Temperature dependence electrical conduction of solution-processed CZTS films in dark and under light

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Abstract. Electrical conduction of solution-processed Cu₂ZnSnS₄ (CZTS) films has been reported in dark and under light in the temperature range of 85 to 300 K. The films show nearest neighbor hopping mode of transport at below 200 K, while above 200 K the films were dominated by thermionic emission over grain boundary barriers, following, Seto’s model for polycrystalline films. The hopping energy and grain boundary barrier height of CZTS films are found be decreases under illumination due to the photoconductivity. The films were pure kesterite CZTS as revealed from X-Ray diffraction and Raman spectroscopy.

1. Introduction

Cu₂ZnSnS₄ (CZTS) is emerging as the most promising absorber material for cost effective thin films solar cells (TFSCs) now a day’s [1]. CZTS is p-type with a direct near-optimal band gap of 1.4 to 1.5 eV and high absorption co-efficient of above 10⁴ cm⁻¹ in the solar spectrum. Hence, it can be regarded as an alternative to conventional TFSC absorbers such as CdTe and Cu(In,Ga)Se₂ (CIGS). Recently, a conversion efficiency of 12.6 % has been achieved by depositing CZTSSe using a hydrazine ink based pure solution [2]. However, the performance of CZTS-based solar cells is still far away from the 20.8 % efficient CIGS devices. To enhance the photo conversation efficiency of solar cells, the basic electrical properties of the CZTS, especially temperature dependence of electrical conductivity is being vigorously studied all over the world [3-8]. Electrical properties of polycrystalline CZTS films in dark have been investigated from 10 to 300 K by various researchers [3-5]. However, under light, the report has been sparse [6-8]. Generally, the electrical conductivity can be governed by (a) Mott Variable Range Hopping (M-VRH), (b) Nearest Neighbour Hopping (NNH) and (c) Thermionic Emission (TE) over Grain Boundary (GB) barriers. The dominant mode of electronic transport was found to depend on the temperature range: TE over GB (150 to 300 K), NNH (70 to 150 K) and M-VRH (30 to 70 K). M-VRH is generally applicable to amorphous kind of materials and at below 50 K where electrons do not have enough energy to cross the potential barrier. Hence, in present case, M-VRH model is not expected in our...
polycrystalline CZTS films. Analysis of the earlier reported data look rather complicated and confusing suggesting quite different conductivity mechanisms in the temperature range of 10 to 300 K. Hence, it is quite difficult to identify the applicability of specific model in specific temperature range. Moreover, experimental results on the temperature dependence of photoconductivity in CZTS films are not reported yet. Hence, it was worthwhile to study the electrical properties of CZTS films in dark and under light. We report, in this paper, electrical transport of solution-processed CZTS films in the temperature range of 85 to 300 K in dark and under light with specific and simplified mode of transport. A simple process for deposition of CZTS films from single precursor solution of metal-thiourea complex has been developed. The solution processed films are pure and free of unwarranted impurity.

2. Experimental

A synthesis and characterization of solution-processed, pure kesterite methanolic CZTS films were reported earlier by Chaudhuri and Tiwari [9]. Hence, in present case a same method was adopted for the synthesis of CZTS films. However, in present study, Ethylene glycol (EG) is used as the main solvent instead of methanol. The precursor ink was prepared by dissolving 0.1 mol/L copper (II) acetate, 0.05 mol/L zinc acetate, 0.05 mol/L tin (II) chloride and 0.5 mol/L thiourea (TU) in 40 ml of EG. All the chemicals and solvents used in present study are of analytical grade supplied by Merck Limited, India. The as-prepared inks were then directly deposited on glass substrates (75 mm X 25 mm) by doctor blade (‘Marshal’ AP-E Basic, India) technique using film applicator. Wet precursor films are then converted into black CZTS films due to metal-TU complex by applying 473 K temperature for 1 hr. in air. For electrical measurements gap cells (~ 2 mm) were fabricated with graphite paint (Ted Pella) as ohmic contact. The electrical conductivity of CZTS films in the temperature ranges of 85 to 300 K in dark and under light were measured by placing the samples in a Liquid nitrogen cryostat (Janis VPF-100, with LakeShore 335 Temperature Controller). A constant 10 V bias was applied for the conductivity measurements. The dark and photocurrent was measured with Source/Meter Unit (Keithly 2611). For illumination, white light of a quartz halogen lamp (Philips 50 W, 12 V) with an intensity 100 mW/cm² was chosen. The amount of light falling on the sample was calibrated by Pyranometer (National Instruments, Kolkata).

