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Controlled synthesis of highly crystalline CVD-derived monolayer $MoSe_2$ and shape evolution mechanism

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ABSTRACT

Ultrathin two-dimensional transition metal dichalcogenides (TMDCs) have shown significant potential for diverse applications in semiconductor industry. The controlled synthesis of TMDCs is a prerequisite for its potential application. Unfortunately, controllable synthesis is still a great challenge. Here, we report an experimental method to induce a broad range of morphologies in highly crystalline, monolayer $MoSe_2$ thin films by H_2 content engineering. A growth mechanism was proposed to clarify the formation process for variable-shaped $MoSe_2$ crystals. We attributed the evolution in morphologies to a result of the variable growth rates of two types of terminations that occur under different growth conditions. Our work provides a foundation for the controlled synthesis of $MoSe_2$, reveals the shape evolution of CVD-derived $MoSe_2$ and broadens the application range based on its shape-dependent properties.

1. Introduction

Emerging 2D semiconducting transition metal dichalcogenides (TMDCs) have become highly sought for their specific application in semiconductor industry [1]. Practical TMDC application requires controllable synthesis of high quality material, including the control of size, shape, and crystallinity. Much of graphene- and MoS_2-based research has focused on morphological control because of their mechanical, chemical catalytic activity, and magnetic properties are highly shape dependent [2,3]. Since other TMDCs have similar characteristics, morphological control during TMDC synthesis is important.

Molybdenum diselenide ($MoSe_2$) has gained attention due to its unique structure and remarkable physical and chemical properties. It has been highly regarded in its potential application in electronics [4] and optoelectronics [5]. Chemical vapor deposition (CVD) has been widely used to synthesize thin films [6,7]. Through CVD method, many $MoSe_2$ shapes have been synthesized including triangles [5], hexagons [8] and snowflake-like morphologies [9]. Unfortunately, a reliable, uniform method to induce specific shapes in $MoSe_2$ thin films is lacking. More importantly, the underlying mechanism behind the formation of different shaped-$MoSe_2$ has not been clarified.

Controlled morphology in thin film synthesis relies on understanding multiple ongoing processes during deposition and growth [2]. It is important to uncover the influence of processing parameters on CVD-derived $MoSe_2$ growth. After testing various processing parameters, we found that the shape of $MoSe_2$ domains are highly dependent upon the H_2 content used during growth process. Slight variation in H_2 content introduced a range of $MoSe_2$ shapes without degrading crystallinity. They were successively formed into hexagon, truncated triangle and triangle. To further investigate film quality, we fabricated field-effect transistors (FETs) based on as-grown $MoSe_2$ samples. Growth mechanisms were proposed to explain the various $MoSe_2$ morphologies film formation process. Our results provide groundwork for controllable synthesis of $MoSe_2$ films, reveal the shape evolution of CVD-derived $MoSe_2$ and broaden the application range based on its shape-dependent properties.

2. Experimental methods

During CVD-derived $MoSe_2$ growth process, 100 mg of Se and 50 mg of MoO_3 were used as precursors to synthesize $MoSe_2$ in a two-temperature zone furnace. A mixture of Ar and H_2 was used as carrier gas and reducing atmosphere. The H_2 content during $MoSe_2$ growth ranged between $49Ar/1H_2$ to $42Ar/8H_2$. The MoO_3 was heated to 750 °C, and maintained for 15 min before naturally cooling down. The Se was kept at 300 °C throughout synthesis process. The AFM, SEM, OM, Raman spectrum, PL spectrum and

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HRTEM were performed to investigate shape evolution and structural properties of as-grown $MoSe_2$ crystals. 20 nm of Ti and 100 nm of Au were deposited as electrodes of devices.

3. Results and discussion

The $MoSe_2$ crystals were grown and growth patterns over different H_2 contents were measured (Fig. 1). When H_2 content was set to $49Ar/1H_2$, only white rhomboidal-shaped nanosheets covered the substrate (Fig. 1a). As H_2 content was gradually increased, the color of the rhomboidal nanosheet transformed into violet (Fig. 1b). With increased H_2 content, the $MoSe_2$ domain shape transformed from hexagonal shapes into truncated triangle, and finally into sharp-edged triangle (Fig. 1c–e). By further increasing H_2 content, the $MoSe_2$ film morphology maintained triangle shape but with decreasing size (Fig. 1f–h).

To confirm the composition and crystal quality of samples depicted in Fig. 1, we performed Raman spectroscopy characterization (Fig. 2). The white rhomboidal (WR) nanosheets showed three characteristic peaks located at 347 cm^{-1}, 364 cm^{-1} and 748 cm^{-1} that could be assigned to MoO_2 [10]. Compared to the WR nanosheets, violet rhomboidal (VR) nanosheets showed two additional peaks, located at 240 cm^{-1} and 287 cm^{-1}, which corresponded to the A_{1g} mode and E^1_{2g} mode of $MoSe_2$ [4]. Our Raman results confirmed that the VR-shaped nanosheets are $MoO_2/MoSe_2$ complex. The characteristic peaks of hexagon (Hex), truncated triangle (Tru) and triangle (Tri) nanosheets located at 241 cm^{-1} and 287 cm^{-1} were assigned to $MoSe_2$ and no characteristic peaks corresponding to MoO_2 appeared in these three Raman spectra. The upshift of A_{1g} mode in $MoSe_2$ Raman spectra may be attributed to the tensile strain release of $MoSe_2$ on MoO_2 [10]. The uniformity of Raman intensity maps in A_{1g} mode further confirmed high homogeneity of these three samples (Fig. 2c–e). The photoluminescence (PL) spectra of these $MoSe_2$ crystals (Fig. 2b) showed a similar spectral profile with a prominent emission peak at ~820 nm, confirming its direct bandgap characteristics [5].

