Research Paper

Study on Growth Parameters for Monolayer MoS₂ Synthesized by CVD Using Solution-based Metal Precursors

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ABSTRACT

Two-dimensional (2D) materials have received a considerable amount of attention owing to their unique properties compared with those of bulk materials, such as ultralow thickness with no dangling bonds and direct bandgap for monolayers. Monolayer MoS₂ with a direct bandgap of ~1.8 eV is representative of 2D semiconductors, which can facilitate a high on/off ratio in field-effect transistors and can have various optoelectronic applications in the visible range. Large area MoS₂ monolayers are generally synthesized using chemical vapor deposition (CVD) methods, where various types of metal precursors are utilized. Here, we report the effects of process parameters on the growth mode of MoS₂ monolayers prepared by CVD using solution-based metal precursors. We investigated various growth modes of MoS₂ flakes depending on the growth temperature and time, Mo-precursor concentration in precursor solutions, and carrier gas amount. The synthesized MoS₂ monolayers revealed typical n-type semiconductor behaviors, which were investigated by optical microscopy, confocal photoluminescence and Raman spectroscopy, atomic force microscopy, and I-V characterization of field-effect transistors. The n-doping effect was reduced by removing unreacted precursors after transferring the MoS₂ layer on new SiO₂/Si substrates.

Keywords: Growth mode, MoS₂ monolayers, Chemical vapor deposition, Solution-based metal precursor, Transition metal dichalcogenides

I. Introduction

Transition metal dichalcogenides (TMDs) have received attention as van der Waals layered semiconductors because of their unexplored physical properties at an atomic level thickness, compared to those of conventional bulk semiconductors. As a representative of TMDs, MoS₂ monolayers have been intensively studied with regard to their optical and electrical properties. A direct bandgap in the visible range allows for potential applications in several areas such as nanoelectronics, nanophotonics, valleytronics, and soft-electronics [1–6]. For such applications, TMDs synthesized via chemical vapor deposition (CVD) methods are widely used [2,7,8]. Sulfurization after spin-casting a metal precursor solution on substrates is one of the promising CVD methods [9–11]. Although the growth mode of monolayers is strongly correlated to various process parameters, the effects of such parameters and processes for their optimization have not yet been reported. In this study, we investigated different growth modes of MoS₂ monolayers synthesized by CVD as functions of the growth temperature and time, solution concentration for metal precursor, and carrier gas amount, where each growth mode was monitored by optical microscopy (OM). After optimizing the growth condition, surface topographies of the as-grown MoS₂ monolayers were studied via atomic force microscopy (AFM). The optical properties and doping effects of the as-grown and transferred MoS₂ monolayers were investi-

gated using micro-photoluminescence (PL) and Raman spectroscopy; field-effect transistor (FET) characteristics were also studied.

II. Experimental details

1) MoS₂ synthesis

MoS₂ crystals were grown on a SiO₂/Si substrate by using two-zone thermal CVD with a 2-inch quartz tube [10]. Prior to the growth process, SiO₂/Si substrates were pre-treated with O₂ plasma (100 W, 2 min) to obtain hydrophilic surfaces. Next, a liquid precursor solution was coated on the SiO₂/Si substrate by using a spin-coater at 3000 rpm for 30 s. The liquid precursor solution consisted of two Mo-precursors, sodium molybdate dihydrate (SMD, Sigma-Aldrich) and ammonium molybdate tetrahydrate (AMT, Sigma-Aldrich), NaOH as a promoter, iodixanol (Opti, Sigma-Aldrich) as a surfactant, and deionized (DI) water for dilution [10]. We mixed these materials to achieve the desired growth condition. We used a fixed solution ratio of NaOH : SMD : Opti = 4 : 0.5 : 0.5 as the reference condition. S-precursor source (S powder, Sigma-Aldrich) in a ceramic boat was placed at zone 1, and the liquid-solution-coated substrate was placed at zone 2. For synthesis, zone 1 and zone 2 were heated to 250 and 800 °C, respectively. The sublimated S at zone 1 (210–250 °C) was carried to zone 2 by N₂ carrier gas (99.9999 %). The carried S atoms reacted with Mo-precursors at zone 2 (700–800 °C), resulting in the synthesis of MoS₂, when the