3. Result and discussion

The X-Ray Diffraction (XRD) of films doctor bladed from inks is shown in the Fig 1. The films shows 2θ values of 28.55°, 32.97°, 47.29° and 56.11° corresponding to d-values of 0.31, 0.27, 0.19, and 0.16 nm, respectively. On comparison with standard XRD lines of CZTS (JCPDS 26-0575), these lines were identified to be reflections from (112), (200), (220) and (312) planes of kesterite phase. XRD pattern matches well simultaneously with that of ZnS.
(JCDPS 65-1691) and Cu$_2$SnS$_3$ (CTS) (JCPDS 27-0198); hence it is quite difficult to differentiate these entire compounds by doing only XRD. Raman spectroscopy is required to distinguish such materials. Inset of the Fig. 1 shows the Raman shift spectra of the CZTS films along with deconvolution of peaks with the help of Gaussian and Lorentzian functions. The spectra show the presence of two peaks: a strong one at 336 cm$^{-1}$ and weaker one at $\sim$ 285 cm$^{-1}$. These peaks are due to the kesterite CZTS and are in good agreement with previously reported data for CZTS [10]. The main peak at 336 cm$^{-1}$ is due to the A1 vibrational mode, arising from the vibrations of S atoms in CZTS lattice while rest of the atoms remains stationary [11]. Absence on any other peaks due to tetragonal CTS (297, 337 and 352 cm$^{-1}$), cubic CTS (295-303 and 355 cm$^{-1}$), orthorhombic CTS (318 cm$^{-1}$), Cubic ZnS (267, 303 and 356 cm$^{-1}$) and Cu$_{2-x}$S (264 and 475 cm$^{-1}$) corroborate the formation of pure kesterite CZTS.

The cross-sectional view of CZTS films observed by Scanning Electron Microscope (SEM) is shown in the inset of the Fig. 2. The thickness of the films is around 5 µm. The film is slightly porous with interconnected granular grains of 0.4 to 0.6 µm. Zhou et al. [12] observed the similar kind of structure in their CZTS films synthesized by solvothermal route.

The current-voltage (I-V) characteristics of CZTS films in dark and light (100 mW/cm$^2$) are linear indicating Ohmic nature of the graphite contacts. As the dark resistance of the films is of the order of $10^8$ ohm and even higher at 85 K, the two-probe method was used to measure the resistivity/conductivity of the films. Room temperature electrical studies in dark reveal that films were p-type with thermoelectric power of + 193 µV/K. The hole concentration, mobility and electrical conductivity ($\sigma$) of films were found to be $1.65\times10^{19}$.
cm\(^{-3}\), 0.35 cm\(^{-2}\) V\(^{-1}\) s\(^{-1}\) and 0.07 S/cm, respectively. These electrical properties are comparable to that of CZTS films prepared in EG [8]. It was seen from the SEM that the films were porous made up of large interconnected spherical grains. Hence, it is obvious that the electrical conductivity and carrier mobility of the corresponding partially densified films are quite low compared to the reported values for CZTS films in the literature [4, 6]. In general, lower values of charge carrier mobility and electrical conductivity is due to the fact that the films are non-well densified made up of large numbers of grains and microporosity. To find out the dominant conduction mechanism in these films, the electrical conductivity (\(\sigma\)) has been measured in dark (\(\sigma_D\)) and under light (\(\sigma_L\)) in the temperature range of 85 to 300 K as shown in the Fig. 2. In general, \(\sigma\) increases slowly with T below 200 K while it increases sharply above 200 K which shows the typical semiconductor behavior of CZTS films. Due to the photoconductivity, the value of \(\sigma_D\) is higher than \(\sigma_L\). The illumination excites electrons in the valence band to the conduction band and hence increases the minority charge carriers (electrons) in the films, which ultimately enhance the \(\sigma\) of CZTS films. In general, both \(\sigma_D\) and \(\sigma_L\) behave in the same way with varying T. Two quite different slopes were observed from the \(\sigma\) vs. 1000/T plot as shown in the Fig. 2, indicating that the conductivity is affected by the two different transport mechanisms, each one is affecting in the different temperature range. Earlier, Kosyak et al. [3] suggested the electrical conductivity of the polycrystalline CZTS below 300 K can be governed by Eq. (1):

\[
\sigma = \sigma_{01} \exp \left( -\frac{T_0}{T} \right)^{\frac{1}{2}} + \sigma_{02} \exp \left( -\frac{E_2}{k_B T} \right) + \sigma_{03} \exp \left( -\frac{E_3}{k_B T} \right) \tag{1}
\]

where \(\sigma_{01}, \sigma_{02}\) and \(\sigma_{03}\) are pre-factors, \(T_0\) is the Mott characteristics temperature, \(E_2\) is the nearest neighbor hopping energy and \(E_3\) is grain boundary barrier height.

