Micrometer-scale WS$_2$ atomic layers grown by alkali metal free gas-source chemical vapor deposition with H$_2$S and WF$_6$ precursors

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Scalable chemical vapor deposition (CVD) of two-dimensional semiconducting materials such as MoS$_2$ and WS$_2$ is a key technology for the application of these materials in real devices. In this work, we demonstrate the growth behaviors of WS$_2$ crystals from gaseous precursors, i.e. H$_2$S and WF$_6$, under alkali-metal-free conditions. The WS$_2$ crystal growth exhibits layer-by-layer growth, and its behaviors, such as nucleation and lateral growth, are well fitted by the Arrhenius equation. The obtained WS$_2$ crystal shows quality comparable to that obtained from metal oxides: the WS$_2$ film shows sharp photoluminescence with a peak width of 54 meV and $n$-type field-effect transistor operation. Optimizing the growth conditions enabled us to obtain WS$_2$ crystals with a grain size of $\sim 1.5$ µm, which is the largest size ever reported for a transition-metal dichalcogenide grown by gas-source CVD without an alkali-metal promoter.

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1. Introduction

Monolayers of two-dimensional (2D) transition-metal dichalcogenides (TMDs) such as MoS$_2$ and WS$_2$ have attracted much attention because of their exotic properties. In particular, monolayers of Group-VI transition-metal-based TMDs such as MoS$_2$ and WS$_2$ are semiconductors with direct bandgaps of 1.1–2.0 eV and they exhibit strong photoluminescence, excellent field-effect transistor (FET) operation with a high on/off ratio, high carrier mobility, and good ambient sensitivity. These fascinating properties of Group-VI TMDs make them candidates for next-generation semiconductor materials for electronic, optoelectronic, and sensing devices.

Chemical vapor deposition (CVD) has been widely investigated as a method to prepare monolayer TMDs. In conventional CVD growth of TMDs, solid sources such as metal oxides and elemental sulfur are used as precursors. TMD crystals with a grain size larger than 100 nm have already been reported by several groups. However, only these methods, but also CVD growth of TMDs from liquid- and gas-phase precursors such as organometallic precursors (metal-organic CVD), $\text{H}_2\text{S}$, and WF$_6$ is now widely studied because it enables better control of the precursor supply compared with solid-source CVD and therefore it is easily scaled to wafer-scale growth, which is important for the industrial application of TMDs. In particular, TMD growth using gaseous precursors such as H$_2$S and WF$_6$ is highly compatible with industrial manufacturing. In fact, wafer-scale (SiO$_2$/Si wafers as large as 300 mm) TMD growth from these precursors has been demonstrated. However, the grain size of the obtained TMDs is still relatively small (typically less than a few hundred nanometers) compared with that of TMDs prepared by conventional CVD using solid sources when an alkali-metal compound, which is a sufficient growth promoter of TMDs, was added. Furthermore, their growth kinetics, such as their temperature-dependent nucleation and grain size evolution, have not been fully investigated despite their technological and scientific importance.

In this work, we report growth behaviors and micrometer-scale growth of WS$_2$ atomic layers from gaseous precursors of H$_2$S and WF$_6$ under alkali-metal-free conditions. Using an Ar-diluted WF$_6$ precursor (WF$_6$ concentration of $\sim 1\%$), denoted as Ar/WF$_6$, and high-temperature (as high as 900 °C) growth conditions, we successfully suppressed WS$_2$ nucleation and observed lateral as well as layer-by-layer growth of WS$_2$. The photoluminescence (PL) spectrum of the WS$_2$ film shows a single PL emission peak at $\sim 2$ eV with a full-width at half-maximum (FWHM) of 54 meV, which is similar to the PL emission spectrum of solid-source-grown WS$_2$. In addition, we confirmed that WS$_2$ growth is a thermally activated process, where the nucleation density and growth rate of WS$_2$ are well fitted by the Arrhenius equation. The suppressed nucleation and promoted lateral growth result in WS$_2$ with the largest micrometer-scale grain size ever reported among TMDs grown using a gaseous precursor without an alkali-metal growth promoter. Following our previous conference paper, we here describe the experimental method in greater detail. We have also added some experimental data, analysis, and discussion regarding the growth-time-dependent coverage evolution, temperature-dependent growth behavior, and the effect of H$_2$S concentration to gain deeper insight in the growth mechanisms.

