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Direct growth of molybdenum disulfide on arbitrary insulating surfaces by chemical vapor deposition†

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We report a direct growth approach of large area, uniform and patternable few layer molybdenum disulfide on arbitrary insulating substrates, including polymer and glass. The method can effectively control the number of layers with 100% surface coverage and avoid transferring process.

The two-dimensional transition metal dichalcogenides, e.g., molybdenum disulfide (MoS_2), trigger increasing attentions due to their potential in a wide range of electronic, optical, mechanical applications.[1–4] The zero-bandgap property makes that graphene is not a real semi-conductor and could not be used directly by the industry. The direct band gap of atomically thin MoS_2 in the visible portion of the electromagnetic spectrum suggests suitable for digital electronics and numerous photonic application.[5] Recently, various electronic and optoelectronic devices have been fabricated using few-layer MoS_2, such as field-effect transistors (FETs),[6] sensors[7–9] and phototransistors.[10] Excellent mechanical flexibility of MoS_2 also makes it an exciting semiconducting material for flexible electronics. The optical properties of MoS_2 can be tuned by stress[11] and the ultrathin film FETs on flexible substrates are robust to mechanical bending.[12] Exfoliated MoS_2 and graphene grown by chemical vapor deposition (CVD) was used to build highly flexible and transparent transistors on a polyethylene terephthalate (PET) substrate.[13] Layer-structured MoS_2 films was stacked and fabricated to Schottky-barrier solar cell though a layer-transfer process on indium tin oxide (ITO) coated glass substrate.[14] MoS_2 offers a wide spectrum response and high photoresponsivity, combined with its optical stability under illumination from ultraviolet (UV) to near infrared (NIR), which can be attractive for touch screen panels for flat panel or flexible display devices.[15] Emerging device applications all require that MoS_2 are supported by an insulating substrate, such as SiO_2, PET, polyimide (PI), ITO or Al_2O_3.

As early as 2005, monolayer MoS_2 was exfoliated using micromechanical cleavage onto insulating substrate.[2] However, this method has limitations in controlling the thickness and size, in addition, and it is difficult to realize scaling-up. CVD is the most reprehensive method to bring closer wide spread practical implementation of graphene in term of size, quality and price.[16] Recently, many efforts have been devoted to explore the controllable CVD growth of MoS_2 primarily on SiO_2/Si substrate using molybdenum compounds or a thin Mo films to react with sulfur powder.[17–20] The reported methods exist the obstacle that the residual of Mo precursors do not tend to react with sulfur atoms completely, for the reason that transferring process are required to remove the various residuals and contaminated substrates.[17–20] Very recently, Lee et al. synthesized layer-controllable and uniform MoS_2 films on wafer-scale Si/SiO_2 and quartz substrates using highly reactive sulfuric precursor to avoid insufficient sulfurization.[21] The synthesized MoS_2 films still need to be transferred onto flexible substrates using polymer supports because of high reaction and annealing temperature (750°C and 1000 °C). The transferring process would inevitably introduce impurities, wrinkles and cracks, degrading the performance of the device.[22] Wu et al. firstly used MoS_2 powder to directly grow triangular MoS_2 monolayer crystallites on sapphire and silicon oxide substrates at 650°C.[23] However, the discontinuities between the crystals lead to a non-uniform charge carrier mobility. Therefore, it is critical important to control the direct growth of large-area, uniform and patternable MoS_2 on various insulating substrates, especially thermolabile substrates.

Here, we present an effective approach to directly grow large-area, uniform, and patternable MoS_2 on arbitrary insulating substrates. We use silicon with 300-nm oxide layer, quartz, cover glass, and polyimide as representative insulating substrates to demonstrate the advantages with regard to the direct growth of MoS_2 films. High reactive sulfur precursor (H_2S) facilitates sufficient sulfurization and homogeneous MoS_2 films synthesized at low temperature. In addition to the capability to obtain large-area, excellent uniform MoS_2 films with 100% surface coverage on insulating substrates, the simplicity and scalability of our method are greatly favorable toward promoting the applications in low-cost, flexible or transparent electrode.

The synthesis process of large-area MoS_2 films is illustrated in Fig. 1a–b. Different thickness (typically 1–10 nm) of Mo films deposited on insulating substrates were used to directly grow MoS_2 to demonstrate our strategy in the atmosphere of Ar and H_2S. The photo of direct-growth MoS_2 films on representative insulating substrates with 100% surface coverage is shown in Fig. 1c. The most commonly used methods involve the redox reaction between molybdenum compounds with sulfur powder. The obtained MoS_2 samples are discontinuous flakes (Fig. S1 in the ESI†).

