Research Paper

Synthesis of Transition Metal Disulfides with Liquid Ammonium Sulfide as a Reliable Sulfur Precursor

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Abstract

We introduce liquid ammonium sulfide as a reliable and carbon-free sulfur precursor for synthesizing large-area transition metal disulfides (TMdS) in chemical vapor deposition. The flux of sulfur during TMdS growth is precisely controlled by passing a known amount of carrier gas through a bubbling system containing liquid ammonium sulfide. However, controlling the flux of sulfur through the conventional evaporation of sulfur powder using a heating belt remains a challenge. By achieving controllability of sulfur flux, we study growth kinetics such as nucleation density and growth rate. Furthermore, the continuous supply of the sulfur precursor results in the growth of a large-area monolayer and a few layers of MoS₂ film. In addition, we present the feasibility of ammonium sulfide as an effective and clean precursor for the growth of a wide range of TMdS, thus enabling it to serve as a universal sulfur precursor.

Keywords: Two-dimensional materials, Transition metal dichalcogenides, Chemical vapor deposition, Precursor, Ammonium sulfide

1. Introduction

Since the discovery of graphene in 2004 [1], two dimensional (2D) materials have been highlighted due to their unique physical and chemical properties such as exceptional high carrier mobility, gigantic magnetoresistance, and thickness-dependent electronic structural changes [2-8], which were not observed in bulk materials. These unique properties allow the developing of unprecedented electronic devices and new functionality of conventional devices with integrated 2D materials [9,10]. Theoretical calculation predicts that 350 monolayer 2D materials are stable at room temperature under ambient atmosphere [11]. The electronic structures of various 2D materials strongly depend on the constituent elements in 2D layer and their thickness [12]. For instance, while graphene consists of carbon atoms in hexagonal lattice and exhibits semi-metallic property, hexagonal boron nitride (hBN) com-

posed of boron and nitrogen atoms in hexagonal lattice is an insulator with energy band gap of ~ 6 eV. In addition, transition metal dichalcogenides (TMdCs) which consists of transition metal and chalcogen atoms exhibits metallic or semiconducting properties. Furthermore, the energy band gaps of TMdCs varies with thickness due to the orbital interaction between layers [13].

To apply these 2D materials in numerous devices, large-area and high-quality 2D materials are highly necessary. Chemical vapor deposition (CVD) is one of the promising methods in terms of high throughput, low cost and high crystallinity for the growth of wafer-scale 2D materials [14,15]. This is evident in the number of research conducted over the past decade to grow 2D materials via CVD [16-20]. Recently, wafer-scale single-crystal graphene and hBN have been successfully synthesized via “epitaxial growth” and “self-collimated growth” on single crystal Cu (111) and liquid Au substrates, respectively. These growths were made possible due to the presence of reliable vapor and liquid phase precursors, which allowed precise controlling of

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the precursors [21,22]. By contrast, the precursors for growth of TMdCs are quite limited to solid-phase precursors due to the absence of vapor or liquid phase alternatives [17-19]. Typically, solid phase precursors such as metal oxides MoO_3 and WO_3 and chalcogen powders such as S, Se and Te are supplied by evaporating with local heating, restricting the continuous and simultaneous supply of precursors. This limits the reproducible and reliable growth of TMdCs. To overcome this problem, volatile metal carbonyls such as Mo(CO)_6 and W(CO)_6 and liquid organochalcogen compounds such $\text{C}_2\text{H}_6\text{S}_2$ and $\text{C}_2\text{H}_6\text{Se}_2$ as alternative precursors have been developed for the growth of TMdCs in metal-organic CVD (MOCVD) [23,24]. Large-area monolayer molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2) film are readily grown via the proposed MOCVD, but the presence of carbon in the precursors hinders the growth of high quality TMdCs. Therefore, it is still highly necessitated to develop new precursors which do not generate carbon radicals during growth, while ensuring a constant and simultaneous supply of precursors.

Here, we introduce liquid ammonium sulfide $(\text{NH}_4)_2\text{S}$ as a new reliable and carbon-free sulfur precursor for the growth of transition metal dichalcogenides (TMdS) family. The sulfur flux is precisely controlled by the flow rate of Ar carrier gas through a bubbling system containing the liquid ammonium sulfide. The nucleation density and domain size of MoS_2 can be controlled by the flow rate of Ar carrier gas. Furthermore, the continuous supply of ammonium sulfide enables the growth of large-area MoS_2 film. Lastly, the growth of WS_2 and ReS_2 are demonstrated, indicating that ammonium sulfide can be regarded as a universal sulfur precursor for the growth of diverse range of TMdS.

