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$AgSbS_2$ and Ag_3SbS_3 absorber materials for photovoltaic applications

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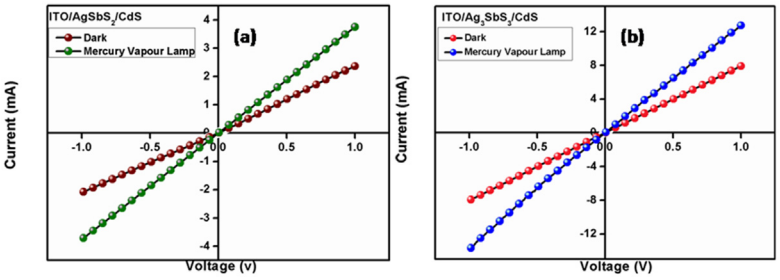
HIGHLIGHTS

- Phase transition from $AgSbS_2$ to Ag_3SbS_3.
- Ag_3SbS_3 film shows higher conductivity.
- ITO/Ag_3SbS_3/CdS shows higher photosensitivity.

GRAPHICAL ABSTRACT



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ABSTRACT

Thermally evaporated Sb_2S_3 and Ag-Sb_2S_3 thin films were prepared by using Sb_2S_3 and Ag nanopowders as precursors. The deposited films were annealed at 250 °C and 300 °C in the air atmosphere and were characterized by using XRD, SEM, AFM, UV–VISible, FTIR and electrical studies. The deposited film showed amorphous in nature at the annealing temperature less than 250 °C whereas the monoclinic structure of Ag_3SbS_3 is noticed in above 250 °C annealing temperatures. AFM studies reveal the morphological change with respect to the annealing temperature. The direct band gap was found to be 2.02 eV, 1.83 eV and 1.74 eV for Sb_2S_3, $AgSbS_2$, Ag_3SbS_3 respectively. FTIR spectra showed the stretching vibrational mode of Ag-O, $AgSO_4$and Sb_2O_3. The electrical conductivity of Ag_3SbS_3 film is better ($\sigma = 1.01$ mho cm^{-1}) than that of $AgSbS_2$ ($\sigma = 0.71$ mho cm^{-1}). The opto-structural and electrical studies revealed that the film Ag_3SbS_3 is identified as the potential absorber for photovoltaic application. The photosensitivity of the ITO: $AgSbS_2$/CdS and ITO: Ag_3SbS_3/CdS thin films is found to be about 58% and 61% respectively.

1. Introduction

Inorganic semiconductors have several advantages such as tunable absorption band due to the quantum-size effect, extinction coefficient and multiple extinction generations by a single photon. Many ternary semiconductors have two attractive features: (a) energy gap E_g close to that (~1.4 eV) for an optimal solar cell absorber and (b) a large absorption coefficient (α) of ~10^4–10^5 cm^{-1}. These two features make ternary metal chalcogenides attractive materials for solar absorbers [1]. As a possible alternative to CIGS-based solar cells, $AgInS_2$ based chalcopyrite semiconductor are also expected to make good solar cell absorber layer. Indeed, the material has a distinguished absorption in the visible and near infrared region because of its large optical absorption coefficient and its band gap energy is between 1.87 eV and 2.03 eV [2]. This material has been prepared by different methods

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such as Hot-Press (HP) method, a direct fusion of Ag, In, and S elements, the vertical gradient freezing (VGS) method and the epitaxy method [2]. However, Indium is a rare earth element and its cost also higher than other materials. So the researchers were replaced this indium by antimony, which is less toxic, low-cost element compares to indium and earth abundant material and nearly equal ionic radius of In (In^{3+} = 0.80 Å, Sb^{3+} = 0.90 Å) [3]. Ag-Sb-S is an emerging semiconductor, which is considered as a high-light absorbing material for sustainable and scalable photovoltaic compared to those of $AgInS_2$ and CIGS [4]. $AgSbS_2$ is a promising candidate (E_g of 1.7 eV and $\alpha \sim 10^5$ cm^{-1}) for a number of applications such as solar cells, semiconductor sensitisers [5], active recording films, micromechanical, optical memories and electrical switching [6]. W.C. Yang et al., and J. Kavinchan et al., were reported the optical properties of $AgSbS_2$. To the best of our knowledge, there are many works have been reported for Cu-Sb-S and Ag-In-S system while paucity in the synthesis and characterisation of Ag-Sb-S. Hence, the objective of the investigation is to deposit $AgSbS_2$ films by thermal evaporation method. To study the optostructural, morphological and electrical characteristics of the films by using X-ray diffraction (XRD), Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), UV-VIS spectrometer, Fourier Transform Infra-Red (FTIR) spectrometer and Electrical studies (I-V). To study the photosensitivity of the ITO: $AgSbS_2$/CdS and ITO: Ag_3SbS_3/CdS thin films under dark and illumination condition.

2. Experimental

The precursors such as elemental silver and antimony sulphide (95.9% purity) were used in this study. The stoichiometry amount of precursors (silver metal powder and antimony sulphide) was taken. This mixture was placed in the molybdenum boat crucible. Distance from the source –to – substrate is 15 cm. Evaporation takes place under a high vacuum of 10^{-5} torr and current was maintained about 150 amps. Duration of evaporation is approximately 5–10 s with the sample crucible temperature of ~2000 °C. In order to get a uniform coating, the precleaned glass substrates were placed in at substrate holder during deposition at room temperature. The film was coated by using HIND HIVAC (model 12-A4UD) vacuum coating unit. The deposited films were annealed at 250 °C and 300 °C. The film thickness was found out by using the cross-sectional view recorded for SEM.

