



## Letter

# Determination of minority carrier diffusion length of sprayed-Cu<sub>2</sub>ZnSnS<sub>4</sub> thin films



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## ABSTRACT

Despite Cu<sub>2</sub>ZnSnS<sub>4</sub>(CZTS) is a potential candidate for solar cell applications, so far, low efficiency values have been reported. In particular, for spray-deposited CZTS, efficiencies lower than 2% are commonly achieved. It is well known that one of the most important parameters governing solar cell performance is minority carrier diffusion length ( $L_n$ ). In this work, CZTS thin film solar cells with different compositional ratios are fabricated in order to study its impact on  $L_n$  values. The  $L_n$  parameter is calculated for sprayed-CZTS layers using external quantum efficiency measurements in conjunction with optical absorption coefficient versus wavelength measurements – for the first time. Values in the range of 0.11–0.17  $\mu\text{m}$  are obtained emphasizing the need for improving sprayed-CZTS crystalline quality.

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## 1. Introduction

Kesterite Cu<sub>2</sub>ZnSnS<sub>4</sub>(CZTS) is a potential absorber material for replacing CdTe and CIGS compounds in solar cell processing due to its high absorption coefficient ( $>10^4 \text{ cm}^{-1}$ ), band-gap close to the optimal single-junction value ( $\sim 1.5 \text{ eV}$ ) and the abundance and low toxicity of the constituents. Among the different CZTS deposition techniques, spray pyrolysis is very attractive for its versatility and low cost. In fact, if this technique were used to obtain CZTS solar cells with high efficiencies, cost/watt of devices would be reduced. However, so far, CZTS efficiency values lower than 2% are commonly reported [1–6]. One of the most important parameters having a great impact on solar cell performance is diffusion length of minority carriers ( $L_n$ ). This parameter is determined predominantly by the mechanism of carrier recombination. Many works have been developed for the measurement of  $L_n$  values in thin film solar cell materials such as SnS, CdTe, SiGeC, CIGS, CZTSSe, GaN, ZnSe, CdSe, GaP, InP [7–15]. In particular,  $L_n$  has shown to be highly dependent on thin film chemical composition, growth conditions, post-thermal and -chemical treatments, as well as doping and defect level [10–15]. Despite some works have reported characterization results on sprayed-CZTS thin films, none of them have dealt with the main hurdles that limit this technology. Particularly, for spray-deposited CZTS thin films, there are no reports on  $L_n$  parameter and its dependence on CZTS compositional ratios. Such study is fundamental to understand poor performances in sprayed-CZTS

solar cells and therefore highly required. In this work, sprayed-CZTS solar cells with different compositional ratios are fabricated in order to study its impact on  $L_n$  values for the first time.

## 2. Materials and methods

## 2.1. Experimental details

The experimental set-up for the preparation of Cu<sub>2</sub>ZnSnS<sub>4</sub> consisted of an aqueous solution containing thiourea, CuCl<sub>2</sub>, SnCl<sub>4</sub> \* H<sub>2</sub>O and (CH<sub>3</sub>COO)<sub>2</sub> Zn \* 2H<sub>2</sub>O. The concentration of solutions was changed in order to obtain different Cu/(Zn + Sn) and Zn/Sn compositional ratios. The solution was sprayed onto Mo substrates heated at 390 °C at constant flow rate of 5 ml/min, using air as carrier gas at pressure of 200 kPa with the nozzle-to-substrate distance of 30 cm during 30 min of deposition time. After deposition, samples were thermally annealed at 580 °C during 30 min – under Argon atmosphere (100 kPa) containing 50 mg of sulfur (Alfa-Aesar, 99.995%) and 5 mg of Tin (Alfa-Aesar, 99.999%) – followed by HCl treatment (10%) for 5 min to remove ZnS secondary phases at surface. In order to complete solar cells, CdS layers ( $\sim 90 \text{ nm}$ ) were deposited by Chemical Bath Deposition onto CZTS ( $\sim 1 \mu\text{m}$ ) followed by the deposition of ZnO ( $\sim 90 \text{ nm}$ ) and ZnO:Al ( $\sim 460 \text{ nm}$ ) layers by pulsed DC magnetron sputtering technique. For CdS preparation, the bath solution was composed of deionized water, ammonium hydroxide NH<sub>4</sub>OH (2 M), NH<sub>4</sub>Cl (0.2 M) – as a pH regulator –, CdCl<sub>2</sub> (0.12 M) and thiourea (0.12 M). The solution (pH = 9.8) was kept under stirring at 75 °C. The deposition time was 15 min. ZnO layers were deposited under

