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Tetrahedrite ($Cu_{12}Sb_4S_{13}$) thin films for photovoltaic and thermoelectric applications

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ABSTRACT

In this paper we have demonstrated the growth of $Cu_{12}Sb_4S_{13}$ thin film through e-beam evaporation from a single source. The source material was pre-synthesised via ball mill method starting from a stoichiometric mixture of elements (Cu, Sb and S) taken in the atomic ratio of 12:4:13. The films were deposited at different beam currents *viz.* 40, 50 and 60 mA. The bulk material and thin films were studied using X-ray diffraction (XRD) and Raman spectroscopy to evaluate phase formation. The films grown at beam current values of 40 mA showed the presence of $Cu_{12}Sb_4S_{13}$ phase along with Cu_3SbS_4 and CuS secondary phases. The films grown at 50 mA and 60 mA are showing Cu_3SbS_4 phase as main phase. These results are in agreement with the Raman studies. The composition of as grown films was analysed using Rutherford backscattered spectrometry (RBS) and proton induced X-ray emission (PIXE) measurements. The Cu content in the films is decreasing with increase in the beam current, whereas the Sb and S content shows increment. The optical absorption measurement was used to determine the optical band gap. The films show a direct band gap value of ~1.8 eV with an optical absorption coefficient of $\sim 10^5\ cm^{-1}$. Temperature dependant Seebeck coefficient and electrical resistivity values were measured for the thin films and the power factor values were calculated. The positive Seebeck coefficient values obtained indicate p-type semiconducting nature of the films. The maximum power factor of 2.30 μW/cm-K^2 at 495 K was obtained for films grown at 40 mA e-beam current. The electrical and optical properties are significantly influenced by the presence of secondary phases and compositional deviation.

1. Introduction

Copper Antimony Sulphide (CAS) compounds have drawn huge attention for energy conversion applications, primarily as thermoelectric materials and recently for their suitable photovoltaic characteristics (Chetty et al., 2015a,b,c; Heo et al., 2015; Lu and Morelli, 2013; Prem Kumar et al., 2016; Rath et al., 2015; Suehiro et al., 2015; Suekuni et al., 2012; Suzumura et al., 2014; Tablero, 2014; Van Embden et al., 2013; Xu et al., 2014). CAS systems are p-type direct band gap semiconductors existing in different phases namely $Cu_{12}Sb_4S_{13}$ (tetrahedrite), Cu_3SbS_4 (fematinite) and $CuSbS_2$ (chalcostibite) (Suehiro et al., 2015). CAS compounds are non-toxic with earth abundant constituents and found naturally in the mineral form (George et al., 2017).

Thermoelectric properties of bulk $Cu_{12}Sb_4S_{13}$ have been widely explored (Chetty et al., 2015a,b,c; Lu and Morelli, 2013; Prem Kumar et al., 2016; Suekuni et al., 2012). High band degeneracy and complex crystal structure give rise to enhanced power factor and low thermal conductivity making them a potential thermoelectric material (Chetty et al., 2015a,b,c; Lu et al., 2013; Suekuni et al., 2012; Tippireddy et al., 2018). The thermoelectric figure of merit, zT ~ 1 (at T = 723 K) is achieved via doping (Lu et al., 2015; Lu and Morelli, 2013). In addition, $Cu_{12}Sb_4S_{13}$ exhibit high optical absorption coefficient ($\sim 10^5\ cm^{-1}$) in the visible region (Heo et al., 2015; Rath et al., 2015) indicating its suitability in photovoltaic applications. Tablaro et al. have reported theoretical band gap value of 1.3 eV for stoichiometric $Cu_{12}Sb_4S_{13}$ compound and the band gap varies for deviations in stoichiometry (Suehiro et al., 2015). The band gap value changes to ~1.4 eV for copper rich, ~1.1 eV and ~0.8 eV for S rich and Sb rich conditions respectively (Tablero, 2014; Van Embden et al., 2013). The experimental studies on thin films have reported band gap values between 1.6 and 1.9 eV (Ramasamy et al., 2014; Tablero, 2014; Van Embden et al., 2013). In addition to optical band gap the carrier concentration of the absorber layer is an important parameter which governs the device

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efficiency. A study has reported that $Cu_{12}Sb_4S_{13}$ shows a high carrier concentration ($\sim 10^{20}\,cm^{-3}$), which increases the probability of charge carrier recombination (Heo et al., 2015). This value is much higher when compared with the effective charge carrier concentration of CZTSe which is reported to be $\sim 10^{16}\,cm^{-3}$ (Taskesen et al., 2018). However, for $Cu_{12}Sb_4S_{13}$ the issue has been addressed through doping Zn^{+2} and In^{+3} in copper site to reduce the carrier concentration to optimal values (Heo et al., 2015).

