Controlled Scalable Synthesis of Uniform, High-Quality Monolayer and Few-layer MoS2 Films

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Two dimensional (2D) materials with a monolayer of atoms represent an ultimate control of material dimension in the vertical direction. Molybdenum sulfide (MoS2) monolayers, with a direct bandgap of 1.8 eV, offer an unprecedented prospect of miniaturizing semiconductor science and technology down to a truly atomic scale. Recent studies have indeed demonstrated the promise of 2D MoS2 in fields including field effect transistors, low power switches, optoelectronics, and spintronics. However, device development with 2D MoS2 has been delayed by the lack of capabilities to produce large-area, uniform, and high-quality MoS2 monolayers. Here we present a self-limiting approach that can grow high quality monolayer and few-layer MoS2 films over an area of centimeters with unprecedented uniformity and controllability. This approach is compatible with the standard fabrication process in semiconductor industry. It paves the way for the development of practical devices with 2D MoS2 and opens up new avenues for fundamental research.

The significance of 2D materials has been manifested by a plethora of fascinating functionality demonstrated in graphene, a monolayer material of carbon atoms. In contrast to graphene, which is a semi-metal with no bandgap by nature, MoS2 monolayers offer an attractive semiconductor option due to a direct bandgap of 1.8 eV. This non-trivial bandgap makes MoS2 monolayers a better candidate than graphene to revolutionize many electronic and photonic devices that are currently dominated by traditional group IV or III–V semiconductor materials. Considerable efforts have been dedicated to achieve scalable synthesis of high quality MoS2 monolayers that is necessary for the development of practical devices. These include sulfurization of MoO3 or Mo layers pre-deposited on substrates, or thermolysis of Mo compound (NH4)2MoS4. However, none of the existing processes provides the capability to exclusively produce uniform MoS2 monolayers over a large area up to centimeters. Additionally, none of these processes is able to precisely control the layer number of MoS2 films. For instance, MoS2 monolayers resulted from these processes always co-exist with by-products of thicker layers. As the properties of MoS2 materials strongly depend on the layer number, this unsatisfactory uniformity and controllability poses a formidable challenge for the improvement of device performance. Here we present a new, self-limiting chemical vapor deposition (CVD) approach that can exclusively grow high-quality monolayer or few-layer MoS2 films over an area of centimeters on various substrates such as silicon oxide, sapphire, and graphite. The layer number of the MoS2 films can be precisely controlled as 1, 2, 3, and beyond. The synthesized film shows unprecedented uniformity with no other layers found by thorough characterizations. It exhibits optical and electrical quality comparable to the MoS2 exfoliated from bulk materials, and can be transferred to other arbitrary substrates.

Results
We grew MoS2 films at high temperatures (≥ 800 °C) using MoCl5 and sulfur as precursor materials (we found the quality of resulting thin films worse at lower growth temperatures). The precursor materials can react at elevated temperatures to produce MoS2 species, which may subsequently precipitate onto receiving substrates to yield MoS2 films (Fig. S1). The layer number of the resulting MoS2 films can be very precisely controlled by controlling the amount of MoCl5 used in experiments or the total pressure in the synthetic setup (details see Studies of growth mechanism in the Supplementary Information). We have successfully grown monolayer or few-layer MoS2 films on various substrates including silicon oxide, sapphire, and graphite. Fig. 1 a–b show optical images of the MoS2...
monolayer and bilayer films grown on sapphire substrates. The optical images of MoS2 monolayer and bilayer films grown on silicon substrates with 280 nm thick silicon oxide (SiO2/Si) are also given as insets. Scratches were intentionally introduced to show the color contrast between the thin film and the substrate (no MoS2 film exists in the scratched area). We confirm the chemical composition of the thin films is MoS2 using x-ray photoelectron spectroscopy (XPS) characterizations (Fig. S2). From the optical images, we can find that the thin films are continuous and uniform over a large area. We can also find that the color contrasts of MoS2 monolayer and bilayer films bear little difference on sapphire but are substantially different on SiO2/Si, the monolayer showing pink color while the bilayer more bluish. This substantial difference in color contrast may provide a facile approach to determine the thickness of 2D MoS2 materials.

