A systematic study of the synthesis of monolayer tungsten diselenide films on gold foil

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ABSTRACT

We report a systematic study of the synthesis of large-area monolayer WSe\textsubscript{2} on gold foil by controlling the growth temperature and the partial pressure of hydrogen during chemical vapor deposition. The gold surface causes surface-mediated growth to form monolayer WSe\textsubscript{2} films. The amount of the tungsten source is controlled by adjusting the partial pressure of hydrogen, which plays a role in the reduction of WO\textsubscript{3} (solid phase) into WO\textsubscript{3-x} (vapor phase). The coverage of monolayer WSe\textsubscript{2} can be effectively controlled by changing either the partial pressure of hydrogen or the growth temperature at a fixed growth time under an Se-rich atmosphere, resulting in 100% coverage of the WSe\textsubscript{2} film. The crystallinity and thickness uniformity are characterized by Raman spectroscopy, photoluminescence, and transmission electron microscopy. This characterization reveals that the quality of the WSe\textsubscript{2} film is comparable to mechanically-exfoliated monolayer WSe\textsubscript{2} and possesses good thickness uniformity.

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1. Introduction

During the past decade, two-dimensional (2D) materials, including metallic graphene and insulating hexagonal boron nitride, have been investigated due to their fascinating properties [1–4]. However, the lack of semiconducting 2D materials prohibits the complete construction of building blocks in 2D electronic devices. Recently, 2D semiconducting transition metal dichalcogenides (s-TMDs) of the composition \( \text{MX}_2 \) (\( M=\text{Mo}, \text{W}; X=S, \text{Se}, \text{Te} \)) have emerged and have been highlighted due to their various energy band gaps in the range from 1 eV to 2 eV. These band gaps depend on the composition of the metal and chalcogen [4–6]. In addition, it is possible to engineer their electronic structure by tuning the chemical compositions of the metal and chalcogen and by applying strain to individual layers [7–10]. Interestingly, when the number of layers is reduced to one, the optical transition is altered from an indirect transition to a direct transition [11].

Among s-TMDs, tungsten diselenide (WSe\textsubscript{2}) is regarded as one of the most important species in the s-TMDC family. While most s-TMDs show n-type characteristic transport behavior in field-effect transistors (FETs), monolayer WSe\textsubscript{2} exhibits p-type characteristic behavior [12,13]. Moreover, it shows a high quantum yield (1.6 x 10^\textsuperscript{-4}) in photoluminescence (PL) [14], a high absorption coefficient in the visible to infrared range, and the valley-dependent optical Stark effect. These characteristics make monolayer WSe\textsubscript{2} appealing for a wide variety of potential applications including digital electronics, optoelectronics, and valleytronics [15].

In order to utilize WSe\textsubscript{2} for such applications, large-area and high-quality monolayer WSe\textsubscript{2} films are in high demand. So far, several methods have been reported for the production of WSe\textsubscript{2} flakes or films. Mechanical exfoliation from bulk WSe\textsubscript{2} produces...
best quality, few-layer WSe\textsubscript{2} flakes, but it is difficult to obtain monolayer WSe\textsubscript{2} films. Furthermore, the size of WSe\textsubscript{2} is limited to only a few micrometers [16,17]. Chemical exfoliation is another route that can be used to generate few-layer WSe\textsubscript{2} flakes on a larger scale [18]. However, these WSe\textsubscript{2} flakes are severely damaged during processing. Chemical vapor deposition (CVD) is a more promising method to obtain large-area and high-quality WSe\textsubscript{2} films. However, while researchers have looked into different precursor materials, such as tungsten oxide, tungsten hexacarbonyl, pure selenium, and dimethylselenium [19–23], few works have investigated the substrate material [24]. Typically, insulating silicon dioxide or sapphire substrates are used for the synthesis of monolayer WSe\textsubscript{2} films. Although monolayer WSe\textsubscript{2} has been successfully synthesized on these substrates, the growth kinetics of WSe\textsubscript{2} are very sensitive to the CVD conditions, including the distance between the precursors and the substrate or the surface morphology of the substrate, which can result in non-uniform thickness and coverage of the sample [22]. To improve the uniformity and coverage of monolayer WSe\textsubscript{2} films, seeding promoter layers have been introduced [25–28]; however, residues of the seeding promoter layer between WSe\textsubscript{2} flakes hinder film completion. More recently, metallic substrates such as gold and graphene have been proposed for the synthesis of other s-TMDCs such as MoS\textsubscript{2} and WS\textsubscript{2} [29–32]. Gold substrates produce centimeter-scale and continuous monolayer s-TMDCs films with large domain sizes (up to ~100 µm). In particular, as-grown s-TMDCs on metal substrates can be directly applied to hydrogen evolution reactions (HERs) without the need for a tedious transfer process. Moreover, this provides an opportunity to study the intrinsic physical and chemical structures of s-TMDCs via scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). However, researchers have yet to explore whether gold is a good substrate for the synthesis of monolayer WSe\textsubscript{2} films. Moreover, the growth kinetics of WSe\textsubscript{2} on Au foil has not yet been studied.

