

Electrochemical preparation and structural characterization of CuGaSe₂ thin films

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Abstract. CuGaSe₂ thin films have been synthesized by one-step electrodeposition on titanium and SnO₂/glass substrates from aqueous solutions that contain thiocyanate ion as a complexing agent. According to composition, and morphology analysis at deposition potential of -0.55V vs SCE (Standard Calomel Electrode) for 20 minutes from aqueous solutions of 4.6mM CuCl, 25.0mM GaCl₃ y 9.2mM SeO₂ in 2.0M de KSCN at pH 2.5 was found the optimum condition for obtain the CuGaSe₂ thin films with good morphology and good stoichiometric. The samples were annealed at temperature of 520⁰C in inert atmosphere for 30 minutes to improve their crystallinity. The obtained CuGaSe₂ thin film has a direct band gap (E_g) of 1.65eV. In addition, the cyclic voltammetry (CV) studies were performed in order to elucidate the electrodic processes that occur for the formation of semiconductor CuGaSe₂. Therefore, the electrochemical behaviour for each ion (Cu⁺, Ga³⁺ and Se⁴⁺), for binary (Cu-Se, Ga-Se, and Cu-Ga) and for ternary (Cu-Ga-Se) systems are described. This material has potential application in solar cells.

1. Introduction

Thin solar cells based on Cu(In,Ga)Se₂ (CIGS) absorber layers have demonstrated 21.7% conversion efficiencies in laboratory devices [1]. Moreover, CuGaSe₂ (E_g=1.65eV and α=1,2x10⁴cm⁻¹) is one of the most-promising wide-gap chalcopyrite absorber and a strong candidate material high open-circuit voltage in thin films solar cells [2]. The current record for thin films solar cell devices with this ternary compounds prepared by physical vapour deposition (PVD), have reached 9.7% efficiencies [3]. This technique produces high-quality materials, but involves a process that is difficult to increased to large-scale. Electrodeposition is an alternative method to obtain good quality and large-scale thin films. However, to obtain high quality layers, parameters such as pH, reactant concentrations, reduction potential, etc., are critical and need optimization, since these parameters influence the deposits stoichiometry and the semiconductor electrical properties [4]. Previously, several research groups have reported the preparation of CuGaSe₂ using electrochemical techniques [5-8]. In this paper, we present the detailed procedure to obtain CuGaSe₂ thin films grown by one-step electrodeposition on Ti and SnO₂/glass from aqueous solutions containing thiocyanate ions.

2. Experimental procedure

The CV studies and the electrodeposition of CuGaSe₂ thin films, were performed in a three-electrode cell, connected to a BAS Epsilon potentiostat. Pt foil was the reference electrode, SCE (Saturated Calomel Electrode) was the reference electrode, and Ti foil or SnO₂/glass was the working electrode.



The electrolytes solutions consists of 4.6-5.0mM CuCl, 5.0-9.2mM SeO₂, 25.0 GaCl₃, and 2.0M KSCN at pH 2.5. The films were grown at different potentials (Table 1) and concentration ratios in the electrolytic medium (Table 2). Annealing at 520^oC in inert atmosphere for 30 minutes improved the the CuGaSe₂ thin films crystallinity. The chemical composition, morphology and crystalline properties of the films were analysed by scanning electron microscopy (SEM, Hitachi Model S-2500) equipped with energy dispersive spectrometer (EDS, Noran System Six Company). The crystal structure was analysed by X-ray diffraction (XRD, Siemens model D5005). The E_g was determined by transmittance measurement using UV-VIS-IR spectrophotometer (Cary 17I).

3. Results and discussions

3.1. Electrochemical studies

The electrochemical behaviour of the individuals constituents, binary and ternary systems were systematic studied in order to elucidate the electrodic processes that occur for the formation of semiconductor CuGaSe₂. Figure 1 shows the CV reduction potentials for the three ions. The thiocyanate ion effect is to shift the Cu⁺ reduction potential in the negative direction to about -0,78V, where metallic gallium is also deposited. Moreover, a reduction peak at -0.68V probably corresponds to Se⁴⁺ reduction to Se⁰.