The AFM images and height profiles of Hex-, Tru- and Tri-shaped $MoSe_2$ crystals were measured (Fig. 3a–c). All three images showed homogeneous color contrast and a step height of ~0.7 nm, confirming a characteristic monolayer. The HRTEM images and corresponding selected area electron diffraction (SAED) patterns confirmed single crystalline nature of samples with hexagonal structure (Fig. 3d–f).

We also fabricated back-gated FETs based on as-grown $MoSe_2$ samples (Fig. 4a–d). The corresponding transfer characteristics of these three samples were shown in Fig. 4e. From the transfer characteristics data, we can extract a mobility of ~16, ~18, ~21 $cm^2 V^{-1} s^{-1}$ for Hex-, Tru- and Tri-shaped $MoSe_2$ using the expression: $\mu = \left(\frac{dI_{ds}}{dV_{bg}}\right) \times \left[\frac{L}{WCV_{ds}}\right]$, where L = 1.5 μm, W = 3 μm, and C = 1.15 × 10^{-8} Fμm^{-2} are the channel length, width and the gate capacitance per unit area (300 nm SiO_2), respectively. The mobility of three samples was comparable to those of exfoliated monolayer $MoSe_2$ [11], confirming a highly crystalline film quality.

Based on the principles of crystal growth, the fastest growing faces become smaller and finally disappear, while the slowest growing faces (i.e. the most stable and energetically favored) be left. It has been reported that the most stable and energetically favored edge structures of MoS_2 are Mo zigzag (Mo-zz) terminations and S zigzag (S-zz) terminations [12], and Mo-zz terminations have sharper, straighter edges than S-zz terminations [13]. Since $MoSe_2$ possesses same crystal structure, it should follow similar principle. The difference between Mo-zz terminations and Se-zz terminations may result in different chemical activity, and further lead to their diverse growth rate under various growth conditions. The H_2 introduced into process may play a role as catalyst. Increasing H_2 content would accelerate the formation of MoO_{3-x}, while excessive H_2 may further reduce MoO_{3-x} to Mo (the detailed analysis can be found in [4]). We assume the growth of $MoSe_2$ crystals begins from a hexagonal nucleus with Mo-zz terminations and Se-zz terminations. When H_2 content was low ($\leq 48Ar/2H_2$), the MoO_3 reduction was not sufficient. This resulted in the WR nanosheets (MoO_2) and VR nanosheets ($MoO_2/MoSe_2$) observed in Fig. 1a and b. When H_2 content increased to $47Ar/3H_2$, the growth rates of Mo-zz terminations and Se-zz terminations were similar, resulting in Hex crystals alternating between curved (Se-zz) and sharp (Mo-zz) edges (Fig. 3a). Along the increased H_2

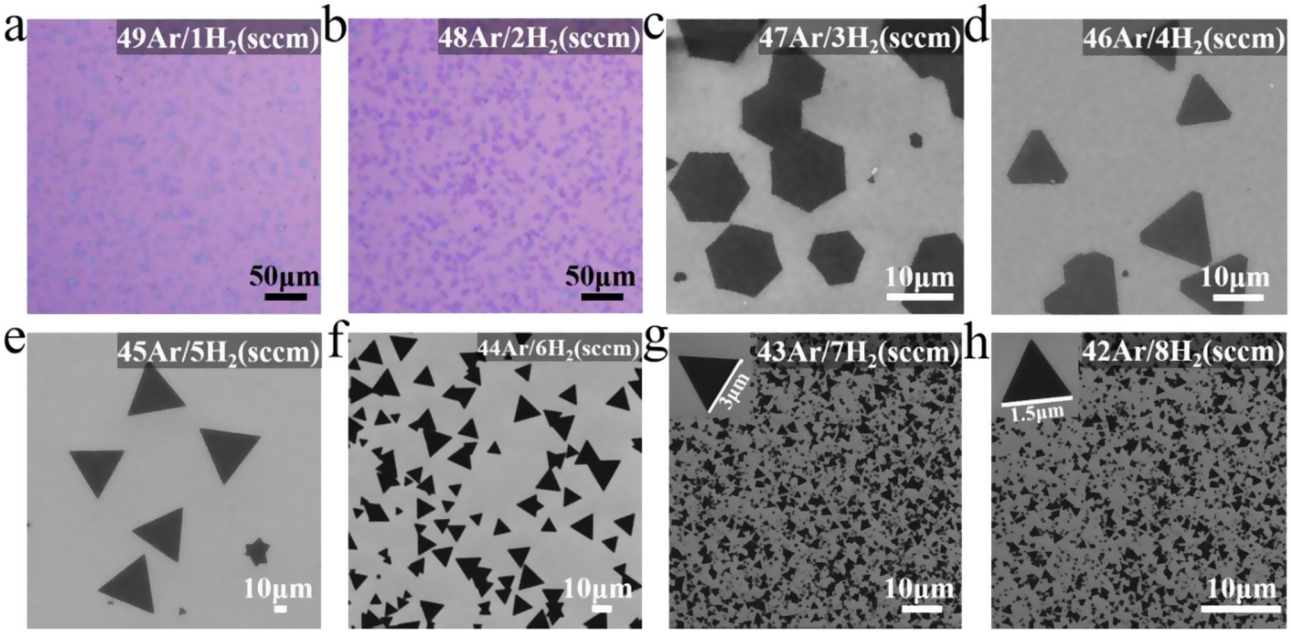

Fig. 1. H_2 content morphological effects in CVD-based $MoSe_2$ nanosheets. (a and b) Optical microscopy images of $MoSe_2$ morphology under low H_2 content. (c–h) SEM images of $MoSe_2$ films grown in an increasing H_2 gradient.