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Effect of precursor ratio on the morphological and optical properties of CVD-grown monolayer MoS$_2$ nanosheets

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Abstract

Atmosphere pressure chemical vapor deposition (CVD) is one of the most powerful methods of synthesizing high quality and large area MoS$_2$ films with a reasonable cost. In our work, the large-scale and high crystalline quality monolayer MoS$_2$ nanosheets were synthesized on Silicon substrate with a 300 nm oxide layer using MoO$_3$ and S powders as precursors by an atmosphere pressure CVD. The results suggest that the surface morphology, crystalline quality and luminescence of CVD-grown MoS$_2$ nanosheets can be tunable by controlling the precursor ratio (the effective Mo: S ratio). Excessive S-rich atmosphere is favor to synthesize large-size and high crystalline quality monolayer MoS$_2$ nanosheets with sharp corners and straight edges. This study may provide insight into the synthesis of large-scale and high crystalline quality MoS$_2$ films.

1. Introduction

In recent years, few-layer MoS$_2$ has attracted a great deal of attentions due to their unique two-dimensional layer structure and remarkable semiconducting performance. All these extraordinary properties benefit few-layer MoS$_2$ for various potential applications in nanoelectronic [1], optoelectronic [2–4], flexible electronics [5] and chemical sensors [6]. Several fabrication approaches of MoS$_2$ have extensively been adopted in the past few years, such as various types of exfoliation [7–9], magnetron sputtering [10], hydrothermal synthesis [11] and CVD [12–16]. Compared to the other fabrication approaches, the CVD method is considered to be one of the most powerful methods of synthesizing high quality and large area MoS$_2$ films with desired morphologies.

It is well known that the structures and properties of MoS$_2$ nanosheets are relevant to the number of layers [17], morphology [18], the domain size [19] and dopants or defects [20], which can be tunable by the growth parameters, including growth temperature [14, 21], carrier gas flow rate [22, 23], source-substrate distance [24] and the ratio between MoO$_3$ and S precursor amount [13, 25]. Both experimental and theoretical results show that the ratio between MoO$_3$ and S precursor amount is critical to the morphology and properties of CVD-grown MoS$_2$ nanosheets. Najmaei et al [12] observed the shape of MoS$_2$ flakes transformed from triangles to hexagons, then to truncated triangles with the decreasing amount of the S precursor. Wang et al [13] proposed the model for the shape transformation of MoS$_2$ nanosheets from triangles to hexagon, then to triangles again with the Mo:S ratio of precursors (>$1:2$, $1:2$ and < $1:2$). Cao et al [26] suggested that the shape evolution of monolayer MoS$_2$ flakes from dodecagons to hexagon and to triangles with the transition of growth environment from the Mo-rich to S-rich atmosphere by using density-functional theory calculations.

In this work, we report the effect of the precursor ratio (the effective Mo:S ratio) on the structural morphology and optical property of MoS$_2$ nanosheets. High crystalline quality monolayer MoS$_2$ nanosheets were successfully synthesized using atmosphere pressure CVD with the precursors of S and MoO$_3$ powder. The morphology, the number of layers, crystalline quality and luminescence characters were investigated by optical microscopy, Raman and photoluminescence (PL) spectroscopy.
2. Experimental methods

Figure 1 shows an illustration of the CVD experimental system for MoS₂ growth. MoO₃ and S powder were used as precursors in an atmosphere pressure to synthesize MoS₂ nanosheets on SiO₂/Si substrates. The CVD experimental system is consist of a single temperature-zone furnace and an additional heating ring upstream to control the temperature of MoO₃ and S powder independently. 30 mg MoO₃ powder (Alfa Aesar, 99.95%) and S powder (Alfa Aesar, 99.999%) were put separately in two different quartz boats, which were located in the furnace centre and the heating ring centre, respectively. The distance of the two boats was about 16 cm for the sake of ignoring the S vapor concentration gradient on the substrates. Silicon substrate covered with 300 nm thick SiO₂ layer was face down to the MoO₃ powder.