Here, we report the synthesis of large-area and high-crystalline monolayer WSe\textsubscript{2} on Au foil. In order to understand the growth behavior of WSe\textsubscript{2} on Au foil, a systematic experiment where the CVD parameters were adjusted was carried out. The coverage and domain size of monolayer WSe\textsubscript{2} can be effectively controlled by adjusting either the partial pressure of hydrogen or...
the growth temperature at a fixed growth time. The thickness and coverage uniformity of a monolayer WSe₂ film is confirmed by Raman and photoluminescence mapping techniques. The domain edge size of WSe₂ was observed to exceed ~300 μm; this was confirmed by optical microscopy and selective area diffraction patterns (SAED) obtained via transmission electron microscopy (TEM).

2. Experimental

To synthesize the monolayer WSe₂ film on catalytic Au foil, pure selenium and ammonium metatungstate (AMT, as the tungsten precursor) were introduced into a two-zone furnace CVD system. To make a clean and smooth gold surface, the Au foil (100 μm, 99.99% iNexus Inc.) was annealed at 1038 °C for 2 h in air. This was followed by chemical mechanical polishing with a diluted Au etchant (GE-8148, Transene) in deionized (DI) water. 8 g of ammonium metatungstate hydrate (463922, Sigma Aldrich) was dissolved in 10 ml of DI water (80 wt%). 40 μl of an AMT solution was dropped onto an Al₂O₃ plate (5 × 20 mm) using a micropipette. The resultant Al₂O₃ plate was dried in an oven in order to evaporate the residual water. 0.2 g of selenium was placed in furnace 1 and the AMT-coated Al₂O₃ plate (positioned below the gold foil in the parallel) was placed in furnace 2, as illustrated in Fig. 1(a).

Furnace 2 was first heated to 930 °C at a rate of 50 °C/min under a nitrogen atmosphere at a flow rate of 300 sccm at atmospheric pressure. After reaching 930 °C, the temperature in furnace 1 was elevated to 420 °C at a rate of 84 °C/min to induce selenium-rich conditions. When furnace 1 reached 420 °C, hydrogen gas was introduced for 5 min to grow WSe₂. After growth, the temperatures of both furnaces were cooled rapidly by opening the furnaces.

In order to transfer the monolayer WSe₂ film onto a target substrate, a typical poly(methyl methacrylate) (PMMA) transfer method was utilized. PMMA was used as a protecting layer and was spun onto WSe₂/Au foils. The gold was etched away with an etchant (GE-8148) for 5 h and the PMMA/WSe₂ film was rinsed in DI water several times. The resultant film (PMMA/WSe₂) was transferred onto a target substrate. Finally, the PMMA layer was removed by the application of hot acetone for 10 min.

The surface morphology of the Au foil before and after growth was characterized by optical microscopy (Axio Imager 2, CARL ZEISS). The thickness of WSe₂ on the 300-nm-thick SiO₂/Si substrate was measured by AFM (SPA 400, SEIKO). The optical properties of the WSe₂ film were resolved by Raman spectroscopy and photoluminescence (PL) mapping at an excitation energy of 2.33 eV (NTEGRA-SPECTRA, NT-MDT). Annular dark-field scanning transmission electron microscopy (ADF-STEM) (ARM200F, JEM) and XPS (K-Alpha, THERMO FISHER) were employed to characterize the atomic structure and for elemental analysis. For TEM measurements, a low acceleration voltage (80 kV) was used to avoid damaging samples during observation.