Figure 1. (Color online) Schematic depicting the CVD growth method based on solution-based metal precursors. Spin-coating of the Mo-precursor solution on SiO₂/Si substrate and its sulfurization. Inset: temperature setting during the growth process.

flow rate of N₂ gas was fixed at 200 sccm. Na ions from NaOH promoted the nucleation and growth of MoS₂ crystals [9]. After completion of the growth process, the temperature of the furnace was naturally quenched below 80 °C.

Figure 1 shows a schematic of our optimized CVD process for the fabrication of triangular MoS₂ monolayers. The inset shows the programed temperature setting for the growth process.

2) MoS₂ transfer

To characterize the electrical properties, the MoS₂ layers were transferred onto new SiO₂ (300 nm)/Si substrates. The transfer process consisted of the following steps: i) Polymethyl methacrylate (PMMA) was coated on MoS₂/SiO₂/Si by using a spin-coater at 1000 rpm for 60 s. ii) The PMMA/MoS₂ layer was detached from the SiO₂/Si substrate in DI water. iii) The floating PMMA/MoS₂ layer on the DI water surface was transferred onto a new SiO₂/Si substrate (treated with O₂ plasma) and dried using a N₂ blowgun. iv) The PMMA/MoS₂ layer on the SiO₂/Si substrate was heated using a hot plate at 80 °C for 5 min. The PMMA supporting layer was removed using acetone and sequentially cleaned using isopropyl alcohol.

3) Characterization

The growth modes and shapes of the MoS₂ flakes for the as-grown samples were observed by OM. The surface morphologies and residues of the as-grown samples were measured by AFM. We identified residues such as the Mo-precursor, promoter, and crater at the surface of the as-grown samples. The PL and Raman spectra for the as-grown and transferred samples were characterized using a micro-PL/Raman mapping system equipped with an objective lens of 0.75 N.A. and a laser beam with a wavelength of 532 nm (XperRam200VN, NANOBASE, Inc.).

To characterize the doping properties, we fabricated FETs by using the In micro-welding method, which is known as a polymer-residue-free process for mentalizations [12,13]. In micro-electrodes were connected to the flake edge of the transferred and annealed MoS₂ monolayers on SiO₂ (300 nm)/Si. Drain current (I_D) curves as a function of the Si back gate bias (V_G) were obtained for various values of the drain bias (V_D) by using a Keithley 2614B Source measure unite.

Figure 2. (Color online) (a) OM images of as-grown MoS₂ as a function of temperatures for zone 1 and zone 2. Scale bar is 30 μ m. (b) Schematic depicting growth mode changes of MoS₂ crystals under temperature variation.

III. Results and discussion

Figure 2(a) shows the OM images of the synthesized MoS₂ flakes on the substrate under temperature variation of zone 1 and zone 2, where the temperatures range from 210 to 250 °C for zone 1 and 700 to 800 °C for zone 2. At a fixed temperature of 700 °C in zone 2, the MoS₂ flakes enlarge as the temperature in zone 1 increases. While small crystal flakes start to form at 230 °C and enlarge at 250 °C in zone 1, no crystal shapes are observed at 210 °C in zone 1. We attribute the failure of MoS₂ formation at a low temperature in zone 1 to the lack of sublimated S flux for MoS₂ synthesis. This is because the size of the MoS₂ flake is proportional to the sublimation temperature of S in zone 1 under a fixed temperature of the synthetic zone (700 °C). MoS₂ flakes with a starfish shape, indicating off-stoichiometry [14], as well as solution residues (Mo-source and promoter) on the facets of MoS₂ flakes and the substance are frequently observed. This is because the sublimation of Mo-precursors at a temperature of 700 °C in zone 2 is not sufficient for the MoS₂ formation reaction. However, at 750 °C in zone 2, the MoS₂ flakes exhibit a curved triangular shape for all zone 1 temperatures and lesser residues are observed. Eventually, MoS₂ flakes with a near triangular shape and size exceeding 60 μ m are synthesized