First of all, the tube was purged by 500 Standard cubic centimeter per minute (sccm) of ultrapure N₂ (99.999%) for 30 min. Then the temperature of MoO₃ powder was heated 5 min up to 100 °C and kept constant at 100 °C for 30 min to sweep water and hosting gases out of the tube. Afterwards, the temperature of MoO₃ powder was heated to 700 °C with a heating rate of 15 °C min⁻¹ and kept at 700 °C for 30 min with 75 sccm N₂ gas. Once the temperature of MoO₃ reached 700 °C, the S powder was heated by heating ring to 190 °C within 5 min. After all these processes, the furnace was cooled down to room temperature by opening the furnace cover, meanwhile the power source of heating ring was taken off. 500 sccm N₂ gas was introduced during the cooling step to prevent as-grown MoS₂ sample oxidation or contamination.

In this work, the same growth procedure was carried out besides the mass of S powder changed, and the mass of S powder was 15 mg, 30 mg, 60 mg, 90 mg and 120 mg, respectively.

The as-grown monolayer MoS₂ nanosheets were characterized by an optical microscope (Olympus BX41RF-LED) and a confocal Raman/PL spectrometer (Renishaw in Via). Raman and PL spectra were collected using Renishaw in Via confocal Raman system excited with a 514 nm laser and with an objective lens of 100×.

3. Results and discussion

3.1. Optical microscopy

Under stable growth conditions, the distribution of the precursors is determined by diffusion and convection. In an atmosphere pressure CVD system, the convection is more dominant in distributing the precursors than the diffusion. This results in the space of S distribution being much larger than MoO₃. Therefore, the effective ratio between Mo and S atoms on the substrate should be equal to the molar ratio of the amount of loaded MoO₃ powder to that of loaded S powder multiplied by a correction factor. In our experiment, the distance of the two boats, loaded S powder and MoO₃ powder respectively, was about 16 cm. The distance far away from MoO₃ source to gas outlet was 800 mm. According to the above analysis, the correction factor is approximatively equal to (160 + 800)mm/800 mm = 1.2. The effective ratio between Mo and S atoms on the substrate is listed in table 1.

The surface morphology of as-grown MoS₂ under different amount of S powder (or the effective Mo:S ratio) is shown by the optical images in figure 2. It can be clearly seen that, with the increase of the amount of S powder, MoS₂ nanosheets undergo an interesting and disciplinary morphology transformation. Under the effective Mo-rich environment (∼15 mg), a large number of MoS₂ nanosheets are randomly aligned on the SiO₂/Si substrate.

![Figure 1. Schematic of the CVD experimental system for MoS₂ growth.](image)

Table 1. The effective Mo:S ratio on the substrate.

| Mass of MoO₃ (mg) | 30  | 30  | 30  | 30  | 30  |
|------------------|-----|-----|-----|-----|-----|
| Mass of S (mg)   | 15  | 30  | 60  | 90  | 120 |
| Mo:S molar ratio | 1:2.25 | 1:4.5 | 1:9  | 1:13.5 | 1:18 |
| Effective Mo:S ratio | 1:1.88 | 1:3.75 | 1:7.5 | 1:11.25 | 1:15 |

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and the morphology of MoS$_2$ nanosheets is mainly $\sim$10 $\mu$m small triangles with straight and smooth edges. However, as the amount of S powder increase ($\sim$30 mg), the growth environment translating from Mo-rich to S-rich, the morphology of MoS$_2$ nanosheets changes to three-point stars or triangles with concave sides, and the length of the concave sides becomes longer and reaches to $\sim$50 $\mu$m (the maximum lateral size $\sim$76 $\mu$m). Then with the increase of the amount of S powder ($\sim$60 mg), there is no obvious change in the edge length of MoS$_2$ nanosheets in the excessive S-rich environment, while the concave sides are found to be filled and the edges of triangle are curved and rough. It is notable that the morphology of MoS$_2$ nanosheets is not equilateral triangle but close to isosceles triangle with two long sides and one short side. Subsequently, the morphology and size of the MoS$_2$ become almost unchanged as the further increasing amount of S powder ($\geq$90 mg), but the edges become more straight and smooth. The morphology of MoS$_2$ nanosheets is more and more closed to equilateral triangle with straight and smooth edges when the amount of S powder increases from 90 mg to 120 mg. It is found that the amount of S powder governs the morphology and edge size of MoS$_2$ nanosheets grown by CVD.