We characterized the synthesized thin films using atomic force microscope (AFM) and Raman spectroscopy. The thickness of the synthesized MoS2 monolayers and bilayers are shown 0.68 nm and 1.40 nm (Fig. 1c–d), in consistence with exfoliated MoS2 (Fig. S3–S5). Fig. 1e shows the Raman spectra collected from the as-grown MoS2 thin films on sapphire with different layer numbers (the Raman spectra for the MoS2 films grown on SiO2/Si is given in Fig. S6). The Raman spectra of exfoliated MoS2 monolayers and bulk MoS2 materials are also given in Fig. 1e as references. Two characteristic Raman modes can be found in the spectra, the A1g mode associated with the out-of-plane vibration of sulfur atoms and the E1g mode related with the in-plane vibration of Mo and sulfur atoms32–34. The full width at half maximum (FWHM) of the E1g peak may be used as an indicator for crystalline quality. We can find the as-grown MoS2 thin films continuous and uniform over a large area, as indicated by the Raman measurements (Fig. 1e and 2b). To further confirm the uniformity across the entire substrate, we performed Raman mapping over an area of 10 µm × 10 µm in the as-grown monolayer film, and plotted the measured frequency difference Δk in a 2D image (Fig. 2c). All the Δk are found in a range of 20.3 – 20.7 cm⁻¹, confirming the film a homogeneous monolayer. To further confirm the uniformity, we performed multiple AFM measurements at different areas on the film, and found similar thickness and surface topology in all the spectra. The profile of the Raman peaks, such as the FWHM, shows negligible difference. This indicates that the synthesized thin film is indeed a homogeneous monolayer with similar crystalline quality across the entire substrate. We also performed Raman mapping over an area of 10 µm × 10 µm in the as-grown monolayer film, and plotted the measured frequency difference Δk in a 2D image (Fig. 2c). All the Δk are found in a range of 20.3 – 20.7 cm⁻¹, confirming the film a homogeneous monolayer. To further confirm the uniformity, we performed multiple AFM measurements at different areas on the film, and found similar thickness and surface topology in all the spectra. The profile of the Raman peaks, such as the FWHM, shows negligible difference. This indicates that the synthesized thin film is indeed a homogeneous monolayer with similar crystalline quality across the entire substrate. We also performed Raman mapping over an area of 10 µm × 10 µm in the as-grown monolayer film, and plotted the measured frequency difference Δk in a 2D image (Fig. 2c). All the Δk are found in a range of 20.3 – 20.7 cm⁻¹, confirming the film a homogeneous monolayer. 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In MoS₂ bilayers, we can find a substantial difference between the imaging provides a credible way to identify the stacking sequence difference in image contrast (Mo atoms show much higher contrast). HAADF imaging is dependent on the atomic number, we can difference indicates an AB stacking sequence in the MoS₂ bilayer, where SCIENTIFIC REPORTS multiple images of MoS₂ monolayer (Fig. 3b) and bilayer (Fig. 3c). This difference indicates an AB stacking sequence in the MoS₂ bilayer, where the Mo atoms of one layer overlap with the position of the sulfur atoms in the other layer (Fig. S13). The experimental observation matches the modeled image for the AB stacking very well (Fig. 3c).

The synthesized thin films show excellent optical quality that is comparable to exfoliated MoS₂. Fig. 4a shows the PL spectra collected from exfoliated and synthesized MoS₂ monolayers. Raman peaks of the MoS₂ materials are also included, and the (photoluminescence) PL spectra are normalized to the intensity of corresponding Raman peaks. The normalization is to better correlate the measured PL intensity with the intrinsic luminescence efficiency of the materials. Two peaks can be found in the PL spectra, ~620 nm and ~670 nm, and can be correlated to the B₃ and A₁ excions of MoS₂, respectively. We can find similar PL peaks from both synthesized and exfoliated MoS₂ monolayer. This suggests a comparable optical quality in the synthesized film with the exfoliated MoS₂. We should note that the synthesized monolayer for the PL measurement was grown on sapphire substrates. For the convenience of comparison with the exfoliated MoS₂, which were dispersed onto SiO₂/Si substrates, the synthesized monolayer was transferred to SiO₂/Si substrates for the PL measurement (see the effect of substrates on PL in Fig. S14). We find that the PL from the MoS₂ monolayer film grown on SiO₂/Si substrates is much weaker than the films grown on sapphire (Fig. S15), probably due to a poorer crystalline quality in the films grown on SiO₂/Si substrates than those grown on sapphire as reported previously. Additionally, the PL efficiency of exfoliated MoS₂ has been well known substantially decreasing with the increase in the layer number due to an evolution of the bandgap with the layer number. We can find that the PL efficiency of the synthesized MoS₂ bilayer is indeed substantially smaller than that of synthesized monolayers (Fig. S16). This suggests that the bandgap of the synthesized MoS₂ film bears a similar dependence on the layer number as exfoliated MoS₂. To illustrate the uniformity of the optical quality, we performed PL mapping over an area of 20 um × 20 μm in the synthesized monolayer. The measurement demonstrates a uniform distribution in the PL intensity (Fig. 4a inset), confirming the uniformity as suggested by the Raman measurements shown in the preceding text.

