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Preparation and characterization of co-evaporated $Cu_2ZnGeSe_4$ thin films

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ABSTRACT

$Cu_2ZnGeSe_4$ (CZGSe), a member of Cu_2–II–IV–VI_4 family, is a promising material for solar cell absorber layer in thin film heterojunction solar cells like Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ which have been explored in recent years as alternate to $CuInGaSe_2$ solar cells. The effect of substrate temperature (523 K–723 K) on the growth of CZGSe films is investigated by studying their structural, morphological and optical properties. Raman spectroscopy studies have been done to identify the phases in addition to X-ray diffraction studies. CZGSe films deposited at different substrate temperatures and annealed at 723 K in selenium atmosphere are Cu-rich and Ge-poor and contained secondary phases $Cu_{(2-x)}Se$ and ZnSe. CZGSe films obtained by reducing the starting Cu mass by 10% were found to be single phase with stannite structure, the lattice parameters being $a = 0.563$ nm, $c = 1.101$ nm. The direct optical band gap of CZGSe films is found to be 1.63 eV which is close to ideal band gap of 1.50 eV for the highest photovoltaic conversion efficiency. The films are found to be p-type.

1. Introduction

Quaternary compound semiconductors of the type Cu_2–II–IV–VI_4 are attracting the attention of the investigators owing to their possible application in optoelectronics and non-linear optical devices [1–3]. Among these, Cu_2ZnSnS_4 (CZTS) and $Cu_2ZnSnSe_4$ (CZTSe) containing non-toxic and abundant elements have been investigated to a considerable extent as alternate solar cell absorber layers to $CuInGaSe_2$ which exhibited a record efficiency of 20.3% [4] but contains expensive and scarce elements — In, Ga. CZTS and CZTSe and $Cu_2ZnSn(S,Se)_4$ thin film solar cells with a laboratory efficiency of 8.4%, 9.15% and 10.1% have been reported [5–7]. Recently, Ford et al. [8] synthesized $Cu_2Zn(Sn_{(1-x)},Ge_x)S_4$ nanocrystals and reported a $Cu_2Zn(Sn_{0.7}Ge_{0.3})S_4$ thin film absorber based solar cell with an efficiency of 6.8%. These results prompted us to look into another member of this family, $Cu_2ZnGeSe_4$ (CZGSe) which is again an attractive candidate for solar cell absorber layer owing to its direct band gap (~1.5 eV) being close to the ideal band gap, high optical absorption coefficient and p-type electrical conductivity [3,9]. The growth and physical properties of CZGSe single crystals were reported earlier [1–3,9–13]. Of late, the synthesis and thermoelectric properties of CZGSe nanocrystals have been reported by Ibanez et al. [14]. Matsushita et al. [15] reported the preparation and characterization of CZGSe thin films. The reported data on CZGSe films are quite meager. Thus there is a need to further investigate these films thoroughly to understand the growth and basic properties for their effective usage in the device fabrication. This paper reports the effect of substrate temperature on the growth of CZGSe thin films deposited by co-evaporation.

2. Experimental details

$Cu_2ZnGeSe_4$ thin films were prepared by the four source co-evaporation technique onto soda lime glass substrates using Hind Hivac Box coater unit (BC-300). Chemically and ultrasonically cleaned glass substrates were used for the deposition. Prior to the deposition, the glass slides were subjected to ion bombardment. Spectroscopically pure Cu (shot — 99.999%), ZnSe (random pieces, optical grade), Ge (99.999%) and Se (99.999+%) (All from Sigma-Aldrich, USA) were used as the source materials. To achieve the desired evaporation rates, each source is pre-calibrated using a quartz crystal thickness monitor. Selenium evaporation rate was kept slightly higher than the stoichiometric requirement to compensate for the loss of selenium due to re-evaporation. The base pressure in the vacuum coating unit was maintained at 5×10^{-4} Pa and the working pressure was 2×10^{-3} Pa. During the evaporation, the substrate holder was rotated using a rotary drive mechanism to ensure uniformity.

In order to investigate the effect of substrate temperature (T_s) on the growth of CZGSe films, the films were deposited at $T_s = 523$ K, 573 K, 623 K and 723 K. A dome-type radiant heater was used to heat the substrate holder to reach the desired temperature. The substrate temperature could be measured using a type K thermocouple kept in close contact with the substrate holder and its temperature could be controlled using a proportional-integral-derivative (PID) controller. Soon after the deposition, the substrates were cooled down to room temperature at the rate of 5 K/min using the PID

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controller. In order to anneal the films in Se atmosphere to improve crystallinity and to compensate for the selenium deficiency, if any, the substrate temperature was increased at the rate of 10 K/min from room temperature to 723 K where they were kept for an hour. Then the substrates were slowly cooled to room temperature at the rate of 5 K/min using the PID controller. The selenium slow evaporation was continued till the substrate temperature reached 573 K.