3.2. Raman spectra

Raman spectroscopy has been proved to be a powerful and nondestructive diagnostic of the number of layers of MoS$_2$ samples. Two prominent Raman modes can be observed in the Raman spectra of MoS$_2$ nanosheets (figure 3). All spectral data is actually the average of more than five measured MoS$_2$ nanosheets for each effective Mo:S ratio. The $E_{2g}^1$ vibration mode originates from the in-plane opposite vibration of two S atoms relative to Mo atom while the $A_{1g}$ vibration mode represents the out-of-plane vibration of two S atoms in the opposite direction. The number of layers of MoS$_2$ samples can be determined by the frequency difference between the $E_{2g}^1$ and $A_{1g}$ vibration mode. The $E_{2g}^1$ and $A_{1g}$ peak frequencies, the frequency difference and intensity ratio between the $E_{2g}^1$ and $A_{1g}$ modes for

![Figure 2. Optical images of MoS$_2$ nanosheets with different effective Mo:S ratio (a) 1:1.88, (b) 1:3.75, (c) 1:7.5, (d) 1:11.25, (e) 1:15.](image-url)
MoS₂ nanosheets grown at various effective Mo:S ratio has been summarized in Table 2. The frequency difference between the two characteristic Raman modes is 17 ∼ 18.6 cm⁻¹. The results are well consistent with the frequency difference of CVD-grown monolayer MoS₂ in the previous reports [27], indicating that all MoS₂ nanosheets grown at various effective Mo:S ratio are dominated by monolayer. Moreover, the E₁₂g/A₁g peak intensity ratio is varied from 2.74 to 4.65 and amplifies to more than 4 when the effective Mo:S ratio decreases to 1:7.5, which suggests that the as-grown MoS₂ samples have good crystalline quality and crystalline quality can be tuned by the amount of S powder. Figure 3(b) shows the full width at half maximum (FWHM) of the Raman peak as a function of the effective Mo:S ratio. The FWHM of the E₁₂g peak becomes narrower from 3.82 cm⁻¹ to 2.65 cm⁻¹ with the decreasing effective Mo:S ratio by means of the increasing amount of S powder, which is close to 3.7 cm⁻¹ of exfoliated monolayer MoS₂ [28], indicating that crystalline quality will be improved in S-rich atmosphere. On the other hand, the FWHM of the A₁g peak becomes wider as the effective Mo:S ratio increases. The broadening of A₁g peak reveals that more and more S vacancies generated under S-rich atmosphere [29].

### 3.3. PL spectra
MoS₂ nanosheets were also characterized using photoluminescence spectroscopy. Two pronounced emission peaks are observed in the PL spectra, representing the A and B direct excitonic transitions, respectively. As shown in Figure 4(a), a stronger intensity peak (A peak) located at 1.78 ∼ 1.83 eV while a weaker peak (B peak) positioned at 1.93 ∼ 1.98 eV, which agrees well with the energy of direct band gap of the exfoliated monolayer MoS₂ [30]. It is notable that only the strong A exciton peak (1.82 eV) without the obvious B exciton peak can be observed for the MoS₂ nanosheets synthesized at effective Mo:S ratio of 1:11.25, suggesting that the as-grown MoS₂ nanosheets are very similar to the freestanding monolayer MoS₂ with low n-type doping density [31]. The energy difference between A peak and B peak is almost unchanged and maintains the value of 0.15 eV (Figure 4(b)), which is in good agreement with the previous reported value for monolayer MoS₂ [30]. The energy difference is attributed to the splitting of valence band due to the strong spin–orbit coupling.

The PL spectra were normalized by Raman A₁g peak intensity (Figure 4(a)). The PL quantum efficiency is closely proportional to the normalized PL intensity [30, 32]. An obvious increasing PL quantum efficiency with the decreasing effective Mo:S ratio suggests that the crystalline quality of the as-grown MoS₂ nanosheet could be improved at a relatively low Mo:S ratio. The best crystalline quality monolayer MoS₂ nanosheets accompany with the normalized PL intensity exceeding 100 were synthesized at the effective Mo:S ratio 1:11.25. These results are in accordance to that of Raman.
The FWHM of B exciton peak become broader from 0.21 eV up to 0.28 eV with the transition from Mo-rich atmosphere to S-rich atmosphere. However, it is almost unchanged in the excessive S-rich atmosphere with the further increase amount of S powder. On the other hand, the FWHM of A exciton peak becomes narrower 0.16 eV down to less than 0.14 eV with the transition from Mo-rich atmosphere to S-rich atmosphere, which indicated that the small effective Mo:S ratio is favor to the improvement of the crystalline quality. Interestingly, for the MoS$_2$ nanosheet of the effective Mo:S ratio being 1:11.25 (excessive S-rich atmosphere), only A exciton peak at 1.83 eV was observed. And the narrowest FWHM of A exciton peak (60 meV) is observed compared to rest of the other Mo:S ratio, which is less than that of exfoliated MoS$_2$ nanosheet on the SiO$_2$/Si substrate (100 meV) [33]. The above results suggest that the MoS$_2$ sample synthesized at the effective Mo:S ratio 1:11.25 is best crystalline quality monolayer MoS$_2$ among all Mo:S ratio.

