllability. Previously, the magnetron sputtering method is infrequently used for 2D material growth, particularly for the TMDs. The main obstacle is possibly the difficulty of controlling the S or Se sources. In contrast to previous CVD methods,$^{22–24,27,28}$ Mo was sputtered to produce energized molecular-sized reactive Mo atoms or clusters that are more reactive than Mo or MoO$_3$ films in the CVD method. Mo atoms react with vaporized S atoms before being placed on hot substrates to form MoS$_2$ layers. Our spectroscopic, microscopic and electrical measurements suggest that this synthetic process can lead to the growth of monolayers, bilayers, trilayers and thicker MoS$_2$ sheets. These MoS$_2$ films are highly homogeneous, and their size is up to several centimeters, which is currently limited by the size of our sample stage. They exhibit optical and electrical qualities comparable to that of the MoS$_2$ synthesized by other methods.

Experimental methods

Characterization

The surface morphology of the samples was examined with a commercial atomic force microscope (AFM, Bruker ICON-PKG). Raman spectra were obtained on a single-gating micro-Raman spectrometer (Horiha-JY T64000) excited with 532 nm laser. The signal was collected through a 100× objective lens, dispersed with a grating of 1800 g mm$^{-1}$, and detected by a liquid nitrogen-cooled charge-coupled device. Photoluminescence (PL) was obtained from the same micro-Raman spectrometer. Note that the Si peak at 520 cm$^{-1}$ was used for calibration in the experiments.

The samples were in situ transferred to an X-ray photoelectron spectroscopy (XPS) chamber for analysis. XPS measurements were performed in a VG ESCALAB 220i-XL system using a monochromatic Al K$_\alpha$ source. The pass energy of the analyzer was set to 10 eV for high measurement resolution.

Transmission electron microscopy (TEM) (JEOL 2100) was used to obtain information of the microstructures. For sample transfer, poly(methyl methacrylate) (PMMA, from MicroChem) was spin-coated on the top of the sample. After baking at 180 °C for 2 min, the PMMA-coated sample was immersed into a 60 °C 2 M NaOH solution to etch the SiO$_2$ until the PMMA with MoS$_2$ film floated on the surface. Subsequently, a lacey carbon TEM grid was used to identify PMMA and the MoS$_2$ film. Finally, the PMMA film was removed by acetone and the MoS$_2$ layers were cleaned by DI water.

Field-effect transistors fabrication and measurements

To fabricate back-gated MoS$_2$ FETs, the metallic drain/source contacts (5 nm Cr/100 nm Au) were fabricated by photolithography, followed by metal deposition and lift-off. Finally, another Au coating layer was made onto the backside of the Si substrate, which served as a back gate contact. The device characteristic curves were measured using a Keithley 4200 semiconductor parameter analyzer.