II. Experimental details

MoS_2 grains and films were grown using a furnace equipped with a 2-inch quartz tube. As sulfur precursor, a bubbler containing ammonium sulfide solution $(\text{NH}_4)_2\text{S}$, 40-48 wt% in H_2O , Sigma Aldrich) was connected with high purity (99.9999 %) argon gas and to the inlet of the quartz tube. 0.02 M sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, ≥ 99.5 %, Sigma Aldrich) aqueous solution was prepared as the molybdenum precursor. The molybdenum precursor solution was spun onto hydrophilic SiO_2/Si substrate with 2500 rpm for 1 min. The molybdenum precursor coated substrate

was placed in the center of the quartz tube. To remove residual gas, the quartz tube was purged with 350 sccm argon for 10 min. The temperature of the quartz tube was then elevated to 850 °C in 15 min (~ 55 °C/min). For growth to commence, 2–20 sccm of argon carrier gas was introduced into the bubbler for 5–20 min. After growth, the supply of $(\text{NH}_4)_2\text{S}$ was stopped by a mass flow controller. The quartz tube was rapidly cooled down (-50 °C/min) by taking out the quartz tube from the furnace. The entire growth process was carried out in atmospheric pressure. In the case of the growth of WS_2 and ReS_2 , sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, ≥ 99 %, Sigma Aldrich) and sodium perrhenate (NaReO_4 , 99.99 %, Sigma Aldrich) aqueous solutions were used as transition metal precursors. The growth temperatures for WS_2 and ReS_2 grains were 850 and 600 °C, respectively. For the growth of ReS_2 , cleaved mica was used as a growth substrate.

To analyze the lateral size, the number of nucleation and the coverage of MoS_2 grains and films, optical microscopy (Eclipse LV150, Nikon) and field emission scanning electron microscopy (FE-SEM, JSM-7100F, JEOL) were used. The thickness and the crystallinity of MoS_2 were confirmed via atomic force microscopy (AFM, N8-NEOS, Bruker), micro-Raman spectroscopy and photoluminescence (PL, XperRAM 100, Nanobase) measurements. Silicon probes (Tap 190-G, BudgetSensors) were used for the non-contact mode AFM measurement. During the Raman and PL measurements, 532-nm laser was used with ≤ 0.1 mW laser power to avoid damages to TMdS.

III. Results and discussion

Figure 1(a) shows the schematic illustration of a CVD system equipped with an $(\text{NH}_4)_2\text{S}$ bubbler. The $(\text{NH}_4)_2\text{S}$ solution constitutes NH_4^+ and S^{2-} ions required for the growth of TMdS. The amount of $(\text{NH}_4)_2\text{S}$ supplied is controlled by the flow rate of argon gas injected into the $(\text{NH}_4)_2\text{S}$ bubbler, and the $(\text{NH}_4)_2\text{S}$ molecules are thermally decomposed to NH_3 and H_2S molecules [25]. Therefore, decomposed H_2S molecules act as sulfur precursors during the growth of MoS_2 . According to our previously reported paper, MoS_2 grains and films are grown through the sulfurization of Na_2MoO_4 coated on SiO_2/Si substrate [26]. Figure 1(b) shows a photograph of bare SiO_2/Si substrate and as-grown MoS_2 film. The color of the bare SiO_2/Si

Figure 1. (Color online) (a) Schematic illustration of CVD set up. (b) Photograph of bare SiO₂/Si substrate and as-grown MoS₂ film. (c) Optical microscopy, (d) AFM topography, (e) Raman intensity mapping images, (f) Raman, and (g) PL spectra of transferred MoS₂ grain, respectively. The AFM, Raman, and PL measurements were taken at the area marked with white-dashed box in the optical microscopy image.

substrate is changed to uniform blue-green after growth. Due to the Fresnel effect, the optical color contrast difference between the SiO₂/Si substrate and MoS₂ grains can clearly be distinguished as shown in Fig. 1(c) [27]. Similar color contrast is observed for all MoS₂ grains, indicating a uniform thickness of MoS₂ grains is attained. To identify the thickness of grown MoS₂ grains, AFM measurement is carried out. Figure 1(d) is an AFM topography image of transferred MoS₂ grain indicated by the white-dashed box in [Fig. 1(c)]. The thickness of MoS₂ grain is ~0.9 nm, which is well matched with reported value of monolayer MoS₂ [28]. Spectroscopic analyses are generally used to investigate the crystallinity of synthetic material. In the case of MoS₂, the vibrational energy difference between two MoS₂ Raman modes (E_{2g}^1 and A_{1g}), provides information on the thickness of MoS₂ as well as its crystallinity. Figure 1(e) shows the Raman intensity mapping image corresponding to the E_{2g}^1 mode of MoS₂. Uniform Raman intensity distribution implies uniform thickness of the MoS₂ grain. Figure 1(f) displays the representative Raman spectrum extracted from the intensity map. The vibration energy difference ($\Delta\omega$) between E_{2g}^1 mode (~386.4 cm⁻¹) and A_{1g} mode (~404.7 cm⁻¹) is 18.3 cm⁻¹, which is in good agreement with the previous report for monolayer MoS₂ [26]. It is noted that carbon impurities are not detected on MoS₂, while amorphous carbon (a-C) Raman modes are clearly observed on MoS₂ grown by organic liquid precursor [23]. Figure 1(g) shows a PL spectrum of transferred MoS₂ grain.

