CZTS absorber layers obtained through sulphurization of metallic precursors: Graphite box versus Sulphur flux

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Abstract

In this work we employed a hybrid method, combining RF magnetron sputtering with evaporation, for the deposition of tailor made metallic precursors, with varying number of Zn/Sn/Cu (ZTC) periods and compared two approaches to sulphurization. Two series of samples with 1x, 2x and 4x ZTC periods have been prepared and thoroughly studied. One series of precursors was sulphurized in a tubular furnace directly exposed to a sulphur flux. A second series was sulphurized in the same furnace but inside a graphite box where sulphur pellets have been evaporated. The SEM/EDS films' morphology and composition analysis revealed a small grain structure but good average composition for all three films sulphurized in the graphite box. As for the three films sulphurized in sulphur flux grain growth was seen with the increase of the number of ZTC periods while, in terms of composition, they were slightly Zn poor. The films crystal structure was analysed through XRD and Raman scattering showing that CZTS is the dominant phase. However, in the case of the sulphur flux films SnS_2 was also detected. Photoluminescence spectroscopy (PL) studies showed an asymmetric broad band emission which occurs in the range 1-1.5 eV. Clearly the radiative recombination efficiency is higher in the series of samples sulphurized in sulphur flux. Furthermore a series of solar cells based on these absorbers were prepared and characterized through J-V measurements. We have found that sulphurization in sulphur flux leads to better film morphology than when the process is carried out in a graphite box in similar thermodynamic conditions. The improvement in the absorber morphology led to solar cells with better performance achieving efficiencies up to 2.4 %.

Keywords: Cu_2ZnSnS_4, Thin Films, Sulphurization, Graphite Box, Sulphur Flux

1. Introduction

Cu_2ZnSnS_4 (CZTS) based solar cells hold the promise of delivering even cheaper PV panels. It is known that CZTS has a direct band gap of about 1.5 eV and an absorption coefficient of 10^4 cm^{-1}, which make this, in principle, a good material for the absorber layer of a thin film solar cell. Demonstrated efficiencies of up to 8.4 % with prospects of improving as well as the use of non-toxic, cheap and abundant elements make CZTS a promising alternative to CIGS [1]. Despite the encouraging evolution in cell performance in recent years, clearly, further improvement is necessary to make CZTS a viable alternative in industrial terms. Several techniques are being used, worlwide, for the deposition of CZTS layers [2-7]. Magnetron sputtering is extensively used in the semiconductor industry to deposit thin films therefore when CZTS is deposited in laboratory with this technique it makes the processes more easily transferable to a large scale production. In order to improve the conversion efficiency, it is important to improve the understanding of the basic properties of CZTS, namely the effect of the deviation from stoichiometry on the electrical, optical and structural properties [8].Those properties are strongly determined by the films defect structure which in turn is likely to depend on the preparation method. The main purpose of this work was twofold. Firstly, compare two commonly used sulphurization techniques, namely sulphurization in sulphur flux [9] or in a closed graphite box [10] and try to identify advantages and disadvantages of one over the other. Secondly, study the influence of the number of ZTC periods, in the metallic precursors, on the properties of the CZTS layers and the corresponding solar cell performance. Two series of stacked Zn/Sn/Cu (ZTC) precursor layers with 1x, 2x and 4x ZTC periods were deposited through our hybrid method, and converted into CZTS films by sulphurizing one in sulphur flux and the other in a graphite box. The morphology and composition were characterized by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The crystalline quality of the films has been studied by X-ray diffraction (XRD) and Raman spectroscopy. The former studies allowed, also, the identification the crystalline phases present in the films. Photoluminescence studies were done to characterize the optical properties. Finally, solar cells based on those CZTS films have been prepared and measured.

