Large Area Synthesis, Characterization, and Anisotropic Etching of Two Dimensional Tungsten Disulfide Films

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Abstract

Emergent properties of tungsten disulfide at the quantum confinement limit hold promise for electronic and optoelectronic applications. Here we report on the large area synthesis of atomically thin tungsten disulfide films with strong photoluminescence properties via sulfurization of the pre-deposited tungsten films. Detailed characterization of the pre-deposited tungsten films and tungsten disulfide films are performed using microscopy and spectroscopy methods. By directly heating tungsten disulfide films in air, we have shown that the films tend to be etched into a series of triangular shaped pits with the same orientations, revealing the anisotropic etching behavior of tungsten disulfide edges. Moreover, the dimensions of the triangular pits increase with the number of layers, suggesting a thickness dependent behavior of etching in tungsten disulfide films. This method offers a promising new avenue for engineering the edge structures of tungsten disulfide films.

Keywords: Crystal Growth, Etching, Raman Spectroscopy, XPS

1. Introduction

Graphene-like two-dimensional (2D) semiconducting transition metal dichalcogenides (TMDs), especially tin disulfide (WS_2), with sizeable band gaps have showed vast potential for electronics [1] and optoelectronics [2] due to exotic physical and electronic properties, recently. WS_2 is a layered semiconductor material with a direct band gap of ~ 1.95 eV [3] in monolayer form. For electronics, the presence of a band gap allows field-effect transistors (FETs) to have high on/off ratios [4], and its ultrathin nature allows the channel length to be reduced relative to those fabricated with conventional semiconductors [5]. For optoelectronics, the direct band gap produces high photoconductivity [6], and strong photoluminescence (PL) [3]. To explore new fundamental properties and to further develop their electronic and optoelectronic applications, synthesis of large-area atomically thin WS_2 layers with uniform properties by a facile and scalable method is an essential requirement.

Recent top-down approaches including mechanical exfoliation [7] and liquid exfoliation [8] to obtain high crystalline WS_2 flakes have attracted considerable attention. However, lateral dimensions of the flakes synthesized by the exfoliation methods are limited to few microns, which limits their applications in large-scale electronics and optoelectronics.

In contrast, chemical vapor deposition (CVD) techniques have great potential in producing large-area WS_2 over macroscopic sizes, which are ideal for integration with current CMOS platform. Typically, CVD growth of WS_2 includes vapor phase reaction or deposition of gaseous metal and chalcogenide feed stocks [9, 10], and sulfurization or decomposition of the pre-deposited films [11, 12].

Among the CVD techniques, sulfurization of the pre-deposited thin films is emerging as a quick and easy way to obtain large-area atomically thin WS₂ films on insulating substrates. Recently, several studies have reported direct sulfurization of tungsten oxide (WO₃) films deposited either by thermal evaporation [12] or by atomic layer deposition (ALD) [11]. However, to the best of our knowledge, large-area growth of atomically thin WS₂ films on silicon dioxide (SiO₂) substrates by sulfurization of the tungsten (W) films deposited by electron-beam (e-beam) deposition has not been reported yet.

In parallel with the recent advances in the synthesis of TMDs, numerous methods have been developed to enable their identification and characterization. PL spectroscopy is a powerful method of probing the electronic structure of TMDs [13]. Recent studies report [14] that molybdenum disulfide (MoS₂) shows laser-dependent PL spectra, where the PL intensity and position are affected by varying the duration and intensity of laser irradiation. To the best of our knowledge, there is no systematic study concerning the effect of laser power on PL spectra of WS₂, which is essential to probing the PL characteristics of WS₂.

Recently, there has been an increasing interest in the nanoscale control of edge structures of TMDs. Nanoscale control of edge structures offers new pathways toward fine tuning the electronic, optical, chemical, magnetic, and catalytic properties of TMDs [15-18]. One way to engineer edge structures of TMDs is heating them in an oxygen (O₂) environment [19, 20]. For example, high density triangular pits with the molybdenum (Mo) or sulfur (S) terminated zigzag edges on the surface of MoS₂ sheets have been obtained upon annealing them in air, which might arise from the anisotropic etching of the active MoS₂ edge sites [19]. Such edge terminated MoS₂ structures find applications in diverse catalytic reactions [21, 22]. As mentioned above, most

studies so far have focused on the oxidative etching of MoS₂. However, to the best of our knowledge, the etching behavior of WS₂ films has yet to be experimentally studied.

