



Study of optical and structural properties of $\text{Cu}_2\text{ZnSnS}_4$ thin films

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ABSTRACT

$\text{Cu}_2\text{ZnSnS}_4$ is a promising semiconductor to be used as absorber in thin film solar cells. In this work, we investigated optical and structural properties of $\text{Cu}_2\text{ZnSnS}_4$ thin films grown by sulphurization of metallic precursors deposited on soda lime glass substrates. The crystalline phases were studied by X-ray diffraction measurements showing the presence of only the $\text{Cu}_2\text{ZnSnS}_4$ phase. The studied films were copper poor and zinc rich as shown by inductively coupled plasma mass spectroscopy. Scanning electron microscopy revealed a good crystallinity and compactness. An absorption coefficient varying between 3 and $4 \times 10^4 \text{ cm}^{-1}$ was measured in the energy range between 1.75 and 3.5 eV. The band gap energy was estimated in 1.51 eV. Photoluminescence spectroscopy showed an asymmetric broad band emission. The dependence of this emission on the excitation power and temperature was investigated and compared to the predictions of the donor-acceptor-type transitions and radiative recombinations in the model of potential fluctuations. Experimental evidence was found to ascribe the observed emission to radiative transitions involving tail states created by potential fluctuations.

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1. Introduction

Among the possible alternatives to replace $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) as absorber layer in thin film solar cells, kesterite $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) appears to have the right properties. This compound only uses abundant elements with low toxicity levels. CZTS is a p-type semiconductor with an absorption coefficient higher than 10^4 cm^{-1} and a band gap close to 1.5 eV [1,2]. Despite these interesting optical properties, the best conversion efficiency attained so far with pure CZTS based solar cell was 6.7% [3] and with $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ based solar cells was 9.6% [4], which are modest values compared with the efficiency reached by CIGS, 20.3% [5]. Growth related problems can explain part of such low efficiency, and according to Chen et al. [6], the formation of stoichiometric CZTS has a very narrow chemical potential region. The fact that best CZTS solar cells are Cu poor and Zn rich favours the growth of other phases during the formation of the film [7]. This means that very controlled conditions must be met during the growth process.

Several research groups followed a procedure consisting in the deposition of precursors by different methods and the subsequent sulphurization/annealing at high temperatures. The deposition of the precursors followed vacuum and non-vacuum methods. In the first

case, DC-magnetron sputtering of metallic precursors was tested by Fernandes et al. [8], RF-magnetron sputtering of stacked binary sulphide precursors by Katagiri et al. [9], co-sputtering by Katagiri et al. [3] and e-beam evaporation by Katagiri et al. [10]. In the second case, non vacuum techniques, spray-pyrolysis was used by Nakayama et al. [11], electro-deposition by Scragg et al. [12] and chemical bath deposition by Todorov et al. [13]. For the sulphurization/annealing of the precursors the main differences between the employed methods were related with the sulphurization atmosphere (S_2 vapour and/or H_2S gas), the annealing temperature, pressure and use or not of a transport gas (like N_2). Additionally, another approach was used by Friedlmeier et al. [14] through thermal co-evaporation.

In this work, we study structural and optical properties of CZTS thin films grown by sulfurization of stacked metallic precursors. Only CZTS with the kesterite structure was identified. The absorption coefficient and the band gap energy were estimated. The photoluminescence (PL) was investigated and was observed an asymmetric broad band. The dependence on the excitation power and temperature of the PL parameters were discussed in the light of existing PL models. The observed PL broad band was explained in the framework of a model of spatial potential fluctuations.

2. Experimental methods

The sample preparation followed an established procedure described elsewhere [8,15]. The used deposition sequence for the

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metallic precursors was Mo/Zn/Cu/Sn. In order to avoid the deposition of Mo in part of the sample, a mask was used, allowing a transmission-based optical characterization. The sulphurization/annealing step was performed in a tubular oven in a mixture of N_2 gas and S_2 vapour at a constant pressure of 5.6×10^{-1} m bar. The sample was sulfurized at a maximum temperature of 525 °C during 10 min. Finally, after the sulphurization process, all studied samples were submitted to a KCN chemical treatment in order to remove the $Cu_{2-x}S$ phases.

