Microstructural and Morphological Properties of Nanocrystalline Cu$_2$ZnSnSe$_4$ Thin Films: Identification New Phase on Structure

Heiddy P. Quiroz$^1$, N. J. Seña$^1$, A. Dussan$^1$

Nano-structured Materials Group, Department of Physics, Universidad Nacional de Colombia, Colombia

hpquirozg@unal.edu.co

Abstract. This paper presents a study of the structural and morphological properties of thin films of compound Cu$_2$ZnSnSe$_4$. Mass (M$_X$) and temperature of the substrate (T$_{S(Cu)}$) of compound copper (Cu), were varied. All samples were deposited by co-evaporation method in three stages. From measurements of X-ray diffraction it was possible to establish with TS increasing the presence of associated binary phases quaternary compound during the growth process of the material. It was found that the main peak around, 2$\theta$ = 27.1°, predominate binary phases Cu$_{1.8}$Se and ZnSe. Measurements of X-ray diffraction were performed to pure binary compounds, showing a peak corresponding to the main peak found around the compound. Raman shifts showed associated binary compounds with the observed by XRD. In this work, we report for the first time the binary phase identification Cu$_{1.8}$Se and ZnSe as part of the structure of the stannite CZTSe. Since the Scherrer equation was found that the crystallite sizes ranged between 30 and 40 nm. A correlation between structure and topography superficial is presented.

1. Introduction

Over the last decades, new photovoltaic materials have been studied on search for new renewable clean energy sources. Cu(In,Ga)Se$_2$ (CIGS) is one of the most promising thin film solar cell materials, with an efficiency about 20% [1]; however their components such as indium (In) and gallium (Ga), have high toxicity levels and limited availability in the earth. Cu$_2$ZnSnS$_4$ (CZTS) and Cu$_2$ZnSnSe$_4$ (CZTSe) compounds are very promising candidates to replace CIGS in thin film solar cell applications thanks to their optical properties (band gap range from 1 to 1.5eV) and absorption coefficient higher than 10$^4$ cm$^{-1}$. [2,3]

Quaternary CZTS(Se) thin films have been produced by pulsed laser ablation [4], one step RF magnetron sputtering [3], co-evaporation of elements [5], sequential evaporation [6] as well as synthesis from melts [7]. However, the understanding of the properties of the different phases is still unclear; there are studies that have addressed their structural, electric, morphological and defect properties of CZTSe thin films grown by others methods. [8,9,10]

In this work we presented a study of the microstructural and morphological properties of thin films of compound Cu$_2$ZnSnSe$_4$ deposited by co-evaporation method in three stages. Parameters deposition
such as mass \( (M_X) \) and temperature of the substrate, \( T_{S(Cu)} \), were varied on large range. Influence of synthesis parameters on properties were investigated from X-ray diffraction (XRD), Raman and Scanning Electron Microscope (SEM) measurements. In this work, we report for the first time the binary phase identification \( \text{Cu}_1.8\text{Se} \) and \( \text{ZnSe} \) as part of the structure of the stannite CZTSe. A correlation between structure and topography superficial is presented.

2. Experimental procedure

Thin films \( \text{Cu}_2\text{ZnSnSe}_4 \) were prepared on Soda Lime-type glass substrates through physical vapor deposition (PVD) in the presence of Se. The substrates were subjected to previous cleaning following a specific process, reported previously [11]. The masses of the precursors used were 0.118 g for Cu, 0.097 g for Sn, and 0.153 g for ZnSe; all had a high degree of purity \((99.95 \pm 0.05\%)\). The deposition process was conducted in three stages. During the first stage, Cu was evaporated in a Se atmosphere at a substrate temperature of \( T_{S(Cu)} = 673 \) K. This stage formed the \( \text{Cu}_2\text{Se} \) composite, as a result of the reaction of the two precursors. During the second stage, Sn was evaporated, again, in a Se atmosphere, but maintaining \( T_{S(Sn)} = 523 \) K; this new layer was deposited over the existing \( \text{Cu}_2\text{Se} \) layer. This stage formed the \( \text{SnSe}_2 \) composite, which in turn reacted with \( \text{Cu}_2\text{Se} \) to give way to the formation of the \( \text{Cu}_2\text{SnSe}_3 \) ternary composite. During the third stage \( \text{ZnSe} \) was evaporated, maintaining \( T_{S(ZnSe)} = 673 \) K, and this was deposited on the ternary layer. The final reaction gave way to the formation of the \( \text{Cu}_2\text{ZnSnSe}_4 \) quaternary composite. The reactions occurring have been considered by other researchers in the fabrication of the composite. [12]

