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Micrometer-Scale Monolayer WS_2 Crystal Grown by Alkali Metal Free Gas Source Chemical Vapor Deposition with H_2S and WF_6 Precursors

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Abstract

Scalable chemical vapor deposition (CVD) growth method of two-dimensional (2D) materials, such as MoS_2 and WS_2, is a key technology for their real device application. In this work, we demonstrate the lateral and layer-by-layer growth of WS_2 crystal from gaseous precursors, i.e., H_2S and WF_6 under alkali-metal free condition. The obtained WS_2 crystal shows comparable quality with that obtained from metal oxide: the WS_2 film shows a *n*-type FET operation and sharp photoluminescence with a peak width of 54 meV. Optimizing growth conditions allows us to obtain WS_2 crystal with a grain size of ~1.5 μm, which is the largest size ever reported among TMDs grown by gas-source CVD without alkali-metal promotor.

1. Introduction

Two-dimensional (2D) monolayer transition-metal dichalcogenides (TMDs), such as MoS_2 and WS_2 have attracted much attention due to their exotic electric properties and great potential for future device applications [1]. To obtain monolayer TMDs, chemical vapor deposition (CVD) growth method has been widely investigated. In particular, CVD growth of TMDs from liquid and gas-phase precursors, such as organometallic compound, H_2S, and WF_6 is now widely studied because it has high compatibility with industrial manufacturing and wafer-scale (up to 300 mm SiO_2/Si wafer) TMD growth have been demonstrated [2-6]. However, the obtained TMD grain size from these precursors is still relatively small (typically under few hundreds of nm, when an alkali metal compound, an efficient growth promotor of TMDs, was not added [4-6]), compared with conventional CVD using solid source [7].

In this work, we report a growth behavior and micrometer-scale growth of WS_2 atomic layers from gaseous precursors of H_2S and WF_6 under alkali-metal free condition. Using Ar-diluted WF_6 precursor (WF_6 concentration of ~ 1%) and high-temperature (up to 900 °C) growth condition, we have succeeded to suppress WS_2 nucleation and observed lateral as well as layer-by-layer growth of WS_2. Micrometer-scale grain size of TMDs grown by gaseous precursor without alkali-metal growth promotor is firstly demonstrated.

2. Experiment

We have grown the WS_2 onto surface-oxidized Si substrate (1 × 1 cm) by a hot-wall CVD setup [6]. WS_2 growth was carried out by flowing 299 sccm Ar, 1–2 sccm H_2S, and 0.03–0.12 sccm mixed gas of Ar/WF_6 (~99:1) under 3 kPa. Characterization of obtained WS_2 was done through scanning electron microscopy (SEM), atomic force microscopy (AFM), Raman and photoluminescence (PL) measurement. Back-gate transistor fabrication was performed by employing standard lift-off processes using a mask-less photolithography and an e-beam evaporator (Cr/Au).

3. Results and discussion

Figure 1 shows typical SEM images of WS_2 at a growth temperature of 800 °C with different growth time. As can be seen in the images, WS_2 crystal shows a layer-by-layer growth: WS_2 at an early stage (Fig.1a) prefers lateral growth rather than vertical growth (Fig. 1b and c), then after merging monolayer WS_2 crystal, 2nd layer growth started (Fig. 1d). At a growth temperature of 800 °C, the maximum WS_2 grain size was 300 to 400 nm (Fig. 2) due to relatively high density of crystal nuclei.

Figure 3 and 4 show a typical Raman and PL spectrum of WS_2 grown at 800 °C. The Raman spectrum shows two-pronounced peaks at 357.6 and 419.2 cm^{-1}, assigned as E'+ 2 LA(M) and A'_1 mode of WS_2, respectively [7]. The peak splitting between E' and A'_1 mode is calculated as 61.6 cm^{-1}, which indicates that the WS_2 crystal is a monolayer [7]. The peak position and full-width half-maximum (FWHM) of the PL spectrum are 1.994 eV and 54 meV, respectively, which are comparable to those of WS_2 crystal grown with a solid source such as WO_3 [7], suggesting comparably high crystal quality of obtained WS_2 in this work.

Field-effect transistor (FET) characteristics of obtained WS_2 film is shown in Fig. 5. Obtained WS_2 shows a typical *n*-type operation with an on/off ratio of $>10^3$. The channel length of the fabricated device is 4 μm, which is much larger than the typical grain size (~400 nm). The polycrystalline nature of the channel would degrade the FET performance; however, it would be improved by optimizing device geometry. For example, shortening the channel length less than the grain size (< 400 nm) makes number of the grain boundaries inside the channel reduce, resulting in improvement of the FET performance. Contact resistance issue should be also mitigated.

Figure 6 shows typical SEM and AFM images of WS_2 obtained with the same growth condition expect for the growth temperatures. As temperature increases, the grain density of WS_2 decreases from 72 μm^{-2} at 700 °C to 0.14 μm^{-2} at 900 °C. The logarithmized grain density is proportional to T^{-1}, which indicates that WS_2 nucleation is thermally activated process: random nucleation of WS_2 by collective crystallization of surface adatom occurred. On the other hand, the grain size of WS_2 increases from ~0.05 μm at 700 °C to ~1.5 μm at 900 °C. The WS_2 grain size grown at 900 °C is up to over 10 times larger than that of the previous reports, where alkali-metal free CVD growth from gaseous precursors was performed [3, 4, 6]. Layer number and crystallinity of WS_2 grown at 900 °C can be evaluated from Raman and PL spectrum, shown in Fig. 7 and 8. The peak splitting between E' and A'_1 peak is 60.6

cm^{-1}, indicates that the crystal is a monolayer. Peak position and FWHM of the PL peak are 1.983 eV and 80 meV, respectively, which is redshifted and broader than that of the sample grown at 800 °C. We speculate that this PL redshift and broadening are caused by strain formed by thermal expansion coefficient difference between WS_2 and substrate, and/or sulfur vacancy formed by re-evaporation of sulfur, since increasing H_2S supply makes WS_2 PL sharp (an FWHM of 59 meV) and strong (Fig. 8). Therefore, WS_2 crystallinity can be further improved by optimizing the growth parameter.