The films were analyzed by studying their composition, structural and optical properties. The film thickness was determined from its deposited mass measured using METTLER microbalance (Model AE240) and the bulk density. It is in the range 0.4–0.45 μm based on the deposition temperature. Spectral transmittance and reflectance of the films were recorded using UV–Vis-NIR double beam spectrophotometer (PerkinElmer, Model LAMDA 950) in the wavelength region 300–2500 nm in steps of 2 nm. X-ray diffraction (XRD) patterns of the films were recorded in the Bragg–Brentano mode in the 2θ range 10°–65° with a step size of 0.03° using SEIFERT X-ray diffractometer (Model 3003TT) with Cu K_α radiation ($\lambda = 0.15406$ nm). Microstructure of the films was recorded using Carl Zeiss scanning electron microscope (SEM) (Model EVO MA15) in the secondary electron image mode with an operating voltage of 20 kV. The cross-sectional image of the film was recorded using Hitachi field emission scanning electron microscope (S-4300 SE/N) with an operating voltage of 20 kV. Elemental composition was determined using Energy Dispersive X-ray spectrometer (EDX), Oxford Instruments, U.K (Model INCA 250) attached to the Carl Zeiss SEM operated at 20 kV. The data acquisition time is 60 s. Raman spectra were recorded using Jobin Yvon T-64000 triple stage spectrometer coupled with confocal microscope (Olympus). Ar^+ laser source ($\lambda = 514.5$ nm) of power 20 mW was used. The integration time kept was 60 s and resolution of the spectrometer is 0.5 cm^{-1}.

3. Results and discussion

3.1. Compositional analysis

EDX analysis data of the films deposited at different substrate temperatures (T_s) and annealed at 723 K is shown in Table 1. The films are non-stoichiometric and mostly Cu-rich and Ge poor. Stoichiometric deviation of germanium is higher, especially at higher substrate temperatures, probably due to re-evaporation from the substrate.

3.2. Structural properties

3.2.1. XRD analysis

Fig. 1 shows the powder XRD patterns of CZGSe films deposited at different substrate temperatures and annealed at 723 K. Fig. 2 shows the narrow scan XRD patterns of these films in the 2θ range 25°–30° with a step size of 0.01° and collection time of 5 s to identify unambiguously the (112) peak of CZGSe from the intense peaks corresponding to secondary phases Cu_2GeSe_3 (CGSe) and ZnSe which are close to it. XRD patterns of films deposited at $T_s = 523$ K [Figs. 1(a) and 2(a)] are found to be multiphase containing Cu_2Se, ZnSe, CGSe along with minor CZGSe phase. XRD pattern of films deposited at $T_s = 573$ K in the lower 2θ range [Figs. 1(b), 2(b)] shows three peaks, the dominant among them being (112) peak of CZGSe with stannite structure [3,15]. The other peaks belong to the binary phases $Cu_{2-x}Se$ and ZnSe. With increase in the substrate temperature from 523 K to 573 K, CZGSe phase is improved with the reduction

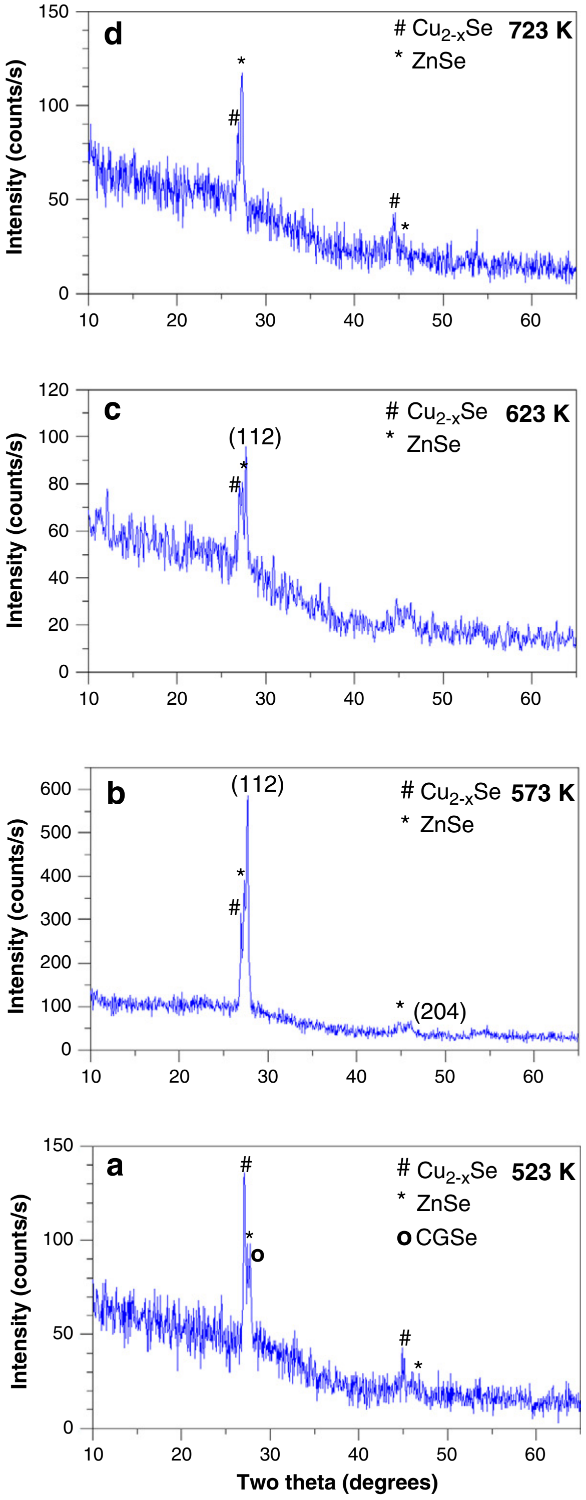

Fig. 1. XRD patterns of films deposited at different substrate temperatures. (a) 523 K (b) 573 K (c) 623 K (d) 723 K.

Table 1
EDX composition data of films deposited at different substrate temperatures.

T_s (K)	T_A (K)	Elemental composition (at.%)			
		Cu	Zn	Ge	Se
523	723	32.3	10.2	12.2	45.3
573	723	29.0	11.5	8.3	51.2
623	723	32.0	13.6	9.6	44.8
723	723	31.7	14.5	7.7	46.1