Study of optical and structural properties of Cu_2ZnSnS_4 thin films

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Abstract

Cu_2ZnSnS_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 Cu_2ZnSnS_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 Cu_2ZnSnS_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 $4 \times 10^4\,\mathrm{cm}^{-1}$ was measured in the energy range between 1.75 and 3.5 eV. The bad 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.

Keywords: Cu_2ZnSnS_4, Thin films, Sulphurization, Photoluminescence, Potential fluctuations
PACS: 68.55.-a, 68.37.Hk, 78.20.-e

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1. Introduction

Among the possible alternatives to replace $Cu(In,Ga)Se_2$ (CIGS) as absorber layer in thin film solar cells, kesterite Cu_2ZnSnS_4 (CZTS) appears to have the

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right properties. This latter compound uses only abundant elements and with low toxicity levels. CZTS is a p-type semiconductor with an absorption coefficient higher than $10^4\,\mathrm{cm}^{-1}$ and a band gap close to $1.5\,\mathrm{eV}$[1, 2]. Despite these interesting optical properties the best conversion efficiency attained so far with CZTS based solar cell was 6.7%[3], which is a modest value compared with the efficiency reached by CIGS, 19.9%[4]. Growth related problems can explain part of such low efficiency, and according to Chen et al[5], the formation of stoichiometric CZTS has a very narrow chemical potential region. The growth of competitive compounds during the formation of CZTS is worsened by the fact that best solar cell results are achieved using Cu poor and Zn rich precursors[6]. This means that very controlled conditions must be met during the growth process.

The methods developed by the several research groups follow a similar procedure. The first part concerns to the deposition of the precursors. Vacuum and non vacuum methods were tested for this process. Conventional thermal and e-beam evaporation were employed by Friedlmeier et al[7] and Katagiri et al[8], respectively.

DC-magnetron sputtering of metallic precursors was tested by Fernandes et al[9], RF-magnetron sputtering of stacked binary sulphide precursors was tested by Katagiri et al[10] and co-sputtering was employed by Katagiri et al[3]. Non vacuum techniques were applied to the growth of CZTS through spray-pyrolisis by Nakayama et al[11], electro-deposition by Scragg et al[12] and chemical bath deposition by Todorov et al[13]. The second part of the growth process consisted of sulfurization/annealing of the precursors. The main differences between the employed methods are related with the sulfurization atmosphere, S_2 vapour and H_2S gas, the annealing temperature and pressure, the use of a transport gas, like N_2 or in a sealed environment.

In this work, we study structural and optical properties of the 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 being 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[9, 14]. The deposition sequence for the metallic precursors used 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 $5.6 \times 10^{-1}\,\mathrm{mbar}$. The sample was sulfurized at a maximum temperature of $525^{0}\,\mathrm{C}$ 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 $\mathrm{Cu}-\mathrm{K}_\alpha$ source ($\lambda = 1.54060\,\text{Å}$). 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.

PL was performed in the temperature range $5-300\,\mathrm{K}$, 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 order of deposition of the metallic precursors was investigated previously[14]. The metallic ratios of $[\mathrm{Cu}]/([\mathrm{Zn}]+[\mathrm{Sn}]) = 0.9$ and $[\mathrm{Zn}]/[\mathrm{Sn}] = 1.3$, obtained in ICP-MS measurements, show that the films are poor in copper and have a larger concentration of Zn compared to Sn. These values are close to the composition of the solar cells with best efficiency[3].

XRD measurements were used in order to identify 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, three 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: $a = 5.424\,\text{Å}$ and $c = 10.861\,\text{Å}$, which gives a value for $c/2a = 2.002$. Since the value of $c/2a$ is close to 2, this indicates that the cell is not distorted.

The morphology of the grown films was investigated by SEM (Fig.2). The micrograph shows a good crystallinity and compactness. 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 $4 \times 10^4\,\mathrm{cm}^{-1}$ in the absorption region ($1.75-3.5\,\mathrm{eV}$). The obtained value for the band gap energy was 1.51 eV, in accordance with values found in the literature[1, 2].

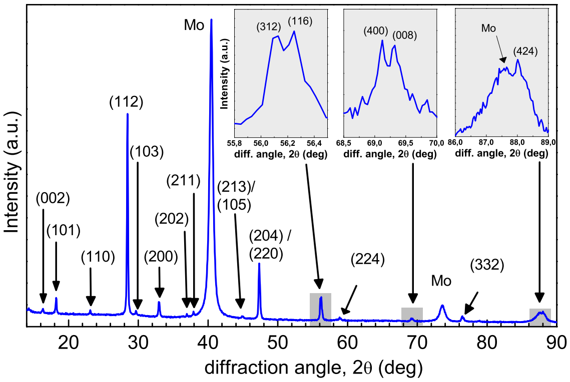

Figure 1: XRD spectrum of a CZTS thin film after the KCN treatment.