Higher PL intensity than MoS₂ Raman signal is observed at the MoS₂ grain, which is another indicator for monolayer MoS₂ [6]. To confirm the crystallinity of MoS₂, the PL spectrum is deconvoluted by three Lorentzian curves at 1.852 eV (A⁻, multiexciton), 1.895 eV (A⁰, neutral exciton), and 1.988 eV (B, neutral exciton), respectively [23]. The full width half maximum value of A⁰ exciton is ~37.8 meV, which is similar to the value of mechanical exfoliated MoS₂ [29]. This suggests that high-quality MoS₂ grains and films are grown with liquid (NH₄)₂S precursor.

One of the great advantages of the liquid precursor is controllability. Based on the controllability of the liquid (NH₄)₂S precursor, the growth kinetics of MoS₂ is studied by controlling of the flow rate of (NH₄)₂S. Figures 2(a)-(d) present the optical microscopy images of as-grown MoS₂ grains with different (NH₄)₂S supply of 2, 5, 10, and 20 sccm, respectively. With 2 sccm of (NH₄)₂S flow rate, various sizes of MoS₂ grains are observed, indicating that the nucleation of MoS₂ grains occurs at different stages with continuous supply of (NH₄)₂S. On the contrary, more uniform lateral size is observed at 20 sccm, implying that the nucleation of MoS₂ grains occurs at similar time. This might be attributed to the fast supersaturation of precursor molecules originated from the higher precursor concentration. Figure 2(e) displays the grain size and the nucleation density variations of MoS₂ grains as a function of the flow rate of (NH₄)₂S from 2 to 20 sccm. While average lateral size of MoS₂ grains grown with increasing flow

Figure 2. (Color online) Optical microscopy images of MoS₂ grains grown with (a) 2, (b) 5, (c) 10, and (d) 20 sccm flow rate of (NH₄)₂S precursor. (e) Statistics of grain size and the nucleation density of MoS₂ grains as a function of the flow rate of (NH₄)₂S.

Figure 3. (Color online) Optical microscopy images of as-grown MoS₂ grains and films with different growth time; (a) 5, (b) 10, (c) 15, and (d) 20 min, respectively. Continuous supply of (NH₄)₂S led to the growth of bilayer and few-layer MoS₂ grains on monolayer MoS₂ film. (e) Statistics of monolayer (1L), bilayer (2L), few-layer (FL), and total MoS₂ coverage as a function of the growth time. (f) Raman E₁_{2g} intensity mapping image corresponding to the red box in (d). (g) Raman and (h) PL spectra measured at region A-C in (f).

rate of (NH₄)S₂ is decreased from ~123 to 54 μm, the number of MoS₂ grains per unit area (10,000 μm²) is increased from 0.87 to 4.01. This is attributed to the increment of the concentration of precursor, which was typically observed in the growth of 2D materials such as graphene and hBN [30,31]. These results further prove that the supply of (NH₄)₂S is successfully controlled by the bubbler system.

Another advantage of the liquid precursor is the sustainable supply of the precursor molecules. Therefore, time-dependent growth is performed to confirm

the continuous supply of (NH₄)₂S precursor. Figures 3(a)-(d) show optical microscopy images of as-grown MoS₂ grains and films for 5, 10, 15, and 20 min, respectively. The lateral size of MoS₂ grains grown for 5 min is ~40 μm, indicating that the growth rate at the initial stage is very high (~160 μm²/min). At 10 min, the grain size increases to ~60 μm, while the number of MoS₂ grains is maintained. It implies that the continuous supply of (NH₄)₂S precursor contributes to the increase in size of the grown MoS₂ grains instead of forming new nucleation sites. With further

Figure 4. (Color online) Optical microscopy images of as-grown (a) WS₂ and (c) ReS₂ grains. Raman spectra of (b) as-grown WS₂ and (d) transferred ReS₂ grains.