In this study, we demonstrate the large-area synthesis of atomically thin WS₂ films on SiO₂ substrates. Briefly, the W films are deposited on SiO₂ substrate by using e-beam deposition method. In the next step, the as-deposited W films are annealed at 500 °C and then sulfurized at 850 °C to obtain WS₂ films. The fundamental morphologic, electronic, optical and chemical properties of the pre-deposited W films and WS₂ films are investigated using optical microscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray photoemission spectroscopy (XPS), Raman spectroscopy and PL spectroscopy. We also systematically investigate the dependence of PL spectra of WS₂ films on laser power. Furthermore, we introduce a simple method to etch WS₂ films with well-oriented triangular-shaped pits by heating them in air.

2. Experimental Section

Materials synthesis: WS₂ films were synthesized via three steps: i) deposition of the W films, ii) annealing of the W films, and iii) sulfurization of the annealed W films. First of all, the W films with a thickness of ~15 nm were deposited on SiO₂ substrates (300 nm thick SiO₂ layer deposited thermally on Si wafer) by e-beam deposition method. The deposition of the films was carried out in a load-lock chamber (Temescal BJD 1800) at a base pressure of ~10⁻⁶ Torr and deposition pressure of ~10⁻⁵ Torr, with an average growth rate of 1 Å/s. Next, the as-deposited W films were annealed at 500 °C in open air for 60 min in order to oxidize the films in a single-zone vacuum tube furnace with 2-inch diameter quartz tube (MTI GSL-1200X-50). The annealed W films were then put at the center of the heating zone, and 250 mg of S powder (99.5%, Alfa Aesar) was put in a ceramic boat at the upstream where S starts evaporating when the

temperature of the center of the tube is 525 °C. High-purity argon (Ar) gas with a constant flow of 100 sccm was used as the carrier gas. After that, the furnace was pumped down to remove the air, and the pressure was stabilized at 250 Torr. Further, the center of heating zone was heated to 850 °C with a heating rate of 5 °C/min, and it was kept at that temperature for 10 min. Finally it was naturally cooled down to room temperature. The etching of WS₂ films was performed in the same furnace by simply heating them in air at 500 °C for 45 min.

Characterization: The morphology of WS₂ films was investigated using SEM (FIB NNS450). Raman spectra and PL spectra were collected using a Horiba system with a 532 nm laser. All spectra were calibrated using the 520.5 cm⁻¹ line of a Si wafer. XPS characterization was carried out by using a Kratos AXIS ULTRADLD XPS system equipped with an Al K α monochromated X-ray source and a 165-mm mean radius electron energy hemispherical analyzer. The vacuum pressure was kept below 3x10⁻⁹ torr, and the neutralizer was applied during the data acquisition. AFM analysis was performed using a commercial AFM system (Multimode, Veeco) in tapping mode.

3. Results and Discussion

The morphology and thickness of the W films before and after annealing are determined by AFM analysis. The AFM height image (**Figure 1a**) of the as-deposited films reveals island type morphology with a height of about 15 nm. The simultaneously recorded AFM phase contrast image (**Figure 1b**) reveals an additional contrast on the surface of islands, which may be attributed to the ‘native oxide layer’.

Figure 1 AFM height and corresponding phase images for the as-deposited (**a, b**) and annealed (**c, d**) W films on SiO₂ substrates, respectively. The AFM height and phase contrast images are taken in an area of 2x2 μm^2 . The insets in (**a**) and (**c**) show the height profiles for the island morphologies.