3. Results and discussion

3.1. Synthesis of centimeter-scale monolayer WSe₂ film on gold foil

The CVD system was equipped with two zone furnaces, as illustrated in Fig. 1(a). AMT is converted into a tungsten trioxide...
above 500 °C and is vaporized in the form of WO3(s) after being reduced by hydrogen [33,34]. Eventually, it reacts with selenium to form WSe2 on the catalytic Au substrate. Fig. 1(b) shows an optical image of WSe2 domains on Au foil. Interestingly, WSe2 flakes can be grown across Au grain boundaries, which are indicated by the white dashed line in Fig. 1(b). In the binary phase diagram of Au–Se or Au–W, there is no solubility and no alloy formation of Se or W in with the Au bulk at the growth temperature [35]. This behavior may lead to surface-mediated growth on the Au surface. Fig. 1(c–d) present the Raman mapping image for the E1g phonon mode and the representative Raman spectrum of WSe2, respectively. Triangle islands are clearly observed on the Au foil in the Raman mapping image, indicating that the triangle islands are indeed WSe2 (Fig. 1(c)). The characteristic phonon modes (E1g near 250 cm−1 and A1g near 260 cm−1) of WSe2 are clearly detected [36,37]. To analyze the chemical composition of WSe2, the sample was further characterized by X-ray photoelectron spectroscopy (XPS). Fig. 1(e–f) show the XPS core level spectra of W 4f and Se 1s, respectively. The core levels of W 4f7/2, W 4f5/2, and W 5p3/2 are observed at 32.28, 34.48, and 37.88 eV, respectively (Fig. 1(e)). The core levels of Se 3d5/2 and Se 3d3/2 are also detected at 54.68 and 55.58 eV, respectively (Fig. 1(f)) [22]. In addition, the Au 5p2/3 peak from the gold substrate is shown (at 57 eV) [38]. The stoichiometry between W and Se was determined to be ~1:2. The blue shifts of the W 4f and Se 1s peak positions (~0.5 eV), relative to the reference position, reflect the electron transfer from WSe2 to the Au foil [30]. By optimizing the growth conditions of WSe2, we successfully synthesized a centimeter-scale monolayer WSe2 film. Fig. 1(g) and its inset show an optical image and a graphical schematic of the WSe2 film on Au foil, respectively, showing that the size of the WSe2 film was 4 cm2. Unlike the WSe2 islands on the Au foil in the optical image (Fig. 1(b)), the uniform color contrast over the entire gold surface in Fig. 1(g) implies that the Au surface was fully covered by the monolayer WSe2 film. The fully-covered monolayer WSe2 film was then transferred onto 300-nm-thick SiO2/Si using a conventional PMMA-supported wet-transfer method. Fig. 1(h) shows the optical image of the continuous monolayer WSe2 film. The inset of Fig. 1(h) shows a photograph of the large-area monolayer WSe2 film. To characterize the film’s surface roughness and thickness, the sample was analyzed by atomic force microscopy (AFM); this was conducted in the yellow-square region of Fig. 1(h). A very clean surface with some wrinkles (induced by the transfer process) can be observed in Fig. 1(i) [29,31]. The height profile in the inset of Fig. 1(i) (taken along the white-dashed line) shows that the thickness of the film is around 1 nm, which confirms that our WSe2 film is a monolayer [22].