Results and discussion

Fig. S1 (see the ESI$^\dagger$) schematically illustrates our experimental setup for growing MoS$_2$. The MoS$_2$ layers are first grown on c-plane sapphire (Al$_2$O$_3$) and SiO$_2$/Si. The as-grown MoS$_2$ thin films show uniformity and continuity across an area of centimeters under an optical microscope or by the naked eye. Fig. 1(a) shows an image of MoS$_2$ thin layer grown on sapphire. The as-grown MoS$_2$ layer is in faint yellow color and found to have specular reflection without grain boundaries. In addition, the absence of grain boundaries was confirmed via atomic force microscopy (AFM) measurement at the micrometer scale. Combining these measurements, large-area continuous and uniform MoS$_2$ film is indicated. The size of the synthesized films is limited by the dimensions of our sample heating holder. The surface morphology is further characterized by AFM at different areas on the film, which exhibit similar surface morphology across the film. A typical AFM measurement (5 µm × 5 µm) is presented in Fig. 1(b), which demonstrated an atomically flat surface. The AFM images confirm that the synthesized film possesses a continuous and smooth surface (root-mean-square (RMS) roughness <0.2 nm) without any step or void. The roughness values are comparable to the values for the substrate itself. The thickness variation is found to be negligible, indicating that the films were highly uniform. Similar uniformity can also be achieved for the thicker synthesized MoS$_2$ films (see Fig. S2 in the ESI$^\dagger$). A larger-scale AFM image given in Fig. 1(c) shows the edge of the MoS$_2$ film. In Fig. 1(d), the height profile drawn at the edge reveals a film thickness of ~0.7 nm, which agrees well with one atomic layer of MoS$_2$. The layer thickness and uniformity assignment are further confirmed by Raman spectroscopy, as subsequently discussed.
We controlled the layer thickness via growth parameters, including deposition time, substrate temperature, and growth power. To demonstrate the control on thickness of atomically thin MoS2 layers, Fig. 2 shows the Raman spectra collected from the as-grown MoS2 thin films on sapphire for variable thickness. The Raman spectra for the MoS2 films grown on SiO2 are given in Fig. S3 of the ESI.† By comparing the Raman spectra in Fig. 2 and S3,† we found that the MoS2 film on sapphire exhibits narrower and stronger Raman peaks than that on SiO2, which suggests better crystalline quality of MoS2 film on sapphire than that on SiO2/Si. The better crystalline quality of MoS2 film grown on sapphire is due to the fact that sapphire is atomically flat with a step height of 0.22 nm, which is sufficiently low to ensure the growth of continuous MoS2 film. In addition, dipole–dipole interactions exist between S and Al atoms on sapphire, which align the MoS2 layers in a better manner.35 In Fig. S4 of the ESI,† the Raman spectra were collected with lower (0.74 mW) and higher (11 mW) laser intensities. It is shown that the Raman spectrum under 11 mW laser intensity exhibits a strong signal without burning the sample. Moreover, the peak positions and their separation do not depend on the excitation laser intensity, which confirms that there is no laser heating effect. Therefore, 11 mW is used for the following measurements. As shown in Fig. 2a, the MoS2 films exhibit two Raman characteristic bands at \( \sim 406 \text{ cm}^{-1} \) and \( \sim 386 \text{ cm}^{-1} \), corresponding to out-of-plane \( (A_{1g}) \) and in-plane \( (E^{1g}) \) vibration modes, respectively. The full width at half maximum (FWHM) of the \( A_{1g} \) peak of the synthesized MoS2 monolayer is \( 4.4 \text{ cm}^{-1} \), close to that of the exfoliated monolayer, \( 3.7 \text{ cm}^{-1} \), which suggests a good crystalline quality for our synthesized film. As expected, these two bands shift with MoS2 layer thickness. In addition, the frequency differential \( (\Delta k) \) between \( A_{1g} \) and \( E^{1g} \) modes has been used to identify the layer number of MoS2. In general, the \( E^{1g} \) vibration softened, whereas the \( A_{1g} \) vibration stiffened at higher layer numbers. This is demonstrated in Fig. 2(a), in which the \( A_{1g} \) is blue-shifted and \( E^{1g} \) is red-shifted with an increase in film thickness. \( \Delta k \) of the synthesized thin film increases from 19.3 to 24.3 cm\(^{-1}\) from monolayer to bulk, respectively. The assignment of \( \Delta k = 19.3 \text{ cm}^{-1} \) to monolayer is in agreement with previous reports.22,27,36 The thicknesses of the bilayer (2L) and trilayer (3L) are confirmed by transmission electron microscopic (TEM) measurement. Note that the optimized process reported herein reproduces homogeneous MoS2 bilayers or multilayers fairly easily. However, the monolayer MoS2 is more difficult to achieve, which is attributed to the growth kinetics of this process.

The uniformity of the layers is quantitatively assessed by conducting numerous Raman spectra at random spots over a typical \( \sim 1 \text{ cm} \times 1 \text{ cm} \) sapphire substrate. Fig. 2(b) shows...
Raman spectra for each measured spot for a monolayer MoS$_2$. It is known that the peak width of the Raman peak is also sensitive to the crystalline quality, and therefore the FWHMs of all $E^\prime$ and $A_{1g}$ modes are also analyzed. As shown in Fig. 2(b), the variation of $\Delta k$ and FWHMs are reasonably small: ±0.27 cm$^{-1}$ for $\Delta k$ and ±0.16 cm$^{-1}$ for FWHMs. These results confirm that the synthesis method described herein can provide highly homogeneous films with similar crystalline quality across the entire substrate. In addition, shear or breathing Raman modes would appear at low frequency for multilayers. The absence of these modes crossing over the surface of our sample suggests the formation of uniform monolayers on a large scale.