The Cu-Ga-Se system voltammogram (Figure 2) presents a multiplicity of cathodic peaks that by comparing with the electrochemical behaviour of the binary systems each process was analysed. At cathodic potentials between -0.35 to -0.75V a peak is observed which is attributed to the formation of binary phases Cu_{2-x}Se [9,10]. At more negatives reduction potentials, beyond -0.75V, two reduction peaks were observed which are assigned respectively to Cu and Ga metallic, respectively. Furthermore, in the Ga-Se system, a cathodic peak was observed at -0.52V corresponding to the formation of Ga₂Se₃, which could to gallium incorporation in the film, increasing its concentration (Table 1). These studies suggest that the formation of CuGaSe₂ could occur through the reaction [8]:

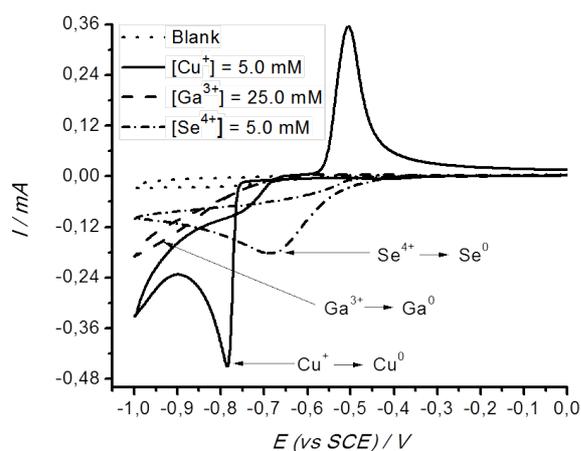
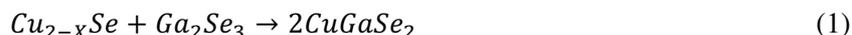


Figure 1. CV obtained on Ti from the precursor ions Cu⁺, Ga³⁺ and Se⁴⁺, respectively.

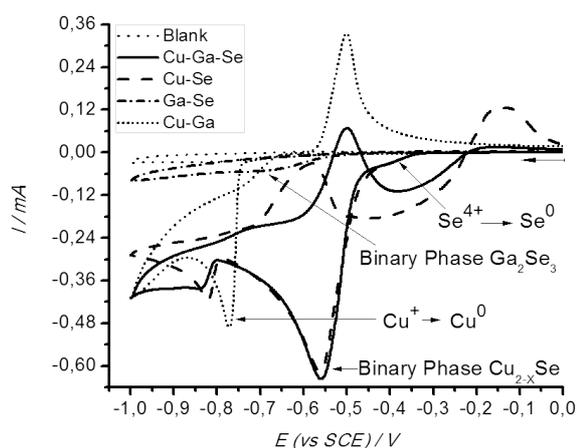


Figure 2. CV of binary and ternary systems obtained on Ti.

3.2. Compositional and morphology studies

The atomic composition and morphology of the Cu-Ga-Se films were analysed by EDS and SEM, respectively. Table 1 summarizes the influence of deposition potential on the film compositions and morphology. In all cases, a solution containing 5.0mM CuCl, 25.0mM GaCl₃ and 5.5mM SeO₂ was

used. In the range between -0.35 and -0.45V, the amount gallium is too low, this is because the reduction reaction of Ga^{3+} to Ga^0 cannot take place, the gallium insertion into the film proceed by formation of gallium oxide or hydroxide [7]. In addition, in this range a Cu_{2-x}Se phase is also deposited, giving an induced deposition mechanism [10]. The micrograph image (Figure 4) showed dispersed deposits attributed to copper selenide phases.

At -0.55V cathodic potentials, it is observed that gallium atomic concentration increases due to gallium, incorporation in the film by metal selenides formation (Figure 2). At this potential, Cu_{2-x}Se formation is observed (Figure 2). In the range between -0.55 and -0.75V it can be seen that the Ga/Cu ratio remains almost constant. This demonstrates that the stoichiometry of the films is independent of the applied deposition potential in this range. Additionally, the synthesized films have a stoichiometric ratio very close to the ternary compound CuGaSe_2 (Figure 3, Table 1) but with Cu_{2-x}Se excess. Moreover, the micrograph image (Figure 4) showed a homogeneous granular morphology.