3.2. Systematic studies of WSe2 growth

To understand how the growth kinetics vary with different CVD parameters, we studied the effect of the growth temperature and the flow rate of hydrogen. Since tungsten trioxide is thermally stable up to ~1400 °C, as opposed to molybdenum trioxide which is only stable to ~800 °C [34], hydrogen is required for the reduction of tungsten trioxide in order to vaporize tungsten oxide: WO3(s) + H2(g) → WO3-s(x)(g) + H2O(g). Fig. 2(a) shows optical images of WSe2 on Au foil as a function of the growth temperature (860, 900, and 930 °C) and the flow rate of hydrogen (2, 5, and 20 sccm) at a fixed growth time (5 min). Triangle-shaped WSe2 domains grew on Au foil at 860 °C with 2 sccm of H2 gas. When the flow rate of hydrogen increased to 20 sccm, the density of WSe2 domains and their coverage were further increased. This can be
attributed to the increase in the tungsten source caused by the additional reduction of tungsten oxide. At a growth temperature of 900 °C and a hydrogen flow of 2 sccm, the domain size of WSe₂ increases and the shape of the WSe₂ domains becomes dendritic. However, the domains return to a triangle shape under a hydrogen flow rate of 5 sccm. 97% coverage of the WSe₂ film was obtained in a hydrogen flow rate of 20 sccm at 900 °C. The observed dendrite formation may be attributed to two factors: 1) the diffusion-limited growth and 2) the trade-off between growth and etching process by hydrogen. For the first scenario, there may be an insufficient amount of the tungsten precursor for growth at high temperatures due to the high desorption rate of the precursor on the surface, which could result in dendrite formation [39]. However, as the amount of the tungsten precursor increases (or as the flow rate of hydrogen increases), triangle-shaped WSe₂ islands were observed; this supports the idea that the growth behavior is changed to attachment-limited growth. For the second scenario, higher flow rates of hydrogen might etch unstable WSe₂ flakes more efficiently during the growth process, which is similar to what occurs with MoS₂ on Au(WSe₂(s) + 2H₂(g) → W(s) + 2H₂Se(g)) [13,30]. This results in a reduction in the growth rate. Therefore, triangle-shaped WSe₂ domains are grown. In our case, these two scenarios could occur simultaneously, affecting the shape of WSe₂ flakes. A similar trend was also observed at a higher growth temperature of 930 °C. The largest domains of WSe₂ exceeded 300 nm in edge length, which is larger than the previously reported values for CVD-grown WSe₂. Optimized conditions for monolayer WSe₂ films in this work were obtained at a growth temperature of 930 °C and an H₂ flow rate of 5 sccm. The color contrast of the gold surface in the optical image is quite uniform, as indicated by the red box in Fig. 2(a). When the hydrogen flow rate was increased to 20 sccm (at 930 °C), we also found that multi-layer WSe₂ islands grew on the monolayer WSe₂ film, as shown in the inset of the bottom-left image in Fig. 4(a). This implies that excess amounts of the tungsten precursor at high temperatures may promote the growth of multi-layer WSe₂. Fig. 4(b–c) summarize the edge length and surface coverage values of WSe₂ domains on Au foil as a function of the growth temperature and hydrogen flow rate. The edge length in the triangular domains strongly depends on the growth temperature. However, the coverage is influenced by both the growth temperature and the hydrogen flow rate. Consequently, the edge length and coverage can be easily controlled by adjusting the growth temperature and hydrogen flow rate.

3.3. Optical properties of monolayer WSe₂ film

To estimate the thickness uniformity, the quality, and the optical properties of the monolayer WSe₂ film, the transferred sample was further characterized by Raman spectroscopy and PL. Fig. 3(a) shows an optical mapping image of the WSe₂ film transferred onto a 300-nm-thick SiO₂/Si substrate. The region between SiO₂ and WSe₂ is clearly distinguished by the optical contrast. Fig. 3(b) shows a Raman mapping image for the E’₂g peak intensity in the region shown in Fig. 3(a). Typically, the E’₂g intensity is proportional to the number of layers [37]. The E’₂g intensity in the mapping image is quite uniform, implying that the number of layers is the same over the whole region. Fig. 3(c) shows the representative Raman spectrum taken from the region highlighted by the yellow circle in Fig. 3(b). The characteristic peaks of the E’₂g (247 cm⁻¹) and A₁g (258 cm⁻¹) modes of WSe₂ are clearly observed. Interestingly, the B₂g mode, which is the Raman active mode of multi-layer WSe₂, is absent from the inset of Fig. 3(c). This confirms that WSe₂ has indeed formed a monolayer, which is in a good agreement with the AFM results. The full width at half maximum (FWHM) of the E’₂g peak is a very useful value that can be used to estimate the quality of WSe₂ samples; i.e., smaller FWHM values indicate superior quality. The FWHM mapping image extracted from Fig. 3(b) is quite uniform, implying that the quality of the monolayer WSe₂ film is the same over the whole region. Furthermore, we carefully compared the FWHM values of mechanically-exfoliated monolayer WSe₂ on SiO₂ (ME), CVD-grown WSe₂ on SiO₂ (WSe₂/SiO₂), and as-grown WSe₂ on Au (WSe₂/Au). These values are plotted in Fig. 3(e). The FWHM of WSe₂/SiO₂ (3.5 cm⁻¹) is comparable to that of ME (3.4 cm⁻¹), indicating that the quality of WSe₂/Au is similar to that of ME. However, the FWHM of WSe₂/Au is -2.5 times larger (8.9 cm⁻¹) than the others. To understand the large FWHM of WSe₂/Au, the peak positions of the samples were further analyzed. While the peak position of E’₂g for both WSe₂/SiO₂ and ME is ~247 cm⁻¹, this is located at ~250 cm⁻¹ for WSe₂/Au. This red-shift in the E’₂g peak position may be due to the compressive strain caused by the Au substrate during the cooling process after growth at high temperature [30]. The thermal expansion coefficient (α) of gold and WSe₂ are 14 × 10⁻⁶/K and 2.42 × 10⁻⁶/K, respectively [40]. Since the growth process is conducted at 900 °C, the compressive strain can be applied to WSe₂ during the cooling process approximated to 0.2% by dT/(α₅Au - α₅WSe₂). PL is more sensitive than Raman spectroscopy for revealing defects or selenium vacancies [113]. Fig. 3(f–g) show the PL mapping image for the exciton emission near 1.66 eV, which corresponds to the optical band gap of WSe₂, and the representative PL spectrum, respectively [41–43]. Typically, monolayer WSe₂ shows a strong PL intensity due to the direct optical transition in the energy band. Alternatively, the PL intensity is weak for multi-layer WSe₂ due to the indirect optical transition. The strong and uniform PL mapping image suggests that only monolayer WSe₂ is grown over the whole region and that the film has reasonable quality.

