Growth of Single-Layer MoS$_2$ by Chemical Vapor Deposition on sapphire substrate

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Abstract: Single-layer molybdenum disulfide (MoS$_2$) has attracted a significant amount of interest owing to its excellent electrical, optical, and mechanical properties. In this paper, we study that the effects of the distance between the molybdenum source and substrate as well as the substrate angle on the morphology, size, and structure of MoS$_2$ films grown from molybdenum trioxide (MoO$_3$) sulfide on sapphire substrates via the Chemical Vapor Deposition (CVD) by using Scanning electron microscopy (SEM), Raman spectra and Photoluminescence spectra (PL). On the results show that the distance between the substrate and molybdenum source affects the controllable growth of MoS$_2$ films. When the substrate is too close to the molybdenum source, it results in increasing amount of non-reduced MoO$_3$ particles which were deposited on the substrate. When the distance between the substrate and molybdenum source is too large, only a small amount of MoS$_2$ is deposited on the substrate. High-quality MoS$_2$ films can be prepared when the molybdenum source and substrate are 9.5 cm apart. When the substrate is inclined 30° and placed downstream of the molybdenum source with a distance of 9.5 cm, the size of the prepared single-layer MoS$_2$ is approximately 100 μm, which is greater than that of MoS$_2$ prepared on the horizontal face-up substrate.

1. Introduction
With the development of semiconductor device fabrication technology and the size of devices approaching miniaturization, two-dimensional transition metal disulfide (TMD) has received widespread attention for its excellent electrical, optical, and mechanical properties$^1$. As a type of TMD, MoS$_2$ is the best representative. MoS$_2$ possesses a graphite-like structure, and the single-layer MoS$_2$ consists of a “sandwich” structure such as “S-Mo-S”$^2$. The distance between layers of MoS$_2$ is 6.5 Å, which are connected to each other by a weak Van Der Waals force. The study found that MoS$_2$ exhibits many excellent properties, such as high luminous efficiency, as the number of layers decreases, high electron mobility rate (up to 200 cm$^2$/V·s), and a direct band-gap structure ($E_g$ = 1.8eV)$^3$. Therefore, MoS$_2$ can be employed in the fabrication of sensitive photodetectors$^4$, light-emitting diodes$^5$, field effect transistors with high-current on and off ratio$^6$, and microelectromechanical nanometer resonators. Single-layer MoS$_2$ has attracted significant attention for a wide range of applications. It is considered as a potential candidate in atomic-scale semiconductor science$^7$. The main methods to prepare single-layer MoS$_2$ include auxiliary tape mechanical exfoliation$^2$, liquid-phase exfoliation$^8$, lithium ion intercalation and physical vapor deposition$^9$, etc. The auxiliary tape mechanical exfoliation method strips multilayered materials into less or single-layered materials using adhesive tape. Although this method is simple and easy to
operate, the size and thickness of the film cannot be controlled and cannot be produced in large sizes\textsuperscript{[10]}. In the liquid-phase exfoliation method, MoS\textsubscript{2} nanoparticles are prepared from MoS\textsubscript{2} powder into a suitable solution by ultrasonic, centrifugal, and vacuum drying\textsuperscript{[11]}. Although this method can be used in large-scale production, it is difficult to obtain single-layer MoS\textsubscript{2} because stripping is conducted in a liquid environment, and it takes a long time. In the lithium ion intercalation method, MoS\textsubscript{2} is immersed in lithium-containing solvents and proton solvents successively, which enable lithium ions to react with proton solvents between the layers of body material, thus enlarging the interlayer spacing of MoS\textsubscript{2} to achieve the peeling effect\textsuperscript{[12]}. However, the preparation process is complex and lithium metal is expensive owing to the shortage in supply. Physical vapor deposition is a physical change only morphological changes. MoS\textsubscript{2} powder is evaporated and converted into a gas phase, and subsequently deposited on the substrate. This method is easy to operate and has uniform film formation, however, impurities in the raw materials are difficult to remove.

Chemical vapor deposition (CVD) is a method that produces high-quality MoS\textsubscript{2} films with uniform morphology and controllable size by the chemical reaction between molybdenum and sulfur sources at suitable temperature and gas flow. In summary, CVD is an efficient method to synthesize large single-layer MoS\textsubscript{2} films. CVD can be roughly divided into two types: one-step method and two-step method\textsuperscript{[13]}. One-step CVD produces MoS\textsubscript{2} by evaporating the molybdenum source and sulfur source, this method is used in our experiment. In the two-step method, molybdenum is deposited on the substrate using a sputtering process, placed in a sulfur atmosphere, and reduced to graphite-like MoS\textsubscript{2} at high temperature.

