Characterization of High Quality, Large-Scale Growth of Monolayer WS2 Domains via Chemical Vapor Deposition Technique

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Research Article

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Abstract

WS\textsubscript{2} flakes have been grown successfully on SiO\textsubscript{2} substrate via chemical vapor (CVD) deposition method by reduction and sulfurization of WO\textsubscript{3} using Ar/ H\textsubscript{2} gas and sulfur evaporated from solid sulfur powder. The prepared samples were characterized by optical microscopy (OM), atomic force microscopy (AFM), scanning electron microscopy (SEM), Raman spectra and photoluminescence (PL). Large domain WS\textsubscript{2} monolayers are obtained by extending the growth time. The perfect triangular single-crystalline WS\textsubscript{2} flakes with an average length of more than 35 µm were achieved. The sharp PL peak (∼1.98 eV) and two distinct Raman peaks (E\textsubscript{2g} and A\textsubscript{1g}) with a ∼ 71.5 cm\textsuperscript{-1} peak split indicating that relatively high quality WS\textsubscript{2} crystals with a regular triangle shape can be synthesized. Higher growth time shows larger triangular-shaped of WS\textsubscript{2}.

1- Introduction

Two-dimensional (2D) materials have attracted widespread research attention in order to be used next-generation nanoelectronic devices [1] due to their unique electronic, optical and mechanical properties [2–3]. Thin 2D crystals, such as graphene, have high charge carrier mobility, high thermal conductivity, high mechanical strength, and broadband optical absorption [4–7]. But the zero-band gap of graphene limited its applications in electronic fields. Graphene has low on/off switch ratios in field effect transistors (FETs) and cannot be efficiently switched on/off [8]. Therefore, 2D layered transition metal dichalcogenides (TMDCs) with variable band gap are essential for application in fast switching transistors and novel electronic devices.

Recently TMDCs, like WS\textsubscript{2}, WSe\textsubscript{2}, MoS\textsubscript{2} and MoSe\textsubscript{2} have the same structure as graphene and attracted extreme attention. These materials show very significant properties such as visible-wavelength band gap structure tunability with strain, high carrier mobility, large optical absorption coefficient, high on/off current ratio, and naturally passivated surface (due to the sulfur bonds).

The bulk materials of TMDCs are indirect band gap semiconductors, however with decreasing the number of layers to a single layer, the band gap of these materials transforms from indirect-to-direct because of quantum confinement effect [9]. These unique properties, makes them a promising candidates for broadly used in electronics and optoelectronics applications [10–11].

WS\textsubscript{2} is a promising transition mental dichalcogenides in electronic device applications [12], due to its higher mobility and chemical strength [13].

The structure of WS\textsubscript{2} is made by sandwiching two atomic layers of S and one atomic layer of W through covalent bonds of W-S, where W localized at the body center of a trigonal-prismatic case made by six S atoms [14]. The bulk WS\textsubscript{2} is an indirect band gap semiconductor with band gap of about 1.3 eV [15]. Though, the single crystal WS\textsubscript{2} with a direct band gap (2.05 eV) [16] has promising applications in electrocatalysis [17–18], ultra-thin channel for constructing ultra-short channel FETs, and photodetectors
WS$_2$ with mono layer structure has stronger photoluminescence (PL) than other TMDCs [21]. Because of high nonlinear susceptibility, WS$_2$ is more suitable material for application in nonlinear optical devices [22].

There are numerous methods to obtain nano layer WS$_2$, such as chemical vapor deposition (CVD) [23–24], mechanical exfoliation [25], liquid exfoliation [26]. In addition, pulsed layer deposition (PLD) [27], metal-organic CVD (MOCVD) [28], atomic layer deposition (ALD) [29], and molecular beam epitaxy (MBE) [30], growth techniques have been used to grow higher quality.

Electronic, photoelectronic, and mechanical properties of deposited WS$_2$ extremely depend on thickness and shape of WS$_2$ flakes, so controllable fabrication of WS$_2$ is very essential [31].

