

Cu₂ZnSnS₄ THIN FILM SOLAR CELLS PRODUCED BY THIOUREA COMPLEXES SUSPENSION

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ABSTRACT:

Cu₂ZnSnS₄ (CZTS) thin films are grown by a two step process aimed for low toxicity requirements and relatively low temperature annealing in S₂ atmosphere. The chemical process developed is based on the metal complexation plus the thermolysis of thiourea to form a highly condensed precursor film. The reagents used are copper acetate, zinc acetate and thiourea dissolved in methanol. Ethylene glycol and polyvinyl alcohol are employed as additives to improve filmation. The suspension obtained is deposited by drop-casting on soda-lime glasses with a layer of sputtered molybdenum and annealed at 450 °C in sulfur vapors obtaining a good quality microcrystalline CZTS phases. Preliminary solar cells fabricated using a CdS buffer layer show an efficiency of about 1% .

Keywords: Cost Reduction, Kesterite, CZTS

1 INTRODUCTION

Nowadays the development of thin-films based solar cells, grown with low cost deposition methods, has become fundamental to compete with low cost of the first generation modules.

To increase the competitiveness of the inorganic thin film solar cells not only an easy and scalable approach is necessary to sustain a massive and cheap production, but rare elements must be avoided in all the layers of the solar device, like In, Ga in Cu(In, Ga)Se₂ (CIGS) cells.

A well known alternative to CIGS solar cells is Cu₂ZnSnS₄ (CZTS), where more abundant and less expensive elements are used instead of In and Ga [1].

The cost of natural resources used for CZTS is less than those used for CdSe and CIGS based thin film technologies. The CZTS most stable crystalline form is the kesterite with a direct band gap around 1.5 eV and an high absorption coefficient > 10⁴ cm⁻¹ [2-3].

Conventionally CZTS is produced by thermal treatment of a film containing the three elements as a stack, alloy or inorganic products such as sulfides, selenides or oxides.

Despite the efficiency of CZTS-based solar cells increased up to 8.4% in the last dozen of years, no substrates other than soda lime glasses have been widely used so far, due to the relatively high CZTS growth temperatures normally used (> 500°C).

Aim of this work is to develop a low cost chemical deposition method, allowing the realization of CZTS at lower temperature suitable to use flexible substrates like polyimide.

2. EXPERIMENTAL

All the chemicals used for this study were of analytical grade (99.99 % purity Aldrich chemicals).

The suspension was made by dissolving at room temperature copper (II) and zinc acetate and tin (II) chloride and thiourea in methanol. The thiourea is added in order to have a molar ratio between metals and sulfur of 1:1. The suspension has the milky appearance shown in Figure 1 and it is stable without forming any precipitates for hours.



Figure 1. Test tube containing the suspension ready to be deposited

The final composition of the optimized suspension is reported in Table I.

Table 1. Composition of the suspension.

Reagents	Solvents and binder
CH ₃ COO) ₂ Cu · H ₂ O (0.05 M) + SnCl ₂ · 2H ₂ O (0.025 M) + (CH ₃ COO) ₂ Zn · 2H ₂ O (0.025 M) + H ₂ NCSNH ₂ - 0.11 M	90% MeOH + 10% ethylene glycol + 0,50 ml of PVA

Ethylene glycol and polyvinyl alcohol are employed as additives to improve filmation. The suspension obtained is deposited by drop-casting on soda-lime glass (SLG) with a layer of sputtered molybdenum, as back contact.

Both the morphology and the chemical composition of the CZTS layers were investigated with a Tescan VEGA TS5136XM Scanning Electron Microscope (SEM), equipped for Energy-Dispersive Spectroscopy (EDS). The operating voltage used for all the SEM images is 20 kV, while EDS analyses were performed with a EDAX Genesis 4000 XMS Imaging 60 under the following conditions: operating voltage 20 kV, probe

current 190 pA, probe size 230 nm, working distance 23 mm, calibration with 53 Minerals Standard Mount MINM25-53. The crystal structure of the CZTS films was examined by Raman spectroscopy. Raman measurements were carried out at room temperature with a Jasco Ventuno micro-Raman system in backscattering configuration, equipped with a Peltier cooled charge-coupled device camera and a He-Ne laser (excitation wavelength of 633 nm). The laser power density was chosen to generate the best signal-to-noise ratio without broadening or shift of the Raman peaks due to local heating. CZTS solar cells were fabricated as follow. The junction is formed by chemical bath deposition of a thin (70 nm) CdS layer. A 80 nm intrinsic ZnO buffer layer, which acts as to prevent any shunts, is then deposited by RF sputtering. The TCO layer consisting of 350 nm Al-doped ZnO (AZO) is grown by DC pulsed (2 kHz) sputtering. The cell is finally completed by evaporating aluminum as metal grid contact. The CZTS solar cells were inspected by I-V measurements. I-V measurements were taken under Air Mass 1.5 conditions (simulating terrestrial applications) with a Abet Lot-Oriel Solar simulator with constant incident power density of 1 Sun (100 mW/cm²) and a Keithley 2440 sourceter.

