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Physical properties of spray pyrolyzed Ag-doped SnS thin films for opto-electronic applications

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ABSTRACT

A spray pyrolysis technique was used to deposit the silver doped tin sulfide (SnS:Ag) thin films on glass substrates at the substrate temperature of 350 °C. The variation in structural, optical and electrical properties of SnS with silver incorporation was investigated. The XRD spectra showed the improvement in crystallinity while increasing the doping concentration of Ag. The lower electrical resistivity of 8.63×10^{-1} Ω cm and the optical band gap of 1.33 eV were obtained at 8 at% of Ag.

1. Introduction

Metal chalcogenide compounds have attracted considerable attention in recent years due to their potential application in the fabrication of opto-electronic and photovoltaic devices [1]. Tin monosulphide (SnS) is one of the tin chalcogenide layered semiconductors which is suitable for the development of an absorber layer in heterojunction solar cells [2] because of its favorable optical and electrical properties. Also SnS belongs to IV–VI group of semiconductor compound with orthorhombic crystal structure [3]. It has direct band gap energy (1.2–1.6 eV) with high absorption coefficient ($> 10^4$ cm^{-1}) [4,5]. The theoretical studies also confirmed that the solar conversion efficiency of > 25% can be obtained by using SnS in photovoltaic devices [6].

SnS thin films have been prepared by various physical and chemical deposition methods such as electron beam evaporation, thermal evaporation, spray pyrolysis, spin coating etc., and reported in the literature [7–11]. Among these methods, the spray pyrolysis technique is a simple and relatively inexpensive for producing large area deposition. To improve the optical and electrical properties of SnS films, some dopant elements like In [12], Sb [13], Bi [14], Cu [15], Ag [16] were introduced. In our knowledge, there are very few literatures available on Ag-doped SnS films prepared by a vacuum thermal evaporation technique. No reports are available on Ag-doped SnS films by the spray pyrolysis technique, so we tried to investigate the physical properties of Ag-doped SnS thin films by the spray pyrolysis technique and to estimate their suitability for photovoltaic and opto-electronic devices.

2. Experimental details

Silver doped tin sulfide thin films were deposited onto microscopic glass substrates at a substrate temperature of 350 °C by the spray pyrolysis technique. A detailed description of an automated spray pyrolysis technique has been given in elsewhere [17]. The equimolar precursors of $SnCl_2 \cdot 2H_2O$ (0.1 M) and thiourea (0.1 M) were dissolved separately in isopropyl alcohol and deionized water (3:1 ratio). Equal volumes of these two solutions were mixed together and $AgNO_3$ as a dopant source was added to the starting solution. The [Ag/Sn] ratio was varied from 2 to 10 at%.

The structural properties of the deposited films were studied by the X-ray powder diffraction technique using a JEOLJDX-803 diffractometer ($\lambda = 1.5406$ Å). The surface topography of the films was examined by using the Nano-Surf Easy Scan2 atomic force microscope. The electrical properties of the films were evaluated by an ECOPIA HMS-3000 Hall effect measurement system at room temperature and the optical properties were carried out by using a JASCO V-670 double beam UV–vis–NIR spectrophotometer in the wavelength range of 400–1200 nm.

3. Results and discussion

Structural properties: The XRD patterns of SnS:Ag thin films Q2 with various concentrations of silver are shown in Fig. 1. From this figure, the observed '2θ' values were coincided with the standard

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JCPDS data (39-0354) of SnS. Also it was found that all the films exhibited the preferential orientation along (111) axis with orthorhombic crystal structure. Compared with pure SnS films [17], no new phase was observed for Ag doping, indicating that the incorporation of silver neither changed the structure of SnS nor resulted in the formation of any new compounds. With increasing the doping concentration, it was very clearly observed that the Bragg peaks become more intense, indicating an improvement in crystallinity. In this case, the crystallinity was increased up to 8 at% of Ag doping into SnS thin films and decreased at 10 at% of Ag. The improvement in crystalline quality of SnS thin films with silver doping was probably due to the creation of new nucleating centers from the dopant atoms and it was favorable for the growth of SnS [18]. While the doping concentration was high, the crystalline quality of the films declined due to the following two reasons: (1) the newer nucleating centers reach to their saturation; (2) the difference in ionic radius between Ag^{1+} (1.22 Å) and Sn^{2+} (0.93 Å), when a lot of Ag^{1+} ions go into the lattice sites of Sn^{2+} plane, the lattice distortion is intensified, resulting in larger strain in the films and consequently affecting the normal growth of SnS thin films [19].