We also evaluated the electrical quality of the synthesized MoS₂ monolayer film. We transferred the thin film grown on sapphire to degenerately doped silicon substrates covered with 280-nm-thick SiO₂, and fabricated bottom-gate transistors by evaporating 5 nm Ti/200 nm Au electrodes on top of the MoS₂ thin film. We performed electrical measurements at room temperature and in ambient environment using the degenerately doped silicon substrate as a back gate and deposited Au electrodes as the source and drain. Fig. 4a...
shows typical output characteristic and transfer characteristic (inset) curves of the device. These results indicate that the device is an n-type channel field effect transistor, consistent with other works on exfoliated MoS$_2$ films. The linear dependence of the current $I_{ds}$ on the source-drain bias $V_{ds}$ suggests that the contacts between the MoS$_2$ thin film and the electrodes are ohmic. This ensures that the observed field effect behavior is from the monolayer MoS$_2$ channel rather than Schottky barriers at the contact. From the measurements, we can derive the field-effect mobility of charge carriers in the device as $0.003–0.03$ cm$^2$/V.s by using the expression $\mu = \left[ dI_{ds}/dV_{ds} \right] \times \left[ L/(W C_{i}V_{ds}) \right]$, where $L$ and $W$ is the length and width of the channel, respectively, $C_{i}$ is the capacitance of the gating oxide, and $V_{ds}$ is the bias applied to the back gate. This is reasonably comparable to previous reports on exfoliated monolayers measured in similar conditions (ambient environment, back gating with silicon oxide as the gate oxide). We can thus conclude that the synthesized thin film has a reasonably comparable electrical quality with exfoliated MoS$_2$.

**Discussion**

The observed remarkable uniformity and controllability in the synthesized MoS$_2$ film strongly suggests that this synthetic process is self-limiting, i.e. the growth may be automatically stopped by some intrinsic factors of the synthetic process. Unlike the self-limiting mechanism for the growth of graphene, which is related with the limited solubility of carbon source in the catalyst of copper, our experimental results suggest that the partial pressure of gaseous MoS$_2$ species and the interaction of MoS$_2$ thin films with substrates play key roles in this self-limiting mechanism.

We found in experiments that the layer number of MoS$_2$ thin films increases with the amount of precursor materials (Table S1, Fig. S17–S18) and the total pressure in the synthetic setup (Fig. S19–S20). We can correlate this to the effect of the two parameters on the partial pressure of gaseous MoS$_2$ species $P_{Mo}$, which we find increasing with the amount of precursor materials and the total pressure (details see Supplementary Information). We believe that the partial pressure $P_{Mo}$ plays an important role in control of the layer number.

To elucidate the role of $P_{Mo}$, we examine the dynamics of the synthetic process, and find that the precipitation reaction MoS$_2$(g) $\rightarrow$ MoS$_2$(s) is the rate-determining step, where g and s refer to gaseous and solid phases, respectively (details see Supplementary Information). The precipitation reaction is governed by two pressures, the partial pressure of gaseous MoS$_2$ species ($P_{Mo}$) and the equilibrium vapor pressure (referred as vapor pressure) of MoS$_2$ in solid phase ($P'_{Mo}$). The role of $P_{Mo}$ in control of the layer number is essentially rooted in its role in the thermodynamics and kinetics of the precipitation reaction. The difference between the partial pressure $P_{Mo}$ and the vapor pressure $P'_{Mo}$ provides the thermodynamic driving force for the precipitation reaction. The partial pressure must be larger than the vapor pressure, i.e., $P_{Mo} > P'_{Mo}$ to drive the precipitation of gaseous MoS$_2$ species. Additionally, based on the law of mass reaction, we know that the partial pressure $P_{Mo}$ also dictates the rate of the precipitation, a larger $P_{Mo}$ driving a faster precipitation.

