



# Solid state synthesis and e-beam evaporation growth of $\text{Cu}_2\text{ZnSnSe}_4$ for solar energy absorber applications



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## ABSTRACT

We report the growth and study of  $\text{Cu}_2\text{ZnSnSe}_4$  (CZTSe) thin films that have been grown by e-beam evaporation from pre-synthesized bulk source. Bulk source CZTSe was synthesized via solid state synthesis method. Hot pressed near stoichiometric CZTSe bulk was used as source for the growth of CZTSe thin films by e-beam evaporation. Electron beam current ( $I_b$ ) was varied between few mA to 110 mA to identify the optimal current for near stoichiometric CZTSe thin film growth without any post deposition annealing. Phase formation in bulk as well as thin films of CZTSe was studied using X-ray diffraction (XRD) and Raman spectroscopy. Raman spectroscopy resolved the ambiguity between co existing main and secondary phases in the complicated quaternary CZTSe. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) measurements were performed on the films grown at optimized e-beam current of  $I_b \sim 70$  mA. Scanning electron microscopy (SEM) was used to investigate the surface morphology and the composition was determined from the energy dispersive spectroscopic (EDS) measurements. Optical transmittance and reflectance data were analyzed to calculate the absorption coefficient ( $\alpha$ ) and the band gap ( $E_g$ ) values. The calculated band gap value of  $\sim 1.3$  eV agrees with the reported value for CZTSe. Positive values of the Seebeck coefficient indicated the p-type nature of the thin films.

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## 1. Introduction

Kesterites or quaternary copper chalcogenides with chemical formula  $\text{Cu}_2\text{ZnSn}(S,\text{Se})_4$  has been considered as potential absorber candidates for thin film solar cells. These compound semiconductors consist of non-toxic and earth abundant elements like Cu, Zn and Sn. The band gap for these materials lies in the range of 1–1.5 eV ( $\sim 1$  eV for CZTSe and  $\sim 1.5$  eV for CZTS) and have high absorption coefficient of the order of  $>10^4 \text{ cm}^{-1}$  (Mitzi et al., 2011). Doping of sulfur on selenium site or vice versa in CZT(S, Se) facilitates tuning of the band gap from 1 eV to 1.5 eV. CZTS was first proposed by Ito et al., as a potential solar absorber material (Ito and Nakazawa, 1988). Katagiri et al. reported first solar cell device fabricated using CZTS as absorber material with an efficiency 6.6% (Katagiri et al., 2009). Since then many vacuum and non-vacuum based methods have been employed to fabricate thin films of these materials. CZTSe thin films deposited by co-evaporation and DC Sputtering have shown device efficiencies of

9.15% (Repins et al., 2012) and 9.7% (Brammertz et al., 2013) respectively. Irrespective of the method of deposition, quaternary systems presents difficulty in achieving near stoichiometric films. The secondary phases formed during the thin film formation have to be eliminated either through heat treatment or etching processes. In solution based approaches nanoparticles of CZTSe have been synthesized by hot injection method which is subsequently deposited as thin films by spin coating or doctor blade method (Yang et al., 2014). In solution processed thin films annealing at high temperature is mandate to facilitate grain growth, removal of residual carbon if any, as well as to achieve desired stoichiometry (Mitzi et al., 2011; Tanaka et al., 2007; Wei et al., 2010). Hence a method to obtain near stoichiometric, homogeneous CZTSe thin films with simple processing steps will be of interest from the point-of-view of device fabrication. With this aim we have studied the e-beam growth of CZTSe thin films from the pre synthesized CZTSe bulk source as a function of e-beam current.

Electron beam evaporation is a versatile technique to obtain uniform thin films of high quality on different kind of substrates such as glass and steel. Unlike thermal evaporation, the material loss is minimal in e-beam evaporation due to localized heating

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(Chopra and Kaur, 1969). The key challenge with this method is that the control of evaporation parameters especially for the deposition of compounds and alloys from single source due to difference in the vapor pressure of the constituent elements. But by carefully optimizing the different parameters namely e-beam current, substrate temperature, etc. thin films having stoichiometry close to the source bulk can be obtained. Previously thin films of CIGSe have been grown successfully by making use of pre synthesized single phase compound as source material and a tailored substrate temperature profile maintained during the deposition (Venkatachalam et al., 2009, 2008; Xu et al., 2013). Similarly Caballero et al., have reported the growth of Ge doped CZTSe thin films by flash evaporation from single source precursor followed by heat treatment (Caballero et al., 2015). To the best of our knowledge no report exists on deposition of polycrystalline quaternary CZTSe films by e-beam evaporation from bulk source in a single step. In this reported work, CZTSe thin films have been deposited at a substrate temperature of 373 K and a carefully optimized e-beam current.

CZTSe has also been explored as a potential mid-range thermoelectric material due to its ideal band gap of  $\sim 1$  eV, as well as complex crystal structure leading to low thermal conductivity. Thermoelectric properties of bulk CZTSe synthesized by solid state method and mechanical alloying have shown promising ZT values (Chetty et al., 2013; Liu et al., 2009; Raju et al., 2013; Shi et al., 2009; Tiwari et al., 2016). However, there are no reports on the thermoelectric properties of CZTSe thin films. In this work, in addition to evaluation of structural and optical properties, thermoelectric characteristics of CZTSe thin films have also been studied.

