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Comparison the effects of Se and Te inclusion on the physical and electrochemical properties of SnS thin films

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ABSTRACT

In this research, materials containing pure SnS, Se-incorporation SnS, and Te-incorporation SnS thin films were electrochemically deposited on fluorine-doped tin oxide (FTO) glass substrates using an aqueous solution. Deposition parameters including bath temperature, deposition time, deposition potential, and the pH of the solution have been kept constant for all samples. The synthesized thin films were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), X-ray photoelectron spectroscopy (XPS), electrochemical impedance spectroscopy (EIS), room temperature photoluminescence (PL), and UV–vis spectroscopy. The XRD patterns showed that the crystalline quality of SnS thin film was improved after Se-incorporation; while it was decreased after Te-incorporation. Since Se^{2-} and Te^{2-} have greater ionic radii than S^{2-}, the inter-planar space and the unit cell volume of SnS have been increased after Se- and Te-incorporation. In addition, the morphology of pure SnS thin film was changed from grain-like to columnar sheets-like due to Se- and Te-incorporation. PL spectra showed four peaks including a blue emission peak at 478 nm, a green emission peak at 557 nm, an orange emission peak at 602 nm, and an IR peak at 833 nm, which correspond to Sn vacancies, Sn interstitials, S interstitials, and band-to-band transition, respectively. Moreover, the PL peaks spectra showed a red-shift due to Se- and Te-incorporation. UV–vis spectroscopy analysis exhibited that the absorption properties of SnS were improved because of Se- and Te-incorporation. Therefore, the SnS thin films incorporation with Se and Te impurities were appropriate to be used as an absorber layer in solar cells. The band gap energy (E_g) of pure SnS is decreased from 1.5 ± 0.1 eV to 1.4 ± 0.1 eV due to Se- and Te-incorporation. The Mott-Schottky analysis showed that the conductivity of all deposited samples was *p-type*. The results of EIS demonstrated that the charge transfer resistance (R_{ct}) of the pure SnS film was decreased sharply after incorporation. Also, the photoelectrochemical cell (PEC) performance of pure SnS was improved because of incorporation.

1. Introduction

Tin sulfide (SnS) has been recently the subject of intense research. Since cadmium is a toxic element and gallium, indium, and tellurium are scarce elements, SnS has been introduced as an alternative for CdTe and $Cu(In,Ga)Se_2$ based solar cells [1]. Among IV-VI semiconductors, SnS is an attractive compound owing to its optical and semiconducting properties. SnS is a layered semiconductor with a strong covalent bond between Sn and S. The interlayer space of SnS lattice bounded with Van der Waal's force, which provides suitable sites for incorporating elements [2,3]. SnS is a non-toxic material made from cheap and abundant elements. SnS can be used as a solar absorber, IR detector, and high-efficiency photovoltaic materials [2]. In addition, SnS has *p-type* conductivity, and the direct energy band gap of SnS is 1.3–1.5 eV, which is close to the optimum value for solar cell applications [3,4]. The absorption coefficient (α) of SnS is higher than 10^4 cm^{-1} and the carrier concentration is about 10^{15}–10^{18} which can be controlled by incorporation [5]. SnS has a high carrier mobility of 90 $cm^2/V\,s$ [6]. Because of the high absorption properties of SnS, the SnS quantum-dot is used as a cathode in dye-sensitized solar cells in the visible range [7].

The physical and electrical properties of SnS can be improved by incorporation. So far, much research has been done on the effect of incorporation on the structural, optical, and photovoltaic properties of SnS. The effect of indium alloying was investigated by Kumar et al., who reported the reduced crystalline quality of SnS and a decrease in energy band gap from 1.60 eV to 1.43 eV after In-alloying [8]. Kumar et al. indicated that the optimum amount of Cu-alloying in SnS structure was 8%, suggesting the smallest resistivity and the highest carriers mobility [9]. Reddy et al. studied the Cu-alloyed SnS thin films and found that the Cu-alloying up to 4% leads to a reduction in the energy

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band gap and an improvement in the crystalline quality of SnS [10]. The effect of Cu on the SnS properties is also investigated by Wang et al., who concluded that the full width at half maximum (FWHM) was decreased and the hole mobility and carrier concentration can be controlled by Cu-alloying [11]. In another research, the effect of Ag on the physical properties of SnS thin films was examined. The X-ray diffraction (XRD) results showed that the crystalline quality is improved and the electrical resistivity and energy band gap of SnS thin films are decreased after Ag-alloying [12]. Trianna and Gordillo examined the influence of Bi on the structural and optical properties of SnS thin films. The conductivity of Bi-alloyed SnS showed *n-type* and *p-type* in Bi > 50% and Bi < 50%, respectively [13,14]. In addition, the effect of other elements such as Sb [15] and Fe [16] on the SnS lattice has been examined.

So far, SnS has been deposited via different methods such as vacuum evaporation [17], electrochemical deposition [20–22], chemical bath deposition [18,19], two-stage process (sputtering of Sn film on substrate and then sulfurization) [20], radio frequency sputtering [21], chemical vapor deposition [2], and spray pyrolysis [22]. Among the mentioned methods, electrodeposition is an appropriate technique for SnS deposition because of its simplicity, cost-efficiency, and the ability to adjust the deposition parameters. In this research, the constant-potential electrodeposition is used, by which the polarization and deposition potential are easily controlled. This research aims to compare the effect of Se- and Te-incorporation on the structural, morphological, optical, and electrochemical properties of SnS thin films.