X-ray photoemission spectroscopy (XPS) was used to examine the film-substrate interface chemistry, as well as the electronic structure of the synthesized films. Fig. 3 shows the core-level XPS spectra of Mo 3d, S 2p and the valence band (VB) for MoS$_2$ films on sapphire. The peaks at 229.3 and 232.5 eV are attributed to the doublet Mo 3d$^{5/2}$ and 3d$^{3/2}$ orbitals, respectively, in agreement with reported binding energy values. From the perspective of thermodynamics, the Mo layer would prefer to bind to an oxide surface to form an interfacial Mo–O oxide on an oxidized substrate. However, our XPS analysis shows no evidence of Mo–O peak at higher energy side, suggesting a negligible interfacial interaction, owing to kinetic reasons. As shown in Fig. 3(b), the spin–orbital splitting for S 2p is well resolved into S 2p$_{3/2}$ and 2p$_{1/2}$ at 162.2 and 163.3 eV, respectively. Especially, the S 2p spectrum of the 2L film almost bears the same shape of that of the bulk, which indicates good crystalline structure for the atomically thin film. In addition, as previously demonstrated, 1T-MoS$_2$ and 2H-MoS$_2$ phases display distinguished binding energies for Mo 3d. Our XPS results support the formation of pure phase of 2H-MoS$_2$ crystal structure. The valence band of MoS$_2$ is built up by the hybridization of Mo 4d and S 3p, which exhibits four major features within 0–10 eV. As shown in Fig. 3(c), the electronic states of Mo 4d$^{-2}$ band is readily developed at ~2 eV for monolayer MoS$_2$. The higher binding energy Mo 4d–S 3p orbitals are overlapped with the substrate O 2p peaks and are gradually pronounced with increasing layer thickness. These observations indicate well-developed band formation from hybridized Mo 4d–S 3p orbitals, which indicate long-range in-plane ordering of the MoS$_2$ structure. Along with the development of the valence band structure, the separation between the Mo 3d$^{5/2}$ and Mo 4d$_z$ peaks increases with increase in layer thicknesses (see Fig. S5 of the ESI†). It changes from 227.25 eV for the monolayer to 227.55 eV for the thicker films. This observation confirms the development of the electronic structure of MoS$_2$ film with the previously demonstrated thickness.

To further elucidate the crystalline structure, the as-grown MoS$_2$ film was transferred onto a lacey carbon grid for TEM characterization. A typical high resolution TEM image as well as the selected area electron diffraction (SAED) pattern are given in Fig. 4(a), which reveals the ordered crystalline with hexagonal lattice structure, and the lattice spacing of 0.27 nm.
for (100) planes is observed. The hexagonal atomic arrangement shown in the TEM image and the SAED pattern indicate that the basal plane of the synthesized thin film is (001), i.e. the c-axis of the MoS₂ films is perpendicular to the substrate. Fig. 4(b) is the magnified TEM image of a specific area, which is indicated by a square, in Fig. 4(a). The periodic atom arrangement for Mo is shown, confirming that the MoS₂ film has a crystalline structure. The MoS₂ film on TEM grids exhibit some wrinkles at the edge of the film, which is caused by unavoidable film folding of the free-hanging MoS₂ sheets at the edge during the TEM sample preparation. This, however, permits the assessment of layer numbers under top-view TEM. For instance, bilayer (2L) and trilayer (3L) edges are displayed in Fig. 4(c). This local layer thickness characterization is in agreement with the Raman spectra.

In addition, photoluminescence (PL) measurement at room temperature is shown in Fig. 4(d), exhibiting the layer-dependent optical properties. The PL spectrum for the monolayer MoS₂ exhibits the strongest emission at 1.83 eV, as well as a shoulder at 2.00 eV, which can be correlated to the A and B exciton transition arising from direct gap transitions at the K point. These excitonic energies, as well as the splitting of ∼170 meV, agree well with previous reports,⁴¹,¹⁴,²⁶ which result from the strong spin–orbit coupling due to the breaking of inversion symmetry.⁴⁰,⁴¹ The PL response confirms the direct band transition in the 2H-MoS₂ monolayer. Our results suggest a comparable optical quality as that of other synthesized MoS₂ films.²⁸,⁴² The strong PL intensity for monolayer MoS₂ drops dramatically for bilayer film and falls to zero when the layer number is larger than three. This suggests that the band structure of our MoS₂ film bears a similar dependence with that of exfoliated films, thus further confirming the layer number assignment for our sputter-grown MoS₂ films. We note that, similar to some previous reports,⁴³,⁴⁴ the exciton B peak is less resolved as compared to the mechanically exfoliated monolayer. This could be due to the presence of lattice disorder or residual dopants that decouple the spin–orbital interaction.