2.1. Solar cell fabrication

ITO/$AgSbS_2$/CdS and ITO/Ag_3SbS_3/CdS heterojunction solar cell was prepared as follows:

(1) Ag_3SbS_3 was deposited on ITO substrate by thermal evaporation method.
(2) CdS was deposited on Ag_3SbS_3 by chemical bath deposition according to the earlier report [7].

2.2. Characterisation techniques

The annealed films were characterized by using Scanning electron microscopy (SEM), X-ray diffraction (XRD), Atomic force microscopy (AFM), UV–Visible (UV-VIS) and Electrical studies (I-V). To find the film thickness the cross-sectional view SEM images of the films were recorded using JEOL scanning electron microscope (JS2610LV). XRD patterns were performed using a PAN analytical X′ PERT-PRO diffractometer with CuKα radiation (λ = 1.5406 Å). To investigate the surface morphology and roughness of the grains, the AFM technique was used (nanosurf instrument). Optical spectra were recorded by using Perkin Elmer Lambda 25 UV–Visible spectrometer. Fourier Transform Infra-Red spectra were recorded by using Perkin Elmer (Spectrum Two, model-C9217) spectrometer. I-V studies were performed by the Electrochemical Analyzer (CHI604E electrochemical workstation) with linear sweep voltametry technique. The photo I-V measurements were carried out by linear sweep voltametry (CH instruments CHI60E electrochemical analyzer) under dark and mercury vapour lamp irradiation (Visible light) with the following speculations, applied voltage ± 1 V, scan rate 0.1 V/s, sensitivity = 0.001 A/V. The film of 2 cm length and 2.5 cm breath is used to study the I-V photo conversion of the fabricated ITO: $AgSbS_2$/CdS and ITO: Ag_3SbS_3/CdS heterojunction thin films. A setup of the two-probe device was constructed by simply connecting the two crocodile clips onto ITO: $AgSbS_2$/CdS and ITO: Ag_3SbS_3/CdS heterojunction thin films surface with a typical spacing of 25 mm.

3. Results and discussion

The thicknesses of the films were measured using the cross-sectional view of the SEM images. The films were broken, and the images were recorded on the broken side. The cross-sectional images of the films are shown in Fig. 1, and their thicknesses are given in Table 1.

Fig. 2 (a) shows the XRD pattern of annealed Sb_2S_3 thin film. It can be seen from the diffraction pattern that the prominent peak appears at 2θ = 32.6° along (221) plane with a two weak peaks at 2θ = 25.02° and 2θ = 28.05° belongs to (310) and (021) planes respectively. The peak 2θ = 32.6° (221) shows strong and sharp owing to higher crystalline order and to larger domain size. The results confirm the orthorhombic crystal system of Sb_2S_3 (JCPDS 06-0474). A hump is detected at 2θ = 66.1° belongs to (422) plane of Sb_2O_4 as an impurity. The result agrees with earlier reports on Sb_2S_3 by S. Shaji et al. [8].

When Ag incorporate (0.2 g) into the Sb_2S_3 system, (annealed at 250°) the preferential orientation appears at 2θ = 31.6° occurs along (200) direction. The reveal of peak shift (221 plane to 200), in comparison to Sb_2S_3, is may be due to the partial replacement of a Sb^{3+}ion (radius of 0.90 Å) by Ag^+ ion (radius of 1.15 Å), which makes lattice distortion due to various ionic radii. The observed results are agreed well with the standard JCPDS (17-0456) with the fcc structure of $AgSbS_2$. This result is matched with $AgSbS_2$ by J. Kavinchan et al. [5], W.C. Yang et al. [1], and N. Tipcompor et al. [6], When an increase the annealing temperature to 300 °C (Fig. 2 (c)), that indicates $AgSbS_2$ transform to the monoclinic crystal structure of Ag_3SbS_3 (JCPDS 76-0197). A peak is observed at 2θ = 31.6° belongs to (111) plane of Ag_2O_3 as an impurity phase. The crystallite size was calculated by using Scherrer's formula,

$$D = \frac{0.9\lambda}{\beta cos\theta}\ \mathrm{m} \quad (1)$$

where 'D' is the average crystallite size, 'λ' is the wavelength of incident X-ray beam (1.5406 Å), 'β' is the full width at half maximum value, 'θ' is the angle of diffraction. The average crystallite size was found to be 64 nm, 8 nm and 18 nm for Sb_2S_3, $AgSbS_2$ and Ag_3SbS_3 respectively. The crystallite size reduction in Ag incorporated Sb_2S_3 is due to the lattice distortion caused by the radius difference between the Ag and Sb ions. It is noticed from the XRD analysis, Sb_2S_3 system is found to be orthorhombic and Ag incorporated films showed fcc at 250 °C and the phase transform to monoclinic showed at 300 °C. The film annealed at 400 °C shows amorphous nature (Fig. S1).

In the case of CdS thin film (Fig. S2) (shown in supportive information) some polycrystalline peaks are shown at