Table 1. EDS analysis of Cu-Ga-Se layers obtained at different potentials in aqueous solution with 25.0mM Ga^{3+} , 5.0mM Cu^+ , 5.5mM SeO_2 and 2.0M de KSCN at pH 2.5 (5.0:25.0:5.0).

Potentials (V vs SCE)	Atomic percent (%)			Ga/Cu ratio	Stoichiometry
	Cu	Ga	Se		
-0,35	34,86	7,45	57,69	0,21	$\text{CuGa}_{0,21}\text{Se}_{1,65}$
-0,45	31,36	14,11	54,53	0,45	$\text{CuGa}_{0,45}\text{Se}_{1,74}$
-0,55	27,05	17,78	55,17	0,66	$\text{CuGa}_{0,66}\text{Se}_{2,04}$
-0,65	27,74	18,06	54,20	0,65	$\text{CuGa}_{0,65}\text{Se}_{1,97}$
-0,75	26,40	17,77	56,33	0,67	$\text{CuGa}_{0,67}\text{Se}_{2,13}$
-0,85	28,84	14,96	55,39	0,52	$\text{CuGa}_{0,52}\text{Se}_{1,92}$

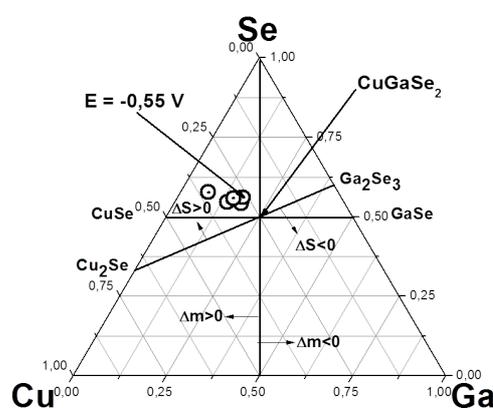


Figure 3. Ternary phase diagram of CuGaSe_2 electrodeposited at different potentials.

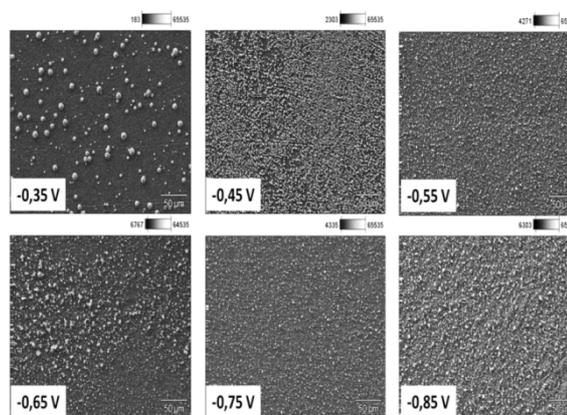


Figure 4. Morphology of CuGaSe_2 electrodeposited at different potentials.

The compositional data obtained in the Table 1 have been expressed into deviation from molecular weight (Δm) and deviation from stoichiometry (ΔS) in Figure 3 and take into account the role of the deviation from the ideal composition. In Figure 3 such a schematic ternary phase diagram for CuGaSe_2 is shown. To describe the $\text{Cu}_x\text{Ga}_y\text{Se}_z$ composition of a point within the ternary field relative to the composition of the chalcopyrite, Groenick and Janse [11] have introduced two independent parameters, i.e. the deviation in molecular weight Δm and the deviation in valence stoichiometry ΔS :

$$\Delta m = \frac{x}{y} - 1, \quad \Delta S = \frac{2z}{x+3y} - 1 \quad (2)$$

where x , y , and z are the atomic concentrations of the individual atoms. As indicated in the Figure 3, ΔS describes compositional deviations from the pseudo binary $\text{Cu}_2\text{Se}-\text{Ga}_2\text{Se}_3$ line, where $\Delta S < 0$

corresponds to anion poor and $\Delta S > 0$ to anion rich material. Δm divides the triangle into Cu-rich and Cu-poor compositions. In our case, it can be seen that the films synthesized at potentials between -0.35 to -0.85V have $\Delta S > 0$ and $\Delta m > 0$, indicating that these films contain an excess of selenium and copper, respectively. This means that these potentials would form the ternary semiconductor with an excess of the Cu_{2-x}Se phase.