The structural characterization of the films was carried out by X-Ray diffraction (XRD) using a Philips PW 3710 diffractometer equipped with a $Cu - K\alpha$ source ($\lambda = 1.54060$ Å). The composition of the grown films was investigated by inductively coupled plasma mass spectroscopy (ICP-MS) using a Thermo X Series. The morphology of the films was investigated by scanning electron microscopy (SEM) with a Hitachi S4100 equipment. The absorption was characterized through transmission and reflection measurements performed with a Shimadzu UV-3600 spectrophotometer.

PL was performed in the temperature range of 5–300 K using a FTIR Bruker IFS 66v spectrometer. The samples were inserted in a flux cryostat in order to change the temperature. The 488 nm line of an Ar^+ laser was used as excitation source and the emission from the samples was detected with a Ge detector cooled to liquid nitrogen temperature.

3. Results and discussion

The deposition order of the metallic precursors was investigated previously [15]. The metallic atomic ratios of $[Cu]/([Zn] + [Sn]) = 0.9$ and $[Zn]/[Sn] = 1.3$, obtained by ICP-MS measurements, show that the films are Cu-poor and have a larger concentration of Zn compared to Sn. These values are close to the composition of solar cells with best efficiency [3].

XRD measurements were used in order to characterize the crystalline phases present in the grown films. The observed reflections are identified in Fig. 1. In addition to three peaks with origin in the Mo layer, all other visible reflections correspond to the CZTS crystalline phase. In particular, two double peaks typical of the kesterite structure, were found. No other crystalline phases have been identified in the films. The above results have been confirmed by Raman spectroscopy measurements (not shown). The main peaks are narrow which indicates that the films have good crystallinity. The lattice parameters have been obtained from the XRD pattern: $a = 5.424$ Å and $c = 10.861$ Å, which gives a value for $c/2a = 1.001$. Since the value of $c/2a$ is close to 1, this indicates that the cell is tetragonal.

The morphology of the grown films was investigated by SEM (Fig. 2). The micrograph shows a good crystallinity and compactness.

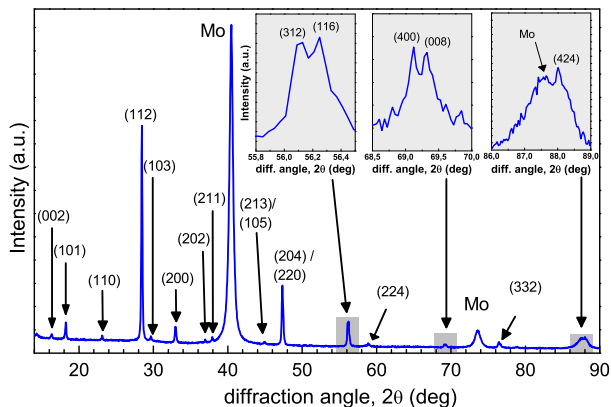


Fig. 1. XRD spectrum of a CZTS thin film after a KCN treatment.

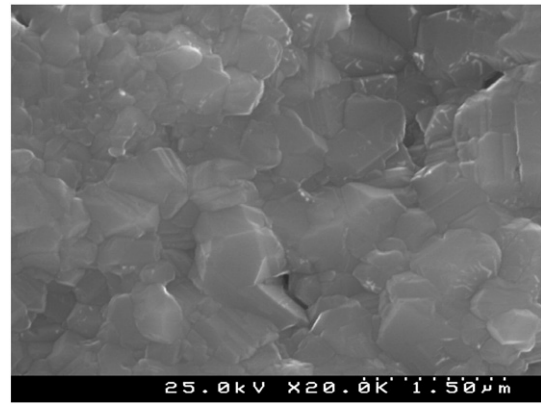


Fig. 2. SEM micrograph of the surface of a CZTS thin film after a KCN treatment.

The changes in the SEM micrographs induced by the KCN treatment clearly showed the removal of $Cu_{2-x}S$ crystallites after this treatment.

