Growth Mechanism of Continuous Monolayer MoS₂ Prepared by Chemical Vapor Deposition

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Abstract. Molybdenum disulfide (MoS₂) is a cutting-edge layer-dependent two dimensional semiconductor which monolayer is direct-bandgap. Nano-scale monolayer MoS₂ has big potential in electronics and optoelectronics devices. In this work we reported the progress in growing continuous single layer MoS₂ by ambient pressure chemical vapor deposition (APCVD). Scanning electron microscope (SEM), Raman, photoluminescence spectra (PL) and atomic force microscopy (AFM) disclose that as-grown films are large-area monolayer and of high quality. SEM observations also clearly reveal the growth process of these films. Figuring out the growth mechanism grants growth of large scale continuous MoS₂, and lays the foundation for wide device applications in the future.

1. Introduction
Transition metal dichalcogenides (TMDCs) are nano-scale two-dimensional semiconducting materials which monolayers are direct bandgap. Recently, much attention has been attracted to its synthesis, properties and applications in nanoelectronics and optoelectronics. MoS₂ is one of the most famous member of TMDCs due to its satisfying optoelectronic properties[1-5]. As for the structure, MoS₂ is made up of one layer of Mo atoms sandwiched between two planes of S atoms, S-Mo-S groups are gathered together weakly by van der Waals forces, while atoms within the layer are bound by strong covalent bonds. MoS₂ is an inherently n-type semiconductor, like many TMDCs have layer-dependent property, its bandgap ranges from 1.29eV to 1.9eV as the thickness decreasing from bulk to monolayer [6-8]. Single-layer MoS₂ is direct band-gap leading to strong photoluminescence phenomenon.

Growing MoS₂ using chemical vapor deposition (CVD) is promising around other growth methods such as physical vapor deposition[9], micro-mechanical exfoliation[10, 11], liquid exfoliation[12] because CVD has great potential in synthesizing large scale films with high quality[13]. Many works have been done to grow monolayer MoS₂ films[14,15], however, understanding the chemistry of large scale continuous MoS₂ films is still a challenge. In this paper, we study growth mechanism of monolayer MoS₂ prepared by APCVD, which is the most commonly used method for the preparation of MoS₂.

2. Experimental Method

2.1. Synthesis of Large-scale Continuous MoS₂ Film
The synthesis of two-dimension MoS₂ occurred within the set up shown in Figure 1. Precursors are molybdenum trioxide (MoO₃) (99.99%, Alfa) and solid sulfur (99.99%, Aladdin). Argon (Ar) acts as the carrier gas in the APCVD system during whole growth process. MoO₃ powder was put in a ceramic boat loaded in the center of 1 inch quartz tube inside of 2 inch tube, whole 1-inch tube is...
adjusted to be at the middle of 2 inch tube. Silicon dioxide/silicon (SiO₂/Si) substrates were placed at downstream about 7 cm away from MoO₃ powder. The substrate was cleaned in acetone, alcohol and deionized (DI) water separately for 15 min. Solid sulfur (S) powder (0.5g) was also loaded in a ceramic boat located at the upstream of the 1 inch quartz tube with 15 cm away from MoO₃ powder. At first stage, the whole two tube was flushed for 25 min with 400 sccm of Ar to drive oxygen away, then furnace was set to 810°C together with Ar flowing at 80 sccm and ramping rate of 40°C/min. When furnace reached the set temperature, simultaneously S evaporated because it was heated up by radiation of the furnace, growth stage started for 4~10 min. At last cooling stage, when growth time finished, the tube reached room temperature in a quite short time by exposing directly to air.

![Figure 1. Schematic depiction of the APCVD setup.](image)

2.2. Characterization of Synthesized MoS₂ Films
Raman spectroscopy and photoluminescence (PL) spectroscopy were achieved by the usage of a confocal spectrometer with a 532nm solid-state excitation laser. The structural and optical features of the film were characterized by Raman and photoluminescence (PL) spectroscopy, respectively. Scanning electron microscope (SEM) was conducted to see the surface topography and structures of the as-grown MoS₂. The surface morphology and thickness of the as synthesized domains were observed by atomic force microscope (AFM).

