Large Area Vapor Phase Growth and Characterization of

MoS₂ Atomic Layers on SiO₂ Substrate

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Abstract

Monolayer Molybdenum disulfide (MoS_2), a two-dimensional crystal with a direct bandgap, is a promising candidate for 2D nanoelectronic devices complementing graphene. There have been recent attempts to produce MoS_2 layers via chemical and mechanical exfoliation of bulk material. Here we demonstrate the large area growth of MoS_2 atomic layers on SiO_2 substrates by a scalable chemical vapor deposition (CVD) method. The as-prepared samples can either be readily utilized for further device fabrication or be easily released from SiO_2 and transferred to arbitrary substrates. High resolution transmission electron microscopy and Raman spectroscopy on the as grown films of MoS_2 indicate that the number of layers range from single layer to a few layers. Our results on the direct growth of MoS_2 layers on dielectric leading to facile device fabrication possibilities show the expanding set of useful 2D atomic layers, on the heels of graphene, which can be controllably synthesized and manipulated for many applications.

KEYWORDS molybdenum sulfide, atomic layers, silicon dioxide, chemical vapor deposition, Raman spectra, high resolution transmission electron microscope

Inspired by recent success in graphene based research¹⁻³, monolayer or few-layer nanostructures derived from other layered materials such as hexagonal Boron Nitride (h-BN) and transition-metal dichalcogenides including MoS_2 , WS_2 etc. have received increasing attention due to their potential for a range of applications⁴⁻⁷. Unlike conductive graphene and insulating h-BN, atomic layered MoS₂ is a semiconductor material with a direct bandgap, offering possibilities of fabricating high performance devices with low power consumption in a more straight-forward manner⁸. In a recent effort to fabricate single-layer MoS₂ transistors, impressive mobility of at least 200 cm^2V^{-1} s⁻¹ has been demonstrated using a halfnium oxide (HfO₂) gate dielectric⁸, a big increase from $0.5 - 3 \text{ cm}^2 \text{V}^{-1} \text{ s}^{-1}$ reported earlier using a silicon oxide gate dielectric¹. However, the traditional mechanical exfoliation method is still employed to obtain the MoS₂ atomic layer with rather modest foot-print, limiting its usefulness in a commercially viable device. Liquid exfoliation of layered materials including MoS₂ has been proposed to be a promising large scale synthesis method for twodimensional nanosheet⁹. Although it is quite facile to create hybrid dispersions or composites using this method, its application into device applications still needs further development. Other methods including hydrothermal methods that were employed to synthesize MoS_2 nanosheet have similar limitations¹⁰⁻¹². Therefore, large area synthesis of monolayer and few-layer MoS_2 that is compatible with current micro- or nano-fabrication processes will greatly facilitate the integration of this fascinating material into future device applications. In the present work, we report that a rather simple and direct elemental reaction between Mo and S can produce large area good quality MoS₂ atomic layers on SiO₂ substrates.

In a typical procedure, samples (Mo thin films deposited on SiO₂ substrates) placed in a ceramic boat were placed in the center of a tube furnace (Lindberg, Blue M, quartz tube). Another ceramic boat holding pure sulfur (1-2g, Fisher Scientific, USP grade) was placed in the upwind low temperature zone in the quartz tube. During the reaction, the temperature in the low temperature zone were controlled to be a little above the melting point of sulfur ($113^{\circ}C$). The quartz tube was first kept in a flowing protective atmosphere of high purity N₂, the flow rate of which was set at 150-200 sccm. After 15 minutes of N₂ purging, the furnace temperature was

gradually increased from room temperature to 500 °C in 30 minutes. Then the temperature was increased again from 500 °C to 750 °C in 90 minutes and was kept at 750 °C for 10 minutes before cooled down to room temperature in 120 minutes. Figure s1 shows a schematic illustration of the reaction condition of this CVD process. Raman spectroscopy (Renishaw inVia) was performed with 514.5 nm laser excitation. Scanning electron microscope (FEI Quanta 400) and high resolution transmission electron microscopy (HRTEM, JEOL-2100) equipped with electron energy loss spectrum (EELS) and GIF filter were employed for imaging and chemical analysis of the samples. X-ray photoelecton spectroscopy (XPS, PHI Quantera) was performed using monochromatic aluminum KR X-rays. MultiPak software was used for XPS data analyses.