2. Methods

We grew WS$_2$ on surface-oxidized Si substrates (1 × 1 cm$^2$) with a $\sim 100$ nm thick SiO$_2$ layer using a hot-wall CVD setup. After the substrates were loaded into a chamber, the chamber was evacuated to $\sim 1 \times 10^{-4}$ Pa and the temperature of the electric furnace was increased. After the temperature reached a set value, Ar, H$_2$S, and the mixed Ar/WF$_6$ (Ar:WF$_6$ ≈ 99:1) were introduced. Unless otherwise

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indicated, the gas flow rate was fixed at 299 sccm for Ar, 1 sccm for H₂S, and 0.03 sccm for the Ar/WF₆ mixed gas and the growth time was fixed at 120 min. The growth temperature and pressure were 700 °C–900 °C and 3 kPa, respectively.

Materials were characterized by scanning electron microscopy (SEM, Hitachi SU-4000) conducted at an acceleration voltage of 1–30 kV. Atomic force microscopy (AFM) images were recorded using a standard AFM system (Park Systems NX10). Raman and PL measurements were carried out using a confocal Raman microscope (Renishaw inVia Qontor) with 488 and 532 nm laser sources for Raman and PL measurements, respectively. All measurements were performed at room temperature.

Back-gate transistors were fabricated via standard lift-off processes using maskless photolithography and an e-beam evaporator to deposit Cr and Au with a thickness of 5 and 50 nm, respectively.

3. Results and discussion

3.1. Growth-time dependent behavior and basic characterization

Figure 1 shows typical SEM images of WS₂ grown at 800 °C and at an Ar/WF₆ flow rate of 0.12 sccm for different growth times. The WS₂ crystal exhibits layer-by-layer growth, i.e. Frank–van der Merwe growth mode, where WS₂ at the early stage [Fig. 1(a)] prefers lateral growth rather than vertical growth [Figs. 1(b) and 1(c)], followed by the initiation of second-layer growth [Fig. 1(d)] after the layer merges with the monolayer WS₂ crystal. Figure 2 shows growth-time-dependent surface coverage. The coverage of the first layer can be linearly well fitted as a function of growth time, indicating a constant growth rate during the growth of the whole first layer and a relatively short incubation time before the start of the growth. This constant growth rate results from the stable supply rate of the gas sources. Under these growth conditions, the maximum WS₂ grain size was 300–400 nm (Fig. 3) because of the relatively high density of crystal nuclei.

Figures 4 and 5 show typical Raman and PL spectra, respectively, of WS₂ grown for 80 min at 800 °C and an Ar/WF₆ flow rate of 0.12 sccm. The Raman spectrum shows two pronounced peaks at 357.6 and 419.2 cm⁻¹, which are assigned as the E’ and A’₁ modes of WS₂, respectively. The shoulder at the lower-frequency side of the E’ peak is the 2LA (M) mode of WS₂. The peak splitting between the E’ and A’₁ modes is 61.6 cm⁻¹, which indicates that the WS₂ crystal is a monolayer. The position and FWHM of the peak in the PL spectrum are 1.994 eV and 54 meV, respectively, which are comparable to those of the peak in the spectrum of WS₂ crystals grown using a solid source such as WO₃ (42–68 meV), suggesting a comparably high crystal quality of the WS₂ obtained in this work.
The FET characteristics of the obtained WS$_2$ film are shown in Fig. 6. The WS$_2$ device exhibits typical $n$-type operation with an on/off ratio of $>10^3$, consistent with previous reports. The channel length of the fabricated device is 4 $\mu$m, which is much larger than the typical grain size ($\sim$400 nm). Therefore, the channel is not single crystal-line but a polycrystalline film, which degrades the FET performance. This degraded performance is one of the reasons why the on/off ratio is smaller than that reported previously; however, it can be improved through optimization of the device geometry. For example, shortening the channel length to less than the grain size ($<400$ nm) reduces the number of grain boundaries inside the channel, resulting in enhanced FET performance. Contact resistance issues should be also addressed.

