Synthesis of large-scale 2-D MoS2 atomic layers by hydrogen-free and promoter-free chemical vapor deposition

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\textbf{A B S T R A C T}

As one of the two-dimensional (2-D) transition metal dichalcogenides, atomically thin molybdenum disulfide (MoS\textsubscript{2}) has attracted significant attention and research interests for micro and nanoelectronic applications. Significant efforts have been made to develop different approaches in order to obtain atomic layer MoS\textsubscript{2}, such as exfoliation, chemical synthesis, and physical or chemical vapor deposition (CVD) processes. In this paper, we report a hydrogen-free and promoter-free CVD growth to synthesize large-area MoS\textsubscript{2} atomic layers. A variety of techniques including optical microscopy (OM), atomic force microscopy (AFM), photoluminescence (PL) mapping, Raman and x-ray photoelectron spectroscopy (XPS), high resolution electron microscopy (HREM) and scanning transmission electron microscopy (STEM) were applied to characterize the film quality, uniformity and layer numbers. High quality centimeter-sized MoS\textsubscript{2} atomic layers were demonstrated, which form a foundation to develop wafer-sized material platform for device fabrication and production.

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1. Introduction

Atomically thin MoS\textsubscript{2}, as one of the prototypes of 2-D transition metal dichalcogenides (TMDs), has demonstrated desirable material properties for low power electronics and optoelectronic applications. These properties include large direct bandgap energy for monolayers [1,2], high carrier mobility [3], excellent current on/off ratio [4], high mechanical strength [5] and flexibility [6], etc. Considerable research efforts and investigation have been motivated to develop techniques to produce MoS\textsubscript{2} atomic layers. These techniques include various exfoliation processes [7-10], physical vapor deposition (PVD) [11-13], and chemical vapor deposition (CVD). For example, direct sulfurization of pre-deposited molybdenum thin film [14] or molybdenum trioxide (MoO\textsubscript{3}) powder with graphene-like promoters [15] were reported, with MoS\textsubscript{2} crystal shapes investigated under different growth conditions [16]. A two-step thermal process [17] to convert MoO\textsubscript{3} to MoS\textsubscript{2} by hydrogen annealing and sulfurization have been demonstrated. A self-limiting CVD approach [18] to grow MoS\textsubscript{2} films with layer numbers precisely controlled over an area of centimeters was also developed by sulfurization of MoCl\textsubscript{4}. And another layer control approach for large-area MoS\textsubscript{2} film was proposed by treatment of the substrate surface with oxygen plasma [19]. Process using magnetron sputtering [20] was also developed to grow MoS\textsubscript{2} films by sputtering Mo metal target in vaporized sulfur ambient at high temperatures (> 700 °C). In summary, the goal of all these processes is to grow high quality large-area MoS\textsubscript{2} film, which is required for large-scale production of practical devices.

In this paper, we report a CVD synthesis method, hydrogen-free and promoter-free, for MoS\textsubscript{2} film growth on SiO\textsubscript{2}/Si substrate. The film thickness, crystalline quality and layer numbers were characterized comprehensively by a variety of spectroscopic and microscopic techniques including OM, AFM, PL, Raman, XPS, HREM and STEM. Our results show that large-area MoS\textsubscript{2} atomic films were attainable with high quality as by other growth techniques, which is favorable for device applications.
2. Experimental

Prior to the CVD process, the SiO2/Si substrate (SiO2 thickness: 280 nm) was cleaned with acetone, Isopropyl Alcohol (IPA) and deionized (DI) water, followed by piranha solution \((\text{H}_2\text{SO}_4: \text{H}_2\text{O}_2=1:1)\) and rinse thoroughly by DI water again. After dried completely, the substrate was loaded in a 2-inch-diameter quartz tube furnace. Fig. 1(a) illustrates the CVD setup for MoS2 growth. Solid powders of MoO3 (99.995%, 50 mg) and S (99.999%, 50 mg) were used as the precursor materials, and high purity argon (Ar) as the carrier gas. An alumina boat was used to contain S and placed upstream relative to the Ar gas flow direction, while another boat containing MoO3 was placed close to the center of the heating zone. At room temperature, the quartz tube was first pumped down to remove the oxygen, followed by constant Ar gas flow started with a 500 sccm rate. While the furnace was heated up with a heating rate of 10 °C/min, the Ar gas flow was adjusted as shown in Fig. 1(b) to 100 sccm when temperature reached 700 °C. The precursor MoO3 and S reacted at 700 °C for 15 min to produce MoS2 spices which precipitated onto the SiO2/Si substrate to form MoS2 thin film. After chemical synthesis, the furnace tube was cooled down to room temperature to unload the substrate.