The as-deposited W films are annealed in open air for 60 min at 500 °C. Annealing is found to induce changes in the morphology and thickness of the films. The AFM height image (**Figure 1c**) of the annealed W films reveals roughly triangular island type morphologies with a height of about 6 nm. While the density of the islands increases, the thickness of the islands decreases upon annealing. This could be explained as follows: It is known that when Tammann temperature (~ 599 °C for WO₃) [23] is achieved, the evaporation of metal oxide thin films can be initiated even though the processing temperature is lower than their melting point (~ 1473 °C for WO₃). It is possible that surface oxidation of the as-deposited W films may occur during deposition. Thus, the as-deposited W films with the native oxide layer might become thinner

possibly due to the partial evaporation of the metal oxide layer upon annealing. The AFM phase contrast image (**Figure 1d**) reveals layered-type island morphologies with one single phase contrast, which can indicate a completed oxidation.

The as-deposited and annealed W films are investigated by XPS analysis. The high-resolution XPS spectra (**Figure 2a**) of the as-deposited films reveal four major peaks at 37.99 eV, 35.87 eV, 33.38 eV and 31.2 eV. The typical doublet W 4f peaks of W are clearly visible in the spectra, which are at 33.38 eV and 31.2 eV [9]. The two upper binding energy peaks at 37.99 eV, 35.87 eV can be attributed to WO₃ [24], confirming the existence of WO₃ in the as-deposited films. It is also found that there is a shoulder at upper energy side of each W peak, and the shoulders are related to WO₂ and WO_x [24]. We can conclude that W, WO₃ and sub-stoichiometry tungsten-oxides exist in the as-deposited film. The high-resolution XPS spectra (**Figure 2b**) of the annealed films reveal only two W 4f peaks at 37.97 eV and 35.87 eV, which are assigned to WO₃. After annealing, the metallic W peaks and the shoulder peaks related to WO₂ or W_x completely disappear. This evidence strongly supports the stoichiometry phase evolution of the as-deposited films.

The XPS data of WS₂ films are also captured to analyze surface composition of the WS₂ films. The two peaks of each core level appear due to spin orbital splitting of W 4f (**Figure 2c**) and S 2p (**Figure 2d**) core levels. The peaks at 38.89 eV, 35.40 eV, and 33.2 eV are ascribed to W 5p_{3/2}, W 4f_{5/2}, and W 4f_{7/2} orbitals, respectively. The binding energies for the S 2p_{1/2} and S 2p_{3/2} are located at 164.0 eV and 162.82 eV, respectively. The binding energies of the W and S elements are consistent with the W (+4) and S (-2) oxidation states in WS₂, further confirming the formation of a pure WS₂ phase [25].

Figure 2 High resolution XPS spectra of W 4f core levels of the as-deposited **(a)** and annealed **(b)** W films. High resolution XPS spectra of W 4f **(c)** and S 2p **(d)** core levels of WS₂ films.

To study the effect of annealing on the growth of WS₂ films, we have synthesized WS₂ films by sulfurizing the as-deposited and annealed W films. It is observed that sulfurization of the as-deposited W films leads to thick WS₂ films with poor coverage (**Figure 3a, b**). However, thinner WS₂ films with high coverage are obtained by sulfurization of the annealed W films (**Figure 3c, d**). For clarification, monolayer, few-layers and thick regions of WS₂ films and the substrate are indicated by arrows on the high magnification SEM images (**Figure 3b, d**), as confirmed by Raman and PL spectroscopy. We can conclude that the WS₂ growth is substantially improved by annealing the as-deposited W films before sulfurization.

The growth mechanism of WS₂ films can be explained as follows. The reaction of S vapor with WO₃ islands result in WS₂ nuclei. This reaction includes a transition to WO_(3-x) species along with the subsequent formation of oxisulfides. As the reaction proceeds, a complete

conversion to WS₂ occurs, and thinner WS₂ layers expand from the edges of WS₂ nuclei, in a similar manner as in MoS₂ [26].

Figure 3 Low and high magnification SEM images of WS₂ films obtained by sulfurizing the as-deposited **(a, b)** and annealed **(c, d)** W films, respectively.