In order to study the recombination mechanisms in CZTS, 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[15–18], as well as, in chalcopyrite-type semiconductors[19–23]. 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

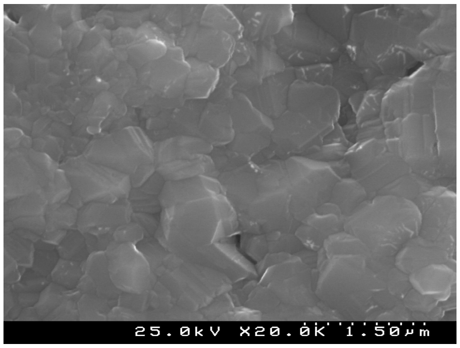

Figure 2: SEM micrograph of the surface of a CZTS thin film after the KCN treatment.

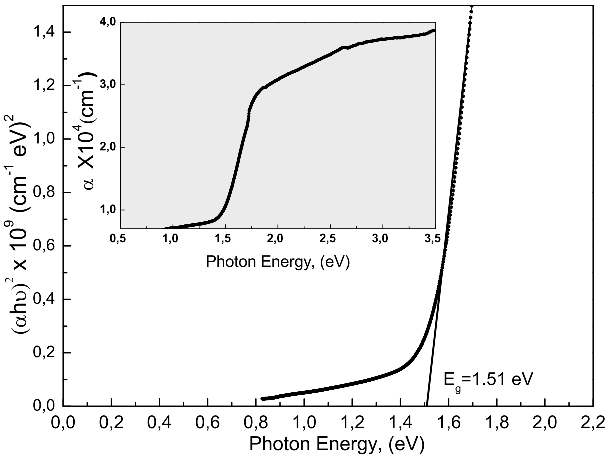

Figure 3: Plot of $(\alpha h\nu)^2$ vs. $h\nu$ for the estimation of the band gap energy of a CZTS thin film grown on a SLG substrate. The plot of the absorption coefficient is shown in the inset.

created by several types of defects. Additionally, at low temperatures, the Coulomb interaction between electrons and 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 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[24]. 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[25]. Usually, the most observed tran-

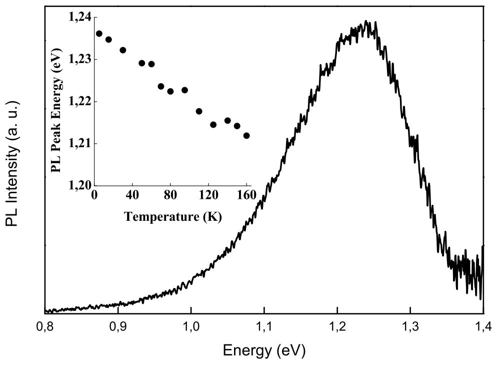

Figure 4: PL spectrum at 5 K for a CZTS thin film grown by sulphurization of metallic precursors. The excitation source was the 488 nm line of an Ar$^+$ laser. The inset shows the dependence on the temperature of the peak energies for a excitation power of 20 mW.

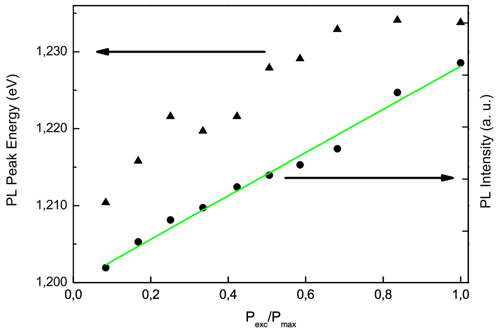

Figure 5: Dependence on the excitation power of the peak energies and PL intensity at the temperature of 10 K. The excitation was done with the 488 nm line of an Ar^+ laser. The excitation power were normalized to the maximum value. The data in part b) was fitted by equation 1, respectively.

sitions 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 are expected to show also similar electronic properties.

The study of the peak energy dependance on the excitation power and temperature contributes to the distinction between the above two models[19, 23]. 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 dependance on the excitation power (P) given by

$$I \propto P^m \tag{1}$$

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[26]. 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 semiconductors the exciton recombination is not observed[24]. Also, the shift ($\sim 0.26\,\text{eV}$) 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 suggests 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 tails states in the CZTS semiconductor.

The increase of the temperature revealed a red shift for the peak energy by $\sim 24\,\text{meV}$ in the range $5-160\,\text{K}$ (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 of the solar cells with best reported efficiency. The measurement of the absorption coefficient in the absorption region gave values in the range 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 $1.24 \pm 0.01\,\text{eV}$. 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.

Acknowledgements

P.A. Fernandes and P.M.P. Salomé thank the financial support of the Fundação para a Ciência e Tecnologia (FCT), through the PhD grants SFRH/BD/49220/2008 and SFRH/BD/29881/2006, respectively. The authors acknowledge the FCT/CAPES joint project "Novos materiais para células fotovoltaicas: calcopirites, kesterites e nanoestruturas de semicondutores III-V". FCT is also acknowledged for the financial support of the national electronic microscopy network (grant REDE/1509/RME/2005).

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