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Structural and optical properties of MoS_2 layers grown by successive two-step chemical vapor deposition method

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ABSTRACT

We have studied a successive two-step chemical vapor deposition (CVD) method to prepare large-scale MoS_2 thin films using a horizontal hot wall furnace. The CVD growth was followed by evaporation of the MoO_3 precursor on ~2.5 × 2.5 cm^2 SiO_2/Si substrates in the first step and a temperature ramp for sulfurization as a second step. Synthesized films were systematically analyzed by various structural and optical measurements. Crystallinity of the synthesized MoS_2 tri-layer films exhibited a typical 2H-MoS_2 structure and uniformly covered the whole substrate. MoS_2 field effect transistors were fabricated by using the obtained CVD-MoS_2, and these showed n-type behavior with an on/off ratio of about 10^3.

1. Introduction

Atomically thin two-dimensional (2D) materials such as graphene have attracted significant attention due to their extremely high carrier mobility *via* linear dispersion of Dirac fermions and other exotic physical properties that result from electron quantum mechanical confinement [1–3]. However, the lack of a band gap prevents graphene from replacing conventional semiconductor material based devices in electronics and optoelectronics [4,5]. Alternatively, other 2D materials analogous to graphene, such as layered transition metal dichalcogenides like molybdenum disulfide (MoS_2), have exhibited promising physical, chemical, optical, and mechanical properties [6–10]. Natural bulk crystal 2H-MoS_2 has a sandwich-like structure where metal atoms are between two planes of chalcogenide atoms [11]. Because of vertical stacking due to the relatively weak van der Waals interaction between S–Mo–S atomic layers, these layers can be easily exfoliated using the Scotch tape method [11,12]. Bulk MoS_2 is a semiconductor material with an indirect band gap of ~1.2 eV; when confined to a monolayer, it becomes a direct band gap material with a band gap of ~1.8 eV [13]. Transistors based on mechanically exfoliated monolayer MoS_2 flakes on SiO_2/Si substrates have shown a high current on/off ratio (~10^8), a low subthreshold swing (~70 mV/dec), and a high mobility of 200 cm^2/Vs in a HfO_2–MoS_2–SiO_2 configuration [7]. Moreover, an indirect–direct band gap transition, the absence of dangling bonds, and broken inversion symmetry have been previously reported [14–16]. Therefore, atomically thin MoS_2 has great potential for optical electronic nano-devices and flexible, transparent electronics [17–19].

The synthesis of large-area, uniformly layered MoS_2 has been widely investigated in the past few years. The Scotch-tape based exfoliation method for peeling off atomically thin 2D material provides high quality materials and is one of the most extensively investigated methods [20]. However, it lacks systematic control of thickness, size, and uniformity, which makes it inappropriate for wafer-scale electronic applications. Recently, chemical vapor deposition (CVD) methods for atomically thin single- or few-layer MoS_2 growth have been reported [21–26]. For example, Zhan et al. demonstrated a simple growth technique to achieve MoS_2 thin films [21]. Mo metal thin films were pre-deposited on the Si substrate followed by a vapor phase sulfurization process in a sulfur atmosphere. A similar approach has been achieved by Lin et al., where they pre-deposited molybdenum trioxide (MoO_3) as a precursor instead of Mo metal films [23]. Although these methods can produce scalable production of 2D MoS_2, several weaknesses remain. Such pre-deposited samples (especially Mo metal films) normally become oxidized under ambient conditions, and lack control of the number of layers and continuity of grains.

In this study, a facile CVD approach for large-scale synthesis of layered MoS_2 is presented. Synthesis of large-area layered MoS_2 was carried out by evaporating MoO_3 and sulfur powder separately in the same chamber. This process can prevent the re-oxidation effect, and the MoS_2 films were directly grown on an amorphous SiO_2/Si substrate without pre-deposition of Mo or MoO_3 thin films.

2. Experiments

For MoS_2 CVD growth, MoO_3 (99.999% purity) and S (99.999% purity) powder were used as the precursor and the reactant materials, respectively. One gram of reactant was placed in an alumina boat and was positioned upstream of a horizontal hot wall furnace with a 2-inch

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quartz tube. Another alumina boat with ~13 mg of MoO_3 powder and carefully cleaned SiO_2/Si substrates (270-nm-thick oxide layer) was placed downstream. The ~2.5 × 2.5 cm^2 receiving substrates were placed on a quartz plate facing upwards. During the growth process, the furnace was heated to 800 °C with a heating rate of 17 °C/min in an ultrahigh-purity N_2 atmosphere at a 200-sccm flow rate, as shown in Fig. 1(a). Initially, the MoO_3 containing boat was slightly offset from the center of the furnace at ~780 °C and was maintained for 15 min. This procedure involves MoO_3 thermal vaporization and further diffusion to the SiO_2/Si substrates by N_2 carrier gas. Afterwards, the furnace was shifted to the left side and was then heated to 1000 °C at 20 °C/min, followed by holding for 10 min at 1000 °C, as shown in Fig. 1(b). The second step was used to evaporate sulfur powder at ~130 °C in order to inject sulfur vapor into the quartz tube to grow layered MoS_2 films. Before removal from the quartz tube, the furnace was manually opened and was exposed to a flow of 500-sccm N_2 for fast cooling.

A poly(methyl methacrylate) (PMMA) based transfer technique was employed to characterize the synthesized MoS_2 films. Polymer layers were prepared by spin-coating PMMA on MoS_2/SiO_2/Si chips at 2000 rpm for 45 s. The PMMA coated stack samples were immersed into 6:1 buffered oxide etchant (BOE), which etched away the SiO_2 layer, allowing removal of the PMMA/MoS_2 stack. The floating PMMA supported layers were retrieved from the solution using a desired substrate. PMMA was removed by immersion in warm acetone, followed by isopropanol and then rinsing with deionized water.