In our previous work, the effects of temperature, gas flow, raw material quantity, and time on the morphology and size of MoS\textsubscript{2} were studied. However, the effect of the distance between the molybdenum source and substrate as well as the substrate angle on the morphology of MoS\textsubscript{2} has not been considered\textsuperscript{[14]}. In studying the angle in which the substrate is placed, MoS\textsubscript{2} disulfide thin films were successfully prepared on horizontal face-up substrates by Liu H et al\textsuperscript{[15]}. MoS\textsubscript{2} thin films were produced on face-down inverted substrates by Wang S et al\textsuperscript{[16]}. In this paper, the single-layer MoS\textsubscript{2} was prepared by CVD based on sapphire, and on the basis of the preliminary work, the effect of the position of the substrate and the way of the substrate placement on the size and morphology of MoS\textsubscript{2} films was studied.

2. Experimental conditions and methods

First, ultrasonic cleaning of substrates with acetone, alcohol and deionized water for 10 minutes, and then dry the substrates with nitrogen. The molybdenum source and sulfur source are molybdenum trioxide (MoO\textsubscript{3}) and sublimed sulfur (S) respectively. MoO\textsubscript{3} powder (10 mg) was put in a double-open quartz boat and placed in a high-temperature area of the furnace, sulfur powder (10 mg) was put in another double-open quartz boat placed in a low-temperature area of furnace (Figure 1). The clean substrate is placed downstream of the molybdenum source. Before the reaction, the quartz tube was evacuated to 5 Pa or less to remove air, and then 99.9\% high-purity argon was injected into the quartz tube to restore normal pressure. After the process is repeated three times, the 70 sccm argon carrier flow is continuously accessed as a protective atmosphere until the end of the reaction. Next, the reaction temperature program of the furnace is set according to the reaction conditions. The first step is to raise the temperature of MoO\textsubscript{3} to 600 °C in 30 min to start the evaporation, the second step is to raise the temperature of MoO\textsubscript{3} to 810 °C at 5 °C/min, the sulfur is also heated for evaporation in the second step. The sulfur vapor driven by argon gas reacts with the molybdenum source, MoO\textsubscript{3} vapor can be fully reduced by sulfur vapor after 20 min. After the reaction is finished, argon is continuously injected to cool it to room temperature.

![Figure 1. the CVD system for growing MoS\textsubscript{2}](image-url)
Figure 2 is two different placement modes of the substrate. Figure 2 (a) shows that the substrate was placed face up and positioned horizontally downstream of the molybdenum source. Figure 2 (b) shows that the substrate was placed face up and tilted 30° downstream of the molybdenum source.

![Figure 2. Image of substrate placement mode. (a) Substrate placed face up and positioned horizontally; (b) substrate placed face up and tilted 30°](image)

Reaction principle: firstly, the furnace heating caused the MoO$_3$ and sublimed sulfur to transform from solid to gas phase (formula 1 and 2). Secondly, driven by argon flow, MoO$_3$ was initially reduced to MoO$_{3-x}$ by sulfur, and then MoO$_{3-x}$ was reduced to MoS$_2$ by sulfur (formula 3 and 4). Finally, MoS$_2$ was deposited on the downstream substrate.

\[
\begin{align*}
S (s) & \rightleftharpoons S (g) \quad (1) \\
MoO_3 (s) & \rightleftharpoons MoO_3 (g) \quad (2) \\
MoO_3 (g) + S (g) & \rightleftharpoons MoO_{3-x} (g) \quad (3) \\
MoO_{3-x} (g) + S (g) & \rightleftharpoons MoS_2 (s) \quad (4)
\end{align*}
\]

In this work, the morphology and size of MoS$_2$ samples were characterized by SEM. The thickness and number of layers of MoS$_2$ were characterized by Raman spectra, PL spectra and AFM.

SEM produces various effects through the interaction between the electron beam and sample, the acceleration voltage was 20 kV, which produces an image full of stereoscopic sense with high magnification. The morphology of MoS$_2$ can be clearly seen by SEM, the layer number of MoS$_2$ was roughly judged according to the contrast of color between MoS$_2$ and the substrate.