### 3.2. Temperature-dependent growth behavior

Figure 7 shows typical SEM and AFM images of WS$_2$ prepared under the same growth conditions except for the growth temperature. The grain size of WS$_2$ increases from $\sim$0.05 $\mu$m in the film grown at 700 °C to $\sim$1.5 $\mu$m in the film grown at 900 °C, which is more than 10 times larger than the grain size reported elsewhere in cases where TMDC films were grown via CVD from gaseous precursors in the absence of an alkali metal. The temperature-dependent WS$_2$ grain-size evolution is explained by the Arrhenius equation:

$$r \propto \exp\left(-\frac{E_a}{k_B T}\right),$$

where $r$, $E_a$, $k_B$, and $T$ are the grain inradius [Fig. 8(a)], activation energy, Boltzmann constant, and the absolute temperature, respectively. The plot of $r$ as a function of $T$ and the corresponding fitting result are shown in Fig. 8(b). Here, because $r$ is approximately proportional to the WS$_2$ growth rate, $E_a$ in Eq. (1) is the activation energy of the WS$_2$ formation processes from gaseous precursors. Possible origins of the obtained $E_a$ are surface diffusion, decomposition and/or reaction of precursors and their incorporation into a WS$_2$ crystal. The extracted $E_a$ value is 1.9 eV, which is similar to the $E_a$ of graphene grown via CVD from CH$_4$ on Cu (2–5 eV) and the attachment barrier of MoS$_2$ growth from solid-source onto SiO$_2$ (2.0 eV).

As the temperature increases, the grain density of WS$_2$ decreases from 72 $\mu$m$^{-2}$ at 700 °C to 0.14 $\mu$m$^{-2}$ at 900 °C. The temperature-dependent grain density evolution is shown in Fig. 9. The grain density evolution is explained by the following equation:

$$N_s \propto \exp\left(-\frac{E_a}{k_B T}\right),$$

where $N_s$ is the grain density at the saturation regime. The grain density was well fitted by the equation, which indicates that WS$_2$ nucleation is a thermally activated process, where the activated surface diffusion and coalescence of adatoms results in random nucleation of WS$_2$. The calculated $E_a$ value is 3.1 eV, which is also similar to the $E_a$ of graphene grown on Cu (1–9 eV). The results shown in Fig. 9 also suggest that the dominant factor determining the density of WS$_2$ nuclei is unchanged under these growth conditions. As can be seen in the Fig. 7 and PL properties shown in the next chapter, at a growth temperature of 900 °C, re-evaporation of WS$_2$ seems to occur, because raised growth temperature makes WS$_2$ crystal round and broadens PL FWHM when the growth conditions except temperature are fixed. Therefore, according to the Robinson and Robins
model,31,32) the desorption energy of adatoms would be the determinant factor of $E_a$ in these growth conditions. The Robinson and Robins model also points out the existence of the other mechanism, relating to the surface diffusion. However, we consider that the diffusion barrier is unlikely to be the dominant barrier in our case because of the following reason. The model indicates that $E_a$ becomes 3 times of the diffusion barrier when the surface diffusion of adatoms determines the nucleation density. In our case, $E_a$ is $\sim 3.1$ eV, corresponding to $\sim 9.3$ eV for diffusion barrier, which is much larger than the typical value of diffusion barrier for TMDs growth (up to 4 eV).34) Therefore, the diffusion-limited nucleation would not be the case in our growth conditions.

The two aforementioned results related to temperature-dependent grain density and growth rate strongly suggest that WS$_2$ growth from gaseous precursors is well explained by the conventional growth kinetics model of a thin film. We speculate that this thermally activated behavior of WS$_2$ growth originates from the gaseous nature of the precursors, where the highly diffusive nature of gaseous precursors inhibits inhomogeneous nucleation that is often observed in solid-source CVD.11,23) Note that in our case, WS$_2$ nucleation and growth would not be largely affected by a reaction between WF$_6$ and SiO$_2$. Root mean square surface roughness of a SiO$_2$ surface does not change before and after 900 °C growth (0.244 and 0.266 nm, respectively), which indicates that WF$_6$, H$_2$S, and SiO$_2$ would not react during the growth. Thus, in contrast to the case of amorphous Al$_2$O$_3$,21) thermally-grown SiO$_2$ surface is inert even in our growth temperature range, and it would not be involved in WS$_2$ nucleation and growth.