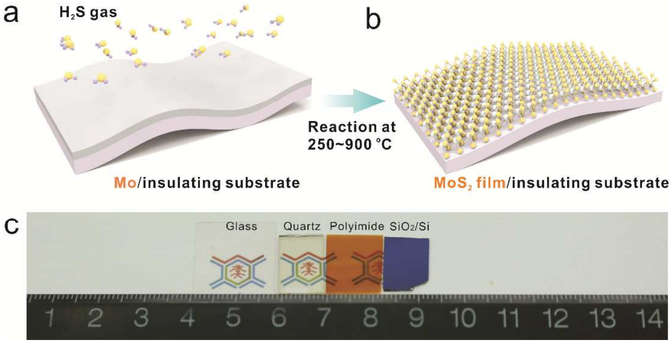

Fig. 1 Schematic illustration of the direct-growth process. Large-area MoS_2 film could be synthesized on arbitrary insulating substrates with 100% surface coverage of MoS_2.

Raman spectra is used to demonstrate the typical features of MoS_2 directly grown on the insulating surfaces at 900 °C (Fig. 2a). The out-plane vibration of S atoms (A^1_g) at ~404.9 cm^{-1} and in-plane vibration of Mo and S atoms (E^1_{2g}) at ~383.1 cm^{-1} are exhibited with a frequency ~21.8 cm^{-1} (grown on SiO_2/Si substrate), reflecting two-layers MoS_2 according to the measurements of exfoliated samples in previous works.[24] Our approach to obtain large-area and high-quality films is tolerant to the deposited substrates, which also can be directly grown on transparent insulating substrates, e.g. quartz, as shown in Fig. 2a of the red line. The typical two peaks of E^1_{2g} and A^1_g at ~382.2 cm^{-1} and ~404.2 cm^{-1} respectively, with a frequency ~22 cm^{-1}. With the variation of substrates, the quality and thickness of MoS_2 films do not show significant difference. The high crystallinity of the MoS_2 directly grown on SiO_2/Si substrate is explored by high-resolution transmission electron microscopy (HRTEM) (Fig. 2b). The corresponding 2D fast Fourier transformation (FFT) pattern shown in Fig. 2d exhibits only one set of diffraction spots, indicating the single crystalline nature of the film. In Fig. 2e, a false 3D image from a Fourier enhanced TEM micrograph of the marked area in Fig. 2e highlights the perfect atom-scale crystal structure of the MoS_2. The (100) lattice plane, with an interlayer spacing of 0.27 nm is clearly displayed in Fig. 2e, thus MoS_2 in-plane lattice constant a (MoS_2) was determined to be ~0.31 nm, which is in agreement with the bulk value of 0.315 nm. The uniformity of MoS_2 films is one of key factors to determine its properties and applications. Fig. 2c displays the typical AFM image of directly grown MoS_2 on 300-nm thick SiO_2/Si substrate. No obvious wrinkles and cracks are observed. The corresponding 3D surface image of the direct-growth MoS_2 is shown at Fig. S2a†, indicating excellent flatness achieved using our direct growth technique. Based on the above characterization results and analysis, we demonstrate that large-area and high-quality MoS_2 can be directly grown on insulating surfaces.

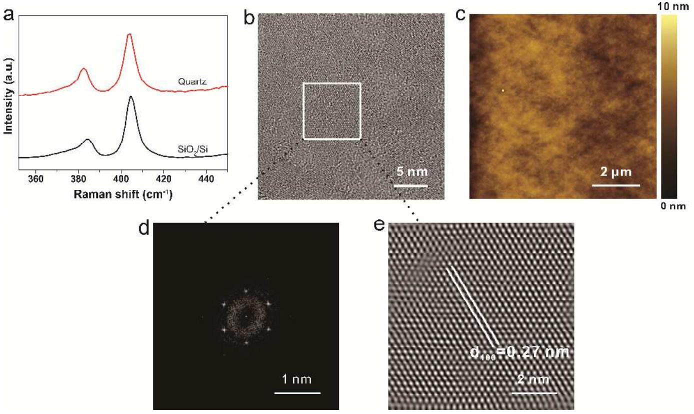

Fig. 2 Direct-growth uniform MoS_2 films on 300-nm thick SiO_2/Si, quartz at the growth temperature of 900 °C. (a) Raman spectra of direct-growth MoS_2 on SiO_2/Si and quartz. (b) High-resolution TEM image of two-layer MoS_2 directly grown on SiO_2/Si substrate. (c) AFM profile of uniform MoS_2 films directly grown on SiO_2/Si with 100% full coverage. (d) 2D FFT of the TEM presented in (b). (e) A false 3D image originated from Fourier enhanced TEM micrograph of the marked area in Fig. 2b.

