Synthesis of a chalcopyrite material, based on CuIn$_{1-x}$Ga$_x$Se$_2$ (X = 0.3 y 0.5), for application as semiconductor layer, deposited by a low-cost technique

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Abstract. The current work reports the synthesis and characterization of a photovoltaic material based on the CuIn$_{1-x}$Ga$_x$Se$_2$(X = 0.3 y 0.5) system, making use of the doctor blade method. For this purpose, homogeneous inks were obtained and worked under previous stoichiometry arrangement. The deposition process of thin films, were made in a heating plate on conventional glass substrates, previously washed and treated for this purpose. Once the layers of Cu, In, and Ga were deposited by chemical bath, a thermal treatment was performed at 550 °C for 30 min in a conditioned oven, in which the selenium process was performed. The obtained films were characterized by X-ray diffraction, Raman spectroscopy, solid-state impedance spectroscopy, UV spectroscopy and scanning electron microscopy techniques. The identification of the main crystalline phase could be corroborated, as well as the conductive and optoelectronic behavior of the solids in accordance with reported in literature. Simultaneously, it was checked that the method used allows obtaining layers of an optimum thickness, in order to be used as an absorbent layer in the design of solar devices.

1. Introduction

Current photovoltaic industry has made use of different semiconductor materials to be applied as absorbent layers in the solar cells manufacture, within these are: polycrystalline and monocrystalline silicon (first generation), which present a low absorption coefficient and an indirect band gap, materials in thin layer (second generation), such as cadmium telluride (CdTe), CuIn$_{1-x}$Ga$_x$Se$_2$ (CIGS), CuInSe (CIS), etc. These materials are characteristic to exhibit a direct band gap and a high absorption coefficient, since it is constituted of a multi-union system, of different semiconductors p-n mainly of groups III and V of the periodic table (third generation) [1-3].

According to reported references materials based on chalcopyrite structure such as (Cu(In, Ga)Se$_2$) and CdTe, can be synthesized by different chemical or physical methods: physical vapor deposition (PVD), chemical vapor deposition (CVD), hydrothermal, among others, with high efficiency values (around 22%) and high physico-chemical stability. Previous properties have allowed its easy adaptability to several substrates, as well as its reproducibility at industrial level [3-6]. Although these advantages, these materials display some drawbacks such as the shortage in different elements used, the toxicity of some atoms such as cadmium, and the high manufacturing costs caused by the synthesis conditions, in which the material must be treated. For this reason, the objective of the research focuses on obtaining a semiconductor material with a composition based in CuIn$_{1-x}$Ga$_x$Se$_2$(X = 0.3 y 0.5),...
deposited over a vitreous substrate in order to evaluate its structural, morphological and electrical properties, for its possible application as an absorbent layer in a solar device.

2. Experimental

2.1. Deposition of CIGS material and later selenization

The procedure to obtain the inks is based on the production of solutions from corresponding metallic precursors as gallium acetyl acetone Ga(C$_5$H$_7$O$_2$)$_3$, copper nitrate Cu(NO$_3$)$_3$, indium oxide (In$_2$O$_3$) and metallic selenium (Se) all with 99.9% purity. The dissolution of all metal cations was made in 5.0 mL of HNO$_3$ 68%, in order to dissolve oxides and metal precursors in accordance with Zhang, et al 2014 and Castellanos, et al. 2017 [7,8]. The used proportions were (1:0.7:0.3:2) and (1:0.5:0.5:2), the process was developed under stirring conditions and constant temperature (80 °C), until the productions of homogenous and stable solutions, which were conserved at room temperature.

The deposition of the inks was carried out on conventional glass substrates, which were cut with 2.5 cm × 2.5 cm dimensions, for each test, the substrates were treated for 30 minutes in ultrasonic bath using an ethanol-water mixture, for subsequent drying in oven at 120 °C. For the deposition of inks using the doctor blade method and using approximately 0.05 mL, the process is repeated to complete 5 layers of materials, which were treated between 50 °C – 80 °C for 5 minutes. The obtained films were calcined in a furnace to carry out the selenization process (550 °C for 30 min ), in order to generate the optimum crystallization of the semiconductor over substrate.

