Study of optical and structural properties of CZTS thin films grown by co-evaporation and spray pyrolysis

R Moreno1, E A Ramirez1 and G Gordillo Guzmán1
1 Universidad Nacional de Colombia, Bogotá, Colombia.
E-mail: rmorenom@unal.edu.co

Abstract. Results regarding optical and structural properties of Cu2ZnSnS4 (CZTS) thin films prepared by co-evaporation using a novel procedure are compared with those obtained with CZTS films grown using a solution based route. The lattice strain \( \varepsilon \) and crystallite size \( D \) of CZTS films prepared by co-evaporation and by spray pyrolysis were estimated through X-ray diffraction (XRD) measurements using Williamson–Hall-isotropic strain model. The results of estimated average crystallite size of CZTS films by Scherrer and Williamson–Hall plot methods were compared with AFM (atomic force microscopy) measurements. It was found that the average crystallite size measured by Williamson–Hall plot methods agree quite well with AFM results. Further, information regarding the influence of preparation method on both, crystalline phases and the formation of structural defects was achieved through Raman and Urbach energy measurements.

1. Introduction

Cu2ZnSnS4 is emerging as a potential material that has several promising attributes for efficient, inexpensive solar cells made from abundant and nontoxic elements [1]. The first CZTS solar cell was reported by Katagiri et al. in 1997 with an efficiency of 0.66% [2]. In 2008, Katagiri’s group reported an energy conversion efficiency of 6.7% [3]. Until recently state of the art CZTSSe thin-film solar cells were limited to 11.1% power conversion efficiency, being achieved via a hydrazine slurry approach [4]. Other vacuum and non-vacuum-based deposition techniques have also been successful in fabricating CZTSSe solar cells with efficiencies above 8% [5]. In 2013 Solar Frontier announced a world record for CZTS cell efficiency, reaching 12.6% [6].

This paper reports results concerning optical and microstructural properties of Cu2ZnSnS4 thin films prepared by both co-evaporation of precursors and spray pyrolysis from a solution containing chlorides of metallic precursors and thiourea, dissolved in dimethyl sulfoxide (DMSO). The influence of the preparation method on the crystallite size and formation of micro structural defects was studied through X-ray diffraction measurements using the scherrer and Williamson-Hall equations. In addition, we report results related to the influence of the preparation method on the crystalline phase and formation of structural defects, obtained through measurements of Raman spectroscopy and Urbach Energy.

2. Experimental

The Cu2ZnSnS4 films were prepared by co-evaporation of Cu, Sn and ZnS in presence of sulphur (evaporated from a Knudsen cell) using an evaporation source consisted of a cylindrical graphite crucible, which includes two coaxial chambers. The purpose of using the coaxial source is to improve the homogeneity in chemical composition of the CZTS films both laterally and in depth, which is not
possible using laterally separated crucibles to evaporate the precursors. Cu and Sn evaporate from the same camera considering that they have similar evaporation temperature, while the ZnS evaporates in a separate chamber due to the fact that this evaporates at a lower temperature. To achieve simultaneous evaporation of Cu, Sn and ZnS, the coaxial source was built with a special design, which allows generating a temperature profile such that the chamber containing the ZnS is at a temperature around 980°C and the chamber containing Cu+Sn at a temperature around 1300°C.

The preparation of Cu2ZnSnS4 films following a solution based route was done using a solution containing copper chloride (0.01M), zinc chloride (0.005M), tin chloride (0.005M) and thiourea (0.04M) as source of metal and sulphur, respectively and dimethyl sulfoxide (DMSO) was used as solvent. A spray pyrolysis deposition system was used to deposit the CZTS thin films; this consist in a pneumatic spray nozzle that employ nitrogen as carrier gas and a solution flow rate of 15L/min. CZTS films were deposited on soda lime glass substrates held at a temperature of 350°C. Post deposition annealing was also carried out in a furnace installed inside a vacuum chamber, kept at a temperature of 500°C for 30 minutes. The camera is initially evacuated to a pressure of 10⁻⁴ mbar, then nitrogen is introduced until it reaches a pressure of 20mbar and finally the furnace temperature was ramped up at 10K/min until the annealing temperature is reached.