### 3.4. Possible growth mechanism

It is well known that the morphology evolution of CVD-grown two-dimension transition metal dichalcogenides is determined by the change in precursor ratio [13, 34]. However, the intermediate shape of three-point star (figure 2(b)) is not interpreted in detail in the previous literature. Therefore, we would explain it by the edge attachment growth model, as shown in figure 5.

Assuming the formation of a hexagonal monolayer at the stage of MoS$_2$ growth, as S powder amount of 15 mg (Mo-rich atmosphere), the growth rate of S-terminated zigzag edge is faster than that of Mo-terminated zigzag edge in the Mo-rich atmosphere, resulting in the formation of equilateral triangles with Mo-terminated zigzag edge. As the S powder amount is increased up to 30 mg, the growth environment changing from Mo-rich atmosphere to S-rich atmosphere, due to the growth rate of Mo-terminated zigzag edge is over three times than that of S-terminated zigzag edge, the S-terminated edges deviate from established zigzag edges and become curved [35]. Therefore, the morphology of MoS$_2$ nanosheets transforms to three-point star. If further increasing the quantity of S powder, Mo:S ratio is much smaller than 1:2, indicating the formation of an excessive S-rich atmosphere. The shape of MoS$_2$ nanosheets ended up with triangles instead of three-point stars. To understand the morphological evolution of MoS$_2$ nanosheets from three-point star to triangle, the activation barriers of three elemental atomic motion processes should be involved. The first is the activation barrier ($V_c$) against atoms crossing an island corner from one edge to a neighboring edge via a corner site. The second is the edge diffusion barrier ($V_e$). The third is the activation barrier against atoms at kink sites moving to the neighboring positions ($V_k$). Generally, $V_k > V_c > V_e$ [36, 37], therefore, the island corners act as reflecting sites and the kink sites act as
absorbing sites for atoms diffusion along the edges. In other words, the precursor molecules prefer to be adsorbed at the kink sites in the middle of edges. As a result, the concave part of the edge of MoS₂ nanosheets is gradually filled until the edges become more and more straight. The crystalline grain eventually becomes an equilateral triangle with straight zigzag edges and sharp corners. If further increasing the quality of S powder, the morphology and size of MoS₂ nanosheets do not seem to change besides the edges become more and more straight. Moreover, the size of MoS₂ nanosheets also can be tuned by the effective Mo:S ratio, as shown in figure 2. With an abundant supply of S vapor, a large number of MoS₂ species are formed by the sulfurization of MoO₃. Because of the aforementioned low edge diffusion barrier, more and more MoS₂ species are absorbed on the surface of the substrate and only need to diffuse a relatively short distance to coalesce into the previously formed nuclei. Consequently, the edge size of MoS₂ nanosheets increases with the decreasing of Mo:S ratio.

4. Conclusions

In conclusion, monolayer MoS₂ nanosheets have been synthesized on SiO₂/Si substrate under the different amount of S powder ranging from 15 mg to 120 mg by an atmosphere pressure CVD. The morphology, the number of layers, crystalline quality and luminescence characters of as-grown MoS₂ nanosheets were systematically investigated by optical microscopy, Raman and PL spectroscopy. The results demonstrate that the small effective Mo:S ratio (excessive S-rich atmosphere) is favor to the improvement of the crystalline quality and edge size of MoS₂ nanosheets. Moreover, A possible growth mechanism of MoS₂ nanosheets with various shapes has been proposed according to the transformation of the effective Mo:S ratio. This work paves way for the synthesis of large-scale and high crystalline quality MoS₂ films.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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