The samples were characterized through XRD measurements by using a Philips X’Pert Pro diffractometer by PANalytical, equipped with a Cu-K\( \alpha \) source: 1.540598 Å, 40 kV, 40 mA and an X’Celerator detector. The software used to compare the samples was the XPert High-Score Plus through Rietveld refinement in the range of \( 10^\circ \leq 2\theta \leq 80^\circ \) with angular steps of 0.026\(^\circ\). All the samples, including the binary samples for their comparison with the analyses presented, were scanned at the same spectral range. The Raman measurements were carried out in the high-resolution Horiba Jobin Yvon Confocal Raman spectrometer, Labram HR high-resolution model equipped with a CCD detector (1024x256-pixel resolution), a 633-nm He/Ne laser, and a 785-nm diode laser. The Labspec Software was used to operate the equipment, as well acquire and treat the data, varying the Raman displacement from 100 to 500 cm\(^{-1}\).

The samples were about 0.6 µm thick. Sample thickness was obtained from Uv-Vis-IR spectrophotometry measurements and corroborated with profilometry techniques. SEM images were obtained in a scanning electron microscope FEI QUANTA 200.

3. Results and discussion

Fig. 1-a shows the X-ray diffraction spectrum obtained for the sample with optimal reproducible conditions of CZTSe quaternary compounds prepared by co-evaporation method in three stages: \( T_{S(Cu)} = 673 \) K, \( M_{Cu} = 0.118 \) g, \( T_{S(ZnSe)} = 673 \) K, \( M_{ZnSe} = 0.153 \) g. It is observed, that characteristic phase have a preferential orientation on the plane \((1\ 1\ 2)\). Crystal structure simulated is presented in the inset of figure 1-a.

Diffractogram obtained (see figure 1-a) presents a Stoichiometry coinciding with that of \( \text{Cu}_2\text{ZnSnSe}_4 \). Position of the peaks and diffraction planes were identified using Rietveld method and XPert HighScore Plus program. A single phase is observed with Stannite-type structure [13,14] and spatial group of conventional symmetry \( I \ – \ 42m \) [15,16].

2
Figure 1. a) Diffraction pattern of Cu$_2$ZnSnSe$_4$ quaternary sample. Crystallographic structure in reference to the atomic location of the composite’s atoms can be observed in the inset. b) Raman spectrum for the sample in a). Inset of the figure detail of the peak form $\nu = 195$ cm$^{-1}$ for the CZTSe sample with Gaussian fit.

Figure 2 shows the diffractograms of the CZTSe films when varied the substrate temperature during the Cu evaporation stage. It was observed, that new phases are evident in the spectra on structure of the quaternary when $T_{S(Cu)}$ change from 573 to 773 K. Main peak $2\theta = 27.1^\circ$ is characterized by a splitting with the change of $T_{S(Cu)}$ from optimal value. Crystal size was calculated using the Scherrer equation and reported in table 1.

Figure 2. XRD spectra of the Cu$_2$ZnSnSe$_4$ composite varying: a) Substrate temperature during Cu evaporation and b) Mass of ZnSe. Figure inset shows detail of double peak for $2\theta = 27.1^\circ$.

From analysis of binary compounds used as precursors in the synthesis of Cu$_2$ZnSnSe$_4$, allowed determining that the phases accompanying quaternary phase, are associated to secondary phases of ZnSe and Cu$_{1.8}$Se (see Figure 3). It is observed that, changes in temperature influence the formation double peak around $2\theta = 27.1^\circ$ evidencing a contribution of ZnSe and Cu$_{1.8}$Se at very close angles.

Raman measurements permitted evidencing the presence of these binary phases previously observed in the figure 3, identified for shifts Raman around peak 195 cm$^{-1}$ (see figure 1-b). In this figure, an overlapping is clearly observed of peaks associated to the binary composites, Cu$_{1.8}$Se $\sim$192,2 cm$^{-1}$ and ZnSe $\sim$198,7 cm$^{-1}$.
Figure 3. Broadening of peak $2\theta = 27.1^\circ$ for the samples shown in Figure 2-a. The XRD spectra of the ZnSe and Cu$_{1.8}$Se binary composites are presented comparatively and the crystal structures of the binary phases. The dash line red is indicating the main peak for binary compounds ZnSe and Cu$_{1.8}$Se.

Figure 4 shows micrographic SEM of CZSTe thin films varying the $T_{S(Cu)}$ between 573K and 773K. These images evidenced the grains formation on the surface that change of size with increasing of $T_{S(Cu)}$. Table 1 shows the crystal size and mean size grain obtained from XRD spectra and SEM measurements, respectively.

![Figure 3](image_url)

Figure 4. SEM images of thin films CTZSe varying $T_{S(Cu)}$: a) 573K, b) 673K and c) 773K.