2.2. Characterization

The obtained films were characterized by X-ray diffraction (XRD) technique, using a PANalytical X'pert PRO-MPD apparatus, equipped with an Ultra-fast XCelerator detector in Bragg-Brentano arrangement, using radiation the CuK$_x$ = (λ = 1.54186 Å) between 5° and 90° with steps of 0.02°. Subsequently, the analysis was made by means of Raman spectroscopy with the help of a Raman spectrometer, DXR Smart Raman, between 50 cm$^{-1}$ – 3370 cm$^{-1}$, with a cooled CCD detector −51 °C and a laser diode (785 nm), in order to determine the optoelectronic behavior of the material. The band-gap value was determined using a HACH DR6000 UV – VIS spectrophotometer, where a wavelength sweep was carried out from 190 nm – 1100 nm. Simultaneously the conductive capacity of the material was analyzed with the help of solid-state impedance spectroscopy using a GAMRY potentiostat-galvanostat, with a frequency between 100 Hz to 1.0 MHz. The morphology and thickness of the layer was evaluated by scanning electron microscopy (SEM), using a Carl Zeiss EVO – MA10 equipment, with possibility analysis of energy dispersion spectrometry of X-rays (EDS).

3. Results and discussion

The structural characterization has been carried out after deposition of inks and subsequent thermal treatment of the materials. The results show the formation of a crystalline phase of Cu(In$_{1-x}$Ga$_x$)Se$_2$, with the presence of diffraction signals in accordance with previous literature [7]. In Figure 1., it is clear to observe the obtained materials with main diffraction planes along (1 1 2), (1 0 3), (2 2 0)/ (2 0 4), (3 1 2)(1 1 6) facets, with a tetragonal crystalline system, which structure corresponds to the I – 42d space group; this is characteristic for chalcopyrite type materials [9]. In agreement with obtained results, it was possible to define that stoichiometry of material correspond with the CuIn$_{0.7}$Ga$_{0.3}$Se$_2$ material, which exhibit a high intensity in the signals attributed to selenization process.

The obtained value from crystal size confirms the effect of different stoichiometries on the material, since the inclusion of gallium atom in the crystalline structure that produces a contract in distance between atoms of crystal, in comparison with the material whose stoichiometry is CuIn$_{0.7}$Ga$_{0.3}$Se$_2$ where the proportion of gallium atom in the structure produce a larger crystal size (30.36 nm), which favors the formation of desired phase, decreasing the presence of secondary phases [10]. Simultaneously this will cause better semiconductor performance, since the crystallinity of the solid is greater.
In Figure 2, the Raman spectrum shows the presence of secondary phases in the synthesized materials, which can be corroborated through the vibrational modes identified in the region of 174 cm$^{-1}$, that is related to the main interaction of the peak dominant of the chalcopyrite phase in terms of $A_1$ vibration mode, where the symmetrical vibration of the material is found. The signals found around 228 cm$^{-1}$ are attributed to the vibrational mode $B_2/E_2$, [11-13] which correspond to the asymmetric vibrations that are generated in the crystal structure CuInGaSe$_2$ (CIGS). In accordance with Mousavi S, et al. 2016 the signal found around 258 cm$^{-1}$, it is attributed to the presence of the secondary phases of Cu$_x$Se [13-15]. Previous results are confirmed with a high intensity of signals in the material whose stoichiometry corresponds to $(CuIn_{1-x}Ga_xSe_2)_X = 0.5$, verifying that an increase in the amount of gallium, inside in the consolidation of the chalcopyrite structure and consequently, undesired phases are generated under thermal treatment.

In turn, the results obtained are consistent with what was found by DRX, since having a lower intensity of the main signal (Raman spectroscopy and DRX) will obtain a material with the presence of secondary phases, which are formed during the heat treatment due to the presence of selenium in the environment.

In the Figure 3 and Figure 4, is clear the micrographs of the cross section and of the upper part of the materials deposited on the vitreous substrates, where the formation of a dense layer of different thickness for each material can be observed (CuIn$_{0.5}$Ga$_{0.5}$Se$_2$ = 6.325 µm y CuIn$_{0.7}$Ga$_{0.3}$Se$_2$ = 1.518 µm). Previous results are concordant with reported by Fraga D, et al. 2017, in which the morphology of these solids is not directly related to the proposed stoichiometry. In turn, the films thickness which ratio is $X = 0.3$ is optimal for the design of thin-layer solar cells, because the material offers a denser and compact morphology, which would generate a better coupling between the substrate and the layer absorbent [16,17].