## 2. Experimental methods

The growth of thin films consists of two steps. In the first step bulk CZTSe has been synthesized by the conventional solid state method. For the preparation of bulk CZTSe compound 5 N pure constituent elements namely Cu, Zn, Sn and Se were taken in the stoichiometric ratio. All elemental precursors used for the synthesis of CZTSe were obtained from Alfa Aesar. The individual elements are weighed with an accuracy of  $\pm 0.02$  mg and taken in molar ratio of 2:1:1:4 as per the chemical composition of CZTSe. The elements were sealed in a quartz ampoule at a pressure of  $7.5 \times 10^{-5}$  mbar. The sealed ampoule was heated in a muffle furnace to a temperature of 923 K at a heating rate of 2 K/min. The furnace is maintained at this temperature for a period of about 48 h before it is allowed to cool down to the room temperature. For annealing, the ingot was crushed and cold pressed to form the pellets and vacuum sealed before annealing at a temperature of 1073 K for 96 h. The annealed ingot was crushed into fine powder and packed into graphite dies for subsequent hot pressing under a pressure of 30 MPa at 773 K for 1 h in a 5 ton Vacuum Hot Press built by Vacuum Technologies Bangalore. Near stoichiometry in the synthesized bulk was confirmed before using it as source material for e-beam evaporation.

The films are deposited on well cleaned soda lime glass substrates using Hind Hivac thermal and e-beam evaporator (Model 12A-4D). The substrates were cleaned following the standard procedure, where primary cleaning was done with chromic acid. Subsequently the substrates were cleaned in distilled water and ultrasonically cleaned in acetone for 10 min. Cleaned substrates are mounted on the substrate holder fitted with thermocouple. Pre synthesized pellet of CZTSe was kept in graphite crucible for evaporation. The deposition was carried out under a high vacuum of  $5 \times 10^{-5}$  mbar. The substrate temperature was maintained at 373 K throughout the deposition with the help of PID controller. Substrates were kept static in the line of sight of the crucible in

order to obtain the uniform thin films. The supply voltage was kept constant at  $\sim 5$  kV and the beam current ( $I_b$ ) was varied. The films were deposited utilizing our different e-beam current values ( $I_b$ ) from 10 mA to 110 mA.

XRD measurements were done with Cu  $K_\alpha$  radiation having a wavelength of  $\sim 1.54$  Å using PANalytical X'pert powder diffractometer in Bragg Bernanto geometry on bulk and thin films of CZTSe. Powders from hot pressed CZTSe pellets and e-beam deposited thin films are subjected to the Raman spectroscopy studies in backscattering mode. Non polarized Raman spectra for the thin film were recorded by Horiba Jobin-Yvon (HR 800) spectrophotometer with 488 nm Ar ion laser. Band gap measurements on the deposited thin films were done by diffused reflectance UV-Vis spectroscopy (Specord 200 plus UV-Vis spectrophotometer Analytik Jena Germany) fitted with integrating sphere. SEM studies were carried out on the as deposited thin films with ZEISS SUPRA scanning electron microscope. EDS measurements were done with the OXFORD instruments attached with the SEM. Transmission electron microscopy studies were done with JEOL transmission electron microscope. Samples for TEM measurement were prepared by floating off very thin CZTSe thin film deposited on glass substrate using dilute hydrofluoric acid (HF). Resistivity and Seebeck measurements were performed on the LINSEIS LSR-3 instrument in the temperature range of 323–460 K.

## 3. Results and discussion

### 3.1. CZTSe bulk

#### 3.1.1. Structure and phase analysis

XRD data of heat treated, annealed and hot pressed samples were analyzed to identify the phase purity. The sample heated to 923 K was a mixture of binary and ternary phases. Therefore the samples were subsequently annealed and hot pressed to improve the phase purity. Typical XRD patterns obtained for the annealed and hot pressed CZTSe bulk is presented in Fig. 1a and b respectively. XRD analysis of the annealed CZTSe bulk showed the formation of CZTSe phase along with less intensity diffraction peaks corresponding to  $\text{CuSe}_2$ . All the observed peaks are indexed with reference to the ICDD file No. 04-003-8817 for CZTSe. In order to eliminate the secondary  $\text{CuSe}_2$  phase and obtain single phase CZTSe hot pressing of the annealed powders was carried out. The XRD pattern obtained for the hot pressed CZTSe bulk is shown in Fig. 1b. It is clearly seen from the figure that reflection corresponding to  $\text{CuSe}_2$  disappeared after hot pressing. The appearance of sharp peaks indicated the grain growth and improved crystallinity after hot pressing. All the peaks are indexed and found to match well with the standard data for the CZTSe compound. The crystallite size for the annealed and hot pressed CZTSe was calculated by Scherrer formula given below:

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where 'D' is the crystallite size in nm, ' $\lambda$ ' is the wavelength of  $\text{CuK}_\alpha$  radiation in nm, ' $\beta$ ' is full width at half maximum value (FWHM) in radians of the maximum intensity peak. The crystallite sizes calculated for the annealed and hot pressed CZTSe bulk samples are 53.5 nm and 61.7 nm respectively.

It is a well-established fact that the phase confirmation in quaternary CZTS/Se compounds cannot be ascertained by XRD studies alone due to its overlapping diffraction peaks with the peaks due to sub systems (Siebentritt and Schorr, 2012). In particular, ternary  $\text{Cu}_2\text{SnSe}_3$  (CTSe) and binary ZnSe exhibit very similar XRD patterns leading to uncertainty in phase corroboration. This ambiguity in this system occurs due to the fact that Cu existing in +1 state

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