Conference Paper

Characterization of Thermally Evaporated In_2S_3 Films for Solar Cell Application

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Indium sulphide (In_2S_3) is one of the best alternatives for CdS as a buffer layer in CuInGaSe_2 -based thin film heterojunction solar cells. In this work, In_2S_3 films were prepared by thermal evaporation of In_2S_3 powder onto glass substrates at different temperatures that vary from 200°C to 300°C . The as-grown films were characterized using appropriate techniques to evaluate the chemical and physical properties. The X-ray diffraction analysis revealed that all the films were polycrystalline in nature with a strong (109) plane as the preferred orientation and consisted of tetragonal and cubic phases. The crystallite size and the lattice parameters are calculated. The scanning electron micrographs indicated smooth surface with fine grains. The optical analysis revealed a high optical transmittance for the layers with a direct optical band gap that varied in the range of 1.8–2.2 eV.

1. Introduction

Indium sulphide (In_2S_3) is a chalcogenide semiconductor that belongs to the III–VI group of semiconductors with interesting fundamental properties, useful for various device applications [1, 2]. It shows n-type electrical conductivity and has a wide direct band gap of ~ 2.3 eV [3–5]. Depending on the growth conditions, In_2S_3 exists in three different crystallographic forms, namely α , β , and γ . The α -phase shows cubic crystal structure while the β - In_2S_3 phase crystallizes in tetragonal structure and γ - In_2S_3 in trigonal structure. Among these three phases, β - In_2S_3 is found to be stable at room temperature.

In recent years, In_2S_3 has proved to be an important alternative buffer layer to CdS in the fabrication of Cu(In,Ga)Se_2 -based solar cells with solar conversion efficiencies $>15\%$. In_2S_3 layers have been synthesized using a variety of chemical as well as physical techniques. These include chemical vapour deposition [6], atomic layer epitaxy [7], chemical spray pyrolysis (CSP) [8], chemical bath deposition [9], metal-organic chemical vapor deposition [10], thermal evaporation [11], and successive ionic layer adsorption and reaction [12, 13]. In this

study, In_2S_3 films were formed on glass substrates by vacuum thermal evaporation. The effect of substrate temperature on the structural and optical properties were reported and discussed.

2. Experimental Procedure

In_2S_3 thin films were deposited by vacuum thermal evaporation using Hind Hi Vac Box Coater (model BC: 300). 4 N pure In_2S_3 powder, obtained from Sigma-Aldrich, was used as the source material and evaporated from molybdenum boat. The boat was covered with quartz wool to avoid spattering of the some material during evaporation. The deposition was carried out at a vacuum of 2×10^{-5} mbar on ultrasonically cleaned glass substrates. The distance between the source and substrate is kept as 7 cm. A 1KW radiant heater is used to heat the substrates. The substrate temperature (T_s) was varied in the range of 200 – 300°C .

The as-grown layers were characterized to study the properties using appropriate techniques. The morphological and chemical details were studied using Hitachi scanning electron microscope (SEM) connected with an Oxford energy

dispersive X-ray analyzer (EDAX). The structural properties were evaluated using Seifert GE—X-ray Diffraction system—XRD 3003TT with a CuK_α radiation source ($\lambda = 1.542 \text{ \AA}$) in the 2θ range of $20\text{--}70^\circ$. The optical properties such as optical transmittance, energy band gap, refractive index, and extinction coefficient were determined from the transmittance versus wavelength spectra. These measurements were recorded using PerkinElmer Lambda 950 UV-Vis-NIR double beam spectrophotometer in the wavelength range of 300–2500 nm.

3. Results and Discussion

The visual observation indicated that all the grown layers appeared dark brown in color, homogeneous, and free from pin holes. The scratch tape test revealed that the layers were strongly adherent to the substrate surface. The films had a varying thickness of approximately 510–580 nm.

3.1. Morphological Analysis. Figure 1 shows the SEM pictures of In_2S_3 films formed at three different substrate temperatures. It could be observed that the films formed at 200°C had smaller grains, and the grain size increased with the rise of substrate temperature. Although the grain size is increased with the increase of substrate temperature, however, the surface of the films became more rough and nonuniform.

3.2. Compositional Analysis. The EDAX measurements on In_2S_3 layers revealed the presence of In and S peaks without any other impurity elements. The films formed at 200°C had shown higher S content that slowly decreased with the increase of substrate temperature. Figure 2 shows the typical EDAX spectrum of In_2S_3 film formed at a temperature of 300°C . The spectrum indicated In and S peaks of nearly equal intensities, and the elemental composition determined was In = 49.07 at.% and S = 50.93 at.%.