2. Experimental

2.1. Materials and processing

In the present research, materials containing pure SnS, Se-incorporation SnS, and Te-incorporation SnS thin films were prepared using three-electrode electrochemical processing. The cathode was a 3-mm thick fluorine-doped tin oxide (FTO) coated glass substrates (TCO30-8) purchased from the Solaronix Co., Switzerland. The surface resistivity and dimension of FTO substrates were 8 Ω/square and 1 cm × 2 cm, respectively. A platinum sheet and a saturated calomel electrode were used as the anode and reference electrodes, respectively. Before initiating the deposition process, FTO substrates were cleaned precisely with ethanol/acetone for 15 min in an ultrasonic bath and then rinsed with double-distilled water. An aqueous bath containing 2 mM $SnCl_2$ (Merck) and 16 mM $Na_2S_2O_3$ (Merck) was applied to deposit pure SnS thin film. The Se-incorporation and Te-incorporation SnS thin films were obtained by adding an appropriate amount of 4 mM SeO_2 (2 mL) and 4 mM TeO_2 (4 mL) to the main bath, respectively. The deposition time and the bath temperature were 30 min and 60 °C, respectively. The diluted H_2SO_4 was added dropwise to adjust the pH of the solution to be 2.1. In addition, the applied deposition potential remained at −1.0 V via a potentiostat/galvanostat (potentiostat, Autolab, A3ut71167, Netherlands). The deposition parameters were constant for all samples. After the electrodeposition process, the deposited thin films were extracted from the bath, rinsed with deionized water, and dried with warm air.

2.2. Characterization

The structural properties of deposited thin films were analyzed by Philips X′Pert-MPD X-ray diffraction. A TESCAN field emission scanning electron microscopy (FESEM) equipped with an energy dispersive X-ray spectroscopy (EDS) was used to observe the morphological properties of deposited thin films. X-ray photoelectron spectroscopy (XPS, VG-Microtech ESCA-2000) was used to investigate the elemental analysis of as-deposited thin films. In this test, the percentage error was ± 0.03 eV. Optical properties were examined using a Varian-Cary Eclipse photoluminescence (PL) with an excitation wavelength of 325 nm and Lambda 950-Perkin–Elmer UV–visible spectroscopy, respectively. In the UV–vis analysis, the angles of the incident for reflectance and transmittance were 15° and 0°, respectively. The unpolarized light was used, and specular reflectance was measured. The current-voltage (*I-V*) characteristics under dark and illumination (using a 100-W xenon lamp) were recorded using linear sweep voltammetry (LSV). The impedance studies were characterized in the 0.5 M Na_2SO_4 electrolyte. In this experiment, the cathode, the anode, and the reference electrode were the as-deposited films, a platinum wire, and a saturated calomel electrode (SCE), respectively. The electrochemical impedance spectroscopy (EIS) (Nyquist plot) was obtained under frequencies ranging from 0.01 to 10^5 Hz. The Mott- Schottky (M-S) analysis was done under a dark condition at a constant frequency of 1 kHz. The current density-voltage (*J-V*) characteristics of photoelectrochemical (PEC) solar cell were measured under a 100 mW/cm^2 (1.5 Air Mass) illumination. The PEC solar cell devices were prepared using the deposited thin films as working electrodes (WE). The FTO sheets were sealed in a sandwich cell as the counter electrodes filled with the I^-/I^{3-} (redox couple) electrolyte. All electrical measurements were recorded using an AutoLab PGSTAT 320 N potentiostat.

3. Results and discussion

3.1. Cyclic voltammetry

Cyclic voltammetry (CV) analysis was used for investigating the electrochemical processes of SnS deposition. Fig. 1 shows the CV for a solution of 2 mM $SnCl_2$ and 16 mM $Na_2S_2O_3$ (pure SnS) at a scan rate of

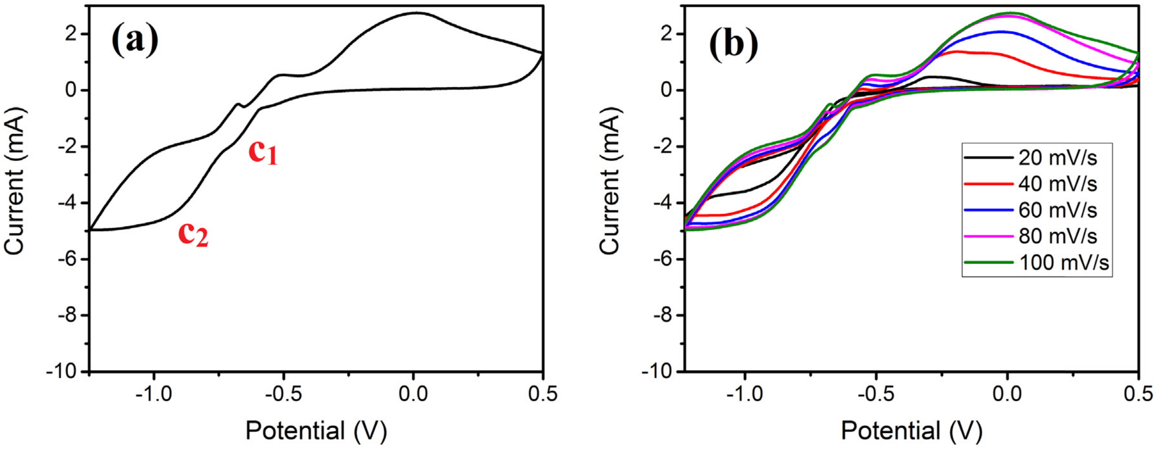

Fig. 1. Cyclic voltammetry of pure SnS solution containing 2 mM $SnCl_2$ and 16 mM $Na_2S_2O_3$ on FTO glass substrate, (a) at 100 mV/s, and (b) at different scan rates.