The observed dependence of the layer number of MoS$_2$ films on experimental parameters (the amount of precursor materials and the total pressure) suggests that a larger partial pressure $P_{Mo}$ tends to give rise to a thicker film (Fig. S21–S22). While a larger $P_{Mo}$ can cause a larger precipitation rate, we do not think that this kinetic effect would be the major reason for the observed control of layer number. Should the precipitation rate be the major mechanism for the control, it would request a perfect control in timing to stop the precipitation right at the end of the formation of each individual layer, in order to produce the observed uniform MoS$_2$ films with precisely controlled layer number. This is most unlikely in our synthetic setup. The growth of large-area, highly uniform MoS$_2$ thin films in our experiments suggests that this precipitation is a self-limiting process, i.e. the precipitation automatically stops at the end of the formation of each individual layer.

We believe that the self-limiting mechanism may lie in a thermodynamic balance between the partial pressure of gaseous MoS$_2$ species ($P_{Mo}$) and the vapor pressure of MoS$_2$ thin films ($P'_{Mo}$) on the substrate. The vapor pressure of MoS$_2$ thin films could depend on, more specifically, increase with the layer number. As $P_{Mo}$ is required larger than $P'_{Mo}$ to provide the thermodynamic driving force, the precipitation of gaseous MoS$_2$ species may be automatically stopped at a specific layer number by control of $P_{Mo}$. For instance, an exclusive growth of MoS$_2$ monolayer could be achieved by controlling the partial pressure $P_{Mo}$ between the vapor pressures of MoS$_2$ monolayer ($P'_{Mo,1}$) and bilayer ($P'_{Mo,2}$) films as $P'_{Mo,1} < P_{Mo} < P'_{Mo,2}$. In this case, the larger vapor pressure of MoS$_2$ bilayers may automatically prevent the continuous growth once a MoS$_2$ monolayer film is formed, regardless a continuous supply of MoS$_2$ species. This indeed matches our observations that the layer number of MoS$_2$ films shows a step-function dependence on the amount of precursor materials (Table S1). Our hypothesis on the self-limiting mechanism can also be supported by the observed dependence of the layer number on growth temperatures. We find that the layer number of MoS$_2$ films increases with the temperature of receiving substrates decreasing (Fig. S23). This can be understood that the vapor pressure of MoS$_2$ thin films $P'_{Mo}$ decreases with the temperature, and the same partial pressure $P_{Mo}$ can drive a deposition of thicker films at lower temperatures.

The dependence of the vapor pressure of MoS$_2$ thin films on the layer number might be related with the interaction with substrates.
The vapor pressure indicates a capability of atoms escaping from solid phase into gas phase. The interaction of MoS₂ overlays with substrates could substantially suppress the escaping of MoS₂ atoms, and subsequently cause a decrease in the vapor pressure. This interaction with substrates is expected to relax with the layer number (Fig. S24). As a result, the vapor pressure of MoS₂ thin film may increase with the layer number. Similar suppression effects of substrates on the vapor pressure have been well demonstrated in other materials adsorbed on substrates, for instance, polymers8. This dependence of vapor pressures on the layer number of MoS₂ films may provide the possibility of self-limiting growth. We also find in experiments that a precise control of the layer number generally tends to be more difficult for thicker films, for instance, larger than 4, often resulting a mixture of layer numbers. This suggests that the difference between the vapor pressures of MoS₂ films with neighboring layer number (\(P_{Mo,n+1} - P_{Mo,n}\) n refers to the layer number) tends to shrink with an increase in the layer number, which makes the selective growth more difficult.