3.3. XRD Measurement. Figure 3 shows the X-ray diffraction (XRD) patterns of In_2S_3 films formed at different substrate temperatures. All the three spectra revealed the polycrystalline nature of the layers with a dominant (109) plane in addition to other peaks related to the (107), (222), (301), (511), and (444) planes of In_2S_3 . Among the different peaks observed, the (107), (109), and (301) planes correspond to the tetragonal crystal structure while, the (222), (511), and (444) peaks to the cubic structure. The various planes observed in this study are in agreement with the JCPDS card nos. 73-1366 and 65-0459. There were reports in the literature on the existence of mixed phases, both tetragonal and cubic, in In_2S_3 films [14]. In this study, however, a continuous increase in the intensity of the peaks related to tetragonal structure with the rise of substrate temperature could be noted from the XRD spectra with a decrease in intensity of the peaks that correspond to the cubic phase.

The lattice constants, a and c , were determined for the tetragonal phase using the equation

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}, \quad (1)$$

(a)

(b)

(c)

FIGURE 1: SEM pictures of In_2S_3 films grown at (a) 200°C , (b) 250°C and (c) 300°C .

where d is the inter planar spacing and (hkl) are the Miller indices. The evaluated values of $a = 7.169 \text{ \AA}$ and $c = 32.329 \text{ \AA}$ are in agreement with the JCPDS data. The average crystallite size was calculated for the layers formed at different substrate temperatures using the Debye-Scherrer formula [15] and using the full width at half maximum of the (109) peak. The value varied from 11.8 nm to 37.9 nm with the increase of the substrate temperature from 200°C to 300°C . This shows an improvement in the crystallinity of the films with the rise of a substrate temperature, a common phenomenon observed in polycrystalline thin films.

3.4. Optical Studies. The optical transmittance spectra of In_2S_3 films grown at different substrate temperatures are shown in Figure 4. All the spectra showed a high optical transmittance with a sudden fall in transmittance near the

FIGURE 2: EDAX spectrum of In_2S_3 film grown at 300°C . FIGURE 3: X-ray diffraction spectra of In_2S_3 films. T and C in the above figure refer to tetragonal and cubic crystal structures, respectively.

fundamental absorption edge, indicating the presence of direct optical transition in the layer. Further, the optical transmittance of the film decreases with the increase of the deposition temperature, which might be due to the increase of the surface roughness and nonuniformity of the film leading

FIGURE 4: Transmittance versus wavelength spectra of In_2S_3 films.

FIGURE 5: Absorption coefficient versus photon energy plots.

to more light scattering. The optical absorption coefficient, α , was calculated using the relation

$$\alpha = -\frac{1}{d} \ln T, \quad (2)$$

where d is the thickness of the film and T is the transmittance.

Figure 5 shows the variation of absorption coefficient α , with photon energy $h\nu$ for In_2S_3 layers deposited at different temperatures. The optical band gap of the films is determined using the $\log \alpha$ versus $h\nu$ plot for α values in the region where

the transmittance falls off rapidly ($T < 5\text{--}10\%$). The band gap values determined from the plot increased from 1.8 eV to 2.2 eV with the increase of substrate temperature indicating a red shift. This widening of band gap with growth temperature might be due to a decrease of the midband gap states as reported by Dow and Redfield [16]. The slight variation of "S" composition with the rise of substrate temperature also might be responsible for the change of energy band gap of the layers. The calculated values of energy band gap are in good agreement with the values reported in the literature where such a large variation in the energy band gap was observed [17, 18]. The refractive index and extinction coefficient were evaluated using the transmittance data using the formulae reported in the literature [19] at a wavelength of 725 nm and were found to be 1.6439 and 0.0199, respectively.

4. Conclusions

In_2S_3 films were prepared on the glass substrates by thermal evaporation technique at different substrate temperatures. All the films were polycrystalline with the (109) plane as preferred orientation. Also, the layers showed a presence of both tetragonal and cubic phases where the later tend to minimize with the rise of substrate temperature. The evaluated crystallite size increased from 11.8 nm to 37.9 nm. All the layers showed a high optical transmittance, and the energy band gap increased with the rise of substrate temperature and varied in the range of 1.8–2.2 eV.

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