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Controlled synthesis and optical properties of polycrystalline molybdenum disulfide atomic layers grown by chemical vapor deposition

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ABSTRACT

We report a scalable growth of mono to few-layer molybdenum disulfide (MoS_2) atomic layers on different substrates by chemical vapor deposition (CVD). The effects of the source material (sulfur and MoO_3 powder) and the growth temperature were systematically optimized for the growth of both highly crystalline and large area MoS_2. The deposited film thickness could be precisely controlled by varying the growth temperatures, and this was confirmed by Raman and AFM results. The monolayer, bilayer, and multilayer MoS_2 could be obtained at 650 °C, 700 °C, and 750–800 °C, respectively. The mobility value of ~0.89 cm^2/V s and current on/off ratio in the order of ~10^4 was estimated for monolayer MoS_2. The mobility value increased to ~7.6 cm^2/V s for the bilayer MoS_2. Our results pave the way for the controlled synthesis of high-quality transition metal dichalcogenide materials, which are an attractive option for applications in electronic and optoelectronic devices.

1. Introduction

Graphene has opened new avenue in the field of low-dimensional material [1–4] and layered transition metal dichalcogenide (TMD) [5,6]. Recently, two-dimensional (2D) molybdenum disulfide (MoS_2) has received much attention due its intrinsically semiconducting property, which is absent in graphene [7–10]. MoS_2 is a first and representative member of the TMD materials family, which possesses attractive optical and electrical properties such as strong photoluminescence (PL) [7,11], controllable valley and spin polarization [10,12], high carrier mobility of ~50–200 cm^2/V s at room temperature [13,14] and ~1000 cm^2/V s at low temperature [15], large on/off ratio (~10^8) [16], low subthreshold swing (SS, ~70 mV/decade) [8] in field effect transistors and band gap tunability from direct (mono) to indirect (few layers) (~1.8–1.2 eV). A scalable synthesis method for high-quality MoS_2 film is necessary for practical applications and much attention has been paid to obtaining this method. The various methods have been reported for large-area MoS_2 films on different insulating substrates: chemical synthesis of MoS_2 nanosheets by liquid exfoliation [17,18], thermal decomposition of $(NH_4)_2MoS_4$ by post-annealing [19] and a chemical vapor deposition (CVD) method [20–26]. Ahn et al. [27] demonstrated that the CVD growth of MoS_2 thin films yielded large, uniform and continuous films on the scale of several inches directly on polyimide (PI) substrates at lowest temperatures 150 °C–300 °C. Also, they have mentioned that the novel report of the direct deposition of a 2D crystal on a soft substrate without using any transfer method, which causes many structural defects. The carrier mobility of ~3.7 cm^2/V s was derived from the Hall measurement, which had a structural integrity well enough for electronic devices. In addition, the humidity detection analyses performed for MoS_2 thin film synthesized on PI substrate and it revealed its potential for flexible sensor devices. Ji et al. [28] successfully synthesized centimeter scale, strictly monolayer and high-quality MoS_2 on the nearly lattice-matching mica substrates, with the growth of epitaxial mechanism. They obtained high PL helicity (~0.35) at room temperature for the transferred sample, which was evident of the ultrahigh quality of MoS_2. The magnetron

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sputtering route prepared MoS_2 film exhibited *p* type performance with an on/off current ratio of ~10^3 and hole mobility up to ~12.2 cm^2/V s proposed by Tao et al. [29]. They mentioned that this strategy paves new ways towards the large scale controlled growth of various two dimensional semiconductors with the feasibility of controllable doping in order to realize the desired *p*- or *n* type devices. The higher thickness and controllable growth of uniform MoS_2 thin films was prepared on the wafer-scale *via* a spin-coating route. They used the formulation of a dimethylformamide-based MoS_2 precursor solution mixed with additional amine- and amino alcohol-based solvents (*n*-butylamine and 2-aminoethanol) for the formation of MoS_2 thin films over a 2-inch wafer scale SiO_2/Si substrate. Also, FET performance was measured for layered MoS_2 thin films [30]. Wu et al. exploited the low pressure vapor–solid growth of a MoS_2 monolayer using MoS_2 powder as a source [31]. In recent times, the detailed characterization performances were carried out for an atomically thin MoS_2 film prepared by atomic layer deposition (ALD) on a sapphire substrate [32]. However, the previous reported methods have some limitations in terms of the controllability of layer thickness and wafer-scale uniformity. In addition, most of the synthesized MoS_2 films report very low carrier mobility (0.003–0.8 cm^2/V s) [20,22,24,33,34] Thus, improving the synthesis process for high uniformity, high crystalline quality and low-cost are significantly challenged. Herein, we demonstrate the development of the large-area synthesis CVD approach, which can exclusively grow high-quality mono, bi and few-layer MoS_2 films on the different substrates such as silicon oxide and sapphire. This approach offers an important advantage such as uniform layer thicknesses over a wafer scale, and also controllable film thickness by changing their material source and growth temperature. It exhibits superior optical and electrical properties compared to the MoS_2 exfoliated from bulk materials. The fabricated MoS_2 back-gate transistors showed a rather high mobility of ~7.6 cm^2/V s and a large on/off ratio in the order of 10^4. Our present synthesis approach demonstrates the controlled growth of the MoS_2 layer with high crystalline quality, making them promising materials for applications in high-performance nanoelectronics and optoelectronics applications.