Single layer WS$_2$ with a size of hundreds of microns has been produced by CVD method [32–34]. Cong et al. deposited high quality WS$_2$ (with a maximum size of 178 µm) by direct sulfurization of WO$_3$ powders at 750°C in CVD system [35]. Rong et al. [36] and Sheng [37] grown large WS$_2$ flakes by using two furnace systems that the sulfur powder is located in the low temperature zone, and the WO$_3$ powder is located in the high temperature zone.

We employed chemical vapor deposition for preparing our sampled due to its good balance between material quality, yield, and cost.

Growth of high quality WS$_2$ thin film is significant because of engineering and integration of large-scale device applications. The growth of monolayer WS$_2$ is always a big challenge, especially for the large-scale monolayer WS$_2$.

In this study, the large-scale monolayer WS$_2$ was successfully deposited. One of the attractive advantages of 2D materials is that their properties are tunable by controlling the number of layers. Clearly, TMDCs with a tunable number of layers are appropriate for several applications including energy, electronics, optoelectronics, and catalysis applications [38-41].

In this paper, we deposited the synthesis of mono layer triangular WS$_2$ thin films with large size by CVD method and investigated the effect of growth time on the flake size, Morphology and optical properties. We use optical microscopy, Raman spectroscopy, photoluminescence (PL), scanning electron microscopy (SEM) and atomic force microscopy (AFM) to characterize growth formation, crystallinity and existence of monolayer growth.

2. Experimental Details

WS$_2$ thin film was deposited on SiO$_2$ substrate via chemical vapor deposition method. Fig. 1 shows the PCVD of WS$_2$ was carried out inside a tube furnace. Prior to deposition, all the substrates were ultrasonically cleaned in acetone; ethanol and deionized (DI) water for 10 min, respectively. The
sulfurization of tungsten three oxide (WO$_3$) powders to deposit WS$_2$ nanostructures has been broadly approved [42-43]. The mixed of 1.02 g WO$_3$ powder and 0.0170 g NaCl is placed in the alumina boat. The boat was put at the center of the tube furnace and another boat containing 0.60 g sulfur powder was placed in the other end of tube, which is used as the precursors of the synthesizing WS$_2$. The SiO$_2$ substrate at the growth region was placed face-down above the boat with mixed of WO$_3$ powder and NaCl. Moreover, the mixture gas of Ar/H$_2$ is always injected during the reaction (Ar (SCCM) = 40 and H$_2$ (SCCM) = 30). The operating pressure during growth was approximately 0.075 Torr. The furnace was heated to 250°C and kept at this temperature for 10 min. Then during 33 minutes, the temperature reaches 800°C for the growth of WS$_2$ and kept at this temperature for 5, 10, 15 and 20 min respectively, then cool down rapidly. The evaporation of WO$_3$ requires a higher temperature than the sulfur evaporation. By insertion the sulfur powder at different places outside of the main heating area of the furnace, it evaporated at different times relative to the substrate temperature.

CVD-based vapor phase is powerful growth method for organizing high quality 2D materials. As shown in Fig. 2, three different stages of the CVD process like nucleation, growth, and coalescence are important for optimization film deposition and determines the final film quality. The nucleation density must be modified to achieve a suitable number of nuclei that will finally merge together to form a continuous film with single crystal domains.

Optical and electronic properties of 2D materials are mainly dependent on their size, morphology, phase, etc. that can be controlled in CVD growth processes.

### 3. Result And Discussion

#### 3.1. Structural properties of tungsten sulfide layers

##### 3.1.1. Optical microscope

Fig. 3 shows the optical images of WS$_2$ products grown on SiO$_2$ substrates. The perfect triangular shape with sharp edges and large scale WS$_2$ flakes have also been detected in all samples, which exhibit isolated triangular morphology with lateral dimensions up to several tens of micrometers. The triangular shape is the most thermodynamically stable morphology of atomically thin TMDCs, determined by the directionality of chemical bonding and interactions of the orbitals of the hexagonal lattice [44]. All the flakes show distinct color contrast between the core and outer area, signifying a thickness variation between the core and peripheric regions.