The transmittance and reflectance measurements were performed using a Varian–Cary 5000 spectrophotometer and the film thickness was determined using a Veeco Dektak 150 surface profiler. The XRD measurements were performed with a Shimadzu-6000 diffractometer and Raman spectroscopy with a Thermo Scientific DXR Raman spectrometer with a DPSS laser of 785nm, 15mW focused with a 50X objective.

3. Results

3.1. Optical properties

In Figure 1 are compared transmission spectra of CZTS deposited by co-evaporation with those of a CZTS film grown by spray pyrolysis. It is observed that both type of CZTS films exhibit high transmittances indicating that the photon absorption occurs predominantly via band to band transitions. Curves of (αhν)² vs hν are also depicted in Figure 1. The absorption coefficient α was calculated through the relation [7]: \[ \alpha = -\frac{1}{d} \ln \frac{1}{T} \left( \frac{1}{T} - \frac{1}{R} \right) \]. Where T(λ) and R(λ) are values of transmittance and reflectance experimentally obtained and d the film thickness. The Eg values obtained from the intercept with the axis hν of the curve of (αhν)² vs hν were 1.45eV for samples prepared by co-evaporation and 1.48 for samples prepared by SP.

![Figure 1. Curves of spectral transmittance and of (αhν)² vs hν, corresponding to typical CZTS films deposited by co-evaporation and spray pyrolysis.](image-url)
Structural defects give rise to distortion of the bands generating tails of states that extend the bands within the gap causing a decrease of the slope of the transmittance curves (see insert of Figure 1). Absorption via transitions between states of tails of bands was evaluated through the calculation of the absorption coefficient near the band edge $\alpha_E$ that has an exponential dependence on photon energy and Urbach energy $[8]$ ($\alpha_E = \alpha_0 \exp \left( \frac{h\nu - E_u}{E_u} \right)$, where $E_u$ is the Urbach energy, $E_i$ and $\alpha_0$ are constant. Thus, a plot of $\ln \alpha$ vs. $h\nu$ should be linear and Urbach energy can be obtained from the slope. The $E_u$ values obtained from the slope of the transmittance curves, were 22.98 meV for samples prepared by co-evaporation and 43.17 meV for samples prepared by SP. Considering that Urbach energy is related to density of localized states in the band gap induced by structural disorder (stress and dislocation) $[9]$, can be concluded that the co-evaporated CZTS films present an improved crystallinity, as compared with those grown by SP.

### 3.2. Structural characterization

In Figure 2 are compared XRD pattern of typical CZTS thin films deposited by both co-evaporation and spray pyrolysis. It is observed that the CZTS samples present reflexions corresponding only to the Cu$_2$ZnSnS$_4$ phase (AMC cart #99-100-5143). The formation of single phase CZTS compounds was also proven from Raman spectroscopy measurements.

![Figure 2. XRD spectra of CZTS film prepared by co-evaporation and by spry pyrolysis. Inset shows a scan around the (112) reflexion.](image)

The scans around the (112) reflexion shown in inset of Figure 2 show that the full width at half maximum (FWHM) value corresponding to the studied CZTS films is different, indicating that crystallite size of CZTS films is affected by the deposition method.

Initially the crystallite size value is calculated using Scherrer’s formula to compare with the values obtained from the Williamson-Hall (W–H) models and AFM analysis results. The crystallite size $D$ of CZTS films is estimated from the Scherrer’s equation $[10]$ as: 

$$D = \frac{k \lambda}{\beta_{hkl} \cos \theta_{hkl}}.$$ 

Where $D$ is the crystallite size (nm); $K$ is the shape factor ($K=0.9$), $\lambda$ is the wave length of the X-rays (for CuKa radiation); $\theta_{hkl}$ is Bragg diffraction angle and $\beta_{hkl}$ is the instrumental corrected broadening of the hkl diffraction peak measured a half of its maximum intensity. In addition to the instrumental X-ray peak broadening, lattice strain and crystallite size are the other two independent factors that contribute to the total peak broadening. The strain induced broadening $\beta_s$ is given by the relation $\beta_s = 4\varepsilon \tan \theta_{hkl}$. Now the total peak broadening is represented by the sum of the contributions of crystallite size and strain present in
the material. Assuming that the strain present in the material is uniform, the W–H equation \([11]\) for the total peak broadening is given by:

\[
cos \theta_{hkl} = \frac{k^2}{D} + 4 \sin \theta_{hkl}.
\]

