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Effects of Ge- and Sb-doping and annealing on the tunable bandgaps of SnS films

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ABSTRACT

SnS, Ge- and Sb-doped SnS films with single orthorhombic SnS phase were fabricated via solvothermal routes and subsequent spin-coating, respectively. The substitution solubilities of Ge and Sb in SnS are about 6 and 5 at.%, respectively. The bandgaps of Ge- and Sb-doped SnS films can be tuned in the ranges of 1.25–1.35 and 1.30–1.39 eV, respectively. The possible mechanisms for the tunable bandgaps of Ge- and Sb-doped SnS films are discussed. For the Ge- and Sb-doped SnS films subjected to annealing at 200–350 °C in N_2, the bandgaps of 200 °C-annealed films remain unchanged, while those of 300 °C- and 350 °C-annealed films decrease with the annealing temperature because of the evaporation of Ge and Sb respectively.

1. Introduction

SnS exhibits p-type electrical conduction and high absorption coefficient with a direct bandgap around 1.3 eV [1]. It is a promising alternative to the lead chalcogenides in the photovoltaic (PV) applications because of the environmental sustainability. It also has potential applications in field effect transistor, electrochemical capacitors, and photocatalysts [2]. To maximize the conversion efficiency, the band gap of an ideal PV absorber layer should be around 1.3 eV for the single-junction cell and 1.0–1.9 eV for the two-junction cell [3,4]. These requirements can be achieved by tunning the bandgaps of PV materials via adjusting their size or chemical compositions [5–10]. However, it is difficult to tune the bandgaps of SnSe and SnS nanocrystals through control of the nanocrystal's size within the quantum confined regime because of their layer crystal structure which readily results in the formation of the sheet-like morphology instead of 0-dimensional particles [6,7,11,12].

Recently, the tunable bandgaps of Sb- and Bi-doped SnS films were reported [13,14], showing that the bandgap first decreases and then increases with the dopant concentration. However, our previous studies showed that the bandgap of $Sn_{1-x}Sb_xSe$ nanocrystals increases with the Sb concentration (x) in the range of 0.1–0.2 [15]. Therefore, further exploration on the synthesis and characterization of cation-doped SnS is still attractive. In addition, Sb is a potential n-type dopant. Low and high concentrations of Sb dopant may tune the p-type SnS to the intrinsic and n-type ones respectively, permitting the construction of p–i–n structure and p–n homojunction for improving the efficiency of SnS-based solar cells [16]. The Sb-doped SnS(6% Sb) films with low resistivity (about 2.6×10^{-2} Ω-cm) and high absorption coefficient may also have potential applications in optoelectronic devices [14]. In the present study, the tunable bandgaps and annealing effect of Ge- and Sb-doped SnS films were explored.

2. Experimental

For Ge-doped SnS samples, a mixture of $SnCl_2 \cdot 2H_2O$ (1.0 mmol for undoped SnS and 0.8 mmol for Ge-doped SnS), GeI_4 (x mmol, x = 0.0, 0.4, 0.6, 0.8), CH_4N_2S (1.0 mmol), and oleylamine (OLA) (30 ml) was stirred for 2 h and then heated at 230–270 °C in N_2 for 12 h. For Sb-doped samples, $SnCl_2 \cdot 2H_2O$ ((1 − x) mmol, x = 0.00, 0.02, 0.04, 0.06), $Na_2S \cdot 9H_2O$ (1 mmol), and $SbCl_3$ (x mmol) powders were dissolved in ethylene glycol (EG) (32 ml) and then stirred for 2 h. The solutions were loaded into a 40 ml teflon-lined stainless steel autoclave and then heated at 160–180 °C for 12–24 h followed by slow cooling to room temperature, respectively. The products synthesized in EG and OLA were sequentially washed in deionized water (12 ml) and ethanol (12 ml), and in hexane (12 ml) and ethanol (12 ml), respectively, for several times. For each wash, the dissoluble by-product was separated by centrifugation at 3500 rpm for 3 min. The whole process repeated for six times. Finally, the powder was dried at about 50 °C. The films were fabricated on the glasses by spin-coating at room temperature and then annealed in N_2 at 200–400 °C for 20 min. The phases in the samples were analyzed using a Rigaku MultiFlex X-ray diffractometer (XRD) with CuK_α radiation. The scanning speed was 4°/min. The microstructure

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and chemical compositions of samples were analyzed using scanning electron microscopy (SEM, Zeiss Auriga 35–50) operated at 5 kV and transmission electron microscopy (TEM, JEOL JEM-2100 F) operated at 200 kV, and energy dispersive spectroscopy (EDS, Bruker QUANTAX 200)/SEM operated at 10 kV. The optical properties of samples were characterized using UV–vis absorption spectroscopy (Hitachi, U-4100) with the scanning speed of 300 nm/min in the range of 400–2000 nm.