The band gap energy of the grown CZTS thin films was estimated considering the plot of $(\alpha h\nu)^2$ vs. $h\nu$ (Fig. 3). The absorption coefficient was extracted from the transmittance and reflectance of the films grown on SLG substrates. As shown in the inset of Fig. 3, the absorption coefficient varies between 3 and 4×10^4 cm^{-1} in the absorption region (1.75–3.5 eV). The obtained value for the band gap energy was 1.51 eV, which is in accordance with values found in the literature [1,2].

In order to study the recombination mechanisms, PL from CZTS thin films was measured. The temperature of the samples was varied from low (5 K) to higher values (160 K) until the complete extinction of the luminescence was obtained. In Fig. 4 we show the spectrum at low temperature (5 K). The observed broad band has a maximum of intensity at 1.24 ± 0.01 eV and a full width at half height of ~ 0.17 eV. The shape of the band clearly shows an asymmetry which remains as the temperature is increased. In the low energy side the energy dependence of the PL intensity is exponential, whereas in the high energy side the fall of the intensity is steeper. Similar bands with asymmetrical shapes were observed in CZTS grown by other methods [16–19], as well as, in chalcopyrite-type semiconductors [20–24]. This is the first time PL results are reported for CZTS thin films grown through the sulphurization method.

In general, the radiative transitions in lightly doped semiconductors can involve free carriers in the bands and/or carriers bounded to potentials wells created by several types of defects. Additionally, at low temperatures, the Coulomb interaction between electrons and

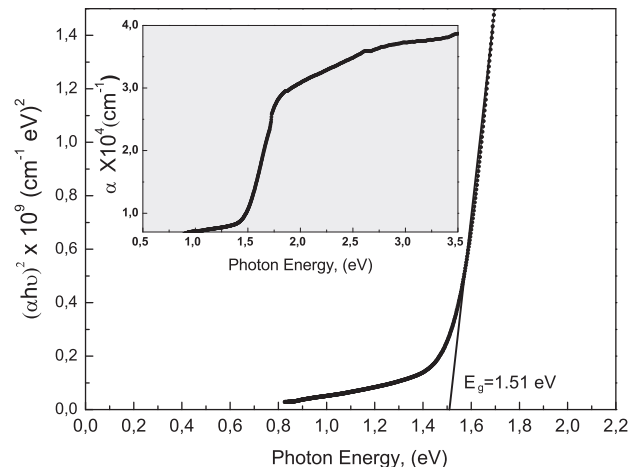


Fig. 3. Plot of $(\alpha h\nu)^2$ vs. $h\nu$ for the estimation of the band gap energy of a CZTS thin film grown on a SLG substrate. The plot of the absorption coefficient is shown in the inset.

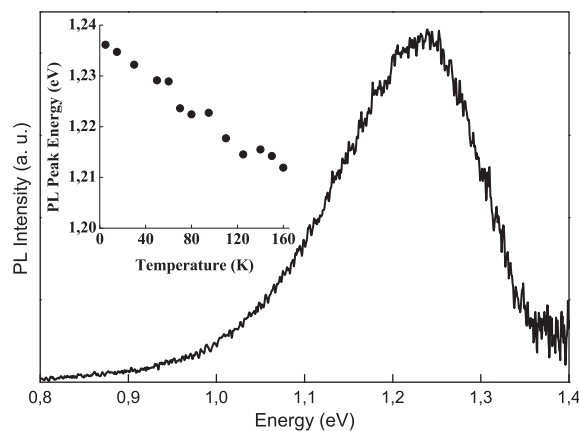


Fig. 4. PL spectrum at 5 K for a CZTS thin film grown by sulphurization of metallic precursors. The excitation source was the 488 nm line of an Ar^+ laser. The inset shows the dependence on the temperature of the peak energies for an excitation power of 20 mW.