supply of (NH₄)₂S precursor, monolayer MoS₂ film is successfully grown within 15 min. In addition, the growth of bilayer and few-layer MoS₂ grains occurs at the grain boundary of monolayer MoS₂ film, similar to our previous reports [23,26]. This might be attributed to the aggregation of Na₂MoO₄ precursor on the grain boundary of the monolayer MoS₂ film. For 20 min, further growths of bilayer and few-layer MoS₂ grains are observed. Figure 3(e) shows the statistics of monolayer (1L), bilayer (2L), and few-layer (FL) MoS₂ coverage as a function of the growth time. With high growth rate at the initial growth stage, the coverage of 1L MoS₂ is already ~70 %, and linearly increased to 100 % in 15 min. The coverage of both 2L and FL MoS₂ grains increase with increasing of the growth time. To analyze the grown MoS₂ film, Raman and PL measurements are carried out. Figure 3(f) shows a Raman intensity mapping image at E_{2g}¹ mode corresponding to the red box in [Fig. 3(d)]. Due to the different thickness of MoS₂, stronger Raman intensity is observed at 2L and FL MoS₂ grains than that of 1L MoS₂. Figures 3(g) and 3(h) present three Raman and PL spectra extracted from different regions (A-C) in the mapping image. Different $\Delta\omega$ values of ~19, 22, and 25 cm⁻¹ in the Raman spectra are observed at each region, indicating that each region has 1L, 2L, and FL MoS₂ thickness. Higher PL intensity which originates from the direct band gap transition in 1L thickness is also observed at 1L MoS₂. Therefore, 2L and FL MoS₂ grains are grown on 1L MoS₂ film,

implying that the growth behavior of MoS₂ is according to the Stranski-Krastanov model.

In order to confirm the versatility of (NH₄)₂S precursor, the growth of tungsten disulfide (WS₂) is demonstrated. Na₂WO₄·2H₂O aqueous solution is used as tungsten precursor instead of the use of Na₂MoO₄·2H₂O solution. Figure 4(a) shows an optical microscopy image of as-grown WS₂ grains. Equilateral triangular shaped WS₂ grains are grown with uniform grain size (~10 μm). Two representative WS₂ phonon modes (2LA (M) mode at 349.2 cm⁻¹ and A_{1g} mode at 415.3 cm⁻¹) are clearly observed in the Raman spectrum as shown in Fig. 4(b). The $\Delta\omega$ value between the two modes is ~66 cm⁻¹, which is similar to the previously reported $\Delta\omega$ value of monolayer WS₂ [32]. As another example, the growth of rhenium disulfide (ReS₂) is carried out by sulfurization of the NaReO₄ coated substrate. Figure 4(c) shows an optical microscopy image of circular-shaped ReS₂ grains grown on sapphire substrate. The observed circular shape of ReS₂ grains might be attributed to the high diffusion of adatoms which originates from the higher growth temperature at 600 °C than previously reported growth of hexagonal grains at 450 °C [33]. Similar growths of other circular shaped 2D materials are observed at higher growth temperature [21]. To identify the layer thickness of ReS₂ grains, Raman spectroscopy measurement is carried out. Figure 4(d) shows a Raman spectrum of ReS₂ grains transferred on SiO₂/Si substrate. Two ReS₂ phonon modes are clearly observed at ~154 (E_g mode) and ~212.7 cm⁻¹ (A_g mode). Additionally, very weak E_g like Raman modes are observed between 280–380 cm⁻¹, which is well in agreement with previously reported 1L ReS₂ Raman signals [33]. Therefore, both 1L WS₂ and ReS₂ grains are successfully grown with the use of (NH₄)₂S liquid precursor. Consequently, our proposed (NH₄)₂S liquid precursor can be used as a universal sulfur precursor for the growth of other TMdS.

IV. Conclusions

In summary, we report the use of liquid (NH₄)₂S solution as a universal sulfur precursor for CVD growth of TMdS. Based on the advantage of the liquid precursor, the growth kinetics are studied by controlling of the precursor flow rate and the growth time. The lateral size and the number of nucleation sites of MoS₂ grains are controlled by the flow rate of (NH₄)₂S precursor. With increasing of the growth time

to 15 min, centimeter-scaled MoS₂ film is successfully grown. After further supply of (NH₄)₂S precursor, the growth of MoS₂ is governed by the Stranski-Krastanov model. Furthermore, the growth of WS₂ and ReS₂ using (NH₄)₂S precursor are also demonstrated. We believe that our approach not only open a facile way for the high quality reliable growth of TMdS but also helps the commercialization of TMdS in the near future.

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