With the purpose to define the band gap value of the synthesized materials, an analysis has been made with the help of UV spectroscopy, using the Tauc equation [3]. The Figure 5, it is determined that substitution of gallium atom in the structure generates a considerable change in the same, directly affecting the semiconductor behavior. This results can be observed in Table 1, where it is clear that the material with the lowest proportion of gallium displays a close value to the optimum band gap (1.2 eV) [18,19]; it therefore follows that the ratio of gallium produces deficiencies in the optoelectronic characteristics of the material, increasing the distance for the electron to pass from the Valencia layer to
conduction; Simultaneously the thickness of the layer and the specific defects generated can present a recombination.

**Figure 3.** SEM micrographs of the deposited material CuIn$_{0.7}$Ga$_{0.3}$Se$_2$, upper part of the substrate and cross section.

**Figure 4.** SEM micrographs of the deposited material CuIn$_{0.5}$Ga$_{0.5}$Se$_2$ upper part of the substrate and cross section.

**Figure 5.** Determination of the Band gap value of the synthesized materials, (a) CuIn$_{0.5}$Ga$_{0.5}$Se$_2$, (b) CuIn$_{0.7}$Ga$_{0.3}$Se$_2$. 
Table 1. Optoelectronic and conductivity values found for the CIGS material deposited in thin layer.

| Material                  | Band-gap value (eV) | Conductivity value (Siemens) |
|----------------------------|---------------------|-------------------------------|
| CuIn$_{0.5}$Ga$_{0.5}$Se$_2$ | 1.434               | 2.99 × 10$^{-7}$              |
| CuIn$_{0.5}$Ga$_{0.5}$Se$_2$ | 1.382               | 1.22 × 10$^{-4}$              |

Table 1 showed results in terms of impedance spectroscopy (IS), where it was observed by the Nyquist diagrams means [20] that the material with greater of gallium doping, Figure 6, has as a capacitor behavior at low frequency values, it means that behaves in a resistive way, accumulating charge inside the semiconductor [21]. In the opposite way, it was found that for the material with the least amount of gallium, it will have a more resistive behavior at high frequency values. Those results are in agreement with the investigations carried out by Adel Ch, *et al.*, 2016, who reported a maximum resistivity value of 6044 Ω, for the CuIn$_{1-x}$Ga$_x$Se$_2$ ($X = 0.3$) [22]; simultaneously, these values were verified in the investigation, by conductivity and band-gap calculations means, Table 1.

![Figure 6](image)

**Figure 6.** Graph of Nyquist (Z'vs. Z") for the samples synthesized. (a) CuIn$_{0.5}$Ga$_{0.5}$Se$_2$, (b) CuIn$_{0.7}$Ga$_{0.3}$Se$_2$.

Finally, with the results obtained, it can be deduced that the material whose characteristics (physical-chemical and electrical) are optimal to be used as an absorbent layer in a solar cell, will material be the one that presents in its stoichiometry lower gallium content (CuIn$_{0.7}$Ga$_{0.3}$Se$_2$), since it will generate a lower presence of impurities, increasing its crystallinity, with a better behavior as a semiconductor; the above, corroborated according to the studies carried out by different authors, among which stand out: Fraga D, 2017; Chiou Ch y Penga H, 2017; Jinlian B, *et al.*, 2018, who, from different synthesis methods, obtained the type material chalcopyrite with different stoichiometries, observing an optimal result in the material CuIn$_{1-x}$Ga$_x$Se$_2$ ($X = 0.3$) [3,21,23].

4. Conclusions

With the results obtained in the characterization by X-ray diffraction, it was proved that the materials deposited (doctor blade) and thermally treated (CuIn$_{1-x}$Ga$_x$Se$_2$ $X = 0.3$ y 0.5), generate a crystalline structure of chalcopyrite type with a tetragonal crystalline system, corresponding to the space group $I-42d$ (1 2 2). Simultaneously it was corroborated that depending on the stoichiometry used, there is the presence of secondary phases, which directly affects the electrical behavior of the material, that proved...
with the values of conductivity and band-gap found for each solid. Accordingly, it is concluded that the solid that has better characteristics to be used as an absorbent layer, whose stoichiometry is CuIn$_{0.7}$Ga$_{0.3}$Se$_2$, which giving an answer to the need to synthesize a semiconductor which generates optimal results, in the design of a solar device.

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