As can be seen from Fig.3, uniform WS$_2$ thin film can be obtained in a large domain monolayer. The monolayer WS$_2$ thin film obtained in a more controlled and repeatable manner. In Fig. 3a, WS$_2$ flaks were found to have nucleated randomly on the SiO$_2$ substrate with domains up to 10 micrometers. The orientation of the triangles was relatively disorder. From the optical images (Fig.3b), there was no
significant change in comparison to Fig. 3a. In contrast, with increasing growth time, larger scale triangular \( \text{WS}_2 \) thin films are synthesized.

Under suitable conditions, the domains can merge together to form continuous thin films.

When the growth time increases, the perfect triangular shape monolayer \( \text{WS}_2 \) flakes can be achieved with higher density. A continuous monolayer \( \text{WS}_2 \) thin film growth and moreover the area of the film continues to increase. This result shows that the film can realize the lateral growth and vertical growth at the same time. Therefore, it can be inferred that at a suitable growth temperature and growth time, the growth mechanism of the \( \text{WS}_2 \) crystal on the \( \text{SiO}_2 \) substrate is lateral growth at the beginning, and when the crystal area is sufficiently large, both lateral and vertical growth can carry out [45]. While large area samples can be obtained by longer growth time, significant overgrowth may occur. To avoid the multilayered, the growth time is a very important parameter.

The edge lengths of the large triangular flakes are estimated to be \( \sim 35 \) micrometers, which are larger than those of the flakes, obtained at lower growth time. With increasing growth time, the nucleation particles increase because of sufficient time of the evaporating particles for diffusion and migration on the substrate, thus the large island forms.

### 3.1.2. SEM

The magnified view of SEM images of fabricated single layer \( \text{WS}_2 \) films is shown in Fig. 4. We study the effect of the growth time on the morphologies of \( \text{WS}_2 \) flakes. Based on the SEM images, the \( \text{WS}_2 \) crystal starts to grow, and the monolayer \( \text{WS}_2 \) films and flakes can be obtained. Small and single crystal \( \text{WS}_2 \) triangles with sharp edges were observed at lower growth time. At higher growth time, the 2D \( \text{WS}_2 \) flakes with larger size are formed.

It is verified that with increasing growth time, both the size and density of \( \text{WS}_2 \) crystals increased. During growth time, triangles \( \text{WS}_2 \) monolayers coalesce together and continuous monolayer growth was happened. The average size of a \( \text{WS}_2 \) single crystal increased from 10 \( \mu \text{m} \) to 35 \( \mu \text{m} \).

The SEM images confirm the uniformity over a large area, which is greatly required for application in the device. The increase in total area coverage is related to increase in crystal size and increase in nucleation density.

### 3.1.3. AFM

In order to obtain detail about morphological information of the \( \text{WS}_2 \) nanostructure atomic force microscopy characterizations were conducted.

Fig. 5 shows 2D and 3D AFM images of deposited \( \text{WS}_2 \) thin films at different growth time. The films surface is covered completely by \( \text{WS}_2 \) flakes. The \( \text{WS}_2 \) flakes exhibit flat with sharp edge.
Through the study, we found an interesting thing, as shown in Fig.5a-d. There was a great difference in torsion angles on the two connecting triangles. With a great difference in torsion angles, a grain boundary will appear on the interface of two different triangles. However, the multilayer films are only concentrated on the grain boundary. This growth can be observed when two triangles connecting at the grain boundary with great difference in torsion angles. For connecting triangles with a small difference in torsion angles or triangles that do not connect with each other, this phenomenon does not appear. The appearance of the grain boundary will result in the disorder of the growth that results in an overlapping growth of two triangular grains with different orientations in the grain boundary. This phenomenon also reported in Lan et.al. work.