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the following sputtering conditions:  $1 \times 10^{-3}$  mbar (O and Ar flows of 1 and 19 sccm, respectively) and 100 W during 12 min at room temperature while ZnO:Al films were obtained under  $7 \times 10^{-4}$  mbar (Ar flow of 20 sccm), 120 W and 120 °C during 60 min. Measurement of optoelectronic properties was carried out using a 91160–1000 simulator under similar conditions to the AM1.5.

The chemical compositions of samples were measured by XRF (Fischerscope XDV-SDD). The optical properties of films were recorded using a UV/VIS spectrophotometer in the interval of 300–1000 nm at room temperature using a Perkin Elmer Lambda 950 UV/VIS Spectrometer. The spectral response measurements were made using a monochromator Oriel Corneston 130. The photocurrent was measured as a function of wavelength on each device and on calibrated standard Si solar cell (with known spectral response used as reference). Then, the external quantum efficiency (EQE) is found by sequence of analysis using standard silicon solar cell response and the response of the device under test.

## 2.2. Theoretical details

The  $L_n$  parameter of CZTS films can be evaluated assuming that short-circuit current density contribution ( $J_{sc}$ ) at any given wavelength  $\lambda$  can be approximated by [7–10]:

$$J_{sc}(\lambda) = q[1 - R(\lambda)]N_{ph}(\lambda)[L_n/(L_n + 1/\alpha)] \quad (1)$$

where  $R(\lambda)$  is the reflectance of the cell,  $\alpha$  is the optical absorption coefficient,  $N_{ph}$  is the incident photon flux. This expression is expected to be valid in the range of wavelength where  $\alpha$  is small such that the corresponding absorption length of the absorbed photons is within the CZTS layer, away from both CdS/CZTS junction and the CZTS back contact. On the other hand, it is well known that EQE is related with  $J_{sc}$  by the following equation:

$$EQE(\lambda) = \frac{J_{sc}(\lambda)}{qN_{ph}(\lambda)} = \frac{hc}{q\lambda} SR(\lambda) \quad (2)$$

where SR is the Spectral Response (ratio of the current generated by the solar cell to the power incident on the solar cell). From Eqs. (1) and (2), it is observed that a plot of  $EQE^{-1}$  versus  $\alpha^{-1}$  should be a straight line with an intercept on the  $\alpha^{-1}$  axis equal to  $L_n$ .

## 3. Results and discussion

The current density–voltage characteristics for sprayed-CZTS solar cells processed under different Cu/(Zn + Sn) and Zn/Sn compositional ratios are illustrated in Fig. 1; details of optoelectronic parameters are given in Table 1. The first thing to highlight from this table is the fact that CZTS solar cell efficiency is improved when Cu/(Zn + Sn) and Zn/Sn compositional ratios approach to 0.85 and 1.25, respectively which correspond to the optimal ratios required for a high CZTS solar cell efficiency [16]. One of the main reasons of this performance is the minimization of secondary phases for optimal compositional ratios as previously reported [4]. Under our experimental conditions, the maximum efficiency was 0.82% which is as low as other reported [1–5]. The efficiency enhancement is mainly related with  $J_{sc}$  improvement as displayed in Table 1. As a result, Cu/(Zn + Sn) and Zn/Sn compositional ratios play a fundamental role in  $J_{sc}$  and therefore on  $L_n$  values. For stoichiometric compositional ratios – Cu/(Zn + Sn)  $\sim$  1 and Zn/Sn  $\sim$  1 –, the lowest solar cell efficiency is reached because of a major secondary phases impact on solar cell parameters as previously shown [4]. A disadvantage of spray pyrolysis technique for processing CZTS solar cells is the relatively low Fill Factor values (<36%), which are due to high series resistance and low shunt resistance values. One of the main limiting factors concerning