Figure 3. (Color online) (a) OM images and schematics depicting growth mode change of MoS₂ flakes as a function of (a) AMT ratio in the Mo-precursor solution, (b) carrier gas amount, and (c) deposition time, under the reference growth condition. Scale bar is 30 μm .

at 800 $^{\circ}\text{C}$ in zone 2, indicating the exact stoichiometry of the Mo and S composition for MoS₂. While multilayers form at a lower temperature (210 $^{\circ}\text{C}$) in zone 2, uniform monolayers are synthesized at higher temperatures (230 and 250 $^{\circ}\text{C}$). These growth modes according to the synthesis temperatures are schematically summarized in Fig. 2(b).

Figure 3(a) shows the OM images of the synthesized MoS₂ flakes as a function of the AMT ratio in the Mo-precursor solution (top) and corresponding schematics depicting the growth mode (bottom). As the AMT content increases under the reference growth condition, the flake size increases to 100 μm for an AMT ratio of 0.5 owing to the sufficient amount of the Mo source. Moreover, the curved facet of the triangular shape changes to a flat facet, indicating the exact stoichiometry for MoS₂ [14]. While large-area growth of MoS₂ can be achieved using a sufficient amount of AMT, an excess amount of AMT will promote multilayer growth. The effects of carrier gas amount are displayed in the OM images and schematics shown in Fig. 3(b). While the crystals are not formed at a smaller gas amount of 100 sccm owing to a lack of S vapor flux, triangular MoS₂ monolayers are synthesized at 200 sccm. However, when the gas amount reaches 300 sccm, enlarged and curved triangles with multilayers are observed owing to an overly high flux of S vapor. This suggests that an optimum amount of

Figure 4. (Color online) (a) AFM topography of as-grown MoS₂ monolayers and (b) height profile for the selected line A. (c) Magnified AFM topography of (a) and (b) height profile for the selected line B.

carrier gas is essential for forming homogeneous monolayers. Figure 3(c) displays the effects of the deposition (or growth) time on the growth mode of MoS₂. As the deposition time increases from 18 to 22 min, the size of MoS₂ flakes increases and multilayers form at 22 min because of sufficient nucleation time for multilayer formation.

Under the reference condition optimized through the above processes, the surface morphology of the as-grown MoS₂ was investigated using a tapping mode AFM, and the acquired topography image is shown in Fig. 4(a). The height of the MoS₂ flake with triangular area is higher than the substrate area. While unreacted promoters of a residual particle shape are observed on the entire sample, they are selectively accumulated at the facet edges of the MoS₂ flakes, which is typically observed in MoS₂ prepared by CVD using solution-based metal precursors [10]. Figure 4(b) shows the height profile of line A in Fig. 4(a). The height difference between the substrate and MoS₂ layer reaches ~ 0.7 nm, indicating the typical monolayer thickness of MoS₂ [8,10]. Figure 4(c) presents a magnified topography image of Fig. 4(a). Typical craters are clearly observed on the samples, which is attributed to craters originating from the unreacted Na₂MoO₄ [10]. The height profile of line B in Fig. 4(c) is displayed in Fig. 4(d), where the measured crater depth reaches ~ 5 nm and the accumulated height of promoter residues at the facet boundary is over 17 nm. Such unreacted promoters and craters can be easily removed by undertaking transfer processes in water [10].