3.4. Atomic structure analysis

In order to evaluate the atomic structure and chemical composition of monolayer WSe₂, samples were analyzed by TEM. Fig. 4(a) shows a low-magnification TEM image of a triangle-shaped monolayer WSe₂ island on a TEM grid, as indicated by the yellow-dashed line. The crystal structure was characterized by analyzing the selective area electron diffraction (SAED) pattern. Fig. 4(b) shows the SAED patterns that correspond to the numbered regions in Fig. 4(a). The SAED pattern from region 1 shows single-set hexagonal spots, indicating that WSe₂ possesses a hexagonal structure, which is in good agreement with the previous results [44]. The two red circles in (b) are assigned to the (10–10) and (11–20) planes. Interestingly, the hexagonal spots in all of the regions have the same orientation, as indicated by the yellow-dashed lines, implying that the triangle-shaped WSe₂ island is a single crystal. The presence of monolayer WSe₂ was confirmed by counting the folded edge of the layer (Fig. 4(c)). A moiré pattern in the folded monolayer WSe₂ film was observed, which is attributed to the misorientation of the folded monolayer film. A misoriented angle of 31.7° was confirmed by the fast Fourier transform (FFT) image shown in the inset of Fig. 4(c). The atomic structure was further characterized by Annular Dark Field (ADF) -STEM. Fig. 4(d) displays an ADF-STEM image of monolayer WSe₂. Typically, the intensity of an atom in an ADF-STEM image is proportional to its atomic number. Therefore, bright tungsten atoms (purple) and dark selenium atoms (yellow) are easily distinguished. A well-defined hexagonal structure, consisting of tungsten and selenium atoms,
appears to be present. This proves that WSe₂ was successfully synthesized. Moreover, the d-spacings of the (10\text{-}10) and (11\text{-}20) planes were determined to be 0.28 and 0.16 nm, respectively, which are in good agreement with a previous report [45]. Fig. 4(e) presents the EDX spectrum of WSe₂, showing that the stoichiometry of tungsten and selenium is almost 1:2. As a consequence, we were able to grow high-quality monolayer WSe₂ with our approach.

4. Conclusion

In summary, we conducted a systematic study focusing on the synthesis of monolayer WSe₂ films on Au foil by controlling the CVD parameters. The absence of solubility and alloy formation of tungsten and selenium in/with the gold bulk at high growth temperatures leads to surface-mediated growth, resulting in the formation of a monolayer WSe₂ film. The growth kinetics were controlled by adjusting the hydrogen flow rate and growth temperature. While the lateral grain size of WSe₂ increased with increasing growth temperature, the surface coverage was strongly affected by both the hydrogen flow rate and growth temperature. Under optimum processing conditions, a surface coverage of 100% was achieved. Optical and TEM characterizations suggest that the quality of the monolayer WSe₂ film is comparable to mechanically-exfoliated monolayer WSe₂ and its thickness is highly uniform over the whole region. Our approach not only promotes real applications of monolayer WSe₂ films, but also should serve to catalyze the development of new synthesis methods for other s-TMDs.

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References
