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Preparation and characterization of molybdenum disulfide films obtained by one-step atomic layer deposition method

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ABSTRACT

High crystalline MoS_2 films are prepared by one-step ALD without followed high-temperature annealing. $MoCl_5$ and H_2S are used as precursors, while Si and Al_2O_3 are used as substrates respectively. The obtained MoS_2 films are characterized by Atomic Force Microscopy (AFM), Raman spectroscopy, Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), indicating they possess structures in high quality. Experimental results demonstrate the film grain sizes can be tuned from ~20 nm to ~100 nm at various growth temperatures from 420 °C to 480 °C and excellent crystal performance can be guaranteed from 430 °C to 470 °C. Meanwhile, the growth temperature should not exceed 480 °C due to decomposition of the functional groups. Furthermore, Al_2O_3 can do better than Si as a substrate for the film building for more necessary hydroxyls during initial reaction on its surface. The average growth rate of the high crystallinity MoS_2 film is ~4.3 Å/cycle for Al_2O_3 substrate and ~3.8 Å/cycle for Si substrate.

1. Introduction

Recently, MoS_2 has attracted wide attention because of its distinctive properties. MoS_2 is a two-dimensional (2D) layered transition-metal semiconductor material. Molybdenum and sulfur atoms form a hexagonal network with stable covalent bonds in the layer. Meanwhile, the layers are stacked by Van der Waals forces. Unlike graphene, the band gap of MoS_2 varies with the number of layers. The indirect bandgap can gradually change to direct bandgap of MoS_2 converted from bulk to a single layer material, making it have promising application values in many fields [1–7].

Generally, MoS_2 films obtained from mechanical exfoliation are preferred as they possess perfect crystalline structures. However, the production efficiency from this method is extremely low. Furthermore, because of the limitations in size scale, films obtained from exfoliation cannot be adopted in large-scale applications such as integrated circuit fabrication. Fabricating ultra-thin MoS_2 crystalline films (single layer or few layers) with high quality and large area is in great demands [8–11]. Till nowadays, considerable efforts have been made to obtain large-area MoS_2 films from different methods [12–15]. Polycrystalline MoS_2 can be grown on SiO_2 substrate through chemical vapor deposition (CVD) using sulfur and MoO_3, which demonstrates the possibility of band-gap engineering in polycrystalline films by tailoring the grain size [16]. Another promising and straightforward method is to prepare a Mo-containing thin film and then sulfurize it at high temperature, by which large-area monocrystal MoS_2 film can be obtained on sapphire [17,18]. At the same time, it is found that higher temperature is advantageous to improve the quality of MoS_2 film [19,20]. For deposition on high aspect ratio structures such as a pore or a trench, CVD method cannot offer conformal deposition because more material is deposited at the opening [21]. Comparatively speaking, ALD can generate conformal film on the substrate with rather complex structure because of its self-limiting reaction [22–24]. Moreover, the thickness of film obtained from ALD can be easily and precisely controlled by defined ALD cycles [25,26]. According to the existed work, general precursors for MoS_2 films by ALD method are $MoCl_5$ and H_2S, $Mo(CO)_6$ and dimethyldisulfide (CH_3SSCH_3, DMDS), $Mo(CO)_6$ and H_2S, and the reported temperatures for film building are 300 °C, 100 °C and 155–225 °C respectively [27–30]. Furthermore, it is difficult to get films with high crystallinity at these temperatures, and annealing process at high temperature (at least 800 °C) is usually followed [27,28]. Meanwhile, it indicates when the growth temperature increases, the crystallinity of the film will be significantly improved [25]. Unfortunately, decomposition will occur for $Mo(CO)_6$ and DMDS above 200 °C [26]. However, $MoCl_5$ and H_2S can guarantee the stability at the 700 °C [31–35], which makes them suitable for building high crystallinity MoS_2 film. As has been said, substrate and growth temperature is very important to the quality of the grown MoS_2 films.

For one-step ALD, it means that the film can be directly grown on the substrate without any pre-treatment or post-treatment, such as spinning some graphene-like molecules onto the substrate to promote film growth and post-annealing at high temperature to improve the film properties. In this work, we report a one-step ALD for producing

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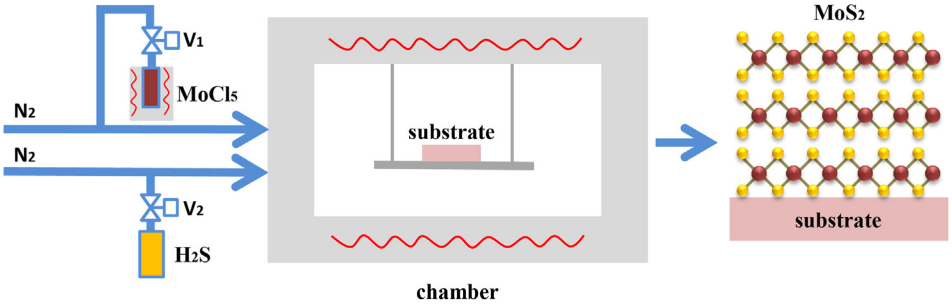

Fig. 1. Schematic illustration of ALD MoS_2. MoS_2 film can be obtained by Mo precursor ($MoCl_5$ gas) and S precursor (H_2S) alternately exposed onto the substrate.

MoS_2 film with high crystallinity at moderate temperatures (420 °C–490 °C). In this way, films with different grain structures can be directly formed on Si and Al_2O_3 substrates by using $MoCl_5$ and H_2S as precursors without followed high-temperature annealing. The structures of the obtained films were characterized. Moreover, influences of substrate and growth temperature on the films were also investigated.