3. Results and discussion

3.1. Synthesis of Ge- and Sb-doped SnS films

The synthesized SnS and $Sn_{0.8}Ge_xS$ (x = 0.4, 0.6, 0.8) powders are of orthorhombic SnS phase (JCPDS 039-0354) as shown in Fig. 1, where the XRD peaks of Ge-doped powders shift to higher diffraction angles as compared with that of the SnS powder. From EDS/SEM analyses, the chemical compositions of SnS and the three Ge-doped SnS powders are Sn:Ge:S = 52.7:0.0:47.3, 49.5:2.3:48.2, 46.7:4.7:48.7, and 45.8:6.2:48.0 in atomic% (at.%), respectively, hereafter these samples are referred as SnS, SnS(2.3% Ge), SnS(4.7% Ge), and SnS(6.2% Ge), correspondingly. The substitution of Ge for Sn in SnS reduces its lattice constant because the ion radius of Ge^{2+}, 0.073 nm, is smaller than that of Sn^{2+}, 0.093 nm. The substitution solubility of Ge in the SnS lattice may be about 6 at.% because when the dopant concentration exceeded this limit, e.g. the $Sn_{0.8}Ge_{1.0}S$ sample, only a trace amount of the powder could be synthesized.

The $Sn_{1-x}Sb_xS$ (x = 0.00, 0.02, 0.04, 0.06, 0.08, 0.10) powders synthesized in an autoclave are of orthorhombic SnS (JCPDS 039-0354) as shown in Fig. 2, where the XRD peaks of Sb-doped powders shift to higher diffraction angles as compared with that of the SnS sample. However, for the $Sn_{1-x}Sb_xS$ (x = 0.08, 0.10) powders no further shift in their XRD peaks is observed, revealing that there may be a limit in the substitution solubility of Sb in the SnS lattice. Meanwhile, no XRD peaks of impurity phases are observed. From EDS/SEM analyses, the chemical compositions of SnS and the three Sb-doped SnS powders are Sn:Sb:S = 52.4:0.0:47.6, 47.5:3.8:48.7, 47.3:4.7:48.0, and 46.6:5.4:48.0 in at.%, respectively, hereafter these samples are referred as SnS, SnS(3.8% Sb), SnS(4.7% Sb), and SnS(5.4% Sb), correspondingly. The substitution of Sb for Sn reduces the lattice constant of SnS because the ion radius of Sb^{3+}, 0.076 nm, is smaller than that of Sn^{2+}, 0.093 nm.

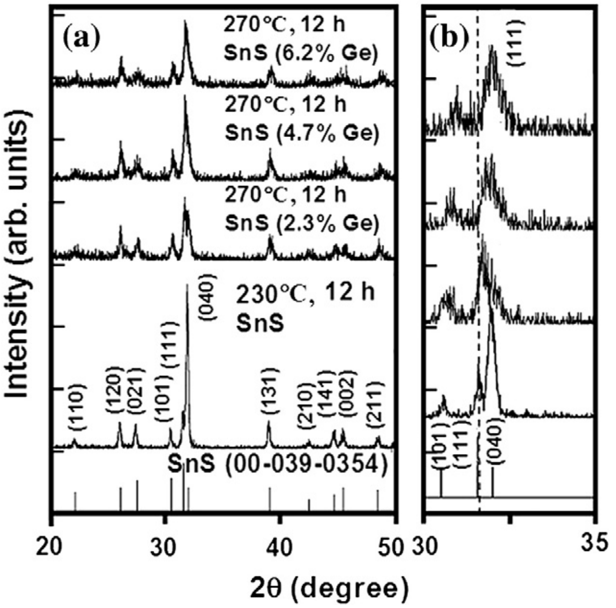

Fig. 1. (a) XRD patterns and (b) expanded (111) peaks of SnS and Ge-doped SnS samples synthesized in OLA at 230 and 270 °C for 12 h, respectively.