There was not a clear report about relationship between rotation angles of 2D materials and the number of layers and their growth parameters. The shape and edge structure are essentially dependent on the reaction conditions, such as substrates, growth time, gas flow rate, precursor concentration growth temperature, and etc.

### 3.2. Optical properties

#### 3.2.1. Raman

Raman spectra have been generally used to detect the heterostructure, verify the composition and phase distributions, internal and external strain, thickness and uniformity, and stacking sequence of 2D TMDs. It studies the scattering spectrum with different incident light excitations to obtain molecular vibration and rotation information. The optical phonon modes of WS\(_2\), related to the in-plane vibrational and out-of-plane vibrations mode. For bulk WS\(_2\) material, the Raman spectrum has two different vibration peaks, \(E_{2g}\) and \(A_{1g}\) peak, where the \(E_{2g}\) and the \(A_{1g}\) peaks are placed at a wave number of about 350 and 420 cm\(^{-1}\) respectively. When the film thickness decreases, the interlayer interaction weakens [46]. The spectral position of two Raman modes (\(E_{2g}\) and \(A_{1g}\)) in TMD materials can be used to identify the layer number [47-48].

The frequency difference (\(\Delta \omega\)) between the \(E_{2g}\) and \(A_{1g}\) modes monotonically decreases with decreasing the thickness of WS\(_2\).

Fig. 6 show the corresponding Raman spectroscopy of the WS\(_2\) thin films over a frequency range of 100–800 cm\(^{-1}\) at room temperature with laser excitation at 532 nm.

All the Raman spectrum consist of two major peaks at \(\sim\) 345 cm\(^{-1}\) [49-50] and at \(\sim\) 417 cm\(^{-1}\) [51-53] and confirms the formation of WS\(_2\), meanwhile a small hump at \(\sim\)520 cm\(^{-1}\) is due to the Si substrate [54]. The expected resonance at 3LA (M) would spectrally overlap with the first silicon peak at 520 cm\(^{-1}\) [55-56].

The frequency difference between the \(E_{2g}\) mode and \(A_{1g}\) mode is about 71.5 cm\(^{-1}\). The height of the \(E_{2g}\) peak is about three-times than that of the \(A_{1g}\) peak that can recognize the Raman spectroscopic
characteristics of monolayer WS\(_2\) \[36\].

The weak Raman peak at 230.7 cm\(^{-1}\) associated to the first order modes of A\(_{1g}\) (M)-LA (M) \[57\]. The peak around 580 cm\(^{-1}\) is commonly corresponding to A\(_{1g}+\)LA (M) \[58-59\]. According to studies by other authors, the low intensity Raman peak at 700 cm\(^{-1}\) is generally attributed to 4LA (M) \[53, 60\].

As shown in Fig. 6, the E\(_{2g}\) peak had a small shift to lower wavenumbers at samples 2, 3 and 4, while no shift has been detected in wavenumbers of the A\(_{1g}\) mode in all samples.

The shift of two vibrational modes of WS\(_2\) is very important, as the materials goes from monolayers to a few layers. When the number of layers increases, because of suppression of atom vibration by the Van der Waals force, higher force constants appears, resulting the blue shift of A\(_{1g}\) that relates to the predicted stiffening \[61\]. Redshift of the E\(_{2g}\) peak with increasing the number of WS\(_2\) layers is due to change in the structure based on the stacking of different layers or long-range Coulombic interlayer interaction have a key role \[62-63\].

However, the intensity E\(_{2g}\)/A\(_{1g}\) ratio is used to identify surface information of the WS\(_2\) film \[64\] and also is sensitive to the number of layers \[65-66\]. In general, the intensity of Raman spectra increases from single layer to bilayer \[67\].

The ratio of E\(_{2g}\)/A\(_{1g}\) is about 3 for all samples with a small difference. This ratio is reported for the monolayer WS\(_2\) \[68-69\]. We can see, with increase in growth time of WS\(_2\) layers, the ratio of E\(_{2g}\)/A\(_{1g}\) has not obvious change. The difference was small while not proportional to the number of layers.

