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Research paper

A facile way to control phase of tin selenide flakes by chemical vapor deposition

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ABSTRACT

Although two-dimensional (2D) tin selenides are attracting intense attentions, studies on its phase transition are still relatively few. Here we report a facile way to control the phase growth of tin selenide flakes on mica and SiO_2/Si by only adjusting nominal Sn:Se ratio, which refers to the amount of loaded SnO_2 and Se precursors. High normal Sn:Se ratio induced SnSe flakes, conversely $SnSe_2$ flakes formed. It could be used as a practical guide to selectively synthesize pure phase of single crystalline 2D layered chalcogenide materials similar to tin selenides.

1. Introduction

Two-dimensional (2D) layered chalcogenide materials (LCMs) have attracted tremendous attention in modern materials science due to their unique properties and diverse applications in electronics, optoelectronics and thermoelectronics [1–5]. As a member of the big 2D family, tin chalcogenides have become a subject of intense researches [6]. As the important member of IVA-VIA group, tin selenides may cater well to the industrial demands for next-generation electronics and optoelectronics. Bulk SnSe is a p-type semiconductor with an indirect band gap of ~0.9 eV and a direct band gap of ~1.3 eV. However, 2D SnSe nanostructures are expected to possess a tunable band gap in the range of 1.0–1.5 eV which falls within the optimal bandgap for solar cells, rendering it great potential applications in the fields of photovoltaics and optoelectronics [6–9]. On the other hand, $SnSe_2$ is an intrinsically n-type semiconductor with a bandgap of ~1.0 eV [10], whose potential applications include lithium ion batteries [11], phase change memory [12], and high drive current FET [13,14]. The high work function (~5.3 eV) of $SnSe_2$ makes it easy to form an Ohmic contact with metal, which is very important for the fabrication of devices [14].

Chemical vapor deposition (CVD) has been proposed as a successful method to synthesize high quality 2D LCMs including tin chalcogenides. Considering the high sensitivity of different phases to the growth conditions, it is very difficult to selectively synthesize pure phase of tin selenides. The phase transition of tin sulfides was realized by addition of H_2 [15] and regulating the temperature [16] by CVD. Boscher et al. [17] obtained SnSe and $SnSe_2$ thin films on glass via atmospheric pressure (AP) CVD. Huang et al. [18] also studied the effect of growth temperature on the phase of the products. The SnSe and $SnSe_2$ hierarchical nanostructures were controllable synthetized by a facile solvothermal method with the help of surfactant [19]. From above experiments [17,18], the temperature plays an important role on the phase of tin selenide films. However, the critical temperature of the tin selenide phase transition varied from 650 °C [17] to 510 °C [18]. Recently, SnSe flakes were obtain in lower temperature (340–390 °C) [20]. The SnSe phase formed in 340–650 °C, so the substrate temperature maybe is not the key role on the phase transition of tin selenide.

In the previous works [17,18], the substrate temperature changed the reactive Sn:Se ratio, as a result the phase transition happened. In this letter we selected a proper proportion of SnO_2 and Se precursors to synthesize 2D SnSe or $SnSe_2$ flakes with lateral sizes of over ten micrometers under the same temperature by APCVD. The reactive Sn:Se ratio is controlled by the proportion of loaded SnO_2 and Se precursors named as the term of "nominal Sn: Se ratio". Our experiments show the phase of tin selenides changes from SnSe to $SnSe_2$ by simply increasing the weight of Se powder. That is, we could obtain the selected phase of tin selenides by using appropriate ratio of SnO_2 and Se precursors. Meanwhile, the phase transition was realized on various substrate such as mica and SiO_2/Si. Systematic investigation shows the normal Sn: Se ratio plays a crucial role on the phase controlled growth of tin selenides.

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2. Experimental procedure

2.1. Synthesis of 2D crystals on various substrates

The synthesis strategy of 2D tin selenide flakes is schematically illustrated in Fig. 1a. The experiments proceeded in a furnace equipped with a quartz tube (2 in. in diameter), which includes two heating zone: high temperature (HT) zone and low temperature (LT) zone. Typically, SnO_2 powder (99.9%, Alfa Aesar) of 20 mg loaded in an alumina boat was placed in the center of the HT zone, and another alumina boat filled with Se powder (>99%, Alfa Aesar) was mounted about ~13 cm upstream from the SnO_2 powder. The clean substrates (mica, SiO_2/Si) were placed in the LT zone. Then, the tube was pumped to the pressure down to 1 Pa to remove the air. After that, the tube was filled with a high-purity argon (Ar) gas to reach an atmospheric pressure. Next, the HT zone and LT zone were heated to 850 °C and 530 °C respectively. The temperature of Se powder was ~350 °C. After 10 min of growth, the furnace is left to cool naturally to room temperature. During the whole growth process, Ar flow rate of 20 sccm was used as the carrier gas.