3. Results and Discussion
The structural properties and quality of MoS₂ film was illustrated by Raman spectroscopy. In figure 2a, the sample shows two typical peaks. The in-plane vibration mode results in \( E_{2g}^1 \) peak locating around 384.9 cm\(^{-1}\), this mode is caused by two S atoms vibrating oppositely versus the Mo atom within the S-Mo-S unit. And the two S atoms vibrating perpendicularly to the plane is called out-of-plane vibration mode, this mode leads to peak \( A_{1g} \) which is close to 405.1 cm\(^{-1}\). The frequency difference (\( \Delta K \)) between \( E_{2g}^1 \) and \( A_{1g} \) indicates the number of layer in atomic layered MoS₂[16]. \( \Delta K \) in this work is 20.2 cm\(^{-1}\), which means that it is monolayer MoS₂ film. Besides 20.2 cm\(^{-1}\) is in agreement with exfoliated monolayer MoS₂ crystal’s \( \Delta K \) [17], which suggests that as-synthesized films have highly crystallized structure. Figure 2b shows PL spectrum of this film which has two emission peaks existing. An obvious PL peak is located around 679.9 nm, this sharp PL signal is caused by A1 excitation of MoS₂. The resonance of B1 excitation in MoS₂ gives the spectrum a wide shoulder peak locating at 628.5 nm. The excitonic transition between maximal splitted valance band and minimal conduction band brings about A1 and B1 excitations[18].
Figure 2. Spectroscopic characteristic of MoS2 films. (a) Raman spectrum of single layer MoS2. (b) PL spectra of MoS2 at the same sampling spot in Raman characterization.

AFM was used to testify the thickness and topography of the film (figure 3). The knifing along the white line which covers substrate and MoS2 domain in figure 3a shows height image in figure 3b. The step height is ~0.75 nm which means the thickness of MoS2 is ~0.75 nm, matching good with range of 0.65-0.9 nm of CVD grown monolayer MoS$_2$[19]. The color in the AFM image reflects the thickness. The MoS$_2$ region’s thickness is roughly consistent, indicating an uniform monolayer.

Figure 3. (a) AFM 2D image of MoS$_2$ domain on the bare substrate. (b)Step height image of the white line in (a).

Figure 4a-d are the SEM figures of MoS$_2$ nanofilms under various growth time. In this experiment, the reaction time are set to 4, 6, 8 and 10 min respectively to observe the MoS$_2$ films growth process. Figure 4a presents the result of the reaction time at 4 min, MoS$_2$ domains locate randomly on the substrate and the number of domains is small. It is worth attention that as reaction time increased from 4 min to 10 min, as demonstrated in figure 4b-4d, with reactants diffuse on the wafer surface continuously, density of MoS$_2$ crystals increased and MoS$_2$ domains tended to join together then finally reached a continuous film on the substrate. Figure 4d shows a continuous film with high uniformity.

In a CVD system when the partial pressure of the reactant in the gas is high, it will lead to gas-phase reactions which means reactions occur in the gas phase. The solid is first produced then lands on the wafer thus resulting in poor uniformity of film. High flow rate of carrier gas Ar ensures
relatively low reactant pressure then leading to solid surface reactions. Under such circumstance reaction occurs on the wafer surface and solid forms the deposition film. In our work, quite high reaction temperature (810°C) guarantees high reaction rate. The whole deposition depends on the diffusion of reactants. As the time increasing, more and more reactants diffuse on the surface thus leading to high density of domains. Early landed crystals act as nucleation sites and newly synthesized particles adsorb in the originally landed crystals’ edges due to higher reactivity from edges’ atom vacancy [20], then finally extended to a large scale and continuous MoS2 films.

Figure 4. SEM images of different morphologies with different growth times. (a-d)growth time from 4min to 10 min, every 2 min as an interval.

4. Conclusions
In conclusion, large scale continuous monolayer MoS2 film was in situ synthesized by chemical vapor deposition. AFM and Raman characterizations show that as-synthesized MoS2 films are monolayer and SEM images present the coverage of films are big. PL spectrum reveals the films have good optical features. Our study elaborates on the growth process of MoS2, including vaporization of S and Mo precursors, diffusion of reactants and merging of MoS2 nanoparticles to form continuous films. Our work studies the growth chemistry of continuous large scale MoS2 single layer film, and suggests a way to control the growth of film for larger coverage.

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6. References
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