Raman spectra is a method for studying molecular structure by the inelastic scattering effect of molecules on photons. The peak of the Raman spectrum of MoS$_2$ is closely related to the thickness of MoS$_2$. When the number of MoS$_2$ layers is reduced, the Van Der Waals force is gradually increased. At this time, the corresponding peaks E$_{2bg}$ of sulfur atoms that vibrating in the horizontal plane show a blue shift, while the corresponding peaks A$_{1g}$ of sulfur atoms that vibrating in the vertical plane show a red shift, which causes the difference in wavenumber to decrease. The wavenumber difference between A$_{1g}$ and E$_{2bg}$ of the monolayer MoS$_2$ film is approximately 21 cm$^{-1}$
[17], therefore, the thickness of the material can be reflected by the wavenumber difference. The wavelength of Raman spectra was 532 nm with a spectral range of 200 to 1000 nm, a spectral resolution of 1 cm$^{-1}$, a grating groove density was 1800 L/mm, and a spatial resolution of 0.5 μm in the lateral direction and 2 μm in the longitudinal direction.

PL spectra refers to the process in which a substance re-emits photons or electromagnetic waves when it absorbs photons or electromagnetic waves of a certain frequency. The multilayer MoS$_2$ is an indirect band-gap semiconductor material with a band gap of approximate 1.2 eV and almost no fluorescence peaks. These demonstrate wide direct band gaps and two strong PL fluorescence peaks appearing near 1.8 eV and 2.0 eV when MoS$_2$ is changed from bulk to less or monolayer[18]. The characteristic peak corresponding to 1.8 eV is the direct band gap of MoS$_2$, and the characteristic peak corresponding to 2.0 eV is the energy band split caused by the spin orbit coupling of MoS$_2$. The wavelength of PL spectra was 700 nm, and its groove density was 150 L/mm.

AFM is a micro-cantilever which is very sensitive to weak forces. One end of the micro-cantilever is fixed, the other end of the micro-cantilever possesses a tiny probe below it. When the probe is close to the surface of the sample, there is a weak repulsion force between the probe and the atoms on the
surface of the sample, so that the sample surface can be analyzed in depth. The height difference between the substrate and the MoS\textsubscript{2} deposited on the substrate surface can be measured by the interaction between the tip of the probe and the surface of the MoS\textsubscript{2} sample. AFM was used to confirm the flake’s thickness.

3. Experimental results and analysis

Figure 3a is the picture of the distances between the molybdenum source and substrate in Figure 3 (b–f) : 5 cm, 6.5 cm, 8 cm, 9.5 cm, and 11 cm, respectively. Figure 3 (b–f) are compared SEM images of the substrate placed face up and horizontal at different distances downstream of the molybdenum source.

Figure 3 (b) is a sample SEM image of area a. The substrate is almost full of MoO\textsubscript{3} particles owing to the small distance from the molybdenum source. The MoO\textsubscript{3} concentration is too high before it can be reduced by sulfur deposited on the substrate. Figure 3 (c) is a sample SEM image of area b. There are a few small triangular of MoS\textsubscript{2} on the substrate, and there are more MoO\textsubscript{3} particles. Since sulfur vapor can only reduce part of MoO\textsubscript{3} to MoS\textsubscript{2}, the excess MoO\textsubscript{3} is deposited on the substrate surface. Figure 3 (d) is a sample SEM image of area c. The surface of the substrate is clean and produces a regular triangular of MoS\textsubscript{2} with a size of approximate 50 μm in equidistribution, but it's not large enough. Although MoO\textsubscript{3} and S vapor can react adequately by argon, MoS\textsubscript{2} does not have enough growth time because the substrate is still close to the molybdenum source and the contact time between MoO\textsubscript{3} and S vapor is short. Figure 3 (e) is a sample SEM image of area d. It shows that the triangular MoS\textsubscript{2} with the size of approximate 80 μm deposited on substrate, for which the size is larger than that of Figure 3 (d) with the distance between molybdenum source and substrate of 8 cm. Figure 3 (e) also shows that the MoS\textsubscript{2} is a regular triangle with no redundant edges and uniform surface morphology, which is obviously contrasted with the substrate, the preliminary judged is the single-layer MoS\textsubscript{2} film. Owing to the suitable distance between molybdenum source and substrate provides sufficient reaction time for MoO\textsubscript{3} and sulfur vapor. Figure 3 (f) is a sample SEM image of area e. It can be seen that there is a small amount of MoS\textsubscript{2} on the surface of the substrate. The reason is that the substrate is too far from the molybdenum source, the corresponding concentration of MoO\textsubscript{3} is too low, leading to the small amount of MoS\textsubscript{2} produced by the reaction which is difficult to nucleate; therefore, a small amount of triangular MoS\textsubscript{2} is grown on the surface of the substrate.
Figure 3. Samples SEM image of the substrate placed face up and positioned horizontally (a) the map of the distances between the MoO$_3$ and substrate; (b) Area A; (c) Area B; (d) Area C; (e) Area D; (f) Area E