As illustrated in Fig. 1a, thin layer of Mo (typical thickness 1 ~ 5 nm) was predeposited on SiO₂/Si by e-beam evaporation at a rate of ~ 0.1 A/s. Sulfur was introduced and reacted with Mo at 750°C forming very thin MoS₂ film (form single layer to few layers), as illustrated in Fig. 1b. The as-prepared MoS₂ atomic layers on SiO₂ substrates are readily available for further characterizations as well as device fabrications. It is also easy to transfer the thin layers onto arbitrary substrates by etching away the SiO₂ using KOH solution (\sim 15M). Fig. 1c shows a released MoS₂ atomic layers floating on the surface of the alkaline solution. The lateral size of the MoS_2 layers is simply dependent on the size of the substrates used (~0.8cm×0.8cm as shown in Fig. 1c), suggesting that the process is scalable and films of any size can be grown with good uniformity. The thickness of the MoS₂ atomic layer grown directly relates to the thickness of the pre-deposited Mo metal on the substrate and hence the thickness of the layers can be controlled. The MoS_2 atomic layers can then be transferred onto arbitrary substrates (including TEM sample grids) for further characterizations and processing. Figure 1d shows an optical image captured from the edge of a typical MoS_2 on a SiO_2 substrate (285nm). The light purple area in the top-right corner marked by a yellow arrow shows a very thin area (1-2 layers), while most of other areas are few-layered MoS_2 in purple. Fig. 1e shows the corresponding SEM image. The morphologies reveal that the on-site growth of MoS_2 on SiO_2 substrate can produce very thin, continuous and uniform atomic layers. Fig. 1f shows

a SEM image of a large size MoS_2 in uniform. More optical and SEM images can be found in supporting information Figs. S1. In our experiments, we tried various substrates (Si, SiO₂, Al₂O₃, Cr, Au, Au / Cr bi-layer) to deposit Mo on them using ebeam evaporation. All other substrates (Al₂O₃, Cr, Au and Au/Cr) were pre-deposited thin films on silicon wafers. The growth of MoS₂ on different substrates is compared in the supporting information (see Supplementary Information Figs. S2 and S3).

To further confirm the quality of the MoS₂ atomic layers prepared by our CVD method, Fig. 2a shows the morphology of an atomic MoS₂ layer covering on the TEM grid with a rolled-up edge, and Fig. 2b shows the edge area. Fig. 2c and 2d shows the two-layered and three layered MoS₂ samples. The interlayer spacing was measured to be ~6.6 \pm 0.2 Å. Fig. 2e and 2f are HRTEM of MoS₂ atomic layers. Circle in 2e indicates the Moiré patterns. The hexagonal structure could be clearly found in Fig. 2f. Fig. 2g and 2h are diffraction patterns, showing single-layered and double-layered areas. Fig. 2i, 2j and 2k shows elemental mappings. Fig. 2i is the original images and Fig. 2j and 2k are Mo and S elemental mappings, respectively. The EELS results are also shown in Fig. 21 and 2m. The EELS spectrum obtained from the location, indicated by the red dot in Fig. 2i, reveals the characteristic peaks of Mo at 35 eV (N-edge) and S at 165 eV (L-edge)¹³. The ratio of Mo and S is about 1:2, which is confirmed by the XPS data (see Supplementary Information Figs. S4).