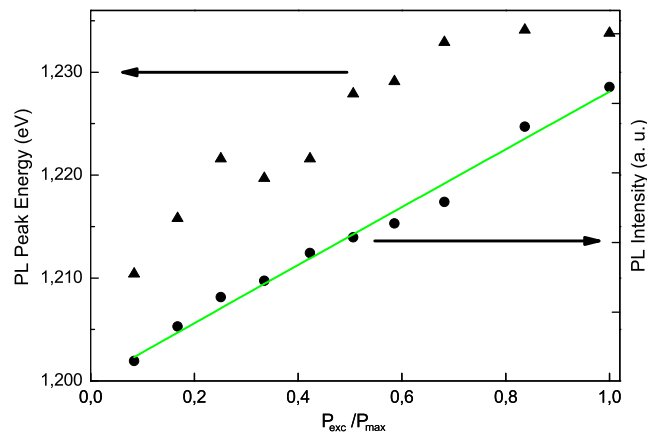


Fig. 5. Dependence on the excitation power of the peak energies and PL intensity at the temperature of 10 K. The excitation was done with the 488 nm line of an Ar^+ laser. The excitation powers were normalized to the maximum value. The data in part b) was fitted by Eq. (1).

holes can result in the formation of excitons which can recombine radiatively before or after they become bound to potentials wells in the crystals. In the case of heavily doped and highly compensated semiconductors, the occurrence of a large concentration of impurities, most of them charged, creates potential fluctuations which are responsible for the appearance of tail states in conduction and/or valence bands [25]. In some cases, these tails can penetrate deep in the band gap. In the particular case of chalcopyrite-type semiconductors different transitions have been identified [26]. Usually, the most observed transitions are the ones involving donor–acceptor pairs (DAP), in which the charge carriers are located in discrete levels inside the band gap created by donor and acceptor impurities, and the transitions involving tail states. The material class of kesterites, to which CZTS belongs, has a crystal structure very similar to that of chalcopyrites, therefore similar electronic properties are expected.

The study of the peak energy dependance on the excitation power and temperature contributes to the distinction between the above two models [20,24]. For DAP transitions it was observed that as the excitation power increases the peak energy shifts to higher energies by a few meV per decade, while the observed blue shift for the model involving potential fluctuations is much higher. On the other hand, as the temperature increases the peak energy suffers a blue shift for DAP-type transitions whereas the shift is for lower energies for the model of fluctuating potentials.

In Fig. 5 we show the experimental behaviour measured for our CZTS thin films. The excitation power values were normalized to the highest one. The experimental range of values was limited to around one decade due, on one hand, to the low signal/noise ratio of the emission and, on the other hand, to the annealing of the film with its consequent destruction for higher excitation power values. A blue shift of ~ 23.5 meV per decade was observed which could be well described by the model of potential fluctuations.

The observed experimental dependance of the PL intensity on the excitation power is shown in Fig. 5. The PL intensity follows a dependence on the excitation power (P) given by

$$I \propto P^m \quad (1)$$

where m is an adjustable parameter. The fitting to the experimental data gives $m = 0.99$. For $m > 1$ the transitions involve the recombination of excitons whereas for $m < 1$ the radiative recombination involves defects [27]. In our work, the obtained value do not suggests a clear type of transition. This could be understood in the scope of a model of potentials fluctuations. The appearance of tails in the bands will not allow the existence of excitons in the material. Actually, for

heavily doped and highly compensated semiconductors the exciton recombination is not observed [25]. Also, the shift (~ 0.26 eV) of the peak energy of the emission from the gap energy is too high for excitonic transitions. Moreover, the value of m is not low enough to suggest the involvement of defects levels as should be the case for DAP-type transitions. So, we consider that the observed emission could be ascribed to radiative transitions involving tail states in the CZTS semiconductor.

The increase of the temperature revealed a red shift for the peak energy by ~ 24 meV in the range of 5–160 K (see the inset in Fig. 4). This behaviour is opposite to the one observed for DAP-type transitions and is in accordance with the prediction for the model of potentials fluctuations. In this way, this result supports the previous interpretation of the observed PL as radiative recombination involving tail states created by potential fluctuations.

4. Conclusions

The sulphurization of metallic precursors allowed the formation of single phase thin CZTS films grown on SLG substrates with kesterite structure. The obtained films had a composition poor in copper and rich in zinc which is close to the one observed for solar cells with best reported efficiency. The measurement of the absorption coefficient in the absorption region gave values in the range from 3 to $4 \times 10^4 \text{ cm}^{-1}$ and an estimation of a band gap energy of 1.51 eV. The PL revealed an asymmetric broad band with a maximum of intensity at 1.24 ± 0.01 eV. The dependance of this band on the excitation power and temperature showed a behaviour typical of radiative transitions involving tail states created by potentials fluctuations.

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