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Growth and characterization of Cu_2SnSe_3 thin films

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Abstract

Thin films of Cu_2SnSe_3, a potential candidate for acousto-optic device applications in IR region were prepared by co-evaporation onto glass substrates. Powder X-ray diffraction (XRD) pattern revealed that the films were polycrystalline in nature with sphalerite structure. The lattice parameter was found to be $a = 0.573$ nm. Grazing incidence X-ray diffraction (GIXRD) studies indicated that the surface layers contain Cu_2SnSe_4 as the secondary phase. Average grain size obtained from scanning electron micrograph was found to be 0.6 μm. Optical absorption studies revealed two direct-allowed transitions, one corresponding to the transition from the acceptor level to the bottom of the conduction band (0.74 eV) and the other corresponding to the transition from the spin-orbit splitting level to the conduction band minimum (1.12 eV). The films were found to be p-type with a carrier concentration of 1.85×10^{20} cm^{-3} and Hall mobility of 1.79 $cm^2\ V^{-1}\ s^{-1}$. Temperature dependence of electrical conductivity studies in the range 123–373 K indicated three acceptor states with activation energies of 60, 15 and 5 meV.

Keywords: Cu_2SnSe_3 thin films; Co-evaporation; Optical absorption; Electrical conductivity; Structural properties

1. Introduction

Ternary and multinary compound semiconductors are currently being investigated due to their variety of applications in the areas like opto-electronics, non-linear optics, electro-optics, acousto-optics, etc. [1–3]. There is a wide range of semiconductors with different optical band gaps, refractive indices, electrical resistivity and other properties to suit the devices of interest. The compound semiconductors of I_2–IV–VI_3 family, which are three-fold derivatives of II–VI binary analogs, have attracted the attention of investigators recently for acousto-optic applications due to their low band gaps, low melting points, high mean atomic weight and high refractive indices. Some studies on single crystals [4–13] and nano crystals of these materials [14,15] are reported. However, to the best of our knowledge, no data on thin films of I_2–IV–VI_3 compounds are reported in literature. Investigations on thin films of these compounds are quite relevant for application in thin film wave-guides, LEDs, etc. An attempt is, therefore, made in our laboratory to prepare thin films of Cu_2SnSe_3, a member of above family.

Thin films of ternary compound semiconductors were successfully prepared earlier by using several thin film deposition techniques like thermal evaporation, electron beam evaporation, laser evaporation, sputtering and MOCVD. In the present study, we employed three-source co-evaporation to deposit Cu_2SnSe_3 thin films in which individual evaporation rates of the elements can be controlled to achieve the desired stoichiometry. Obtaining single phase and stoichiometric Cu_2SnSe_3 thin films is a difficult task due to re-evaporation of selenium and the possibility of formation of defect compound Cu_2SnSe_4 along with Cu_2SnSe_3 at the same deposition conditions. The present paper reports the growth and characterization of co-evaporated Cu_2SnSe_3 thin films.

2. Experimental

Thin films of Cu_2SnSe_3 were prepared using three-source co-evaporation technique. The films were prepared by evaporation of spectroscopic pure elements of copper, tin and selenium (Aldrich, USA) onto chemically and ultrasonically cleaned soda lime glass substrates in a conventional

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four source vacuum system (HINDHIVAC Ltd. model: BC-300). The evaporation was carried out at a base pressure of 5×10^{-6} mbar and substrate temperature of 673 K. The substrate holder was rotated using a rotary drive mechanism to ensure uniformity. The evaporation rates of copper and tin were fixed according to stoichiometry by controlling the source temperatures. However, selenium evaporation rate was adjusted to be slightly higher than the stoichiometric proportion to compensate for the loss of selenium due to re-evaporation. The thickness and evaporation rates were monitored using quartz crystal digital thickness monitor. After deposition of the films, in situ post-deposition annealing in selenium atmosphere was carried out at a temperature of 723 K in selenium atmosphere for about 45 min. The films were slowly cooled down to the room temperature at the rate of 10 K min^{-1} using PID controller.

The elemental analysis and microstructure of the films were obtained using scanning electron microscope (model: XL30ESEM, FEI Inc.) with energy dispersive X-ray analysis (model: Phoenix, EDAX Inc.) attachment. The spectral transmittance of the films was measured using UV–vis–NIR spectrophotometer (model: V-570, JASCO) in the wavelength range of 350–2500 nm with a scan speed of 100 nm min^{-1} in steps of 2 nm. Spectral reflectance (R_λ) measurements were done in the wavelength range 500–2000 nm.