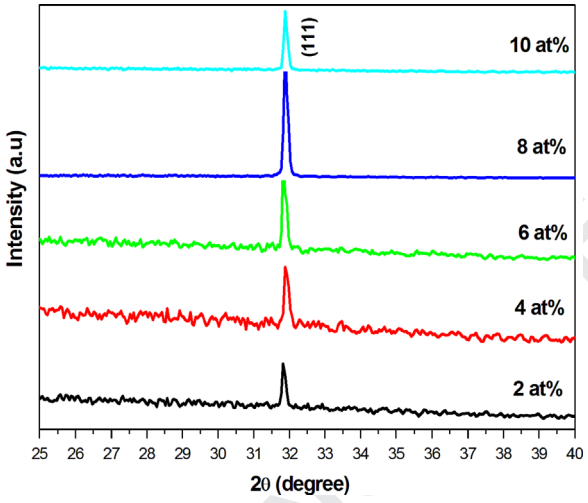

Fig. 1. XRD spectra for Ag-doped SnS films prepared at different doping ratios.

The microstructural parameters such as crystallite size, micro strain and dislocation density were calculated from the XRD data using standard Scherr's relation [20]. The variation in microstructural parameters of Ag-doped SnS films at different doping ratios is depicted in Fig. 2. From this figure, it was identified that the crystallite size found to increase initially from 97 nm for pure SnS [17] to 115 nm for 8 at% of Ag doped SnS films and then slightly decreased to 113 nm for further increasing the doping concentration of 10 at%. Correspondingly, the lattice defects like micro-strain and dislocation density showed a decreasing trend with increasing doping concentration up to 8 at% which may be due to the improvement in crystallinity, and then increased for further increase in doping concentration.

Fig. 3 shows the 3D AFM image of SnS:Ag thin films for the doping concentration of 8 at% and the scanned surface area was 15 μm × 15 μm. From this figure, it can be observed that the film surface was uniform and smooth with densely packed grains. The average roughness of SnS:Ag thin film was found to be about 20.3 nm. Compared with pure SnS films [17] the increase in roughness of the film surface and a lot of pile-up crystal grains form island structure were also observed after Ag doping.

The elemental analysis of SnS:Ag thin films with various doping concentrations of Ag was analyzed by Energy Dispersive Spectroscopy (EDS). From this analysis, it was confirmed that the presence of Sn, S and Ag elements in the films and the atomic percentage of these elements are shown in Table 1. It was observed that upon increasing Ag concentration, the percentage of Sn in the films decreased slightly, whereas the percentage of S was almost constant. It would be presumed that Ag-doping in the films was substitutional.

Electrical properties: Fig. 4 presents the electrical properties (resistivity, carrier concentration and Hall mobility) of SnS:Ag thin films with various Ag-doping concentrations. It can be seen that the semiconducting properties of the films were strongly dependent on the doping concentrations of Ag. As increasing the Ag-doping concentration from 2 to 8 at%, the carrier concentration of the films gradually increased from 5.78×10^{16} to 2.14×10^{18} cm^{-3}; and also the Hall mobility increased from 308.7 to 498.8 $cm^2\ v^{-1}\ s^{-1}$, whereas the resistivity value decreased from 9.79×10^{1} to 8.63×10^{-1} Ω cm. In general, the decrease in resistivity with an increase of Ag concentration may be due to the presence of Ag atoms in SnS structure, which increases the acceptor states. It helps to increase the hole carrier concentration in the valence band and leads to low resistivity at room

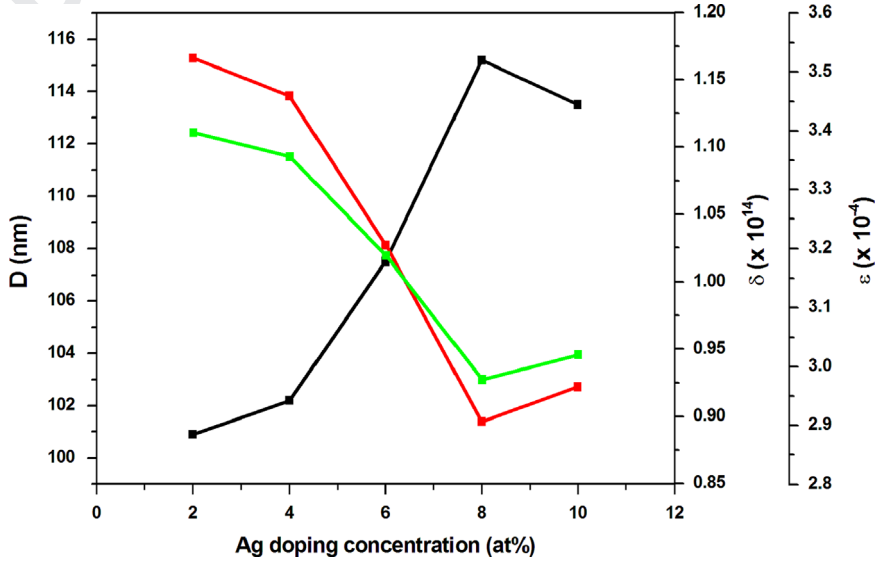

Fig. 2. Variations in crystallite size, dislocation density and micro-strain of SnS films prepared with various Ag doping concentrations.

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