The Synthesis of WS₂ Atomic Layers under Varying Source-Substrate Distance

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Abstract. Although monolayer WS₂ (Tungsten Disulfide) has attracted much interest, controllable synthesis of large-area WS₂ triangles is still challenging. Here, we report salt-assisted CVD growth of WS₂ atomic layers using a kind of sandwich structure in a semi-sealed installation and firstly investigate the effect of the width of the hollow (D₀) of the structure. We demonstrated WS₂ triangles growth up to 300 μm coverage and showed the effect of hollow on the crystal size. By optimizing the width of the domain, large-area WS₂ films were obtained. We utilized optical microscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), Raman spectroscopy and photoluminescence (PL). Our study provides method to fabricate large area WS₂ flakes and the experiment is critical to building scalable devices.

1. Introduction

Since the discovery of graphene in 2004[1], 2D(two-dimensional) materials[2, 3] that has atomically thickness have attracted much attention recently. Although graphene possesses the highest reported electron mobility[4], its zero energy gap blocks the applications in 2D semiconductor. Monolayer semiconducting transition metal dichalcogenides (TMDCs)[5-7] has distinct crystal symmetry and geometrical confinement which make them exhibit unusual electronic properties which are absent in the bulk materials[8-11]. In particular, WS₂ has increased exponentially because it is chemically robust and shows superior carrier mobility compared to MoS₂[12].

WS₂ monolayer have been mostly obtained via mechanical exfoliation[13, 14, 16, 18], chemical exfoliation[19, 20], liquid exfoliation[21, 22], chemical vapour deposition (direct gas-phase reaction using WO₃ with powered sulfur at 900-950°C)[23], and two-step procedure including firstly condensation of thin layer of WO₃ which converted into WS₂ under the same conditions. However, all of the previous methods are not suited for industrial production because of lack of reproducibility and homogeneity at wafer scale. In order to satisfy demand for field-effect transistor[24, 25], hydrogen evolution[19] and photoelectronic technique[5, 26], the synthesis and growth needs to be improved.

Here, we report salt-assisted CVD growth of WS₂ atomic layers using a kind of sandwich structure and firstly investigate the effect of the width of the hollow of the structure. We demonstrated WS₂ monolayer growth up to 300 μm and showed the effect of hollow on the crystal size. By optimizing the width of the domain, large-area WS₂ triangles were obtained by atmospheric pressure chemical vapour deposition (APCVD) method. We utilized optical microscopy, scanning electron microscopy (SEM),
This page contains text about the use of atomic force microscopy (AFM), Raman spectroscopy and photoluminescence (PL) to characterize the sample. Our study provides method to fabricate large area WS$_2$ flakes and the experiment is critical to building scalable devices.

2. Methods

Our strategy on growth of WS$_2$ is to use a double-furnace CVD apparatus and a semi-sealed quartz tube. The gas was supplied directly from the cylinder to the CVD chamber. The double-furnace CVD setup enabled us to realize independently growth temperature of powder sulfur (S) and precursors (WO$_3$). The illustration of the experimental setup of CVD process and the hollow structure were shown in Fig.1a.

One piece of SiO$_2$/Si substrate covered with 10 μL tungsten (W) source (alcoholic tungsten suspension composed of WO$_3$ powders and NaCl crystal) was put with the other piece of clean SiO$_2$/Si substrate placed face down. Then the hollow structure was put into a small one-end sealed quartz tube inside double-furnace CVD apparatus. The center temperature of the tube was raised to 930℃. Sulfur is placed upstream, which was inside the center of the left furnace heating zone.

Firstly, vacuum was maintained at 1 Pa through a simple mechanical pump. Then, using high-purity argon carrier gas with a constant flow rate of 200 sccm in a tube-type electrical heating furnace in the whole experiment, the temperature of furnace was ramped to 200℃ at a rate of 13℃/min followed by a quick 27℃/min ramp to 930℃. At 930℃, the temperature held for 5 minutes. Finally turn off the heating and allow the film to cool down naturally. Fig.1b shows the temperature profile used in this CVD process.