The grain size of CVD-grown and liquid mechanical exfoliated MoS_2 (LE-MoS₂),⁹ as a comparison, could be estimated by the dark-field (DF) TEM images shown in Figure 3. Fig. 3a shows a bright-field (BF) TEM image of a random area in the CVD MoS₂. Fig. 3b and 3c are corresponding diffraction pattern and false-color DF TEM image of area in Fig. 3a, suggesting a poly-crystalline MoS₂ with a grain size ranging from 10 nm ~ 30nm. Fig. 3b contains multi-group six-fold-symmetry spots, which is also seen in CVD graphene.¹⁴ The false-color DF TEM image is taken using an objective aperture filter to cover three spots in the back focus plane, marked by the circle. The colors (red, green and blue) in the DF TEM image correspond to the ones of circles in Fig. 3b. Fig. 3d-3e are the BF TEM image, diffraction pattern and DF TEM image of LE-MoS₂, respectively. The individual six-fold-symmetry pattern suggests the grain size of is larger than 1 μ m or more. This result is further confirmed by the comparison of random edges in CVD and

LE MoS₂, as shown in Fig. 3g and 3h. It can be found 4L and 3L in length of ~10nm, 2L MoS₂ in length of ~20nm in CVD MoS₂, and 4L in length of ~90nm in LE MoS₂.

Raman spectra on as-prepared MoS_2 atomic layers, as well as mechanically exfoliated thin flakes were collected for comparisons. As shown in Figure 4, Raman spectra were collected for single-layered and double-layered MoS₂ samples on SiO₂ substrate. Two typical Raman active modes could be found: E_{2g}^{1} at 383 cm⁻¹ and A_{1g} at 409 cm⁻¹ ¹⁵. These modes of vibration have been investigated both theoretically and empirically in bulk MoS_2^{16-18} , E_{2g}^1 indicates planar vibration and A_{1g} associates with the vibration of sulfides in the out-of-plane direction as illustrated in the inset of Fig. 4a. Some criterion could be used to roughly identify the thickness of the layers¹⁵: (1) Raman peak location and intensity of E_{2g}^{1} and A_{1g} (with same parameters like laser power, collecting time etc.). The peaks were found to be blue-shift for E_{2g}^{1} and red-shift for A_{1g} when the film becomes thinner, which would also result in a weaker signal. In Figs. 4a and 4b, their peaks from E_{2g}^{1} and A_{1g} located at 384.6 cm⁻¹, 405.1 cm⁻¹ and 384.6 cm⁻¹, 406.9 cm⁻¹, respectively, which corresponded to single-layered and doublelayered MoS₂ samples. The spectra in blue are recorded from mechanical exfoliated MoS_2 with a corresponding numbers of layer¹⁵; (2) The peak spacing between E^{1}_{2g} and A_{1g} . In our case, they were 20.6 cm⁻¹ for single-layered and 22.3 cm⁻¹ for double-layer samples; (3) The intensity ratio between the characteristic peaks from MoS_2 and the substrate. For our samples, E_{2g}^{1} /Si were ~ 0.05 and 0.09, again corresponding to single-layered and double-layered MoS₂ samples¹⁵. The Raman intensity ratios for E_{2g}^{1} and A_{g}^{1} are different for the CVD MoS₂ and exfoliated MoS₂. It is because the planar vibration (E_{2g}^{1}) is subject to the nano-scale and random-distributed grains in CVD MoS₂ (Fig. 3c), therefore showing a lower relative intensity compared to mechanical exfoliated MoS₂. It is supported by further studies on the DF TEM image of exfoliated MoS₂ flakes. Their grain size is much larger, typically at the order of microns or more (Fig. 3f). Raman mapping was taken from the dashed area ($35 \mu m \times 45 \mu m$) shown in Fig. 4c, which is a typical edge area of a large size atomic MoS₂ layer prepared by our CVD method. Fig. 4d and 4e represent the intensity mapping (E^{1}_{2g}) and intensity ratio mapping (E^{1}_{2g}/Si) . There were total 576 (24×29) Raman spectra collected from this area. Both mappings show a similar landscape. Intensity ratio mapping provides a more accurate characterization and better resolution for the atomic layer samples with different thicknesses. The thin area was shown in light blue and thick area in red. Raman spectra strongly suggest good quality, uniform coverage of MoS_2 atomic layers (from single layer to a few layers) on SiO₂ substrate.