2.2. Sample characterizations

The fundamental structural and componential properties of the products were comprehensively investigated using optical microscope (OM), scanning electron microscope (SEM) with electron energy dispersive X-ray spectroscopy (EDX), X-ray diffractometer (XRD), Raman spectroscopy and an atomic force microscope (AFM). The morphologies of experimental products were characterized by an OM (Nikon, LV-UEPI), an SEM (FEI, NOVA NANOSEM 450) and AFM (Bruker, Icon). EDX (Oxford Instrument) attached to the SEM and XRD (Bruker D8) with Cu Kα radiation (λ = 1.5418 Å), were used to identify the composition of experimental products. The thickness was measured by the AFM. Raman Spectra were collected on a Renishaw confocal Raman microscope with a 488 nm laser.

3. Results and discussions

In the first experiment, the mica substrates were used to grow tin selenides. After 10 min of growth, we could obtain tin selenides flakes, whose OM images are shown in Fig. 1b–e. The weight of Se powder is changed from 50 mg to 500 mg. It is worth noting that the weight of SnO_2 powder is always 20 mg in our experiments. We observe the shape of final products transfer from square (Fig. 1b) to truncated triangle (Fig. 1d and e) with a transit phase (Fig. 1c). According to previous works [18], the square flakes are SnSe and the truncated triangle flakes are $SnSe_2$. That means we have realized the phase controlled growth of 2D tin selenides by adjusting the nominal Sn:Se ratio. When the Se powder (50 mg) was insufficient, the final products were almost SnSe flakes. If the Se (300 mg or 500 mg) powder is sufficient, the final products tended to be present in the form of $SnSe_2$. When the weight of the Se powder increased from 50 mg to 300 mg, the SnSe flakes transformed to $SnSe_2$ flakes by reducing the nominal Sn:Se ratio.

In order to confirm influence of the substrate type on phase transition, we introduced the SiO_2/Si as substrate to fabricate tin selenide flakes. The phase transition induced by nominal Sn:Se ratio also appeared on the SiO_2/Si substrates, except the growth orientation of the flakes was distinct from mica. Fig. 2a and b shows the typical SEM images of SnSe (50 mg Se powder) and $SnSe_2$ (300 mg Se powder) flakes on SiO_2/Si substrates, respectively. We could find that the SnSe flakes grew obliquely (indicated

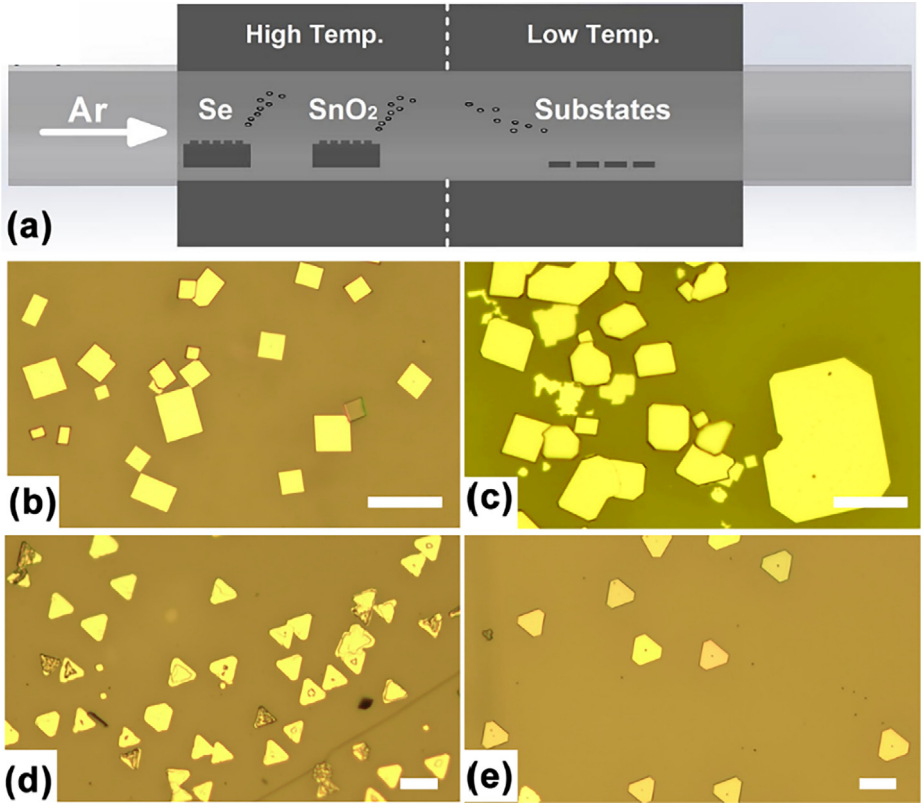

Fig. 1. The experimental setting and OM images of tin selenides flakes on mica substrates. (a) The schematic of the experimental setup. (b, c, d, f) Morphological images of the final products grown with 50, 150, 300, 500 mg Se powder respectively. Scale bar: 20 μm.