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Large area synthesis, characterization, and anisotropic etching of two dimensional tungsten disulfide films

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HIGHLIGHTS

- Large-scale synthesis of WS_2 films is achieved via sulfurization of W films.
- Annealing of W films leads to a substantial improvement in the quality of WS_2 films.
- WS_2 films show laser power dependent photoluminescence characteristics.
- WS_2 films are etched with well-oriented triangular pits upon annealing in air.
- Anisotropic oxidative etching is greatly affected by the thickness of WS_2 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.

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.

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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 WS_2 films on insulating substrates. Recently, several studies have reported direct sulfurization of tungsten oxide (WO_3) 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 WS_2 films on silicon dioxide (SiO_2) 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 (MoS_2) 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 WS_2, which is essential to probing the PL characteristics of WS_2.

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 (O_2) environment [19,20]. For example, high density triangular pits with the molybdenum (Mo) or sulfur (S) terminated zigzag edges on the surface of MoS_2 sheets have been obtained upon annealing them in air, which might arise from the anisotropic etching of the active MoS_2 edge sites [19]. Such edge terminated MoS_2 structures find applications in diverse catalytic reactions [21,22]. As mentioned above, most studies so far have focused on the oxidative etching of MoS_2. However, to the best of our knowledge, the etching behavior of WS_2 films has yet to be experimentally studied.

In this study, we demonstrate the large-area synthesis of atomically thin WS_2 films on SiO_2 substrates. Briefly, the W films are deposited on SiO_2 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 WS_2 films. The fundamental morphologic, electronic, optical and chemical properties of the pre-deposited W films and WS_2 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 WS_2 films on laser power. Furthermore, we introduce a simple method to etch WS_2 films with well-oriented triangular-shaped pits by heating them in air.

2. Experimental section

2.1. Materials synthesis

WS_2 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 SiO_2 substrates (300 nm thick SiO_2 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 WS_2 films was performed in the same furnace by simply heating them in air at 500 °C for 45 min.

2.2. Characterization

The morphology of WS_2 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 Kα monochromated X-ray source and a 165-mm mean radius electron energy hemispherical analyzer. The vacuum pressure was kept below 3×10^{-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 (Fig. 1a) of the as-deposited films reveals island type morphology with a height of about 15 nm. The simultaneously recorded AFM phase contrast image (Fig. 1b) reveals an additional contrast on the surface of islands, which may be attributed to the 'native oxide layer'.

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 (Fig. 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 know that when Tammann temperature (~599 °C for WO_3) [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 WO_3). 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 (Fig. 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 (Fig. 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 WO_3 [24], confirming the existence of WO_3 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 WO_2