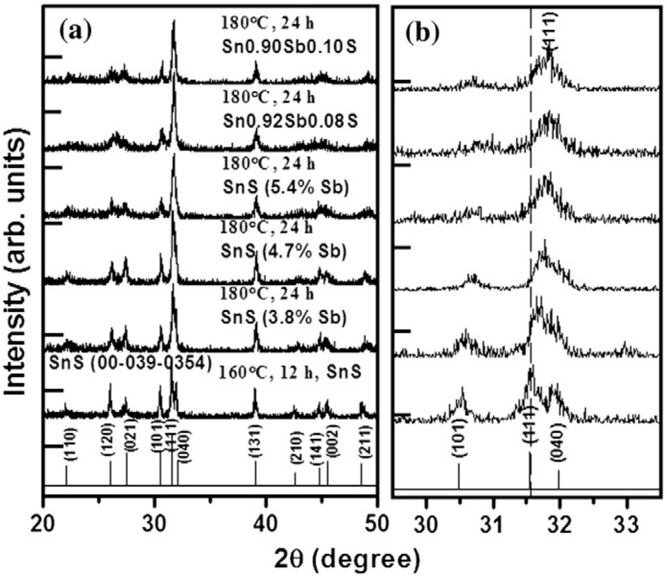

Fig. 2. (a) XRD patterns and (b) expanded (111) peaks of Sb-doped SnS samples synthesized in an autoclave at 180 °C for 12–24 h, respectively.

In the present study, the substitution solubility of Sb in SnS is about 5 at.% which is comparable to a previous report [16]. SnS, Ge- and Sb-doped SnS films were fabricated on the glass substrates by spin-coating at room temperature. These films are composed of nanosheets with 20–50 nm in thickness.

3.2. Tunable bandgaps of Ge- and Sb-doped SnS films

As shown in Fig. 3, the direct bandgaps of Ge- and Sb-doped SnS films are in the range of 1.25–1.35 and 1.30–1.39 eV, respectively, which are obtained from their reflectance spectra by performing the Kubelka–Munk transformation [17,18], showing that the direct bandgaps increase with the Ge and Sb concentrations, respectively. The similar trend was also observed in the $Sn_{1-x}Sb_xSe$ [15] and $Sn_xGe_{1-x}Se$ alloys [19]. The direct bandgaps of SnS, GeS, and Sb_2S_3 are about 1.3, 1.6, and 1.5–1.6 eV, respectively [1,10,20]. One of the causes for the blueshift of the bandgaps of Ge- and Sb-doped SnS films may be due to the hybridization of conduction and valence bands of SnS and GeS, and SnS and Sb_2S_3, respectively. This phenomenon is similar to that observed in $(Ga_xIn_{1-x})_2O_3$ [21] and SnS_xSe_{1-x} [8]. Besides, from XRD analysis the volumetric strains, ΔV/V (V: the volume of SnS unit cell, ΔV: the difference in the volume between SnS and doped SnS unit cells), for SnS(2.3% Ge), SnS(4.7% Ge), and SnS(6.2% Ge) are −1.32, −2.24, and −3.15%, respectively, while those for SnS(3.8% Sb), SnS(4.7% Sb), and SnS(5.4% Sb) are −0.91, −1.38, and −1.73%, respectively. It has been reported that the compressive strain in the films or crystals can induce an increase in the bandgap [22,23].

3.3. Annealing effects on the morphology, chemical compositions, and bandgaps of SnS(6.2% Ge) and SnS(4.7% Sb) films

For the SnS(6.2% Ge) and SnS(4.7% Sb) films subjected to annealing at 200–350 °C, the concentrations of Ge, Sb, and S decreased with the annealing temperature. For example, the concentrations of Ge, Sb, and S decreased from 6.3, 4.3, and 46.8% for 200 °C-annealed films to 1.9, 1.7, and 43.7% for 350 °C-annealed ones, respectively. Meanwhile, severe pitting appeared in the surface of the films annealed at 300–350 °C as shown in Fig. 4. We conceive that during annealing the S atoms in SnS may react with the residual O_2 in N_2 to form SO_2, and then SO_2 readily evaporates together with Ge or Sb because its boiling point is −10 °C.