Thin layer MoS₂ are well suited as a channel material in field effect transistor (FET) applications, exhibiting high mobility, almost ideal switching characteristics and low standby power dissipation. To evaluate the electrical performance of the as-grown MoS₂ sheets, we fabricated bottom-gate FETs on MoS₂ films by evaporating Cr/Au electrodes as source and drain electrodes on top of the MoS₂ thin film, 200 nm thick SiO₂ as a dielectric and Au-coated Si as a back gate. We performed electrical measurements at room temperature in an ambient environment. Fig. 5(a) shows the typical transport
characteristic of a representative device having a channel length of 100 μm and a width of 10 μm as shown in the inset. In contrast to previous results,13,28,30 a p-type field effect behavior is exhibited with an on/off current ratio of ∼103 at ∼20 V gate voltage (Vg) and a bias voltage (Vds) at 4 V. The linear dependence of drain current (Ids)–Vds characteristic curves, see Fig. 5(b), suggests ohmic contact between the film and the electrodes, indicating that the observed field effect behavior is caused by the MoS2 channel rather than Schottky barriers at the contact. Consistent with the transfer curves, Ids increases at a negative gate voltage, indicating that the hole is the majority carrier. From the measurements, the value of hole field effect mobility (μ) of this MoS2 FET is estimated to be ∼12.2 cm2 V−1 s−1 based on the slope of ΔIds/ΔVg, fitted to the linear regime of the transfer curves using the expression

$$\mu = \left( \frac{L C_{ox} V_d}{W} \right) \left( \frac{\Delta I_{ds}}{\Delta V_g} \right). \quad (1)$$

where L and W is the length and width of the channel, respectively, C_{ox} is the capacitance between the channel and the backgate per unit area (∼1.7 × 10−4 F m−2 for 200 nm SiO2). We have performed numerous measurements over several channels and found the mobility ranging from ∼2 to ∼12 cm2 V−1 s−1, which is centered at ∼7 cm2 V−1 s−1. This result is reasonably comparable to those of back-gated FETs made with mechanically exfoliated monolayers measured in similar conditions (0.1–10 cm2 V−1 s−1).13,23,24,27,28 The mobility of the MoS2 FETs could be significantly improved by using local top-gate high-k dielectrics, such as HfO2, as gate materials. We can thus conclude that the synthesized thin film has a reasonably comparable electrical quality with that of exfoliated MoS2. We speculate that by controlling annealing time, annealing environment or the substrate material, the film quality can be further improved, leading to higher carrier mobility.

The p-type doping could be caused by cationic/anionic vacancies/interstitials that are introduced during the deposition process. Tentatively, this is assigned to the S interstitials based on slightly larger S concentration from our XPS measurement (atomic ratio of Mo:S ∼ 1 : 2.06). In addition, recent theoretical calculations predict that the absorption of H2, O2, and H2O on the surface of MoS2 can also result in p-type doping.45 This could mostly occur at the surface defect sites.

The major difference between our one-step sputtering growth method and other growth methods, such as CVD, is the kinetic energy of landing MoS2 molecules. The typical kinetic energies of landing molecules are on the order of tens of eV, even after multiple scattering events within the background gas, the residual energy of which requires in-plane movement. With this energy, the requirement for the nucleation center as required for CVD growth14 is no longer a key issue. Our experimental observations suggest that the Ar pressure and sputtering power play key roles in this growth mechanism. With this difference, different crystal structure imperfections may be introduced as compared to previous methods. This, however, brings new functionalities and opens new possibilities to explore the material properties. In case of CVD growth, S vacancies are normally formed, which lead to n-type doping. While using sputtering method, additional energized S can be incorporated into the lattice to serve as p-type dopants, which is the case as we demonstrated herein. Note that the S interstitials are not observed for the CVD film, suggesting that the excess S vapor itself is not enough for p-type doping, as opposed to the sufficient kinetic energy. Under Mo deficiency conditions, either Mo vacancies or S interstitials will create acceptor levels inside the band gap of MoS2, which lead to p-type doping. Although the detailed growth dynamic studies require further investigation, which are not covered by the current work, we note that the doping type can be modulated via sputtering power and that the p-type doping is related to the Mo deficiency conditions. Moreover, we like to emphasize that the controlled doping study can be easily realized via the use of some alloy targets adopting this strategy.

**Conclusion**

In conclusion, we demonstrated a proof-of-concept, one-step, large-area synthesis of uniform MoS2 films with readily controlled layer numbers using a magnetron sputtering method. This method can be used to produce large-area, good quality MoS2 monolayers and few-layer films with great uniformity and controllability. The electric measurement for the bottom-gate transistor shows p-type semiconductor behavior. The on/off current ratio is ∼1×103, and the hole mobility is up to ∼12.2 cm2 V−1 s−1. This synthesis approach can be readily scaled up to produce wafer-scale 2D MoS2 for the development of practical electronic and photonic devices. This synthesis method could be extended to the growth of other TMDs as well as controlled doping for these systems, opening up new avenues for 2D material studies.