3 RESULTS AND DISCUSSION

Particular attention was made to avoid the formation of cracks in the film during thermal treatments. A critical range between 140 °C and 160 °C has been identified; consequently, after the deposition, the sample was heated in a tubular oven under a slow temperature ramp up to 200 °C in order to remove the organic components and obtain the precursor layer. At this step the thiourea behaves like a sulfurising agent. A slow cooling ($v=1.3^{\circ}\text{C}/\text{min}$) was also crucial to avoid cracks in the precursors film at this stage .

The elemental compositions of the films were investigated with EDX in different points of the samples and the typical chemical composition leads to Cu/Zn+Sn, Zn/Sn and S/metals ratios of around 1, 1.57 and 0.95, respectively.

The Cross section SEM image of a thick sample is reported in Figure 2.

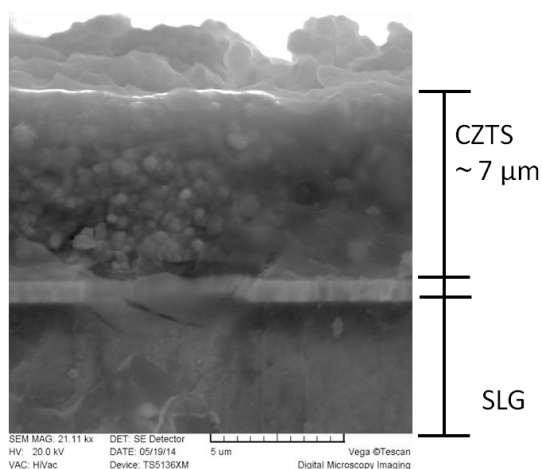


Figure 2 : Cross-section SEM image collected on a thick sample.

The morphology of the sample is shown in Figure 2

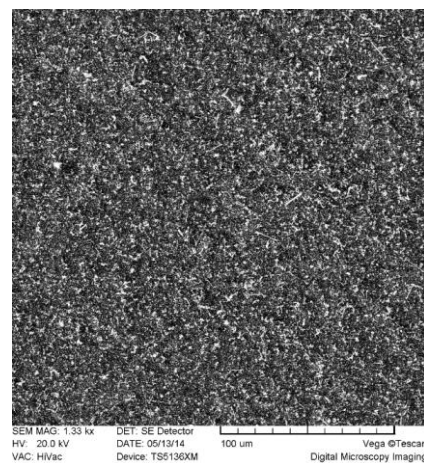


Figure 2: Low magnification top-view SEM micrograph of the CZTS film

The quality and the formation of CZTS phase has been inferred by Raman spectra as the one reported in Fig.3. Values of 339 cm⁻¹, 369 cm⁻¹, 288 cm⁻¹ and 266 cm⁻¹ indicate that CZTS is the main crystalline phase in the samples [4-5]. In some spectra a small peak at 475 cm⁻¹ related to the presence of the secondary phase Cu_{2-x}S, has been observed. If present this peak is not homogeneously distributed on all the sample surface,

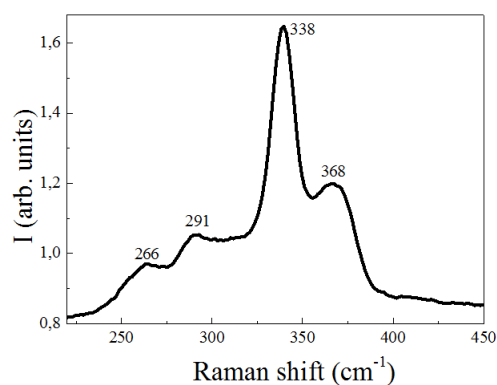


Figure 3: Raman spectrum of the absorber layer, collected on three different position on the sample.

Some solar cells fabricated using a CdS buffer layer shown an efficiency of about 1%. The low efficiency obtained have been associated at the high rugosity of the surface and on the presence of spurious phase on the surface.

According to EDX analysis, some agglomerates of Cu₂S have been identified, on the surface (see Figure 4) in agreement with Raman analysis.



Figure 4:
SEM top-view of a portion of a CZTS film. The bright agglomerate marked in red contains only Cu and S.

4 CONCLUSIONS

The results obtained in this work have shown good prospects for the growth of CZTS by chemical method at the temperature of 450°C. The results also showed the need to further improve the composition of the suspension to reduce the surface roughness and prevent the formation of undesired aggregates which are the main responsible of low efficiency obtained. One possible way forward is to reduce the concentration of copper with respect to the other two metals. A further study on the composition along the thickness of the film could provide information on the position of other secondary phases and suggest other modifications in the composition of the suspension.

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