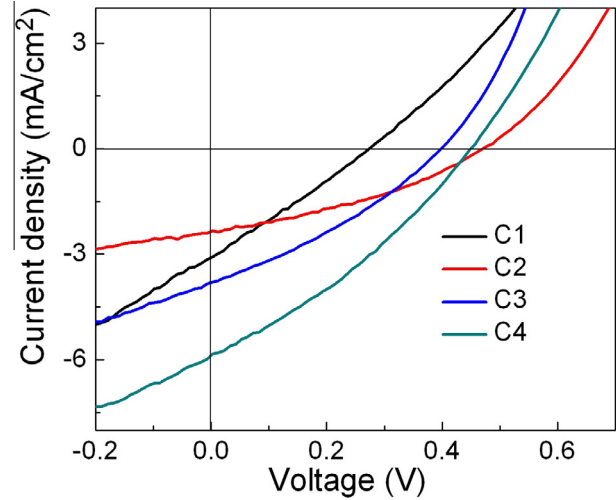


Fig. 1. J–V characteristics of sprayed-CZTS solar cells processed under different Cu/(Zn + Sn) and Zn/Sn compositional ratios.

Table 1

Optoelectronic parameters of sprayed-CZTS solar cells processed under different Cu/(Zn + Sn) and Zn/Sn compositional ratios.

Solar cells	Cu/(Zn + Sn) ( $\pm 0.03$ )	Zn/Sn ( $\pm 0.02$ )	$\eta$ (%) ( $\pm 0.06$ )	$J_{sc}$ (mA/cm²) ( $\pm 0.02$ )	$V_{oc}$ (mV) ( $\pm 0.2$ )	FF (%) ( $\pm 0.3$ )
C1	0.98	1.03	0.23	3.09	274.2	26.8
C2	0.63	1.52	0.39	2.33	470.6	35.7
C3	0.76	1.12	0.48	3.79	398.3	31.9
C4	0.87	1.21	0.82	5.86	440.3	34.0

sprayed-CZTS solar cells is low  $J_{sc}$  (<6 mA/cm²) since values about 20 mA/cm² have been reported for CZTS solar cells with record efficiency [17]. In order to understand low performances in  $J_{sc}$ , EQE measurements were carried out and results are shown in Fig. 2. EQE values lower than 30% are obtained for the best CZTS efficiency; that is, per about three photons in the wavelength range of 540–650 nm, only one electron–hole pair is able to reach the depletion layer. On the other hand, one important parameter that determines the EQE feature is  $L_n$ , which can provide qualitative information about crystalline quality. In order to calculate such

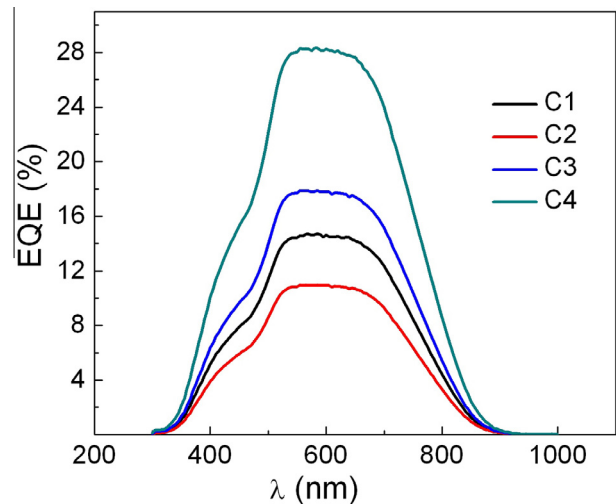


Fig. 2. EQE for sprayed-CZTS solar cells processed under different Cu/(Zn + Sn) and Zn/Sn compositional ratios.