Thinning out the bulk MoS_2 to atomically thin layers can result in the structure of band gap transferring from an indirect to a direct state. The capability of synthesizing uniform MoS_2 with well-controlled layer numbers is especially important for electronics applications. The optical images of few layers directly grown MoS_2 on SiO_2/Si substrates without visible cracks and wrinkles show excellent uniformity and continuity (Fig. S3a–d†). Once a molybdenum metal layer with different thickness was deposited on the substrates, a MoS_2 film having a distinct number of layers could be synthesized (Fig. S4†). Because the whole substrates were covered by the direct-growth MoS_2 films without obvious cracks, the samples were transferred to SiO_2/Si substrates to determine its thickness. The transfer process for 2D atomic materials is inevitable to introduce wrinkles and cracks, in addition, the residues during the transfer process, e.g. impurities between the films and objective substrates or the remaining PMMA on the surface, which seriously decreases the performance and limits its applications. The transferred MoS_2 on SiO_2/Si substrate show obvious wrinkles and residual impurities compared with those direct-growth samples (Fig. S2b and Fig. S4a, c, e, g†). The step measurement of the MoS_2 film was 1.8 nm in Fig. S4a†, which matched to the thickness of two layer characterized by Raman. Increasing the thickness of deposited Mo layer lead to the peak positions of E^1_{2g} and A^1_g moved to 382.3 cm^{-1} and 405.9 cm^{-1}, respectively. And the relative frequency differences increased to 23.6 cm^{-1}, which corresponded to three layered MoS_2 films (red line in Fig. S3e) with the thickness of 2.2 nm (Fig. S4c). Further increasing the thickness of deposited Mo film, the E^1_{2g} vibration blue shifted 1–2 cm^{-1}, whereas the A^1_g vibration red shifted ~1 cm^{-1} (as show in Fig. S3e†). The frequency differences increased to 25–26 cm^{-1}, which corresponded to 6 (4.1 nm)–9 layers (6 nm) in Fig. S4e, g†. Fig. S4b, d, f, h† exhibit the statistical analysis of Raman spectra taken on S3a–d samples dominated by 9, 6, 3, and 2 layers of MoS_2 films, respectively. The relative frequency differences between the modes varied from 22 cm^{-1} to 26 cm^{-1}, which corresponded to 2 to 9 layered MoS_2 films (as shown in Fig. S4†), according to a previous study.[24] Raman mapping images of the peak position differences between A^1_g and E^1_{2g} modes over an area of 10×10 μm (from 2 to 9 layers) show nearly uniform color distribution (Fig. S5†), revealing the thickness variation is negligible. The high reactivity of H_2S with deposited Mo to form MoS_2 films suggests that it is possible to obtain patterned MoS_2 on diverse surfaces. MoS_2 ribbons arrays were directly grown on SiO_2/Si substrate (as shown in Fig. S6†), avoiding transferring process to manufacture devices.

In previous works, MoS_2 films are transferred to transparent insulating substrates including PET, ITO, Al_2O_3 to build photoelectric devices. Their performance is expected to be improved though optimizing the growth process, for example, develop a direct-growth method to avoiding impurities introduced though transfer process. The absorbance and photoluminescence (PL) of 2, 3, 6, and 9 layered MoS_2 films are directly related to the thickness of MoS_2 grown on quartz, as shown in Fig. 3. The resulting UV-vis spectra exhibit excitonic features of A, B, C peaks. A and B excitonic peaks appear between 600–700 nm, while C excitonic peak appear around 430–450 nm in Fig. 4a. The peak position in each MoS_2 films directly grown on quartzes correspond to the band structures. With the layer thickness increasing, the absorbance intensity of the typical peaks increases. The PL response in the energy range corresponding to a direct transition indicated semiconducting behavior in the 2H-MoS_2 films. In general, the relative intensity of the PL band decreased as the number of MoS_2 layers present increased because the indirect electron transitions dominated the direct transitions.[21] The transition wavelength of the directly grown samples exhibits red-shifted position and lower intensity having a higher number of layers (Fig. 3b). Obvious absorbance of A and B excitonic peaks still can be observed when the growth temperature falling into 500–800°C (Fig. S7†), which prove the directly grown samples are tolerant to growth temperature.

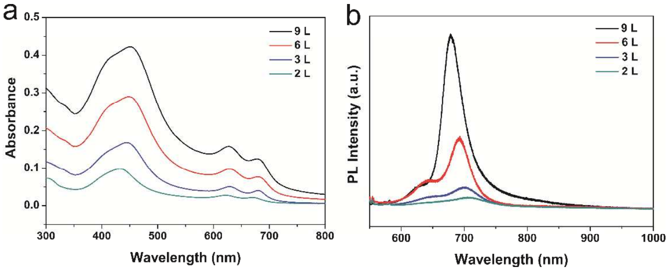

Fig. 3 Optical characterization of direct-growth MoS_2 on quartz. (a) UV-vis absorbance and (b) PL spectra of the MoS_2 grown on quartz at 900 °C having different thickness values.