Field effect transistor (FET) devices were made by photolithography process to determine the electric transport properties of CVD-prepared MoS₂. We use photoresists S1813 and LOR5B to make electrodes patterns with under-cut structures by mask aligner (SUSS Mask Aligner MJB4) and then develop with MF319. Ti/Au Electrodes (5 nm/30 nm) are deposited by e-beam evaporator. The evaporating rate was well controlled about 1 Å/s. The photoresist could be removed by acetone and PG-REMOVER. The electrical measurements were carried out using two Keithley 2400 source meters connected with a CTI Cryodyne Refrigeration System to provide a temperature ranging from 15K to 450K and a vacuum down to 7×10^{-6} Torr. Their electrical transport properties are shown in Figure 5. Fig. 5a is a typical device with an electrode spacing $\sim 9 \,\mu\text{m}$ and the length of the electrodes is $\sim 100 \, \mu m$. Fig. 5b is a typical I-V curve of MoS₂ device with a resistance of ~130 K Ω . For most of the devices, their source current versus bias voltage is linear ranging from 1mV to 1V, suggesting ohmic contacts with our Ti/Au electrodes. The resistivity of our MoS₂ samples are from ~ $1.46 \times 10^4 \Omega/\Box$ to $2.84 \times 10^4 \Omega/\Box$, about two orders of magnitude higher than the CVD-prepared graphene $(125\Omega/\Box)$.¹⁹ Temperature dependence measurement indicates that MoS₂'s resistance increases at low temperatures, as shown in Fig. 5c. The typical mobilities measured are ranging from 0.004 to 0.04 cm²V⁻¹s⁻¹ at room temperature, one to two orders of magnitude less than the mechanical exfoliated MoS₂ samples $(0.1 \sim 10 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1})$.¹ The mobility of MoS₂ at low-field field effect is estimated by $\mu = \left[dI_{ds} / dV_{bg} \right] \times \left[\left(L / (WC_i V_{ds}) \right) \right]$. Here L is the channel length ~9 µm, W is the channel width from 17 μ m to 80 μ m for various devices. $C_i \sim 1.3 \times 10^{-4}$ F m⁻² is capacitance between the channel and the back-gate per unit area. We believe the low mobilities originate from the planar defect - the nano-scale and random-distributed CVD MoS₂ grains, as shown in the DF TEM image in Fig. 3c. Electron hopping among grains would significantly decrease the mobilities in MoS_2 .^{22, 23} In addition, other defects including cationic vacancies, dislocation and adsorption-induced doping effect in the MoS₂ are also possible reasons for the low mobilities, which are always observed in

CVD-prepared two dimensional materials like graphene.¹⁴ The mobility could be significantly improved by annealing the as-prepared samples,^{8, 20} using local top-gate with high- κ dielectric, ^{8, 21} and optimizing the growth conditions. Different from the naturally grown MoS₂ crystal that is n-type semiconductor, we observed that our CVD-prepared MoS₂ is an intrinsic p-type semiconductor at room temperature, as shown in Fig. 5d. Further work would be required to clarify such differences.

The reaction mechanism for synthesizing MoS_2 atomic layers could be simply understood as a direct elemental chemical reaction. In our experiments, the earlier reported precursors used in synthesizing MoS_2 nanostructures²²⁻²⁷ were not selected, since it's very difficult to obtain large area uniform film from those precursors. Metal substrates have also been considered in experiments. In fact, the reactions between S and metals at relevant reaction temperatures make Au almost the only suitable metal substrate. The resulted MoS_2 atomic layers grown on such substrate display many interesting tentlike microstructures (see Supplementary Information Figs. S5 and S6). These suspended, perhaps pre-stressed atomic layers could have some unique properties and also help us learn more about mechanical properties of such atomic-layered MoS_2 samples.

In summary, we have shown here a direct preparation of monolayer and few-layered MoS_2 on SiO_2 substrates using a pre-deposition of Mo film followed by CVD method. The size and thickness of atomic MoS_2 layer depend on the size of the substrate and the thickness of the pre-deposited Mo, which are easily scalable and controllable, making it possible to meet the demands from different applications. Characterization such as HRTEM and Raman indicate the as-prepared MoS_2 are of good quality and crystallinity, and ranges typically from mono-layer to a few layers. Our new large area synthesis method has thus revealed new possibility to prepare large area good quality MoS_2 atomic layer materials, increasing the number of possible candidates to be engineered into 2D structures in the direction provided by the advent of graphene and its applications.