Based on the morphologic analysis a -0.55V potential was selected as the optimum for the CuGaSe_2 deposition, since it requires less energy to produce uniform and homogeneous films. However, it is necessary to do further studies changing the concentration of the ions, trying to reduce the binary Cu_{2-x}Se phase formation. In Table 2, is shown the atomic percent of the deposits, changing the concentration of the precursor ions. It is shown that with the 4.6:25.0:9.2 ion concentrations give a stoichiometric relation close to the expected ternary.

Table 2. EDS analysis of electrodeposited Cu-Ga-Se thin films at -0.55V for 20 minutes from different concentration ratios.

Cu:Ga:Se	Atomic percent (%)			Stoichiometry
	Cu	Ga	Se	
5,0:25,0:5,5	27,05	17,78	55,17	$\text{CuGa}_{0,66}\text{Se}_{2,04}$
4,6:25,0:5,5	26,55	25,36	44,09	$\text{CuGa}_{1,11}\text{Se}_{1,50}$
4,6:25,0:9,2	23,91	23,53	52,53	$\text{CuGa}_{0,98}\text{Se}_{2,20}$

3.3. X-ray diffraction analyses

The XRD analyses of CuGaSe_2 thin films (Cu:Ga:Se=4.6:25.0:9.2) electrodeposited on Ti and $\text{SnO}_2/\text{glass}$ substrates are shown in Figure 5 and Figure 6, respectively. Figure 5(a) shows XRD of as deposited on Ti substrate, in which only shows peaks due to the substrate. After the thermal treatment at 520°C , the peaks corresponding to the chalcopyrite CuGaSe_2 are observed (112), (200, 204) and (312, 116), (JCPDS 75-0104) (Figure 5(b)). Similar results are observed for the films on $\text{SnO}_2/\text{glass}$ under similar conditions (Figure 6(a), (b), (c)). In both substrates the chalcopyrite is the only phase. This is very important results.

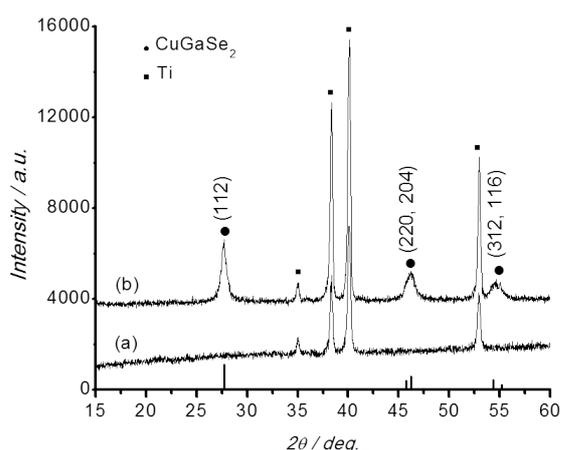


Figure 5. XRD patterns for (a) as-deposited on Ti substrate and (b) with annealing at 520°C for 30 min in inert atmosphere.

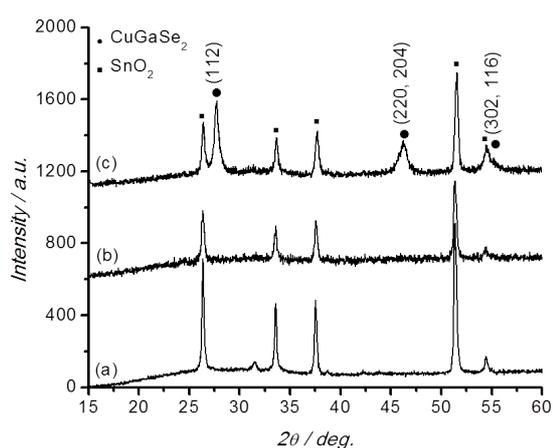


Figure 6. XRD patterns for (a) $\text{SnO}_2/\text{glass}$, (b) as-deposited and (c) with annealing at 520°C for 30 min in inert atmosphere.

3.4. Optical absorption spectroscopy analyses

Using the transmittance (T) values and film thickness (5.6 microns) the absorption coefficient (α) it was obtained. The band gap energy was estimated by extrapolating the linear portion of $(\alpha h\nu)^2$ vs

$(h\nu)$ plot to the intercept on the x-axis. Figure 8 reveals that the obtained CuGaSe_2 thin film has a direct band gap (E_g) of 1.65 eV.

