Growth and characterization of $Cu_2ZnSn(S,Se)_4$ thin films for solar cells

P.M.P. Salomé [a,*], J. Malaquias [a], P.A. Fernandes [a,b], M.S. Ferreira [a], A.F. da Cunha [a], J.P. Leitão [a], J.C. González [c], F.M. Matinaga [c]

[a] Departamento de Física & I3N, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193, Aveiro, Portugal
[b] Departamento de Física, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, Rua Dr. António Bernardino de Almeida, 431, 4200-072 Porto, Portugal
[c] Departamento de Física, Universidade Federal de Minas Gerais, 30123-970 Belo Horizonte, Minas Gerais, Brasil

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Cu_2ZnSnS_4 (CZTS) and $Cu_2ZnSnSe_4$ (CZTSe) with their band gap energies around 1.45 eV and 1.0 eV, respectively, can be used as the absorber layer in thin film solar cells. By using a mixture of both compounds, $Cu_2ZnSn(S,Se)_4$ (CZTSSe), a band gap tuning may be possible. The latter material has already shown promising results such as solar cell efficiencies up to 10.1%. In this work, CZTSSe thin films were grown in order to study its structure and to establish the best growth precursors. SEM micrographs reveal an open columnar structure for most samples and EDS composition profiling of the cross sections show different selenium gradients. X-ray diffractograms show different shifts of the kesterite/stannite (1 1 2) peak, which indicate the presence of CZTSSe. From Raman scattering analysis, it was concluded that all samples had traces of CZTS and CZTSSe. The composition of the CZTSSe layer was estimated using X-ray diffraction and Raman scattering and both results were compared. It was concluded that Se diffused more easily in precursors with ternary Cu–Sn–S phases and metallic Zn than in precursors with ZnS and/or CZTS already formed. It was also showed that a combination of X-ray diffraction and Raman scattering can be used to estimate the ratio of S per Se in CZTSSe samples.

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1. Introduction

The development of Cu_2ZnSnS_4 (CZTS) and $Cu_2ZnSnSe_4$ (CZTSe) solar cells have reached efficiencies up to 8.4% [1] and 3.2% [2], respectively. In 2011 Todorov et al., achieved an efficiency of 10.1% by preparing solar cells with an absorber layer of $Cu_2ZnSn(S,Se)_4$ (CZTSSe) [3]. These results heightened the interest in studying films with a mixture of S and Se as a possible replacement for $Cu(In,Ga)Se_2$ in thin film solar cells since the use of the expensive and scarce element In is avoided.

CZTSSe should have its band gap energy between the one of CZTSe and of CZTS and it should increase with the replacement of Se with, S similar to the case of the chalcopyrite semiconductors, $CuInSe_2$ and $CuInS_2$. This analysis is not straightforward since the exact values of the band gap energy for CZTSe and CZTS are still a debated subject in the literature. For CZTSe, Matsushita et al. [4] and Wibowo et al. [5], refer a value between 1.44 eV and 1.56 eV, but Zoppi et al. report values around 0.9 eV [2]. In 2010, Ahn et al. [6] and Salomé et al. [7] reported a band gap energy close to 1 eV. For CZTS, the reported values range from 1.45 eV to 1.66 eV [8–10], but a value closer to 1.5 eV is widely accepted.

Regarding the CZTSSe crystalline structure, it should crystallize in the same structure as CZTS and CZTSe, which is either stannite, I-42m group 121, or kesterite, I-4m group 82. The structures are similar, differing only in the ordering of Zn and Cu atoms. Since these atoms have very similar X-ray scattering factors, the identification of the crystalline structure is not possible using conventional X-ray diffraction (XRD) [11] and hereafter we will be considering only the kesterite structure. Concerning the CZTSSe lattice parameters, they should be between the ones of CZTSe and of CZTS. Thus, it is expected that in XRD patterns the peaks suffer angular displacements for different atomic ratios of [Se]/[S], for instance the (1 1 2) peak, should be between $27.16°$ and $28.44°$.

In this study, CZTSSe thin films were prepared and were structurally and morphologically characterized. Different types of precursors were used to allow one to decide which may be the best growth procedure for the formation of CZTSSe. A method to estimate the composition of the CZTSSe layer using both XRD and Raman scattering is studied and discussed.

2. Experimental details

2.1. Sample preparation

For the growth of CZTSSe, precursors containing sulphur were selenised. Different types of films were selenized namely,

* Corresponding author. Present address: Ångström Solar Center, Solid State Electronics, Uppsala University, Ångström Laboratory, P.O. Box 534, SE-751 21 Uppsala, Sweden.
E-mail address: psalome@ua.pt (P.M.P. Salomé).

Table 1
CZTSSe samples' growth details.

Sample number	Evaporated precursors	Sulphurization for the formation of CTS	Zn/ZnS Layer deposited	Sulphurization for the formation of CZTS	Selenization
1	Zn/Sn–S/Cu	No	–	No	Yes
2	SnS/CuS	Yes	Zn	Yes	Yes
3	SnS/CuS	Yes	ZnS	Yes	Yes
4	SnS/CuS	Yes	ZnS	No	Yes
5	SnS/CuS	Yes	Zn	No	Yes

metallic/sulphide precursors, ternary Cu_2SnS_3 (CTS)+Zn/ZnS films and finally CZTS films. In Table 1, the growth details for each sample are presented. Depending on the samples, up to a maximum of five process steps were employed. First, precursors were evaporated and in a second step some of the samples were sulphurized to form CTS. The third step consisted on the deposition of a Zn or ZnS layer by RF magnetron sputtering. The fourth step was a sulphurization in order to form CZTS and finally the fifth step was the selenization to form the CZTSSe layer. Note that not all samples are subjected to the same steps.