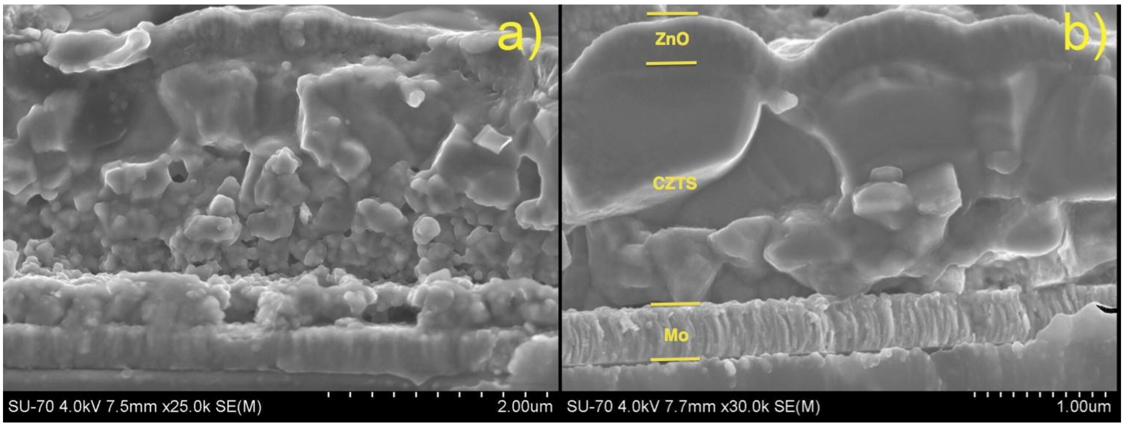

Figure 1: Cross-sectional SEM micrographs for samples sulphurized in a) Graphite box and b) Sulphur flux.

2. Experimental methods

In this work the route followed for the growth of CZTS consisted on the sulphurization of metallic precursors deposited according to a novel approach. The stacked metallic precursors were sequentially deposited by a hybrid RF magnetron-sputtering/evaporation process where Cu and Sn were sputtered from high purity targets while Zn was thermally evaporated (all source materials had a purity of ~99.999%). Prior to the actual precursor deposition the vacuum chamber was pumped down to 10^{-5} mbar and both sputtering and evaporation were carried out under an Ar+10% H_2 atmosphere at a pressure of $4.0 \cdot 10^{-3}$ mbar. The distance between target and substrate was 10 cm. This method allows the deposition of precursors with nx Zn/Sn/Cu (ZTC) periods with good reproducibility. The deposition rates of the individual sources were calibrated so that the precursors content, in Zn, Sn, Cu, is controlled through the deposition time. The precursors were deposited onto Mo-coated soda lime glass substrates. The Mo coating was performed by dc- magnetron sputtering as described by Salomé et al. [11]. Two series of precursors were deposited with n equal to 1, 2 and 4. Here, we will focus mainly on the samples with the best performance of each series.

The precursors were sulphurized in a tubular furnace at a constant pressure of 500 mbar. One series of precursors was directly exposed to a flux of N_2+5% H_2 plus sulphur vapour at flow rate of 40 $ml \cdot min^{-1}$. In this process sulphur is evaporated at a temperature of 230 °C. A second series of precursors was sulphurized in the same furnace but this time the samples were placed inside a graphite box together with 240 mg of high purity sulphur pieces. In both cases the sulphurization was performed at a maximum temperature of 570 °C during 30 minutes after which the samples were allowed to cool down to room temperature at a natural rate. The layers, thus produced, have been finished into complete solar cells by depositing a 50 nm thick CdS buffer via chemical bath deposition (CBD) and subsequent deposition of a i-ZnO/ZnO:Al window layer via RF-magnetron sputtering. The cross-sectional morphology and average composition were analysed by SEM, Hitachi Su-70 equipped with a Rontec EDS system. The crystalline structure of the CZTS films was analysed through a combination of X-ray diffraction with a Philips PW 3710 system and Raman spectroscopy with a LabRam Horiba, HR800 UV spectrometer. Raman scattering was excited with a solid state laser oscillating at 532 nm. Photoluminescence (PL) measurements have been carried out in a FTIR system equipped with continuous flow cryostat and liquid nitrogen cooled Ge detector. The samples have been excited with 514.5 nm laser line from an argon ion laser (Ar^+). The solar cell performance was characterized through J-V measurements in simulated standard test conditions with a home assembled system.

3. Results and Discussion

Even though in the work leading to this paper two series of samples have been prepared and characterized the ensuing discussion will focus on the samples resulting in the best solar cell performance in each series. The composition of the samples has been measured by EDS and the determined atomic ratios are shown in table 1. The values in the table show that the composition of the graphite box sample is very close to the one identified as desirable for achieving high performance solar cells [12], while the sulphur flux sample has Zn poor composition. The latter result means that higher zinc losses have occurred since the precursors were identical. Regarding these compositional differences we must say that they are not surprising since the precursors had been optimized for sulphurization in a graphite box. They, therefore, mean that we must optimize separately the precursors for sulphurization in sulphur flux. Therefore, the precursors for sulphurization in sulphur flux must be optimized separately.

Table 1: Composition of the samples sulphurized in graphite box and in sulphur flux as determined from EDS measurements.