Table 1. Crystal and grain size obtained varying the substrate temperature during the Cu evaporation stage.

| $T_{S(Cu)}$ | Crystal size ± 5% nm | Grain size ± 5% nm |
|------------|----------------------|-------------------|
| 573        | 31,45                | 680               |
| 673        | 45,38                | 610               |
| 773        | 37,11                | 1187              |

When we analyze the effect of the mass of ZnSe in the formation of compound (see figure 2) shows that changes in the concentration of the ZnSe about to $M_{ZnSe} = 0.153$ g (constant for the change of the other parameters) significantly affect the formation of the compound to the point of losing that characterizes phase. This can be attributed to processes of re-evaporation of the material, contributing to the formation of the phase for CZTSe compound.
4. Conclusions
In this work CZTSe nanostructured thin films were fabricated, varying both T$_{S}$ and M$_{x}$ in the Cu and ZnSe composites. It was observed, that variation of these parameters sensibly influences the formation of the CZTSe characteristic phase with presences of secondary phases on structure. From a detailed study of the binary composites by XRD and Raman measurements, was possibly to establish the presence of two new phases around the characteristic peak given for 2θ = 27.1°. Additionally, Raman shifts were identified for Cu$_{1,8}$Se and ZnSe at 195.1 cm$^{-1}$ and 204.8 cm$^{-1}$, respectively. Grain size in CZTSe thin films, was increased with change of temperature around of optimal value for which was obtained the CZTSe characteristic phase.

5. Acknowledgments
This work was supported by Universidad Nacional de Colombia - DIB. We special thank Semiconductor Materials and Solar Energy Group for Laboratory support in sample preparation.

References
[1] Arnulf Jager Waldau, Sol. Energy Mat. Sol. Cells, 95 (2011), 1509-1517.
[2] F. Luckert, D. I. Hamilton, M. V. Yakushev, N. S. Beattie, G. Zoppi, M. Moynihan, I. Forbes, A. V. Karotki, A. V. Mudryi, M. Grossberg, J. Krustok, R. W. Martin, Appl. Phys. Lett., 99 (2011), 062104.
[3] Kentaro Ito, Tatsuo Nakazawa, Jpn. J. Appl. Phys., 27 (1988), 2094-2097.
[4] K. Moriya, K. Tanaka, H. Uchiki, Jpn. J. Appl. Phys., 47 (2008), 602-604.
[5] T. Tanaka, D. Kawasaki, M. Nishio, Q. Guo, H. Ogawa, Phys. Stat. Sol. 3 (2006), 2844–2847.
[6] J. Raudoja, E. Mellikov, M. Grossberg, S. Bereznev, R. Traksmaa, O. Volobujeva, J. Phys. and Chem. Solids, 70 (2009), 567–570.
[7] Louis Grenet, Sergio Bernardi, David Kohen, Christophe Lepoittevin, Sebastien Noe, Nicolas Karst, Arnaud Brioude, Simon Perraud, Henri Mariett, Sol. Energy Mate. Sol Cells, 101(2012), 11-14.
[8] Narjes Beigom Mortazavi Amiri, Andrei Postnikov, J. Appl. Phys. 112 (2012), 033719.
[9] O. Volobujeva, S. Bereznev, J. Raudoja, K. Otto, M. Pilvet, E. Mellikov, Thin Solid Films 535 (2013) 48–51.
[10] P.M.P. Salomé, P.A. Fernandes, A.F. da Cunha, Thin Solid Films 517 (2009) 2531–2534.
[11] F. Mesa, Ph.D. Thesis, Departamento de Física, Universidad Nacional de Colombia, Colombia, 2010.
[12] Alex Redinger, Marina Mousel, Rabie Djemour, Levent Gütay, Nathalie Valle, Susanne Siebentritt, Prog. Photovolt: Res. Appl., (2013) 1-7, Doi: 10.1002/pip.2324
[13] G Suresh Babu, Y B Kishore Kumar, P Uday Bhaskar and V Sundara Raja, J. Phys. D: Appl. Phys. 41 (2008), 205305, Doi: 10.1088/0022-3727/41/20/205305.
[14] Rachmat Adhi Wibowo, Woo Seok Kim, Eun Soo Lee, Badrul Munir, Kyoo Ho Kim, J. Phys. and Chem. Solids, 68 (2007), 1908–1913, Doi: 10.1016/j.jpcs.2007.05.022.
[15] F. Hergert, R. Hock, Thin Solid Films 515 (2007), 5953–5956.
[16] I.D. Oleksyuk, L.D. Gulay, I.V. Dydehak, L.V. Piskach, O.V. Parasyuk, O.V. Marchuk, J. Alloys Compd. 340 (2002) 141.