2. Experimental

2.1. Preparation of MoS_2 films

In order to investigate the effect of substrate on the growth of MoS_2 film, we prepared two different substrates. One was a single side polished bare Si wafer, and the other was an Al_2O_3 wafer. The Si wafer was cleaned by acetone and ethanol successively in an ultrasonic bath. A commercial ALD setup (SUNALETMR-100) from PICOSUN was employed for MoS_2 films building. As precursors, $MoCl_5$ (99.6%) and H_2S (99.6%) were alternately vaporized into ALD chamber under N_2 (99.999%) flow at a rate of 50 sccm. The temperature in ALD chamber was kept from 420 °C to 490 °C under the pressure of 5.3 hPa. The temperature of $MoCl_5$ was kept at 200 °C to guarantee sufficient vapor pressure. The temperature of H_2S was kept at room temperature under the base pressure of 8 hPa.

Schematic illustration of ALD MoS_2 is shown in Fig. 1. To the beginning, chamber and $MoCl_5$ were heated to the preset temperatures and kept for half an hour. Afterward, $MoCl_5$ and H_2S were alternately interfused in the N_2 carrier by gas switching valves (V_1 and V_2). Then they were alternately vented onto the substrate and purged by the N_2 in the ALD chamber. Thus, one growth cycle contains four steps: exposure to $MoCl_5$, N_2 purge, exposure to H_2S and N_2 purge again. By repeating these steps, MoS_2 film with desired thickness can be obtained.

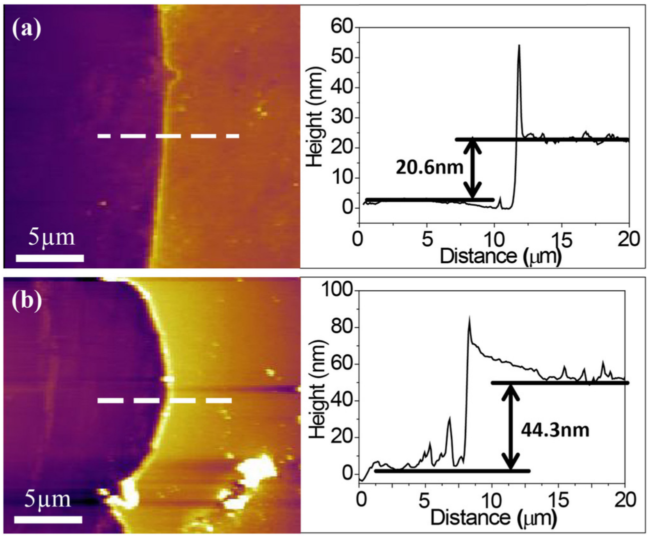

Fig. 2. AFM images and height profiles of MoS_2 films obtained by 100 ALD cycles on (a) Si substrate (b) Al_2O_3 substrate.

2.2. Characterization

The thicknesses and microstructures of obtained films were measured by AFM (MFP-3D-SA, Asylum Research)using contact mode. Contact angle measurement (OCA-15, Dataphysics) was used to study the surface hydrophilicity of substrate. The structures of the obtained films were characterized by Raman spectroscopy (RAM-PRO-785E, Agiltron), SEM (Helios Nanolab 600i, FEI), TEM (G220,FEI) and XRD (Smartlab-3, Rigaku). Raman spectroscopy was carried out by a 514 nm laser. To observe the cross-section of the film using SEM, the film with an Al coating deposited by magnetron sputtering (MSP-300C, KYKY) was etched by focused ion beam (Helios Nanolab 600i, FEI). TEM images were taken using an accelerating voltage of 300 kV. The MoS_2 film was exfoliated from the substrate and transferred on a copper TEM grid. XRD was performed with Cu Kα radiation ($\lambda = 1.54$ Å) at 35 mA and 50 kV.

3. Results and discussion

$Mo(CO)_6$ and H_2S reaction can be given as follows,

$$2MoCl_5 + 5H_2S \rightarrow 2MoS_2 + 10HCl + S.$$

For atomic layer deposition, the binary reaction can be split into two half-reactions,

$$\text{(A)}\ \ Mo—SH^* + MoCl_5 \rightarrow Mo—S—MoCl_4^* + HCl$$
$$\text{(B)}\ \ MoCl^* + H_2S \rightarrow Mo—SH^* + HCl + S$$

where * denotes the surface species.

Firstly, $MoCl_5$ forms chemisorption (A). Then it has a chemical reaction with H_2S (B), and MoS_2 can be obtained. By repeating an ABAB⋯ reaction sequence, MoS_2 film with desired thickness can be grown. Actually, first chemisorption of $MoCl_5$ to the substrate is through hydroxyl functional group. Therefore, the hydroxyl is very important to the initial growth of MoS_2. The reaction can be given as follows,

$$|—OH^* + MoCl_5 \rightarrow |—O—MoCl_4^* + HCl$$

where |— denotes surface.

Elevated growth temperature is conducive to improve the crystallinity of the film. However, as an exothermic reaction, the high temperature is unfavorable for the chemical adsorption. Furthermore, excessive temperature may cause the precursor and functional group to be decomposed, which is fatal to the growth. In order to get a high crystallinity film, the influence of the growth temperature needs to be studied. Therefore, we prepared two different substrates for building films at different temperatures from 420 °C to 490 °C in a chamber at the same time. The one is bare Si (100), the other is amorphous Al_2O_3 covered with rich hydroxyl groups which is got by ALD 500 cycles Al_2O_3 on the Si wafer.