3. Results and discussion

It is found that, in the same growth batch and the same position of substrate (the center of substrate), the distance between the substrate and WO$_3$ precursor source ($D_{ss}$) is important to affect the WS$_2$ triangle size. It is necessary to investigate the effect of the width of the hollow. The effects of hollow size were...
summarized in Figure 2. The initial growth (Figure 2a) was performed with a hollow size of 900 μm in width. These recipes produced isolated islands with several nm, often with spot-like morphology (Figure 2a). Very few sites of triangle growth are present. Upon decreasing the width of the hollow of the structure to 750 μm, some areas of WS₂ triangles were observed and the shapes became more regular. Spot-like configurations (Figure 2b) were produced from several rotationally symmetric grains. The observed change in Fig 2b indicate decreased grain boundaries or decreased defect density. Once the width of hollow was decreased to 450 μm (Figure 2d), the resulting WS₂ flakes exhibited increase in size. The best triangular growth was observed with ~300 μm with the width (Dₚ) of 150 μm (Figure 3a). This observation suggested that structures with big hollow may be detrimental to WS₂.
Fig. 2. Comparisons of optical microscope images (synthesized with different size of hollow). The triangle shapes are as-grown WS2 with a hollow size ($D_{ss}$) of (a) 900 μm, (b) 800 μm, (c) 600 μm, (d) 450 μm, (e) 300 μm, (f) 200 μm, (g) 150 μm, (h) 100 μm in width. Scale bars are 50 μm (Figure 2.a, b, c) or 100 μm (Figure 2.d, e, f, g, h). (h) Typical optical image of WS2 triangle at $D_{ss}$=100 μm. Scale
bar is 100 μm. (i) Median of triangle size (149.3μm) at D_{ss}=200μm. (j) Median of triangle size at different width of hollow (D_{ss}).

4. Characteristics

We have performed AFM measurements (Figure 3c) to demonstrate the layer number of WS$_2$ triangles. The triangles were exhibiting thicknesses around 1.5 nm from the results (Figure 3d).

![Fig. 3. (a) Optical microscope image of as-grown WS$_2$ synthesized with the hollow size of 100 µm. (b) SEM image of the area shown in (a). (c) AFM image of our CVD grown WS$_2$ flakes. AFM step height profile of a typical region.](image)

Raman spectroscopy has been used to study two-dimensional materials, such as the numbers$^{[28, 29]}$, the stacking sequence$^{[30]}$, the external field and doping effects$^{[31, 32]}$, and the internal and external strain$^{[33-36]}$. Here, with the D$_{ss}$ of the structure at 150μm. Figure 2e shows Raman spectra of our WS$_2$ flakes at frequency range of 100-650 cm$^{-1}$ when excited at 532 nm laser at normal room temperature,
matching that of reported literature\(^\text{[37]}\). The Raman spectroscopy measurements detected the in-plane phonon mode (E\(^1\)_2g at 353.4 cm\(^{-1}\)) and out-of-plane phonon mode (A\(^1\)_g at 418.4 cm\(^{-1}\)). The longitudinal acoustic mode at M point (L(A(M)) is obvious at ~350 cm\(^{-1}\). The frequency difference or peak separation (Δk) between the E\(^1\)_2g vibrational mode and A\(^1\)_g vibrational mode was commonly used to determine the layer number of WS\(_2\)[14, 37]. The frequency difference between the E\(^1\)_2g mode and A\(^1\)_g mode is ~65 cm\(^{-1}\) which is consistent with the Raman spectroscopic characteristics of single-layer-thick WS\(_2\) flakes on SiO\(_2\)/Si substrate[14].

PL spectroscopy confirmed the characteristics and monolayer properties of the synthesized crystals. PL measurements (Figure 2c) revealed a sharp emission peak with maximum intensity achieved at 1.97 eV which revealed a strong PL peak between 550 and 750 nm, typical for a monolayer WS\(_2\). The peak is at 632 nm (direct band gap ~ 1.96 eV) which falls in the range of reported PL peak positions for monolayer WS\(_2\) thin films[13, 14, 38, 39].