X-ray photoelectron spectroscopy (XPS) is used to further clarify the structure of MoS_2 directly synthesized at different temperature and substrates. The C1s peak is fixed at 284.8 eV. As shown in Fig. 4a, the Mo (IV) show two peaks centered at 229.1~229.6 and 232.3~232.7 eV, attributing to the Mo $3d_{5/2}$ and Mo $3d_{3/2}$, respectively. And S $2p_{3/2}$ and S $2p_{1/2}$ are centered at 162.3 eV and 163.4 eV, respectively (as shown in Fig. 4b). All the XPS positions of peaks are consistent with the reported values.[17, 19, 22] The small peak at 235.5 eV indicate the residuals of Mo^{6+} grown at 300 °C. The surface oxide is originated from the underlying SiO_2 substrate, and molybdenum oxides are not detected (as shown in Fig. S8†). There are no noticeable changes occurring in the peak shape with a decrease in the temperature, in addition, the ratio of S and Mo is close to 2:1, which further suggest the formation of MoS_2 is independent of growth temperature in our system.

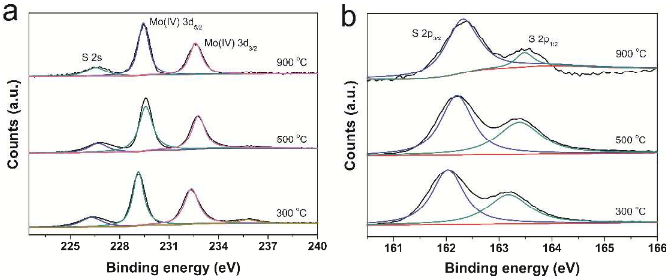

Fig. 4 The characterizations of XPS to shown the composition of MoS_2 on SiO_2/Si substrate. (a) and (b) show the corresponding the binding energies of Mo and S in the few-layer MoS_2, which were grown at 300 °C, 500 °C and 900 °C, respectively.

The growth temperature for reported growth methods of MoS_2 varies from 500 °C to 1100 °C, which limits the direct synthesis of MoS_2 films on thermolabile insulating substrates. Those insulating substrates could survive at high temperature, such as SiO_2/Si, quartz and sapphire are more expensive than plastic, and are not suitable for flexible device applications. The optical properties of MoS_2 attached to plastic are tunable though bending the substrates and electronic prosperities can keep stable, which inspires great potential in flexible photoelectric applications. The exfoliated and transferred MoS_2 films are limited by size and inevitable defects. Therefore, it is important to develop a way to directly grow MoS_2 on thermolabile insulating substrates. Our strategy has extremely high tolerance to various kinds substrates including common glass and polymer, such as PI. We succeed to obtain MoS_2 films on cover glass and SiO_2/Si as low as 250 °C (Fig. S9†). Fig. S9b† shows the typical peaks of MoS_2 directly grown on cover glasses with difference Mo layer thickness at 300 °C, as shown in the photograph of the inset. The MoS_2 films grown on PI at 250–300 °C have been characterized by XPS (Fig. S10†). Obvious signals from Mo(IV) $3d_{5/2}$ (centered at 229.2 eV) and S 2s peak at 226.7 eV are present. When the temperature is higher than 250 °C, the signal from Mo(VI) disappear gradually.

Conclusions

In summary, we demonstrate the direct growth of large area, uniform and patternable few layer MoS_2 films on arbitrary insulating substrates with 100% surface coverage, and the growth temperature can be as low as 250 ^{o}C. The thickness of the synthesized MoS_2 films could be controlled by depositing Mo layers having different thickness values. The AFM characterization exhibit the directly grown MoS_2 films is continuous compared with the transferred samples showing wrinkles, cracks and impurities. The directly synthesized MoS_2 films are also characterized by Raman/PL/UV-vis spectroscopy, XPS, and HRTEM. All analyses reveal almost perfect films uniformity, precisely controlled films thickness values, and high films crystallinity without the presence of an amorphous phase. Our approach is an effective way to directly obtain uniform and layer number controlled MoS_2 films on insulating surfaces especially on low-cost substrates, which would greatly facilitate flexible, stretchable and transparent device applications.

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Notes and references

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†Electronic Supplementary Information (ESI) available: Detailed growth conditions, optical images, Raman spectra, AFM and XPS characterization. See DOI: 10.1039/c000000x/

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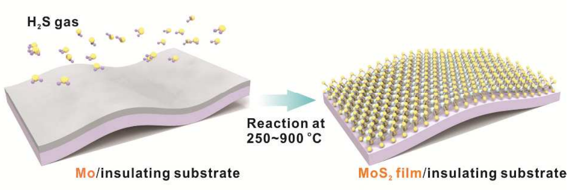

Direct growth of large area, uniform and patternable few layer molybdenum disulfide is achieved on arbitrary insulating substrates by CVD.