A plot taking \(4\sin \theta_{hkl}\) along X-axis and \(\beta_{hkl}\cos \beta_{hkl}\) along Y-axis allow to extract the strain present in the material and the crystallite size from the slope and the intercept of the linear fit made to the plot.

In Table 1 are listed values of crystallite size estimated from Scherrer’s formula and Williamson Hall Equation as well as from AFM measurements, for typical CZTS films prepared by the mentioned methods; values of lattice strain \(\varepsilon\) present in the CZTS films are also listed.

| Deposit. Method | Sherrer’s Equation | Williamson Hall Equation | AFM |
|----------------|-------------------|--------------------------|------|
| Evap          | 127.3             | 130.8                    | 0.0076 | 130 |
| SP            | 78.0              | 80.2                     | 0.0086 | 78  |

It is observed that the lattice strain \(\varepsilon\) of evaporated CZTS films is significantly less than those of CZTS films grown by SP, indicating that evaporated CZTS films grow with improved crystallinity. The results also revealed that the crystallite size of evaporated CZTS samples is much larger than those of Spray pyrolysis deposited CZTS films.

![Raman spectra of CZTS thin films and fitting peaks with Lorentzian functions for (a) co-evaporated sample and (b) SP deposited sample.](image)

Besides X-ray analysis, Raman spectroscopy measurements were done on thin films of CZTS prepared by both, spray pyrolysis and co-evaporation. In Figure 3 the Raman spectra of a typical CZTS film grown by co-evaporation is compared with that of a sample prepared by spray pyrolysis. The fitting with Lorentzian functions curves of the Raman spectrum of the evaporated sample gives evidence of peaks presence at 262, 287, 302, 338, 367 and 374\(\text{cm}^{-1}\) which have been attributed to the \(\text{Cu}_2\text{ZnSnS}_4\) phase [12]. An identical Raman Spectrum was reported elsewhere for stoichiometric \(\text{Cu}_2\text{ZnSnS}_4\) films grown with structure kesterite, measured using a 785nm laser [13]. The Raman spectrum of the sample prepared by SP exhibit the same peaks of the sample evaporated but slightly shifted towards lower values of wave number, indicating that this sample contain only peaks associated with the \(\text{Cu}_2\text{ZnSnS}_4\) phase. The Raman shift has been attributed to the confinement of optical phonons in a small crystalline particle [13]. In both spectra the dominant peaks are located at 338 (334) and 287 (284)\(\text{cm}^{-1}\).
which arises from A1 vibration mode, where only S-anions are involved. The bands at 367cm⁻¹ and 375cm⁻¹ correspond to B1 and B2 vibrational modes with cations moving only along the z direction.

4. Conclusions

Single phase Cu₂ZnSnS₄ thin films with kesterite type structure were grown by both co-evaporation and dimethyl sulfoxide (DMSO) based spray pyrolysis, and their structural properties evaluated through X-ray diffraction measurements using Williamson–Hall-isotropic strain model and Urbach energy estimated from absorption coefficient calculated near the band edge. It was found that evaporated CZTS thin films have values of lattice strain and Urbach energy lower than those obtained for CZTS films grown by SP, indicating that the first type of CZTS samples exhibit a lower density of structural defects than the CZTS films prepared by spray pyrolysis. Considering that Urbach energy is related to density of localized states induced by structural defects, can be concluded that the coevaporated CZTS films present an improved crystallinity.

It was also found that the CZTS films prepared by co-evaporation and SP present Eg values of 1.45eV and 1.48eV respectively and that both type of CZTS films exhibit high transmittances indicating that the photon absorption occurs predominantly via band to band transitions.

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