We have taken Raman and PL spectra from monolayer and few-layers regions of a WS₂ film as indicated by arrows on the optical microcopy image (**Figure 4a**) of the film. The Raman spectra (**Figure 4b**) of monolayer region of the WS₂ film demonstrate the characteristic in-plane vibrational (E_{2g}^1) mode and the out-of-plane vibrational (A_{1g}) mode at $\sim 350 \text{ cm}^{-1}$ and $\sim 416 \text{ cm}^{-1}$, respectively [27, 28]. The frequency difference between the two modes is found to be $\sim 66 \text{ cm}^{-1}$. These results are consistent with what has been reported for WS₂ in the previous studies [29]. The PL spectra (**Figure 4c**) of monolayer and few-layers regions of the WS₂ film are compared. For monolayer WS₂, the PL peak has a maxima at 1.96 eV, which falls in the range of the reported PL peak positions for monolayer WS₂ [7, 29]. The PL peak of monolayer WS₂ is also higher and sharper than that of the few-layers WS₂, which indicates the presence of a direct band gap in monolayer WS₂ [30]. For few-layers WS₂, the PL peak shifts toward lower photon energy

(~ 1.93 eV), and its intensity decreases dramatically, revealing the thickness dependent PL characteristics of WS₂.

Figure 4 a) Optical microscopy image of a WS₂ film. Monolayer and few-layers regions of the WS₂ film and the substrate are indicated by arrows b) Raman spectra of monolayer region of the WS₂ film. c) PL spectra of monolayer and few-layers regions of the WS₂ film. d) Laser power dependent PL spectra of monolayer region of the WS₂ film.

We have also investigated the effect of laser power on PL spectra of monolayer region of the WS₂ film with increasing laser power ranging from 0.1 mW to 0.5 mW with a step of 0.05 mW and 0.5 mW to 5 mW with a step of 0.5 mW (**Figure 4d**), respectively. It is observed that the PL intensity increases with increasing laser power, consisted with the results reported for MoS₂ [14]. Moreover, the PL peak shifts toward lower photon energy as laser power increases. The shift in the PL peak can be attributed to the defect related optical transition [31]. Thus, we

conclude that laser power must be carefully controlled in the applications of PL spectroscopy in order to draw reliable conclusions about the PL characteristics of TMDs.

Furthermore, by directly heating a WS₂ film in air at 500 °C, we show that the WS₂ film is tend to be etched with a series of the triangular-shaped pits with the same orientations (**Figure 5**). The triangular shape of the pits indicates that the WS₂ film is etched preferentially along a specific crystallographic direction that is parallel to the edges of the pits with a preferential edge termination (W-edge or S-edge) [19]. The etching is likely to be initiated at the intrinsic structural defects in the WS₂ film [19]. We also show that the size of the pits are greatly affected by the WS₂ film thickness, where the sizes of the pits increases with the thickness. The sizes of the triangular pits on a multilayers region (with a thickness of about 10.2 nm) of the WS₂ film (**Figure 5a**) is found to be larger than these of the pits on a few-layers region (with a thickness of about 3.2 nm) of the film (**Figure 5b**). This suggests the thickness dependent behavior of the etching on the WS₂ film [32]. These results are similar to previous reports on the etching of MoS₂ [19, 32, 33].

Figure 5 AFM height images showing the formation of the triangular pits on multilayers **(a)** and few-layers **(b)** regions of a WS₂ film. The AFM images are taken in an area of 2x2 μm^2 . The insets in **(a)** and **(b)** show the height profiles for the triangular pits.

4. Conclusion

In summary, we report a facile method for the large-scale synthesis of atomically thin WS₂ films with strong PL properties via sulfurization of the pre-deposited W films. Thermal annealing of the W films before sulfurization is found to substantially improve the quality of WS₂ films in terms of thickness and uniformity. We also find that WS₂ films show laser power dependent PL characteristics, where the PL peak shifts toward lower photon energy, and its intensity increases with laser power. Furthermore, we introduce a simple method to etch WS₂ films with well-oriented triangular pits with a preferential edge termination. The edge sizes of the pits increase with the thickness of WS₂ films. This etching method enables successful formation and modification of the edge structures of WS₂ films with potentially tunable electronic, optical and magnetic properties, which promise various applications ranging from catalysis to energy harvesting.

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