3. Results and discussion

Optical characterizations of synthesized MoS2 atomic film on the SiO2/Si substrate are shown in Fig. 2. Photograph in Fig. 2 (a) displays the color of the as-grown MoS2 under white light. Color contrast clearly shows areas of MoS2 and SiO2. Magnified image of MoS2 film taken under optical microscope is illustrated in Fig. 2(b). It can be seen that the film is uniform and continuous across a large area without grain boundary. The thickness of the MoS2 film was measured by AFM. Fig. 2(c) shows a typical AFM image of triangle-shaped MoS2 crystals with clear grain boundaries attained by our CVD growth. Such triangle shape was also
reported by other publications, for example, \cite{15,16}. With improvement of growth conditions, these crystals now form a continuous form as shown in Fig. 2(d). A scratch was made intentionally for AFM scanning. The height profile of a tri-layer MoS$_2$ film with a thickness of 2.526 nm is shown in Fig. 2(e). The image also confirms the absence of grain boundary in micrometer scale.

PL was performed by a commercial room temperature PL mapping system, VerteX from Nanometrics, Inc., to characterize and confirm the synthesized MoS$_2$ atomic layers. A diode-pumped solid-state laser (532 nm, 50 mW) was applied as the excitation source to scan an area of 3 cm-diameter which covers the whole SiO$_2$/Si substrate, with a scanning spatial resolution of 200 $\mu$m $\times$ 200 $\mu$m. The mapping of $\lambda_{\text{peak}}$ across the whole substrate is shown in Fig. 3(a) using the software equipped in the VerteX system. Typical PL spectra collected from 4 different areas (different colors as in Fig. 3(a)) on the SiO$_2$/Si substrate are illustrated in Fig. 3(b) with signal intensity normalized. These peaks in the PL spectra are around $\sim$670 nm (1.85 eV), which is correlated to the A direct excitonic transition of MoS$_2$. It can be also seen that the PL spectrum of the monolayer MoS$_2$ film shows the strongest emission, and the intensity drops for bilayer and tri-layer films. This confirms that the optical property of as-grown MoS$_2$ films exhibit dependence on layer numbers due to an evolution of the bandgap with the layer no. This result is similar as the exfoliated films and synthesized films reported by other methods \cite{18,20–22}. It is noted that the PL peak corresponding to the B exciton is not clear, which is usually attributed to lattice disorder or residual dopants that decouple the spin–orbital interaction \cite{20,23}.

Raman and XPS spectroscopy was applied to further confirm and evaluate the quality of synthesized MoS$_2$ films. A LabRAM HR
Raman confocal microscope by Horiba Scientific was used for measurement. The wavelength of the input laser was 442 nm. Fig. 4(a) shows a representative characteristic in comparison of signals from areas with and without MoS₂ film. The area without MoS₂ only shows the peak of Si substrate which is at 520.6 cm⁻¹. The area with MoS₂ shows two peaks of 383.6 cm⁻¹ and 405.7 cm⁻¹, which correspond to the E₂g and A₁g vibration modes, respectively. It has been reported that the separation (Δ=E₁g−E₂g) between these two Raman peaks relates to the no of MoS₂ layers [24]. In this area under test, Δ=22 cm⁻¹, which indicates bilayer [18] MoS₂ crystals in this area. Chemical configuration of the synthesized MoS₂ film was analyzed and confirmed by XPS characterization. Fig. 4(b) shows the XPS spectra of as-grown MoS₂ film for Mo 3d and S 2p. Mo 3d spectra peaks at two orbit 2p₃/₂ and 2p₁/₂, respectively. All these peak configurations were characterized by a variety of techniques. The results confirm that the synthesized MoS₂ film have 2h-MoS₂ crystal structure with semiconductor properties [2,26].

HREM and STEM Z contrast images were applied to further elucidate the MoS₂ film and layer numbers. Regular TEM cross-section samples were prepared with a FEI Strata 237 FIB. Prior to FIB milling, a thin layer of Shappie was applied to specimen surface to prevent ion beam damage. HREM and STEM Z contrast images were taken in a FEI TECNAI F20 supertwin TEM with a Fischione high angle annular dark field detector (HAADF). Some representative images are displayed in Fig. 5. As observed in Fig. 5(a), bilayer MoS₂ film is shown in this local area, which is consistent with the STEM Z contrast image in Fig. 5(b) by the two bright lines. These layer numbers are in agreement with the results from our AFM, Raman and PL measurements. Such clear two-layer structure also confirms the crystalline nature of the as-grown MoS₂ material.

4. Summary

In this paper we presented preparation of high quality and large area MoS₂ at crystals by CVD process. Monolayer and few-layered MoS₂ films were synthesized on a centimeter-sized SiO₂/Si substrate. The size and uniformity of the films, the thickness and layer numbers, crystal quality, optical property and chemical configurations were characterized by a variety of techniques. The results confirm that it is promising to grow wafer scale MoS₂ film to realize its applications in electronics.

References


Fig. 5. (a) HREM and (b) STEM Z contrast images show the synthesized monolayer and bilayer MoS₂ films.