Back-gate field-effect-transistors (FETs) on SiO_2 (270 nm)/Si were fabricated using a tri-layer MoS_2 thin film as the channel material to evaluate the electrical performance of CVD-MoS_2. Source and drain electrodes were patterned by using a standard photolithography process, while Ti/Au (10 nm/80 nm) electrodes were directly deposited on top of the tri-layer MoS_2 using an e-beam evaporator (Fig. 6a shows the prepared device). The metal evaporation rates were about 1 Å/s for Ti and 5 Å/s for Au. The devices made from tri-layer MoS_2 were annealed in a furnace at 650 °C for 2 h with 100-sccm Ar gas. Electrical measurements were made using an HP 4156A precision semiconductor parameter analyzer with a homemade probe station.

Scanning electron microscopy (SEM) (Nova NanoSEM, FEI) with an operating voltage of 15 kV and a contact mode atomic force microscopy (AFM) (XE-100, Park systems) were performed to study the surface morphology of as-grown layered MoS_2. The elemental composition of the specimens was obtained by using monochromatic Al K_α source (spot size 15 μm) incorporated X-ray photoelectron spectroscopy (XPS) (ARXPS, Thermo Fisher Scientific) under ~4×10^{-10} Torr of vacuum condition. Energies of core-levels were calibrated against the C1s peak set at 285 eV during analysis. Raman (alpha300, WITec) measurements were performed at room temperature with a $\lambda = 532$ nm exciting laser and a laser spot size of 500 nm.

3. Results and discussion

Tri-layer MoS_2 thin films were grown on SiO_2/Si substrates. As illustrated in Fig. 2(a), a photograph of the ~2.5 × 2.5 cm^2 substrate shows the obtained MoS_2 thin films, which are continuous over the entire area. An optical image of tri-layer MoS_2 is given in Fig. 2(b). The image indicates relatively low color contrast between the SiO_2/Si substrate and the as-grown MoS_2 thin films, consistent with Scotch tape exfoliated MoS_2 flakes on the same substrate [27]. Because of the difference in the thermal expansion coefficient between the substrate and tri-layer MoS_2 thin film, the gap appears in the MoS_2, as previously reported elsewhere [28]. We transferred the PMMA/MoS_2 stack onto a bare substrate with a 270-nm-thick silicon dioxide layer, as shown in Fig. 2(c). Thereby, the number of layers in the specimens could rapidly be identified by optical imaging because the underlying SiO_2 substrate provides high contrast [27]. SEM images shown in Fig. 3(a) reveal the homogeneity and uniformity of the synthesized MoS_2 films. Circular shapes of these grains (90 nm in size) nucleate at high temperatures around 1000 °C.

Further, we found that the number of MoS_2 layers depends on the substrate position and the amount of MoO_3 precursor. The area of growth on the substrate was typically ~1 cm away from the MoO_3 precursor container. For convenient characterization, the growth substrate was equally divided into Regions A, B, C, and D with distances of ~0.5 cm, as shown in Fig. 4(a). According to our experiments, an increase in distance to the growth substrate yields thicker films. In Region A, there is tri-layer deposition of MoS_2 films. Regions B, C, and D correspond to 4 layers, 5 layers, and bulk, respectively. AFM was used to investigate the thickness distribution of CVD-MoS_2 thin films and examine the relationship between the layer number of the synthesized film and the position of the growth substrate. In order to determine thickness, the scratches shown in Fig. 4(c)–(f) were intentionally

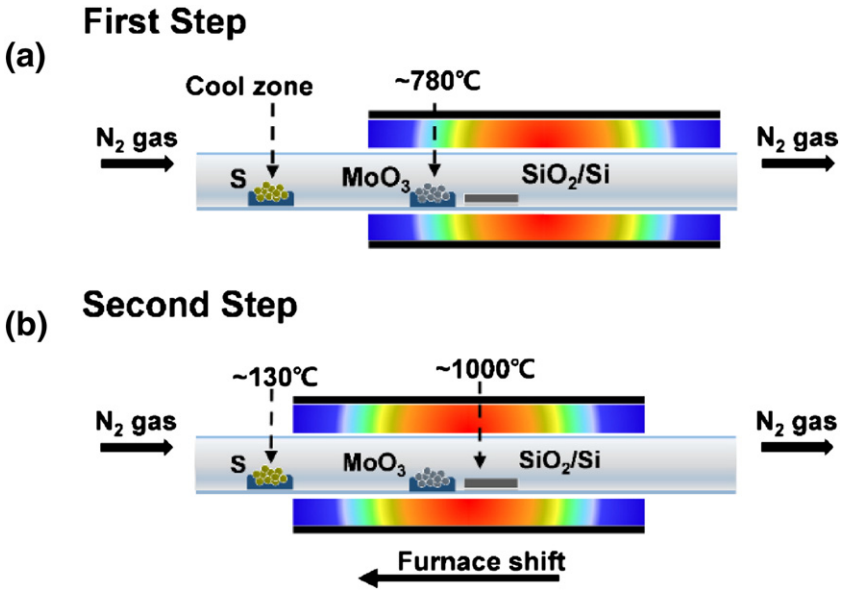

Fig. 1. Schematic diagram of the CVD system setup used for growing MoS_2 thin films on SiO_2/Si substrate. (a) Two distinct heating areas were used, and the temperature of the sulfur powder was just below its melting point. (b) As the furnace moves towards the other side of the quartz tube, the sulfur powder is heated to ~130 °C.