There are various methods reported for the synthesis of bulk, thin film and nano-crystals of CAS and other ternary/quaternary solar absorber compounds (Cho et al., 2017; Heo et al., 2015; Rath et al., 2015; Tablero, 2014 Liu and Chuang, 2012, Tiwari et al., 2017). The synthesis of bulk powder for the thermoelectric applications is conventionally prepared through the solid state melting (Chetty et al., 2015a,b,c; Lu et al., 2015; Prem Kumar et al., 2016; Suekuni et al., 2012) and mechanical alloying process (Barbier et al., 2016; Lu and Morelli, 2013). Lu et al. have proposed a refining process of natural mineral to obtain the desired stoichiometry via ball milling (Lu and Morelli, 2013). Barbier et al. and Harish et al. have shown the synthesis of doped $Cu_{12}Sb_4S_{13}$ by the mechanical alloying process (Barbier et al., 2016) starting from raw elements.

Thin film growth and nano-crystals synthesis of these compounds are often reported that were based mainly on solution processes (Rath et al., 2015; Tablero, 2014; Van Embden et al., 2013). A very few reports have demonstrated the growth of $Cu_{12}Sb_4S_{13}$ using physical vapour deposition (Heo et al., 2015). Heo et al. have reported the thin film deposition using the e-beam evaporation method starting from two independent binary sources namely Cu_2S and Sb_2S_3. Further annealing is done followed by sulfurization to obtain the doped $Cu_{12}Sb_4S_{13}$ (Heo et al., 2015). Rath et al. have demonstrated the growth of $Cu_{12}Sb_4S_{13}$ and $CuSbS_2$ thin films by spin coating metal xanthates precursors followed by annealing under the inert atmosphere (Rath et al., 2015). The reports suggest that the difficulty in synthesis of $Cu_{12}Sb_4S_{13}$ is mainly due to high chances of formation of Cu_3SbS_4 and $CuSbS_2$ secondary phases. The coexistence of these phases is more probable due to almost similar atomic fraction ratios of the constituent elements: tetrahedrite (Cu:Sb:S – 12:4:13) and fematinite (12:4:16). In addition, these phases are sensitive to annealing conditions. The heat treatment of these films may lead to the phase transformation into other Cu−Sb−S systems (Van Embden et al., 2013).

Thermoelectric and PV studies of $Cu_{12}Sb_4S_{13}$ films are interesting from the point of view of scaling down the thermoelectric generator (TEG) modules as well as for applications in thin film solar cells. In this paper, we report the study of growth of $Cu_{12}Sb_4S_{13}$ thin films for PV as well as thermoelectric applications. Our objective is to grow the film by e-beam evaporation technique in a single step using pre synthesised source and optimized e-beam current. The source material is synthesised through viable mechanical alloying starting from pure elements. The structural and compositional variations with respect to e-beam current are studied to optimize e-beam current for single-phase growth of $Cu_{12}Sb_4S_{13}$. The following procedure has previously demonstrated by Tiwari et al for the growth of Sb_2Se_3 thin film (Tiwari et al., 2018). The optical and temperature dependant thermoelectric properties of the films are studied in detail.

2. Experimental details

2.1. Bulk synthesis and thin film growth of $Cu_{12}Sb_4S_{13}$

$Cu_{12}Sb_4S_{13}$ thin films were deposited using mechanical alloyed pre-synthesised bulk compound. The constituent elements namely Copper (99.5%), Sulphur (99.5%) and Antimony (min 99%) were taken in the stoichiometric ratio of Cu:Sb:S = 12:4:13. The mixture was taken in the tungsten carbide jar with ball to powder weight ratio of 10:1 and milled with the rotation speed of 500 RPM for 8 h in toluene medium. The as-milled powder was compacted [cold press] at room temperature using a steel die under a uniaxial pressure of 60 MPa. The compact pellet was used as a source material to deposit the $Cu_{12}Sb_4S_{13}$ thin film using E-beam evaporation. The films were deposited at different beam current (I_B) values of 40 mA, 50 mA and 60 mA keeping voltage fixed at 5 kV for 75 s onto the glass substrates kept at 573 K.