According to the above SEM characterization, high-quality MoS$_2$ with a maximum size of 80 μm can be obtained when the substrate is placed 9.5 cm away and downstream of the molybdenum source. Next, MoS$_2$ was prepared on a substrate inclined by 30° with the other parameters unchanged. Figure 4 are compared the sample SEM image of substrates and molybdenum sources at distance of 9.5 cm. Figure 4 (a) is the SEM image of the sample when the substrate is face up and horizontal. It shows that the size of the triangular MoS$_2$ film is approximately 80 μm. Figure 4 (b) is the SEM image of the sample when the substrate is face up and inclined 30°, the size of the MoS$_2$ film growing on the substrate is approximately 100 μm, which is larger than that deposited on the horizontal substrate in Figure 4 (a). As is known, when substrate placed horizontally, the direction of gas flow diffusion is parallel to the substrate surface, a boundary layer forms near the substrate due to the drag of the gas molecules by the viscous force. The gas in the boundary layer is in a state of low fluidity, and both the reactants and reaction products diffuse through this boundary layer, hence, the boundary layer limits the deposition rate of the film. Changing the placement angle of the substrate increases the gas flow rate ($v$) and Reynolds quasi-number $Re(x)$, reduces the thickness of the boundary layer $δ(x)$, and improves the stability of film deposition (formula 5 and 6). At the same time, when the substrate is tilted, the diffusion per unit area increases, thus increasing both the diffusion flux ($J$) (formula 7) and film deposition.

\[
Re(x) = \frac{\nu x}{\eta} \quad (5)
\]

\[
δ(x) = \frac{5x}{\sqrt{Re(x)}} \quad (6)
\]

\[
J = -D \frac{d\rho}{dx} \quad (7)
\]

(x is the coordinates along the length direction, $\rho$ is fluid density, $v$ is gas flow rate, $\eta$ is fluid viscosity, $D$ is diffusion coefficient)
Figure 4. the sample SEM image of substrates and MoO$_3$ at distance of 9.5 cm. (a) SEM image of the sample when the substrate is face up and horizontal; (b) SEM image of the sample when the substrate is face up and inclined 30°.

Figure 5 (a) is Raman spectra of samples prepared by horizontal face-up and inclined face-up at distance of 9.5 cm between substrate and molybdenum source were compared. It shows that samples prepared on the horizontal face-up substrate possess E$_{2g}^1$ peak of 384.6 cm$^{-1}$, A$_{1g}$ peak of 403.8 cm$^{-1}$, and wavenumber difference A$_{1g}$-E$_{2g}^1$ of 19.2 cm$^{-1}$. It also exhibits that samples prepared on the inclined face-up substrate possess E$_{2g}^1$ peak of 384.7 cm$^{-1}$, A$_{1g}$ peak of 405.4 cm$^{-1}$, and wavenumber difference A$_{1g}$-E$_{2g}^1$ of 20.7 cm$^{-1}$. By comparing Figure 5 (a) and 5 (b), it can be deduced that the peak at 416.5 cm$^{-1}$ wavenumber in Figure 5 (b) is caused by the influence of the sapphire substrate Al$_2$O$_3$. In summary, it can be confirmed that the MoS$_2$ samples prepared by the above two methods are single-layer.

Figure 5 (b) Raman spectra of the grown MoS$_2$ films on sapphire substrates; (b) Raman spectra of the sapphire substrates.

Figure 6 (a) is PL spectra of samples prepared by horizontal face-up and inclined face-up at distance of 9.5 cm between substrate and molybdenum source were compared. It represents that samples prepared on the horizontal face-up substrate show a strong characteristic peak at wavelength $\lambda$ of 665.7 nm. According to the calculated wavelength and electron volt conversion (formula 8), the corresponding transition energy $E$ is 1.86 eV. It also depicts that samples prepared on the inclined face-up substrate display a strong characteristic peak at wavelength $\lambda$ of 664.6 nm and transition energy $E$ of 1.86 eV. By comparing Figure 6 (a) and 6 (b), it can be deduced that the peak at 692.6 nm wavenumber in Figure 6 (b) is caused by the influence of the sapphire substrate Al$_2$O$_3$. In summary, it can be confirmed that the MoS$_2$ samples prepared by the above two methods are single-layer with good photoelectric effect.