![Raman spectrum and photoluminescence](image)

**Fig. 4.** (a) Raman spectrum and (b) room temperature photoluminescence of the as-grown WS\(_2\) films.

The peaks in (a) present the peak positions of the E12g (353.4 cm\(^{-1}\)) and A1g (418.4 cm\(^{-1}\)) modes in the region of WS\(_2\). An excitation wavelength of 532 nm was used for all PL and Raman spectra in this thesis.

We have fabricated the back-gated field-effect transistor (FET) of our as-grown WS\(_2\) (Figure 5a) to further study the electrical properties. The source electrode and drain electrode are defined by laser direct writing lithography system and gilded using magnetron sputtering (100 nm Au). The electronic measurements were conducted using Keithley 4200 SCS electrical performance test equipment. Figure 5b,c displays the I\(_{ds}\)-V\(_{ds}\) characteristic of WS\(_2\) flakes FETs at various gate voltages (V\(_{g}\) = -5.0, -4.5, -4.0, -3.5, -3.0, -2.5, -2.0, -1.5, -0.5, 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 V), showing decreasing current with increasing positive gate voltage, demonstrating p-type behaviour. The non-linear and asymmetrical curves suggested that Schottky contact, caused by the work function difference between the WS\(_2\) (2.1 eV) and the Au (5.1 eV).

Figure 5d, e shows I\(_{ds}\)-V\(_{bg}\) curve that measured at different drain voltage (V\(_{ds}\) = -3.0, -2.5, -2.0, -1.5, -0.5, 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 V), with the back-gate voltage sweeping from -5 to 5 V in steps of 0.05 V. From the above formula, we can calculate the carrier mobility (μ) of the FETs devices:

\[
\mu = \frac{L}{W} \frac{d}{\varepsilon_r \varepsilon_0 V_{ds}} \frac{\partial^2 V_{ds}}{\partial V_g^2}
\]

Where W is the channel width, L is the channel length, \(\varepsilon_0\) equals to 8.854 \(\times\) 10\(^{-12}\) F m\(^{-1}\), \(\varepsilon_r\) equals to 3.9, and d equals to 300 nm (SiO\(_2\) thickness).
The carrier of hole mobility ($\mu$) of our WS$_2$ FETs is 3.5 cm$^2$V$^{-1}$s$^{-1}$. All the curves displayed p-type semiconductor characteristic, most likely because of the effect of alkali metal halides $^{[40]}$. The reason is also because of the effect of the shortage of the W source. The melting point of WO$_3$ is 1300℃ under normal pressure. The lower pressure of WO$_3$ vapor will result in the shortage of the W source, which displays p-type character of FET.

![Device Image](image1)

![Optical Image](image2)

**Fig. 5.** Electronic properties of as-grown WS$_2$ atomic layers. (a) Device image of WS$_2$ transistor. (b) Optical image of WS$_2$ transistors. Scale bar is 100 μm. (c) $I_{ds}$-$V_{ds}$ output characteristics shown in (c) and (d) at different gate voltages (ranges from -5 to 5 V with a 0.5V step). (e) $I_{ds}$-$V_{bg}$ transfer.
characteristics shown in (e) and (f) at different source voltages (ranges from -3 to 3 V with a 0.5V step).

5. Conclusion
In conclusion, we have reported systematic investigation of the width of the hollow of the growth structure with the salt-assisted CVD growth of WS$_2$ atomic layers. Optical characterization show that the addition of the width of the hollow produces detrimental effect to WS$_2$ growth size. We demonstrated that high quality WS$_2$ atomic film can be prepared over 300 μm. PL studies demonstrate uniform emission and excellent crystalline quality. Electronic properties further demonstrate that the p-type WS$_2$ back-gated FET with hole mobility up to 3.5 cm$^2$ V$^{-1}$ s$^{-1}$.

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