\[\text{Figure 2. Temperature dependence electrical conductivity of CZTS films. Inset of the figure shows SEM cross-sectional view of the films on glass.}\]
The first term in the equation denotes M-VRH, second term is due to the NNH and the third term is TE over GB. As discussed earlier, M-VRH is not expected in the present study since a temperature in this investigation is 85 to 300 K which is above 50 K. At intermediate temperatures \(50 < T < 200\), NNH is very plausible, which can play dominant role in the conduction process of semiconductor thin films. NNH needs lowest activation energy for the carrier to hop to the nearest neighboring state from the filled state. NNH type conduction is indicative of some extent of disorder, which leads to the localized states near band edges. This type of conduction is expected because synthesis of the material is carried out at relatively lower temperatures, which may not be sufficient to form a thermodynamically more stable structure, thus leading to a disordered in lattice \([13]\). To check the applicability of the model, \(\ln\sigma Vs 1000/T\) plot was drawn in the temperature range of 85 to 155 K as shown in the Fig. 3(a). Straight line was found, which indicates the existence of NNH conduction at lower temperatures (\(< 200\) K). Hopping energy calculated from the slope is 33 and 30 meV for dark and light, respectively. The values of hopping energy under illumination are less than that of dark due to shift in the position of the Fermi level towards the conduction band under illumination \([14]\).

![Figure 3(a)](image1)

Figure 3 (a) Electrical conduction due to NNH at low temperature; (b) TE over GB mode of transport at high temperature.

It can be seen from the Fig. 2 that the curve (dark and light) deviates from the lower temperature (\(< 200\) K) to higher temperature shows that NNH conduction is not dominating in the higher temperature range. At higher temperature, TE over GB mode of transport is applicable \([3, 8]\). Moreover, interconnected granular CZTS grains was observed in SEM, hence, it is likely that grain boundaries barriers (GBBs) will be formed at the interfaces as observed in polycrystalline semiconductor films \([15]\). Hence, the transport of current (holes) through the CZTS films will be significantly influenced by the GBBs. The transport of charge carriers in such type of films is due to thermionic emission over GBBs as suggested by Seto. If Seto’s model for charge transport is applicable to the CZTS films, then the plot of \(\ln\sigma\sqrt{T}\) vs. \(1/T\) will be linear and the slope will yield GBB. To check the applicability of the model, plot of \(\ln\sigma\sqrt{T}\) vs. \(1/T\) was drawn in the temperature range of 210 to 300 K as shown in the Fig. 3(b). The plots are found to be linear which indicates that the transport of holes in these CZTS films is due to thermionic emission over GBBs. The GBB height in dark is 95 meV while in light it is reduced to 90 meV. When CZTS films are illuminated with light, minority carriers (electrons) are generated which get trapped in the GBs resulting in reduction of GBBs as
compared to dark GBB. Similar results were reported by Ghediya and Chaudhuri [8] and Tiwari et al. [13] for CZTS and CTS films, respectively.

Hopping energy and GBBs are due to the defects. The CuZn antisite defect has the lowest formation energy which acts as an acceptor level located about 0.10–0.15 eV above the valence band maxima (VBM) and is considered to be responsible for the intrinsic p-type conductivity of these materials. The copper vacancy (VCu) has comparatively higher energy of formation than CuZn antisite and contributes to a much shallower acceptor level at ~ 0.02 eV above the VBM. Chen et al. [18] showed that p-type conductivity of CZTS is mainly determined by a CuZn acceptor defect having a quite deep level at $E_a = 0.12$ eV. Hence, similarly the defect GBB energy (> 200 K) observed in present investigation with the identical activation energy (0.095 eV in dark) could be assigned to CuZn acceptor defect. Further, Fernandes et al. [19] also revealed two defect activation energies of 45 meV and 113 meV in CZTS, which agree well with the experimental levels of V Cu and CuZn, respectively. Hence, low hopping energy (0.03 eV in dark) at below 200 K could be assigned to V Cu. A considerable difference in hopping energy at lower temperatures (< 200 K) and GBB at higher temperatures (> 200 K) indicate a clear transition from the NNH conduction to TE over GB conduction in CZTS films.

4. Conclusion

Electrical transport of CZTS films deposited from solution processed inks has been investigated in the temperature range of 85 to 300 K in dark and under light. Analysis of the conductivity data reveal that the transport of charge carriers below 200 K is because of Nearest Neighbor Hopping (NNH) while above 200 K the films were dominated by Thermionic Emission over Grain Boundary barriers (TE over GB). The values of hopping energy and grain boundary barrier height of CZTS films is found to be decreases under illumination due to the photoconductivity.

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