2. Experimental details

Substrates (Si/SiO_2 and sapphire) were ultrasonically degreased by immersion in acetone, methanol, and isopropyl alcohol (IPA) solution and deionized (DI) water prior to MoS_2 layers deposition. After that, the cleaned substrates were dried and baked for 5 min at 100 °C. MoS_2 films were grown in a horizontal split tube furnace equipped with a 2 inch diameter of quartz tube as depicted in Fig. 1(a). Initially, temperature of the furnace was gradually increased to 500 °C in 30 min under argon (Ar) environment to purge the chamber. A ceramic boat containing sulfur powder (0.1–0.3 g) was placed in the low temperature zone as indicated in the schematic. Another ceramic boat containing MoO_3 powder (0.2–0.5 g) was placed downstream in the high temperature zone. The low temperature ceramic boat was heated up to 120 °C to evaporate sulfur atoms. The temperature of the high temperature zone varied from 600 to 850 °C for 60 min with a base pressure of 2×10^{-2} Torr for the film growth.

Synthesized MoS_2 films were analyzed by Raman spectroscopy (Renishawinvia RE04, 512 nm Ar laser) with 1 μm spot size and 30 s scan speed. X-ray photoelectron spectroscopy (XPS) analysis was performed using PHI 5000 Versa Probe (25 W Al Kα, 6.7×10^{-8} Pa) and photoluminescence (PL) properties analysis using PL spectrophotometer with a 512 nm wavelength. FE-SEM (HITACHI S-4700) and atomic force microscopy (AFM) (Vecco Dimension 3100) were used to check surface properties and thickness of layered structures. The crystallinity of film was characterized by in-plane X-ray diffraction (XRD, Rigaku) with Cu-Kα radiation operated at 50 KV and 300 mA.

3. Results and discussion

The growth of MoS_2 atomic layers is governed by the following process. The schematic diagram for CVD growth of MoS_2 is given in Fig. 1(a). At high temperature (600 °C–850 °C), the MoO_3 powder is initially reduced by the sulfur vapor to form volatile suboxide MoO_{3-x}. These suboxide compounds are diffused to the substrate and further react with sulfur vapor to form MoS_2 films [35]. The reaction mechanism is likely to be

$$MoO_3 + \frac{x}{2}S \rightarrow MoO_{3-x} + \frac{x}{2}SO_2 \quad (1)$$

$$MoO_{3-x} + \frac{7-x}{2}S \rightarrow MoS_2 + \frac{3-x}{2}SO_2 \quad (2)$$

where MoO_2 is in an intermediate phase formed when $x = 1$ [1]. Earlier reports mentioned that the amount of precursor materials,

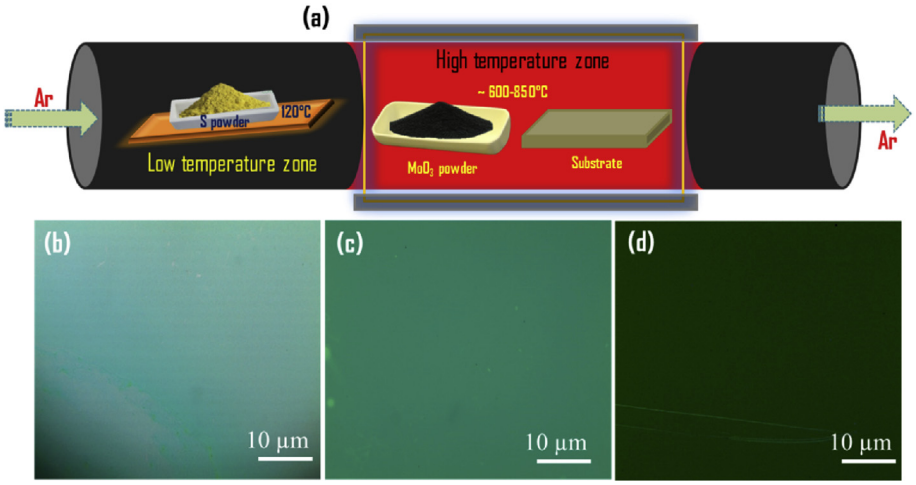

Fig. 1. (a) Schematic representation of the CVD experimental set-up. The sulfur powder was placed on the lower temperature zone at 120 °C. MoO_3 powder and substrate were placed on the high temperature zone for film growth. The growth temperature was varied from 600 to 850 °C. Also, Si/SiO_2 and sapphire substrates were used for the film growth; (b–d) optical microscopy images of MoS_2 atomic layers prepared at difference thicknesses (b) monolayer (650 °C), (c) bilayer (700 °C) and (d) multilayer (850 °C).