Sample	$\frac{[Cu]}{[Zn]}$	$\frac{[Cu]}{[Sn]}$	$\frac{[Zn]}{[Sn]}$	$\frac{[Cu]}{[Zn]+[Sn]}$	$\frac{[S]}{[Cu]+[Zn]+[Sn]}$
Graphite box	1.51	1.92	1.27	0.84	0.90
Sulphur flux	2.05	1.86	0.91	0.97	0.91

The cross-sectional SEM images of the samples are shown in figure 1. A dense structure can be observed. The grain size of the graphite box sample is considerably smaller than the sulphur flux one. Since we are comparing samples with different numbers of ZTC periods namely 1 and 4 for the graphite box and sulphur flux, respectively, it must be said that the series of samples sulphurized in the graphite box all showed morphology similar to the one in figure 1-a). However, in the case of the series of samples sulphurized in sulphur flux a grain growth trend was seen with increasing number of ZTC periods. The cross-section of the sulphur flux sample, in figure 1-b), shows a CZTS layer with a lower half with somewhat small grains and a upper half with large grains about 1 micron across.

Figure 2 shows the XRD results for the sample with 1xZTC period sulphurized in a graphite box, bottom diffractogram, and for the sample with 4xZTC periods sulphurized in sulphur flux, top diffractogram. The latter diffractogram clearly shows that the corresponding sample contains tin disulfide (SnS_2),which is consistent with Zn poor composition. The SnS_2 phase appeared as sparse incrustations visible on the surface of the sample. Both diffractograms point to CZTS being the dominant phase present but do not exclude the possibility of there being additional phases such as ZnS and Cu_2SnS_3 (CTS). The top diffractogram also presents several secondary CZTS diffraction peaks suggesting a better crystallinity of the sample with 4x ZTC periods and sulphurized in sulphur flux.

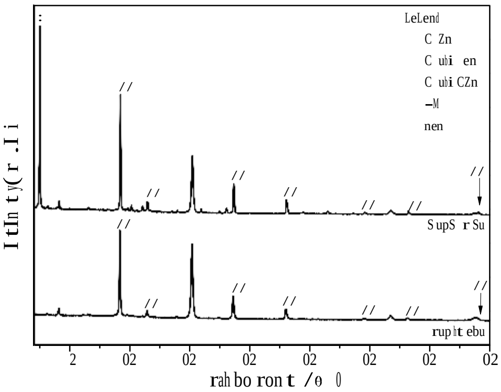

Figure 2: XRD diffractograms for the samples sulphurized in a graphite box (bottom) and in sulphur flux (top).

The crystallinity and phase content of the CZTS films were further analysed through Raman scattering, after solar cells have been made, in the exact same area corresponding to the best performance. The results are presented in figure 3. At first sight Raman spectra of the samples are similar; however a finer analysis reveals some differences. CZTS is known to have strong Raman peaks at 288 cm^{-1} and 338 cm^{-1}, which are clearly present, and a less intense peak structure to the right of the main peak between 348 cm^{-1} and 374 cm^{-1}. The sulphur flux sample shows the structure referred above resolved into peaks at 348.8 cm^{-1}, and 355 cm^{-1} which differs from the broad shoulder seen for the graphite box sample. The 348.8 cm^{-1} peak is assigned to CZTS while the 355 cm^{-1} one is assigned to the CTS phase. This fact is, again, consistent with fact that the sample is Zn poor. The latter peak is not seen in the case of the graphite box sample. On left side of the CZTS peak at 288 cm^{-1} a broad shoulder extending from 230 cm^{-1} to about 280 cm^{-1} is seen in both samples. Besides the typical features of CZTS thin films' Raman spectra discussed above, a peak at 303 cm^{-1} is seen in both samples and is assigned to the CdS buffer layer. Raman scattering structures below 200 cm^{-1} are also seen and have been discussed in [13-15]. Comparing the main Raman peaks, at 338 cm^{-1}, of both spectra we can see that FWHM corresponding to the sulphur flux sample is lower than that of the graphite box sample. This result confirms our analysis of the XRD data which points in the same direction.

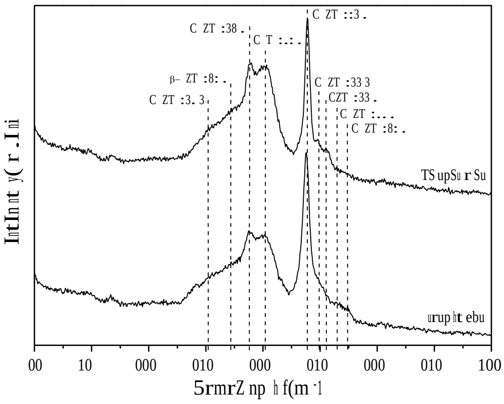

Figure 3: Raman scattering spectra of the samples sulphurized in a graphite box (bottom) and in sulphur flux (top).