2.2. Characterization of $Cu_{12}Sb_4S_{13}$ bulk milled source and thin films

The phase formation in the milled powder and thin films was studied using X-ray diffraction (XRD) and Raman spectroscopy. The films were further subjected to RBS and PIXE to determine the composition. The XRD diffraction data was collected in Rigaku smart lab instrument using Cu-Kα X-rays (λ = 1.54 Å). Horiba Micro-Raman spectrometer with laser source of wavelength 633 nm was used for the Raman studies to examine the phase formation in thin films. FEI Quanta FEG 200 - High Resolution Scanning electron microscope (SEM) was used for the surface morphology studies of as grown films. RBS and PIXE measurements were carried out at CIBA, NUS, Singapore using the 2.0 MeV singletron facility. The electrical resistivity (4-probe technique) and the Seebeck coefficient of the films were measured between 323 K and 495 K using the LINSEIS (LSR-3) system. The measurement was carried out under helium atmosphere (chamber pressure = 1×10^{-1} mbar). The errors in the measurement of electrical resistivity and Seebeck coefficient are 10% and 7% respectively.

3. Results and discussion

3.1. XRD and Raman studies of bulk $Cu_{12}Sb_4S_{13}$

Ball milled CAS powder is examined using XRD. Fig. 1a displays the typical XRD pattern of the ball milled powder, which is matching with the standard ICSD (2857) data of Cu_3SbS_4 with the space group I2m. Further analysis of the XRD pattern showed the existence of CuS and Sb as secondary phases. Fig. 1b shows the de-convoluted Raman spectrum of bulk powder.

The observed vibrational modes at 251.4, 312.5 and 340.9 cm^{-1} are corresponding to Cu_3SbS_4 phase. The peaks at 468 and 464 cm^{-1} are due to $Cu_{1-x}S$ phase (Chalapathi et al., 2017). Although the elemental mixture is taken according to the stoichiometry of $Cu_{12}Sb_4S_{13}$, milling leads to the formation of Cu_3SbS_4 with Sb and CuS secondary phases. Harish et al. have demonstrated the synthesis of $Cu_{12}Sb_4S_{13}$ using a dry milling process at 150 RPM (Harish et al., 2016). They have shown that the Cu_3SbS_4 compound has formed at about 10 h of milling time. Continuation of milling led to the formation of $Cu_{12}Sb_4S_{13}$. Barbier et al have observed the formation of the $Cu_{12}Sb_4S_{13}$ phase after 5 h of dry milling time and at a higher RPM of 600 (Barbier et al., 2016). In the present work, further optimization of the milling conditions is necessary for the formation of single phase $Cu_{12}Sb_4S_{13}$. However, the growth of the thin films with desired stoichiometry is highly dependent on growth parameters such as e-beam current and substrate temperature rather than the stoichiometry of starting material. Therefore, the as formed Cu_3SbS_4 with Sb and CuS secondary phase is used as a source material for the deposition of the tetrahedrite films by optimizing the e-beam current.

3.2. Results of $Cu_{12}Sb_4S_{13}$ thin films

3.2.1. XRD results

XRD patterns obtained for the as-grown films are shown in Fig. 2. For the film deposited at 40 mA beam current the prominent peak was observed at $2\theta = 30.13^{\circ}$(2 2 2) corresponding to $Cu_{12}Sb_4S_{13}$ phase (ICSD #25707) with $I\bar{4}3m$ space group. In addition to the $Cu_{12}Sb_4S_{13}$ phase the film showed the presence of minor secondary phases corresponding to Cu_3SbS_4 at $2\theta = 28.7^{\circ}$ (1 1 2), and CuS at $2\theta = 28.3^{\circ}$ (1 1 1) (Hurma and Kose, 2016).

The XRD patterns of the film deposited at 50 and 60 mA beam

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