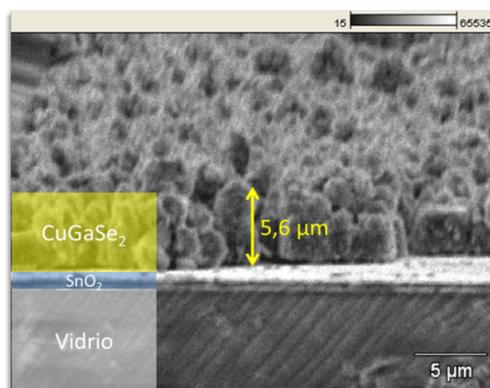
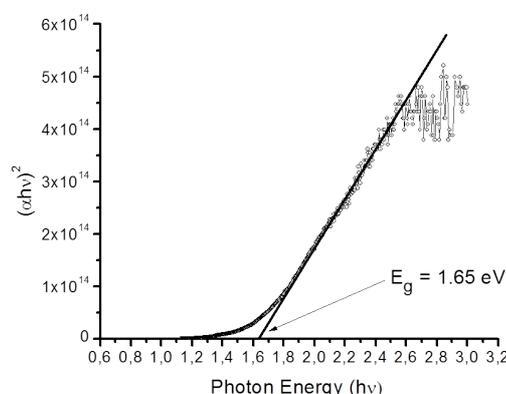


Figure 7. SEM cross-section image of the CuGaSe_2 (5.0:25.0:9.2) with annealed.



Figuras 8. Plot of $(\alpha h\nu)^2$ against photon energy for the CuGaSe_2 thin film on $\text{SnO}_2/\text{glass}$.

4. Conclusions

In this paper, it was found that we could obtain by electrochemical method good thin films of CuGaSe_2 over Ti and $\text{SnO}_2/\text{glass}$ substrate with applying at potential of -0.55V during 20 minutes of deposition. The electrolytic medium was 4.6mM of CuCl , 25.0mM of GaCl_3 y 9.2mM of SeO_2 in 2.0M of KSCN at pH 2.5. Annealing at 520°C in inert atmosphere for 30 minutes improved the CuGaSe_2 thin films crystallinity. The crystal structure of thin films was chalcopyrite type with space group $I\bar{4}2d$, with the direct energy gap of 1.65eV and high optical absorption coefficient. This material has potential application in solar cells.

Acknowledgements

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References

- [1] Jackson P, Hariskos D, Wuerz R, Kiowski O, Bauer A, Frieldmeier T and Powals M 2014 *Phys Status Solidi RRL* **9** 28
- [2] Rusu M, Wiesner S, Fuertes-Marron D, Meeder A, Doka S, Bohne W, Indner S, Schedel-Niedrig T, Giesen C, Heuken M and Lux-Steiner M 2004 *Thin Solid Films* **556** 451
- [3] Saad M, Riaz H, Bucher E and Lux-Steiner M 1996 *Applied Physics A* **62** 181
- [4] Kapur V, Basol B and Tseng E 1987 *Ternary and Multinary Compounds: Proceedings of the 7th International Conference, Snowmass, Colorado* (Pittsburgh: Materials Research Society)
- [5] Oda Y, Minemoto T and Takakura H 2008 *J Electrochem Soc* **155** H292
- [6] Muthuraj J, Rasmussen D and Suni I 2011 *J Electroanal Soc* **158** D54
- [7] Liu F, Yang J, Zhou J, Lai Y, Jia M, Li J and Liu Y 2012 *Thin Solid Films* **520** 2781
- [8] Lee H, Lee J, Hwang Y and Kim Y 2014 *Current Applied Physics* **14** 18
- [9] Vedel J 1997 *Inst Phy Conf Serial* **152** 152
- [10] Kemell M, Saloniemi H, Ritala M, Leskela M and Rauhala E 2000 *J Electrochem Soc* **147-3** 1080
- [11] Groenick and Janse 1978 *Z for Pysikalische Chemie N F* **110** 17
- [12] Manfredy L 2014 *Preparación electroquímica de semiconductores ternarios CuInS_2 y CuGaSe_2* (Mérida: Universidad de los Andes)