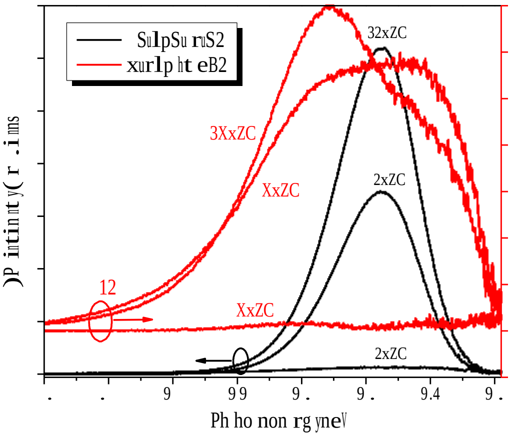

Figure 4: PL spectra at 7 K for a CZTS thin film grown by sulphurization of metallic precursors.

The PL spectra from both series of CZTS films are shown in figure 4. The films sulphurized in the graphite box show a luminescence about 10 times less intense than the ones sulphurized in sulphur flux. This difference in the PL emission intensity may be explained by the difference in the average grain size of the films, see figure 1. It is natural to expect less non-radiative recombination in films with bigger grains and therefore less grain boundary defects. The luminescence from the graphite box samples show two components one peaking at about 1.2 eV and a second peaking at about 1.4 eV while the sulphur flux samples show a much narrower luminescence with an apparent single component peaking close to 1.35 eV. The results in figure 4 also show that increasing the number of ZTC periods in the precursors leads to an increase in the luminescence intensity in both series of samples. Though, in the case of the graphite box, the morphological and structural analysis did not hint to this behaviour, in the case of the sulphur flux it was kind of expected given the observed grain growth. The asymmetric shape and large FWHM of the emission suggests radiative transitions involving tail states created by potential fluctuations in the bands [16]. A deeper understanding of the nature of the electronic transitions giving rise to the luminescence components referred above requires further analysis and studies underway.

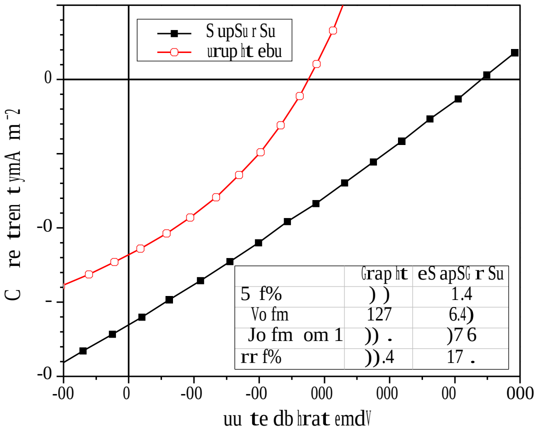

Figure 5: Solar cell J-V characteristics for the samples sulphurized in a graphite box and in sulphur flux.

Figure 5 shows the solar cells J-V curves for the best cell from each sample series. The cell from the sulphur flux sample presents an efficiency that is the double of that from graphite box sample. This is, mostly, the result of a very significant increase in the V$_{OC}$ from 276 mV, in the graphite box sample, to 541 mV, in the sulphur flux sample. This may be explained by a significant reduction in non-radiative recombination with the improvement of the crystalline quality of the sulphur flux CZTS films.

4. Conclusions

A novel hybrid method has been used to deposit precursors with nx ZTC periods with good reproducibility and good CZTS average composition control. The comparison of the chemical composition of the two series of samples showed that the Zn losses are higher in the case of the sulphurization in sulphur flux as a result we conclude that the precursors for sulphurization in sulphur flux need to be different from those optimized for the graphite box. The deviation of the sulphur flux samples to the Zn poor side lead to the formation of SnS$_2$ surface incrustations. The sulphurization in graphite box produces films with small grains and the number of ZTC periods did not influence the size. The sulphurization in sulphur flux produces films in which the grain size increased with the increase of the number of ZTC periods. The PL spectroscopy revealed that increasing the number of ZTC periods in the precursors leads to an increase in the luminescence intensity in both series of samples. The luminescence from the sulphur flux samples was substantially more intense and narrower than in the case of the graphite box samples. This correlates well with the better morphology of the sulphur flux samples. The solar cell results have shown a trend consistent with the morphology improvement seen within the sulphur flux series, where the best conversion efficiency of 2.4% was obtained for the samples with four ZTC periods. The best cell efficiency, for the graphite box sample series, was achieved with the sample with one ZTC and was 1.1%.

5. Acknowledgements

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