3.3. Effect of H$_2$S flow rate

The thickness and quality of WS$_2$ grown at 900 °C was evaluated by Raman and PL spectroscopies, as shown in Figs. 10 and 11. The peak splitting between the E' and A$_1$ peaks is 60.6 cm$^{-1}$, indicating that the crystal is a monolayer. The peak position and FWHM of the PL peak are 1.983 eV and 80 meV, respectively; this peak is thus redshifted and broader than the corresponding peak in the spectrum of the sample grown at 800 °C. We attributed this PL redshift and broadening to strain induced by the difference in thermal expansion coefficients between the WS$_2$ and the substrate and/or to sulfur vacancies formed by the re-evaporation of sulfur. In fact, increasing the H$_2$S supply while keeping the total gas supply rate constant made the WS$_2$ PL peak sharp and strong (Fig. 11 and Table I), indicating the effectiveness of increasing the sulfur-containing-species partial pressure to prevent the formation of sulfur vacancies. However, further increasing the H$_2$S concentration inhibited the layer-by-layer-growth mode of WS$_2$, where second-layer growth before completion of first-layer growth was observed (Fig. 12), resulting in a substantial reduction of the PL intensity (Fig. 11 and Table I). This result is attributable to the degradation caused by H$_2$ etching because the amount of H$_2$ decomposed from H$_2$S increases with increasing temperature. The formed H$_2$ attacks WS$_2$ crystals and forms defects on its surface, promoting the formation of a nucleation site of
of monolayer WS2 crystals from H2S and WF6 and investi-
gated their growth behaviors. Using dilute WF6 as a metal
precursor, we obtained WS2 with a grain size of 1.5 μm and
observed layer-by-layer growth. The temperature-dependent
WS2 nucleation and growth rate were well fitted by the
Arrhenius equation, indicating that the growth kinetics can be
well explained by the general mechanism of thin-film
crystallization, where random nucleation of WS2 by collec-
tive crystallization of surface adatoms occurred. An indus-
trial-compatible gas-source CVD technology enabling the
large-scale growth of high-crystal-quality TMDs should be a
key to realize the application of TMDs in future advanced
devices.

4. Conclusions

We demonstrated alkali-metal-free, micrometer-scale growth
of monolayer WS2 crystals from H2S and WF6, and investi-
gated their growth behaviors. Using dilute WF6 as a metal
precursor, we obtained WS2 with a grain size of 1.5 μm and
observed layer-by-layer growth. The temperature-dependent
WS2 nucleation and growth rate were well fitted by the
Arrhenius equation, indicating that the growth kinetics can be
well explained by the general mechanism of thin-film crystallization, where random nucleation of WS2 by collective crystallization of surface adatoms occurred. An industrial-compatible gas-source CVD technology enabling the large-scale growth of high-crystal-quality TMDs should be a key to realize the application of TMDs in future advanced devices.

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Table I. H2S-concentration dependent FWHM and intensities on PL properties of WS2.

| H2S supply (sccm) | Intensity ratio (arb. units) | FWHM (meV) |
|-------------------|-----------------------------|------------|
| 4.0               | 0.2                         | 79         |
| 2.0               | 1.7                         | 59         |
| 1.0               | 1.0                         | 80         |
| 0.5               | 0.2                         | 91         |

Table II. H2S-concentration dependent FWHM and intensities on PL properties of WS2.

| H2S supply (sccm) | Intensity ratio (arb. units) | FWHM (meV) |
|-------------------|-----------------------------|------------|
| 4.0               | 0.2                         | 79         |
| 2.0               | 1.7                         | 59         |
| 1.0               | 1.0                         | 80         |
| 0.5               | 0.2                         | 91         |

Fig. 11. (Color online) PL spectra of WS2 grown at 900 °C with a H2S flow rate of 0.5, 1.0, 2.0, and 4 sccm. The inset shows the normalized spectra.

Fig. 12. (Color online) AFM image of WS2 grown at 900 °C with a H2S flow rate of 4.0 sccm. Scale bar: 2 μm.

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