3.2.2. PL

The luminescence properties were studied by PL analysis. PL spectroscopy is an effective method to characterize the crystal quality and one of the most direct methods for determining the band gap of monolayer TMDs \[70\]. The change in the band structures from indirect to direct is one of the most important properties of the 2D materials that happened when the samples thicknesses changed to the monolayers. This tells highly efficient emission of the 2D materials \[71\].

Table 1 summarizes the WS\(_2\) Raman spectra as a function of growth time
Monolayer WS$_2$ thin films was characterized by a laser wavelength of 532 nm. Fig. 7 shows PL spectra of monolayer WS$_2$ that presents a sharp emission peak with maximum intensity at 1.97 eV in the investigated range from 1.78 eV to 2.32 eV. Observation of this single peak energy with high intense emission indicates formation high quality of monolayer WS$_2$, which is in good agreement with previous reports [72]. A single sharp emission peak shows the high quality with a good uniformity of the WS$_2$ films.

The peak around 1.97 eV, relates to direct-gap transitions between the spin split valence bands and the conduction band at the K points [25, 73]. This emissions peak is reliable with the reported band gap values [74-75]. The monolayer WS$_2$ possesses a direct energy gap of $\sim 2$ eV [76-77].

As reported by other groups, with increasing the number of layers, the emission intensity dramatically decrease and are supplemented by a low energy peak so, transition to indirect band gap semiconductor happens [78].

The energy and width of predominant emission peaks did not change obviously at different growth time. The PL peak for the WS$_2$ grown at higher growth time is located at 2.01 eV, demonstrating a little blue shift when compared to the other samples. The blue shift of the PL peak might be attributed to the built-in compressive strain [79] or can be happened due to the existence of structural and charged defects, like S-vacancies, as such a defect may cause n-type doping in the WS$_2$ monolayer [80-81].

Samples produced at higher growth time reliably result in the highest PL intensity. Higher PL ratios denote higher optical quality.

### Conclusions

We have confirmed the growth of high quality; large-area triangular WS$_2$ single layers deposited by chemical vapor deposition method with a single step of direct sulfurization of WO$_3$ powders on SiO$_2$.
substrate under different growth time and their structural, morphological and optical properties have been investigated. Most of the mono layer flakes shows smooth surface with triangular shape up to 35 micrometers size. Optical characterization using photoluminescence and Raman spectroscopy of the layers exhibits the identity and monolayer nature of the deposited WS$_2$ crystals nanostructures. Raman spectrum of the WS$_2$ nanostructures indicate two prominent peaks at 345.5 cm$^{-1}$ and 417 cm$^{-1}$ corresponding to the E$_{2g}$ and A$_{1g}$ vibration modes of monolayer WS$_2$. PL spectra show the good uniformity and high quality of the triangles with a single sharp peak at 1.97 eV that correspond to direct band gap emission of monolayer WS$_2$.

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**Figures**
Figure 1

Schematic of the WS2 deposition on the SiO2 substrate. (a) first step, and (b) second step of the growth process.

Figure 2

Different stages of the CVD process: nucleation, growth and coalescence (formation of continuous film).
Figure 3

Optical microscope images of WS2 flakes grown at different growth time, a) 5, b) 10, c) 15, d) 20 min.
Figure 4

SEM images of WS2 flakes grown at different growth time, a) 5, b) 10, c) 15, d) 20 min.
Figure 5

2D and 3D images of WS2 flakes grown at different growth time, a) 5, b) 10, c) 15, d) 20 min.
Figure 6

The Raman spectroscopy of WS2 samples deposited at different growth time, a) 5, b) 10, c) 15, d) 20 min.
Figure 7

PL spectroscopy of monolayer WS2 synthesized under different growth time, a) 5, b) 10, c) 15, d) 20 min.