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Optical properties of thermally evaporated In_2S_3 thin films measured using photoacoustic spectroscopy

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ABSTRACT

In_2S_3 is a III-VI group semiconductor with n-type conductivity and a wide band gap energy, which can be suitable as a buffer layer alternative to CdS in thin film solar cell fabrication. In the present study, In_2S_3 thin films were grown on glass substrates by the thermal evaporation method at a constant substrate temperature of 200 °C. The deposited layers were post annealed in vacuum in the temperature range of 200–300 °C for 1 h. The grazing incident X-ray diffraction and scanning electron microscopy studies revealed polycrystalline nature of the layers with a good surface morphology. The optical properties of these annealed layers were investigated by using photoacoustic spectroscopy and independently by using conventional optical transmission spectroscopy. The photoacoustic spectra of In_2S_3 films showed a sharp fall in the photoacoustic signal at photon energies that increased from 1.95 to 2.74 eV with increasing annealing temperature, which corresponds to the band gap energy of corresponding films. The band gap energy and the refractive index values calculated by using photoacoustic spectra are in good agreement with that determined from transmission spectra.

1. Introduction

CdS thin films are widely used as buffer layer in Cu(In,Ga)Se_2 and CdTe-based heterojunction thin film solar cells and play a vital role in enhancing the efficiency upto 20% [1]. Since Cd is a toxic material and it can cause severe damage to environment on large scale production, the alternative materials are of a great interest for researchers. In this context, In_2S_3 is an important alternative to CdS in Cu(In,Ga)Se_2 and Cu_2ZnSnS_4 thin film solar cells [2,3], because of its eco-friendly nature with wide energy band gap and photoconductive behaviour [4]. It is a n-conductivity type direct band gap semiconductor and has a high quantum conversion efficiency (70–80%) in the visible region [5]. Recently, 16.4% of conversion efficiency has been achieved by using In_2S_3 as a buffer layer in Cu(In,Ga)Se_2 based solar cells, which is close to that achieved using CdS as the buffer layer [6]. Till now, various deposition techniques have been used to prepare In_2S_3 films, which showed significant impact on the behaviour of the grown films. The reported band gap values of In_2S_3 films were varied from 2.0 to 3.3 eV [7,8] depending on the growth techniques and deposition conditions. Barreau et al. [9] reported a band gap of 2.80 eV for n-type In_2S_3 layers grown by physical vapour deposition in oxygen atmosphere. The chemical bath deposited films showed band gap in the range of 2.0–2.8 eV [10], by using atomic layer chemical vapour deposition the obtained band gap is 2.7 eV [11], from thermal evaporation technique the obtained optical band gap values varied in the range of 2.0–2.2 eV [12], in the range of 2.46–2.73 eV from physical vapour deposition [13] and in the range of 2.0–2.8 eV from ultrasonically sprayed layers [14].

In the present study, In_2S_3 films were grown by vacuum thermal evaporation technique at a substrate temperature of 200 °C and annealed in vacuum in the temperature range from 200 °C to 300 °C. The optical properties of the In_2S_3 films were evaluated by using photoacoustic (PA) spectroscopy and compared with the results of optical transmission spectroscopy. The PA spectroscopy is a non-destructive and sensitive technique that gives direct information related to the optical and thermal properties of semiconductors [15]. The PA spectroscopy technique is a very useful tool for effective study of semiconductor films either amorphous or polycrystalline in nature where spectroscopic methods fail, for example, in the case of semiconductor

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films formed on an opaque substrates. There are several advantages of the PA spectroscopy for the optical analysis: it is little affected by the surface morphology and roughness; it detects a signal, which is directly proportional to the generated thermal energy; there are no special demands regarding sample preparation; it exhibits smaller influence of the interference effects on the measured spectra than in the transmission spectroscopy. However, there are only few available reports on photothermal studies of In_2S_3 films. Earlier, the thermal and optical properties of Al-doped In_2S_3 samples were studied with the photothermal deflection (PD) spectroscopy and reported [16]. In this paper, the PA spectroscopy has been used as an investigation tool for determining the optical characteristics of the In_2S_3 films. Very few articles are available on PA spectroscopic studies of In_2S_3 material in the form of single crystal [17] and nano flakes/dendrites type [18], but not in polycrystalline thin film form. Therefore, it is the first report on optical properties of thermally evaporated In_2S_3 films measured by PA spectroscopy.

2. Experimental details

In_2S_3 films were deposited by thermal evaporation technique (Hind Hi Vac box coater BC-300) using In_2S_3 powder (Sigma Aldrich, 99.999% purity) as a source material. The films were deposited on soda lime glass substrates at a constant temperature (T_s) of 200 °C by maintaining a source to substrate distance of 14 cm and deposition rate of 15 Å/sec, while the thickness of the films was maintained as ≈ 200 nm as measured by quartz crystal thickness monitor. The as-grown films were annealed in vacuum (2×10^{-2} mbar) at various temperatures (T_a) in the range of 200–300 °C for 60 min by using a two zone tabular furnace. The structural characteristics of the samples were analyzed by using an Ultima IV X-ray diffractometer in the grazing incidence diffraction geometry (GIXD) at 1 degree of incident X-rays with Cu Kα radiation source (λ = 1.5406 Å). The surface morphology and cross-sectional view of the films were investigated by using a Hitachi S-806 scanning electron microscope (SEM). The optical properties of the films were measured by using a high-resolution PA spectrometer and by using a Photon RT spectrophotometer (Essent Optics).