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Supporting Information Available: Description of CVD setup, additional Raman and XPS characterization results and MoS_2 atomic layer growth on metal substrates. This material is available free of charge via the Internet at http://pubs.acs.org.

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Figure Legends



Figure 1 Illustrations and morphologies of atomic layered MoS_2 . a, Introducing sulfur on Mo thin film that was pre-deposited on SiO₂ substrate; b, MoS₂ films that are directly grown on the SiO₂ substrate. The atoms in back and yellow represent Mo and S, respectively; c, SiO₂/Si substrate (left) and peeled off few layer MoS₂ (right, indicated by the arrow) floating on KOH solution; d, Optical image of one local section with MoS₂ on SiO₂/Si substrate. Most of areas in purple are few-layered MoS₂. The area in light purple is 1-2 layered MoS₂ marked by a yellow arrow; e, Corresponding SEM image. These images show a large size, uniform and continuous MoS₂ atomic layer. f, SEM image of large area MoS₂.



Figure 2 TEM characterizations and chemical elemental analysis of CVD-grown MoS₂. a, One atomic MoS₂ layer covers on the TEM grid; **b**, Edge area of the atomic MoS₂ layer in **a**; **c**-**d**, Two and three layers of MoS₂. The distance between two layers is about 6.5Å; **e**, HRTEM images. The area marked by a circle in e shows the Moir é patterns; **f**, Atomic image of the MoS₂ layer shows a typical hexagonal structure. **g-h**, Diffraction patterns of the atomic layers; **i-k**, Original phase contrast image and corresponding molybdenum and sulfur elemental mappings, indicating the uniform distribution of Mo and S elements in the atomic layer; **1-m**, EELS shows the Mo edge and S edge at ~35eV and ~165eV, respectively. The red dot indicates the area where EELS data was collected.



Figure 3 Comparison of grain size in CVD-grown and naturally formed MoS_2 . a, Random area of CVD-grown MoS2 appear uniform in bright-field TEM images, b, Diffraction pattern taken from of area in a show the MoS2 is polycrystalline, c, a dark-field image corresponding to a with false color, d, Bright-field liquid exfoliated MoS_2 flake, e, Diffraction pattern taken from a region in d showing a single crystal MoS_2 , e, A corresponding dark-field image, g and h, Typical edges of CVD MoS_2 and liquid exfoliated MoS_2 .



Figure 4 Raman signatures of as-prepared CVD MoS₂ atomic layers. a-b, Raman spectra of single-layered and double-layered MoS₂. The thickness of MoS₂ layers can be estimated by evaluating their relative intensity to Si, or the spacing between two vibrating modes (E_{2g}^1 and A_{1g}), as shown in the inset. Spectra in blue in the inset are from mechanical exfoliated MoS₂ (single-layered MoS₂ in **a** and double-layered in **b**; **c**, A typical landscape of MoS₂ atomic layers on SiO₂ substrate. The dotted area is mapped in **d**) (intensity of E_{2g}^1 peak) and **e** (E_{2g}^1 (intensity)), indicating the number of layers.



Figure 5 Characterizations of MoS_2 devices. a, Optical image of a typical MoS_2 device; b, I_{ds} - V_{ds} curve acquired without a gate voltage; c, Temperature dependence of the resistance from 300K to 20K; d, Gate voltage versus drain current shows an intrinsic p-type MoS_2 .

Supporting Information for

Large Area Vapor Phase Growth and Characterization of MoS₂ Atomic Layers on SiO₂ Substrate

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1. Optical and SEM images of CVD MoS_2



Figure S1. (a) and (b), Optical images of CVD-grown MoS2. Inset in a: An zoomout area marked by a white arrow. (c) and (d), SEM images of MoS₂. The MoS₂ size can be easily scalable to the order of millimeters.

2. Schematic of the chemical vapor deposition (CVD) system.



Figure S2. The CVD system to prepare MoS_2 samples

Mo thin films deposited on SiO_2 substrates were placed in a ceramic boat and then loaded into the center of a tube furnace. Pure sulfur in another boat was placed at the upwind low temperature zone in the same quartz tube. During the reaction, the temperature surrounding sulfur was kept to be slightly above its melting point ~113°C.