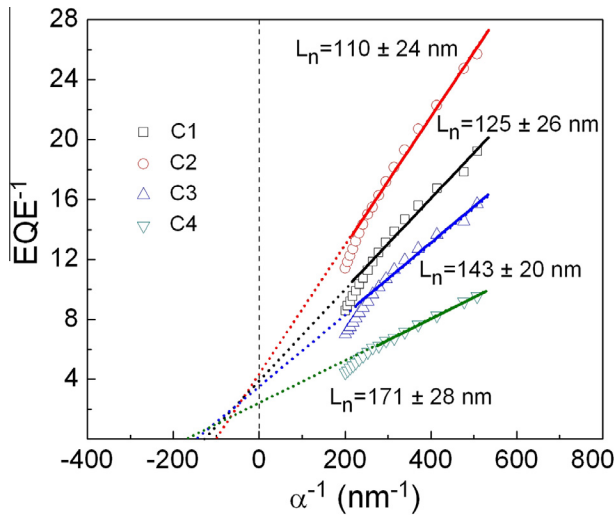


Fig. 3. Calculus of  $L_n$  for sprayed-CZTS as a function of Cu/(Zn + Sn) and Zn/Sn compositional ratios.

parameter, transmittance and reflectance measurements were carried out in CZTS thin films grown under the same conditions. Fig. 3 shows the plots of  $EQE^{-1}$  versus  $\alpha^{-1}$ . The plots are linear for lower values of  $\alpha$  (higher values of  $\alpha^{-1}$ ) and become nonlinear for higher values of  $\alpha$  (lower values of  $\alpha^{-1}$ ). This last behavior is due to a 'buffer layer effect' where the short wavelength fall off corresponds to the band-gap of CdS. By extrapolating the straight lines to  $\alpha^{-1}$  axis, an estimation of  $L_n$  for each CZTS absorber material is obtained. Values in the range of 110–171 nm are calculated. In particular, the sprayed-CZTS solar cell with the highest efficiency showed the biggest  $L_n$  value. From results obtained in Fig. 3 and Table 1, it is demonstrated that Cu/(Zn + Sn) and Zn/Sn compositional ratios have an important impact on  $J_{sc}$  values and so on  $L_n$ . The same tendency obtained for  $J_{sc}$  as a function of Cu/(Zn + Sn) and Zn/Sn compositional ratios is observed for  $L_n$  values. Therefore, Cu/(Zn + Sn) and Zn/Sn compositional ratios near to the optimal ones provide higher  $L_n$  values while the lowest values of  $L_n$  are discovered for non-optimal compositional ratios. Despite  $L_n$  values are in the expected range for polycrystalline thin films, it is important to point out that even the highest  $L_n$  value is far lower than the one reported for CZTSSe (0.75  $\mu m$ ) [18]. Bearing in mind an average absorption coefficient value of  $10^4 cm^{-1}$ , only about 17% of photogenerated electron-hole pairs will contribute to photocurrent. This result is mainly due to a poor sprayed-CZTS crystalline quality since a high density of defects is formed which act as recombination centers as previously demonstrated [19]. Consequently, further studies should be mainly focused on improving crystalline quality of spray-deposited CZTS thin films. Only then,

$L_n$  will be enhanced and thus minority carrier lifetime and solar cell efficiency.

#### 4. Conclusions

In summary, spray-deposited CZTS thin film solar cells were fabricated in order to study  $L_n$  behavior as a function of CZTS compositional ratios to understand poor performances in  $J_{sc}$  values for the first time. For optimal CZTS compositional ratios, higher solar cell efficiencies are obtained which is mainly related with the  $J_{sc}$  enhancement that goes with  $L_n$  increase. Conversely, non-optimal compositional ratios showed relatively low  $L_n$  values. As an important result, low  $L_n$  values in the range of 110–171 nm are discovered; this evidences the need for a further improvement in sprayed-CZTS crystalline quality.

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