The powder X-ray diffraction (XRD) pattern of the films was recorded with Seifert XRD (model: 3003 TT) in Bragg–Brentano (Theta–Theta configuration) mode using Cu Kα (λ = 0.15406 nm) radiation. The pattern was recorded with a scan speed of 0.02° s^{-1} in the 2θ range 10°–70°. The glancing angle attachment with graphite flat monochromator was used to record grazing incidence XRD (GIXRD) pattern of the films. The GIXRD pattern was recorded with the glancing angle (ω) of 0.5°, 1.5°, 2.5° and 5.0°. Peak positions were measured precisely using RAYFLEX ANALYZE software.

The electrical conductivity studies in the temperature range 123–373 K were carried out using van der Pauw technique by using silver paste as ohmic contact. The film conductivity type was determined using hot probe technique and Hall effect measurements were carried out at room temperature in a magnetic field of 14 kG.

3. Results and discussion

3.1. Chemical composition and structural properties

The deposited films are highly uniform and the thickness (t) is around 1 μm. From the EDAX analysis, the atomic percentage of Cu:Sn:Se is found to be 30.66:15.77:53.57. The films are nearly stoichiometric with a Cu/Sn atomic ratio of 1.94 and Se/(Cu + Sn) atomic ratio of 1.15.

The powder X-ray diffraction pattern of Cu_2SnSe_3 films is shown in Fig. 1. The pattern reveals that the films are polycrystalline in nature. There is some ambiguity in the structure of the Cu_2SnSe_3 reported earlier. Palatnik et al. [5] and Sharma et al. [6] reported it as sphalerite structure. Rivet et al. [7] proposed an orthorhombic structure up to 450 °C and sphalerite structure beyond 450 °C due to order–disorder transformation. Recently, Marcano et al. [13] from XRD and differential thermal analysis (DTA) studies reported that Cu_2SnSe_3 crystallizes in monoclinic structure with the space group Cc, and also proposed a sphalerite super-structure. In the present study, we observed the peaks corresponding to sphalerite structure and no peaks corresponding to either the orthorhombic or the monoclinic structures are observed. The calculated lattice parameter is $a = 0.573$ nm. This is in good agreement with the values reported by Palatnik et al. [5] and Marcano et al. [13].

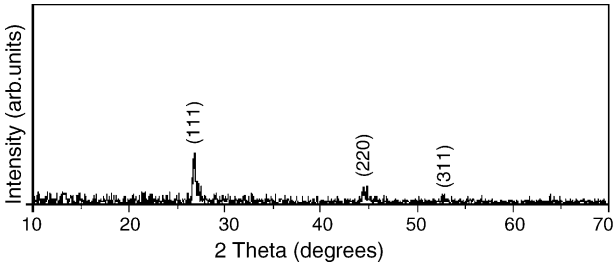

Fig. 1. Powder X-ray diffraction pattern of Cu_2SnSe_3 thin films in Bragg–Brentano mode.

It is also observed that in the above pattern, the peaks are broad and having some asymmetry. The broadness of the peaks may be due to small grain size of the films. The asymmetry might be due to the presence of minor second phase. To detect the presence of any minor phase, GIXRD spectra were taken from which one can elicit structural information as a function of depth.

In GIXRD mode, as the glancing angle (ω) exceeds the critical angle(ω_c), the X-ray beam penetrates into the sample. The critical angle for Cu_2SnSe_3 was calculated using the relations [16]

$$\omega_c = \sqrt{2}\delta$$

$$\delta = N_A \left(\frac{e^2}{2\pi mc^2}\right)\left(\frac{Z\rho}{A}\right)\lambda^2$$

where N_A is the Avogadro's number, Z the average atomic number, A the average atomic mass and ρ the mass density and λ is the wavelength of the X-rays used. The critical angle was found to be 0.3°.

The GIXRD patterns were recorded as stated earlier, for glancing angles (ω) of 0.5°, 1.5°, 2.5° and 5°. The penetration depth for any glancing angle can be calculated using the relation [16]:

$$D(\omega) = \frac{\lambda}{4\pi q}$$

$$q = \left[\sqrt{(\omega^2 - \omega_c^2)^2 + 4(\delta_i)^2} + \omega_c^2 - \omega^2\right]^{1/2} (\sqrt{2})^{-1}$$