In the first step, precursors were sequentially deposited on a Mo coated soda lime glass (SLG) in an evaporation system, with elemental sources of Sn, Cu, Zn and S, therefore allowing the deposition of different sulphides as well as metallic elements. The aimed thicknesses were 807 nm of $Cu_{2-x}S$ and 810 nm of SnS_2 which should provide a film with a [Cu]/[Sn] value close to 2.

In the second step, a tubular furnace was used [10]. The samples were heated up to a maximum temperature of 525 °C in a N_2 flow rate of 40 ml min^{-1}, at an operating pressure of 10 mbar. This pressure was used in order to minimize Sn losses by evaporation. The sulphur evaporation source was a quartz tube filled with elemental S pellets. The evaporation of sulphur was done at 130 °C. The purpose of this step, which was done prior to the incorporation of Zn, was the formation of a Cu–Sn–S phase, probably cubic Cu_2SnS_3 [12], in order to avoid Sn losses [13,14].

In the third step, either Zn or ZnS was deposited by RF magnetron sputtering. The deposition was performed in an Ar atmosphere at a working pressure of 2×10^{-3} mbar. The power densities for Zn and ZnS were 0.41 W cm^{-2} and 0.33 W cm^{-2}, respectively. In situ thickness monitoring was ensured by a quartz crystal monitor and it was aimed to deposit 220 nm of Zn or 570 nm of ZnS. These thicknesses were then confirmed by step profilometry. The fourth step was a sulphurization done in the same conditions as the second step. The final step to form the CZTSSe was a selenization done at a pressure of 1 mbar under an atmosphere of 95% N_2 and 5% H_2 and substrate temperatures of 525 °C [7].

The differences between the samples are precursor layers and on the processing steps prior to the selenization are shown in detailed in table 1. Sample 1 had metallic layers of Zn and Cu, S was only present during the evaporation of Sn with the following order: SLG/Mo/Zn/Sn–S/Cu. This sample was only selenized and the remaining steps were skipped. In the case of the other four samples, the second step to form CTS was performed. In sample 2, after the second step elemental Zn was deposited by RF sputtering and CZTS was formed before the selenization. In sample 3 instead of Zn, ZnS was deposited and CZTS was formed before the final selenization. In samples 4 and 5 after the second step ZnS and Zn were deposited, respectively. In both samples, the step to form CZTS was skipped. All samples were selenized under the same conditions.

These samples allowed us to investigate the structural properties of the different thin films and from their comparison to conclude which is the growth procedure most suitable for the growth of CZTSSe.

2.2. Sample characterization

The cross section of the resulting films was analysed by scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS), the system was a SU-70 Hitachi with a Rontec EDS system and the acceleration voltage used was 25 kV. These measurements can both reveal important information about the morphology and chemical composition of the samples. Conventional EDS however is not capable of providing quantification for the content of S due to the fact that the X-ray emission lines of Mo and S are superimposed. The X-ray emission lines are 2.29 keV for the L_α line of Mo and 2.30 keV for the K_α line of S. One could lower the acceleration voltage so that the Mo layer is not included in the interaction volume, but, in that case, the quantification of Zn and Cu is not ideal since the Cu and Zn L_α lines nearly overlap around 0.9 keV. Since we are dealing with structured layers, the conditions to perform EDS are also not ideal.

The crystalline structure was studied by X-Ray Diffraction (XRD) with XPert MPD Philips diffractometer using the Cu K_α line (1.5419 Å). The XRD allows the estimation of the incorporation of Se by looking at the shift of the kesterite (1 1 2) peak. It is known that for CZTSe this peak is centred at 27.16° and for CZTS is centred at 28.44° thus, for CZTSSe, it is expected that the (1 1 2) peak lies between the values above. The expected peak positions mentioned in this paper are taken from the International Centre for Diffraction Data (ICDD).

The films were also analysed by Raman scattering at room temperature using a Jobin-Yvon T64000 micro-Raman spectrometer equipped with a liquid nitrogen cooled silicon CCD and a BX51 Olympus optical microscope. It was used a 100X objective with a 0.95 numerical aperture to excite and collect the Raman signal in the backscattering configuration. The samples were excited with the 532 nm line of a Verdi^{TM} DPSS laser at 2 mW of excitation power on the sample.

3. Results and discussion

The results of the EDS mapping analysis, with the Se counts in the cross sections, are shown in Fig. 1. The cross section SEM micrographs are also shown. This analysis reveals that for all samples, Se was mainly concentrated in a thin layer close to the surface. These results indicate that the Se diffusion was low. For a more thorough analysis other techniques such as SIMS would be needed. The morphology of the resulting CZTSSe films is depicted in Fig. 2. Sample 1 is the most compact one, showing large grains at the top and smaller ones close to the back. The other four samples share a similar columnar structure. In the case of sample 2 just the columnar structure is observed whereas for sample 3 voids are also present. The micrograph for the latter sample, which had ZnS deposited and CZTS was formed, shows a layer at the top of the sample. Sample 4 has the generic structure that all the other samples show but, at the top, it appears to have a different layer. For this sample ZnS was deposited, and CZTS was