$$E = \frac{hc}{\lambda}$$  \hspace{1cm} (8)

($c=3.0\times10^8 \text{ m/s}; \hspace{0.2cm} h=6.626\times10^{-34} \text{ J-S}; \hspace{0.2cm} 1 \text{ eV}=1.602\times10^{-19} \text{ J}$)
4. Conclusion

In this paper, single-layer MoS\(_2\) film was successfully prepared by CVD, the morphology and size distribution of MoS\(_2\) films prepared by various distance between molybdenum source and substrate and various substrate placement were studied. Through SEM, Raman spectra and PL spectra, the following results were obtained:

(a) The distance between the substrate and molybdenum source affects the controllable growth of MoS\(_2\) film. When the distance between the substrate and molybdenum source is too small, the concentration of MoO\(_3\) is too high, which leads to the deposition of more MoO\(_3\) particles on the substrate surface; When the distance between the substrate and molybdenum source is too large, the concentration of MoO\(_3\) is too low, which results in difficult MoS\(_2\) nucleation, the substrate surface only has trace amounts deposited small triangular MoS\(_2\); When the substrate is placed downstream of the molybdenum source with a distance of 9.5 cm away, the regular and distribution uniform single-layer MoS\(_2\) with size of approximate 80 \(\mu\)m can be synthesized.

(b) The placement mode of the substrate also affects the morphology of MoS\(_2\) films. When the substrate is inclined 30° and placed downstream of the molybdenum source with a distance of 9.5 cm, the size of the single layer MoS\(_2\) is approximately 100 \(\mu\)m which is larger than that of MoS\(_2\) prepared on the horizontal substrate.

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References:

[1] Lei L, Liu Z, Peng H, Wu Z and Jiang S. 2016, J Rsc Advances, 6(114) 113315-21.
[2] Radisavljevic B, Radenovic A, Brivio J, Giacometti V and Kis. 2011, J Nat Nanotechnol, 6(3) 147-50.
[3] Elias D C, Gorbachev R V and Mayorov A S. 2011, J Nature Physics, 7(9) 701-4.
[4] Xu H, Han X, Dai X, Liu W, Wu J and Zhu J, 2018, J Adv Mater, 30(13) 1706561.
[5] Sundaram R S, Engel M, Lombardo A, Krupke R, Ferrari A C and Avouris P. 2013, J Nano Lett, 13(4) 1416-21.
[6] Cho K, Pak J, Kim J K, Kang K, Kim T Y and Shin J. 2018, J Adv Mater, 1705540.
[7] Zheng J, Yan X, Lu Z, Qiu H, Xu G and Zhou X. 2017, J Adv Mater, 29(13) 1604540.
[8] Li H, Yin Z, He Q, Li H, Huang X and Lu G. 2012, J Small, 8(1) 63-67.
[9] Gong C, Huang C, Miller J, Cheng L, Hao Y and Cobden D. 2013, J Acs Nano, 7(12) 11350-57.
[10] Li H, Yin Z, He Q, Li H, Huang X and Lu G. 2012, J Small, 8(1) 63-67.
[11] Smith R J, King P J, Loyda M, Wirtz C, Khan U and De S. 2011, J Adv Mater, 23(34) 3944-48.
[12] Gee M A, Frindt R F, Joensen P and Morrison S R. 1986, J Mater res bull, 21(5) 543-49.
[13] Zhan Y, Liu Z, Najmaei S, Ajayan P M and Lou J. 2012, *J Small*, 8(7) 966–71.
[14] Han S, Yuan C, Luo X, Cao Y, Yu T and Yong Y. 2015, *J Rsc Advances*, 5(84) 68283-86.
[15] Liu H, Si M, Najmeji S, et al. 2013, *71st Device Research Conference*. South Bend, IN(US).
[16] Wang S, Rong Y, Fan Y, Pacios M, Bhaskaran H and He K. 2014, *J Chem Mater*, 26(22) 6371-79.
[17] Balendhuran S, Ou J Z, Bhaskaran M, Sriram S, Ippolito S and Vasic Z. 2012, *J Nanoscale*, 4(2) 461-66.
[18] Eda G, Yamaguchi H, Voiry D, Fujita T, Chen M and Chhowalla M. 2011, *J Nano Lett*, 11(12) 5111-16.