To further examine the role of the interaction with substrates, we studied the growth on different receiving substrates, the traditional three-dimensional (3D) bonded materials such as sapphire (referred as 3D substrates) and highly ordered pyrolytic graphite (HOPG, from Ted Pella) that has a similar layered structure as MoS₂ (referred as 2D substrates). We grew MoS₂ films on these different substrates under identical experimental conditions (the different substrates were placed side by side in the tube furnace). We can find a substantial difference between the films grown on sapphire and HOPG (Fig. S25). With the same experimental conditions, while the film grown on sapphire substrates is monolayer (\(\Delta k 20.4 \text{ cm}^{-1}\)), the one grown on HOPG is bilayer (\(\Delta k 22.4 \text{ cm}^{-1}\)). We can exclude out the possibility that the observed difference in the Raman shifts is caused by the difference in substrates (see Supplementary Information). This result confirms that the interaction of MoS₂ films with substrates plays an important role in the self-limiting growth. The strength of the interaction of 2D material overlay with conventional 3D substrates e.g. sapphire, is well known different from that with 2D substrates (such as HOPG). This difference has been extensively manifested by the van der Waals epitaxial growth of layered materials on 2D substrates9. In our experiment, the different interactions of MoS₂ films with sapphire and HOPG might cause different vapor pressures. Therefore, the same partial pressure of MoS₂ can give rise to a growth of thicker MoS₂ film on HOPG.

In conclusion, we demonstrate a new chemical vapor deposition (CVD) approach that can provide capabilities to produce large-area, high quality MoS₂ monolayer and few-layer films with unprecedented uniformity and controllability. While more studies would be necessary to better understand the growth mechanism, our experimental results strongly suggest that this synthetic process is self-limiting dictated by the balance between the equilibrium pressure of MoS₂ thin films and the partial pressure of MoS₂ species in the vapor phase. As a final note, this synthetic approach can be readily scaled up to produce wafer-scale 2D MoS₂ for the development of practical electronic and photonic devices. It is poised to enable 2D MoS₂ as a useful functional material to revolutionize a wide range of fields including information technology, optoelectronics, chemical/biological sensing, and spintronics.

Methods
MoS₂ thin films were synthesized in a tube furnace as illustrated in Fig. S1. In a typical growth, 1–50 mg of molybdnum chloride (MoCl₇) powder (99.99%, Sigma-Aldrich) was placed at the center of the furnace and 1 g of sulfur powder (Sigma-Aldrich) was placed at the upstream entry of the furnace. Receiving substrates were placed downstream in a distance of 1–7 centimeters away from the center of the furnace. In typical experiments, the furnace was heated up at a rate of 28 °C/min under a flow of Ar gas, held at a setting temperature for 10 min, and then naturally cooled down to room temperature. Typical conditions for high-quality MoS₂ thin film growth include a temperature of 850 °C (the temperature for sulfur source is estimated ~ 300 °C), a flow rate of 50 sccm, and a pressure around 2 Torr. The layer number of the synthetic MoS₂ thin film can be controlled by control of the amount of MoCl₇ precursor or the total pressure in the synthetic setup (see Supplementary Information). The crystal structure of the resulting products were analyzed with transmission electron microscopy (TEM, JEOL-2010) and probe aberration-corrected scanning transmission electron microscopy (STEM, FEI Titan 80–300 STEM) operated at 200 kV under STEM mode. The as-grown thin film was transferred to TEM grid for subsequent characterization. The thickness and surface topology were measured using atomic force microscope (AFM, Veeco Dimension-3000). Raman mapping and photoluminescence (PL) measurements were carried out using Horiba Labram HR800 Raman Microscopy with an excitation wavelength of 532 nm. X-ray photoelectron spectroscopy were performed on SPECS XPS using an Mg Kα x ray source. The field-effect transistor device was fabricated by evaporating Ti/Au (5/200 nm) electrodes directly onto top of MoS₂ films transferred to degenerately doped Si substrates with 280 nm thick silicon oxide. A copper grid (100mesh, 30 micron spacing, Ted Pella) was placed on top of the thin film as mask for the electrode fabrication. This gives a relative large channel with a length \(L = 30 \text{ μm}\) and a width \(W = 230 \text{ μm}\). The electrical measurements were performed in ambient conditions using a probe station (Karl Suss SM6).
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Author contributions
Y.Y. and L.C. conceived the experiments. Y.Y. and C.L. performed the synthesis. Y.Y. performed most of the characterizations and device fabrications. Y.L. carried out the STEM characterization. L.S and Y.Z. performed the Raman and PL mapping. Y.Y. and L.C. analyzed the data. All authors were involved in writing the manuscript.

Additional information
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