PA spectroscopy is the application of the photoacoustic effect for spectroscopic purposes. The basic principle of photoacoustic effect is the generation of acoustic signal, when a material is illuminated with modulated or pulsed light. The PA spectroscopy set-up used in this work is presented in Fig. 1. The light emitted by a Xenon lamp of 300 W light intensity is introduced into an OMNI-300 grating monochromator with the operation range of 600–2400 nm. The monochromated light is modulated by a Standford Research SR540 mechanical chopper and falls on a homemade photoacoustic cell, which contains the sample and a microphone (40AP type condenser microphone with a 26AK preamplifier by G.R.A.S.). The amplitude and phase of the photoacoustic signal (PAS) coming from the sample is measured in the form of sound and vibration by a Standford Research SR830 lock-in amplifier. The whole system is controlled by a computer with the software written in LAB view. Further, two types of measurements can be performed for characterizing the sample in PA spectroscopy: (i) (PAS) versus

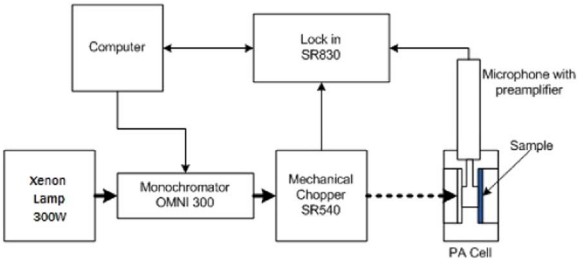

Fig. 1. Experimental set-up of PA spectroscopy measurement unit.

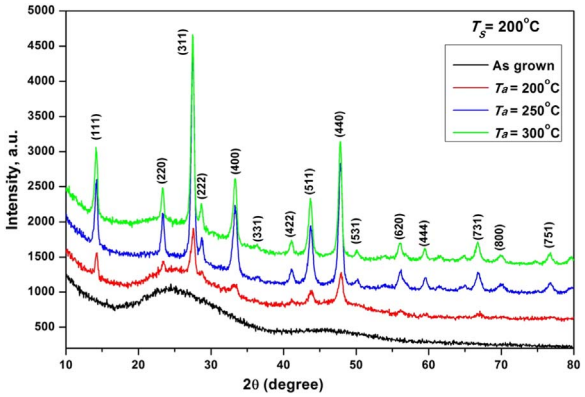

Fig. 2. GIXD patterns of In_2S_3 layers.

wavelength of the light at constant modulation frequency and (ii) PAS versus frequency of modulation at constant wavelength. From the first type of measurement, one can obtain the optical parameters of the sample when the thermal parameters are known, whereas in the latter case, the thermal parameters of the sample can be obtained.

3. Results and discussions

The as-grown In_2S_3 thin films were found to be homogeneous, pin hole free, appeared dark reddish yellow in colour and well adherent to the substrate surface. After the deposition and annealing process, the thickness of the films was ≈ 200 nm.

3.1. Structural analysis

Fig. 2 shows the GIXD patterns of the as-grown and thermally annealed (at three different temperatures 200, 250 and 300 °C) In_2S_3 films. The GIXD pattern revealed that the as-grown films possess amorphous nature, which might be due to insufficient thermal energy to induce crystallization. Zhong et al. [19] also reported the similar behaviour in thermally evaporated In_2S_3 layers deposited at different substrate temperatures (upto 500 °C). Annealing of the as-grown layers triggered the crystallization in the films. The annealed layers exhibited polycrystalline nature with (311) plane as preferred orientation along with the existence of other peaks corresponding to (111), (220), (222), (400), (331), (422), (511), (440), (531), (620), (444), (731), (800) and (751) planes. The presence of these peaks confirmed the existence of cubic structured β-In_2S_3 phase and matches with the JCPDS data file no. 65-0459. Further, it was observed from the figure that the intensity of the dominant diffraction peak increases with annealing temperature, indicating that the crystal quality of the films was improved. This was attributed to the coalescence induced grain growth during the annealing process [20]. Rao et al. [21] also noticed a similar observation, where the crystallinity of thermally evaporated In_2S_3 films increased with the increase of annealing temperature.

The crystallographic parameters like crystallite size (D) and internal lattice strain (ε) were calculated for annealed In_2S_3 films using the following relations and the obtained values were tabulated in Table 1.

The inter-planar spacing (d) was calculated using the Bragg's diffraction law:

Table 1
The crystallographic parameters of the annealed In_2S_3 thin films.

Annealing temperature (°C)	2θ (°)	β (rad)	d-spacing (nm)	D (nm)	ε ($\times 10^{-3}$)
200	27.55	0.0103	0.323	28	10.5
250	27.50	0.0092	0.324	32	9.3
300	27.45	0.0085	0.324	36	8.7