3. Conclusions

we have demonstrated alkali-metal free, micrometer-scale growth of monolayer WS_2 crystal from H_2S and WF_6, and investigated their growth behavior. Industrial compatible gas source CVD technology enabling large-scale and high crystal quality TMDs growth should be a key to realize future TMD-based advanced devices.

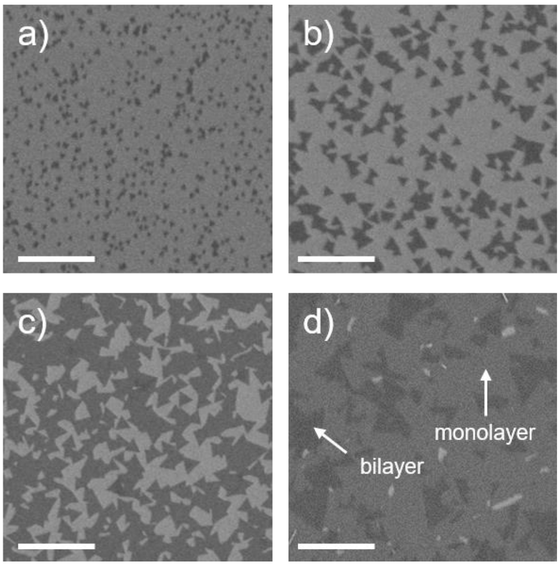

Fig. 1. SEM images of WS_2 grown at 800 °C with various growth time: a): 10; b): 40; c): 40; d): 80min. Scale bar, 500 nm.

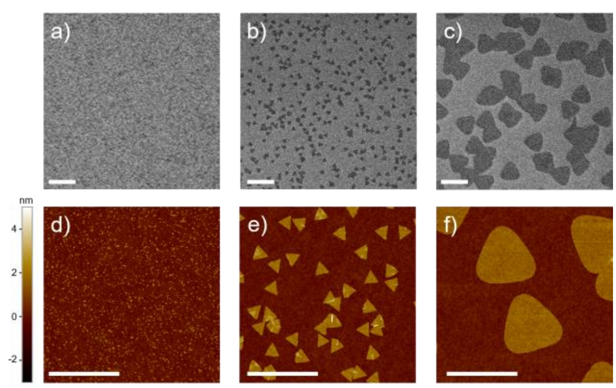

Fig. 6. SEM (upper) and AFM (lower) images of WS_2 obtained with a growth temperature of a) and d): 700 °C; b) and e): 800 °C; and c) and f): 900 °C. Scale bar, 2 µm.

Acknowledgements

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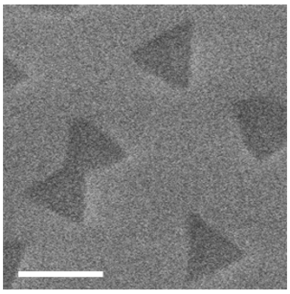

Fig. 2. SEM image of WS_2 grown at 800 °C with a grain size of ~ 400 nm. Scale bar, 500 nm.

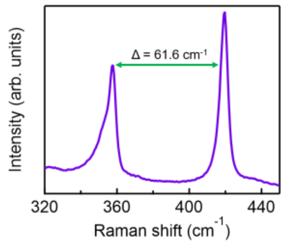

Fig. 3. Raman spectrum of WS_2 grown at 800 °C.

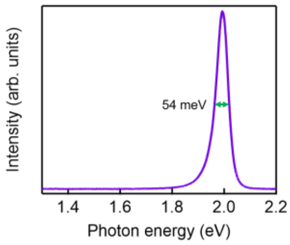

Fig. 4. PL spectrum of WS_2 film grown at 800 °C.

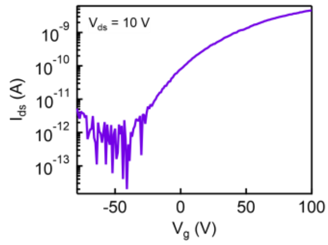

Fig. 5. I_{ds}-V_g characteristic of polycrystalline WS_2 film grown at 800 °C. L/W = 4/100 µm.

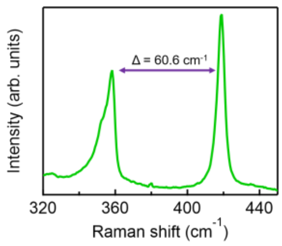

Fig. 7. Raman spectrum of WS_2 grown at 900 °C.

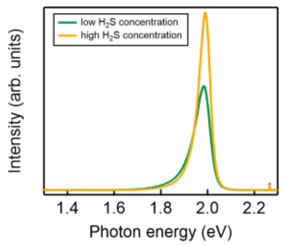

Fig. 8. PL spectra of WS_2 grown at 900 °C with a H_2S flow rate of 1 (low concentration) and 2 (high concentration) sccm.