The quartz tube was first kept in a flowing protective atmosphere of high purity N_2 , the flow rate of was ~ 150-200 sccm (standard cubic centimeters per minute). After 15 minutes of N_2 purging, the furnace temperature was gradually increased from room temperature to 500 °C in 30 minutes. Then the temperature was increased from 500 °C to 750 °C in 90minutes and was kept at 750 °C for 10 minutes before cooled down to room temperature in 120 minutes. Figure S2 shows an illustration of the reaction condition of this CVD process.

3. Raman spectra of CVD MoS₂ grown on various substrates



Figure S3. Raman spectra of MoS₂ samples grown on different substrates.

Raman spectroscopy is used to identify the quality of CVD MoS_2 films grown on 3 different substrates with a 514.5 cm⁻¹ laser. The peaks locate ~385 cm⁻¹ correspond the E_{2g}^1 vibration mode of MoS_2 , and peaks at ~408 cm⁻¹ correspond to the A_{1g} mode.¹ It can be found that thin MoS_2 samples can be grown on various substrates including SiO₂, Au, Si et al. The Raman signal is weak for MoS_2 on Si.

4. XPS spectra of CVD MoS₂



Figure S4. XPS spectra of the MoS_2 thin film showing the typical Mo and S peaks from MoS_2 .

The XPS spectra of the as-grown MoS_2 film for the Mo and S edges are shown in Figure S2. Sulfur is in brown color. It shows 2p1/2 and 2p3/2 core levels at 162.3 eV and 161.2 eV, respectively, marked by the arrows, close to the previous reports (2p1/2: 164.1 eV,², 2p3/2: 161.5 eV ~ 163.4 eV²⁻⁴). The spectrum Molybdenum is in black. The Mo 3d3/2 and 3d5/2 peaks are around ~231.3 eV and ~228.2 eV, indicated by the black arrows, which is almost identify to the bulk MoS_2 samples (3d3/2: 232.3 eV ~ 233.3 eV, 3d5/2: 228.8 eV ~ 230.1 eV)^{2,5,6} The calculated atomic concentration of S and Mo are 68.49% and 31.51%, with a ratio close to 2:1.

5. Syntheses of MoS_2 films on Au substrate and Raman Sepctrum



Figure S5. (a) and (b). Optical images of CVD MoS₂ films on Au substrates. The yellow parts are Au particles. (c) and (d) SEM image of MoS₂ films marked by the red arrows. (f) Raman spectrum of MoS₂ on Au films.

Au is an inert metal and does not react with sulfur in during synthesis of MoS_2 . The thicknesses of gold films are proved to be a key factor in our experiments. Thickness below100 nm was not thick enough and would shrink into isolated micro-balls on silicon substrate after the annealing process during synthesis. Au films with a thickness of ~350nm are finally determined.

Figure S5 shows optical, SEM images and Raman spectrum of typical MoS_2 samples grown on Au substrate with a thickness of 350nm. The Mo thickness is ~ 3 nm. After high temperature annealing, Au substrate shrank into particles (Figure S5b). The MoS_2 films can be found on most of areas marked by the red arrows (Figure S5c and S5d). Raman spectra show the E^{1}_{2g} and A^{1}_{g} mode of MoS_2 . As shown in SEM images, red arrows reveal more details of these films surrounding Au islands and on Au substrate. Also, the suspended MoS_2 film in Figure S5d seems like very thin as they are transparent. Thanks to the highly conductive Au substrate, the MoS_2 films are much clearer under SEM than those grown on SiO₂ substrate.

6. Formation of suspended MoS₂ film.



Figure S6. Illustrations of the formation of suspended MoS₂ film.

The Au and Mo layers are deposited by sputtering and E-beam evaporator, respectively. The MoS_2 film is formed before the Au film shrinks into particles. During the annealing process (750 °C for 10min), the MoS_2 films are deformed when the gold film shrink into particles, forming a suspended MoS_2 film (Fig. S5d).

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