The effects of the residual promoters and craters on the optical properties of MoS₂ were investigated using PL and Raman mapping for the as-grown MoS₂ and transferred MoS₂ on new SiO₂/Si substrates (Fig. 5). The PL intensity map of A exciton peak for the as-grown and transferred MoS₂ are shown in Figs. 5(a) and 5(b), respectively. The overall PL intensity distributions for both cases are homogeneous. However, the PL and Raman spectra exhibit prominent differences. In the comparative PL spectra shown in Fig. 5(c), while the A peak position for the as-grown MoS₂ is in the range of 1.82 eV, that for transferred MoS₂ is blue-shifted to ~ 1.87 eV with an enhanced PL intensity [13], indicating a p-doping effect [15,16]. This result agrees well with the comparative Raman spectra shown in Fig. 5(d).

Figure 5. (Color online) (a) PL mapping image for A exciton peak intensity of (a) as-grown and (b) transferred MoS₂. Comparative (c) PL and (d) Raman spectra of as-grown and transferred MoS₂.

Figure 6. (Color online) (a) Schematic illustration of MoS₂ FET with In electrodes. (b) I_D - V_G transfer curves of the FET with varying V_D .

The doping-related A_{1g} peak of the Raman spectra for the transferred MoS₂ is slightly blue-shifted (~ 1 cm⁻¹) owing to the p-doping effect, in comparison to that for the as-grown MoS₂ [16]. When the residual promoters, possibly acting as n-dopants in the as-grown MoS₂, are removed by water during the transfer process [10], the transferred MoS₂ is in a relatively de-doped condition. Therefore, the de-doping effect for the transferred MoS₂ is attributed to the reduction in n-doping sources via the transfer process.

To confirm the de-doping effect of the transferred MoS₂ monolayers, we measured the I_D - V_G transfer curves with varying V_D for the MoS₂ FET. Figure 6(a) illustrates the MoS₂ FET with In electrode contacts, and Fig. 6(b) shows the measured I_D - V_G characteristics of the FET for various V_D . These I_D - V_G curves exhibit bi-polar characteristic, and the on/off ratio reaches $\sim 10^5$ for a drain voltage of 0.7 V. Notably, while MoS₂ FETs have been reported to typically exhibit n-type behavior for various metal electrodes [1,2,6,9], our FET exhibits bi-polar behavior because of the reduced n-doping effect and a good compatibility between MoS₂ and In contact [13]. Moreover, threshold voltages in the n-type region decrease with reduced V_D and become nearly zero for a V_D of 0.7 eV, in contrast to the fixed current level and threshold voltage in the p-type region. A change in the V_D -induced threshold voltage is exhibited prominently between In and MoS₂, which is attributed to the low work function (~ 4.0 eV) of In, because the V_D dependence of thermionic effect is more sensitive for a small Schottky barrier [17].

IV. Conclusions

We have studied the effects of process parameters on the growth modes for monolayer MoS₂ flakes synthesized by CVD using solution-based Mo-precursors. Based on the variation in growth temperature, Mo-precursor ratio in the solution, carrier gas amount, and growth time, we have optimized the growth mode for triangular flakes with the exact stoichiometry of MoS₂. As the most important process parameter, the growth temperature influenced the flake size and shape as well as the number of layers. As the AMT ratio was increased in the liquid precursor solution, the coverage of MoS₂ flakes also improved. As the carrier gas amount and the deposition time increased, the coverage of MoS₂ flakes and the number of layers also increased. The AFM morphology of the as-grown MoS₂ surface revealed a considerable amount of precursor and promoter residues, which accumulated at the interfaces of the flake facets. The PL and Raman mapping images displayed a uniform contrast for intensities in a single flake; however, the blue-shift of the A exciton peak and A_{1g} peak for the transferred samples indicated de-doping effects resulting from precursor residue removal during the transfer process using DI water. The I_D - V_G transfer curves of the MoS₂ FET with In electrodes exhibited an on/off ratio of $\sim 10^5$ for a drain voltage of 0.7 V. Moreover, the FET displayed typical bi-polar transistor characteristics owing to the de-doping effect of transferred MoS₂ and reduced Schottky barrier effect from In electrodes.

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