Influence of support electrolytic in the electrodeposition of Cu-Ga-Se thin films

A.M. Fernandez^{1,*}, J.A. Turner², B. Lara-Lara¹, and T. G. Deutsch²

**¹Instituto de Energías Renovables, Universidad Nacional Autónoma de México,
Av. Xochicalco s/n, Col Rubén Jaramillo, Temixco, Mor., 62580, México.**

²National Renewable Energy Laboratory, Golden, Colorado, 80401, USA

Abstract

CuGaSe₂ is an important thin film electronic material that possesses several attributes that make it appealing for solar energy conversion. Due to its properties it can be incorporated in to various devices, among the greatest highlights are photovoltaic cells, as well as its potential use as photocathodes for hydrogen production, via the photoelectrolysis. There are several methods of its preparation, most notably electrodeposition that has the potential for large areas and high volumes. Electrodeposition of ternary and/or quaternary semiconductors generally proceeds via the formation of a binary, which is subsequently reacted to form the ternary compound. Several conditions must be controlled to form binary compounds that include the use of complexing agents, buffers, temperature, etc. In this paper, we discuss the effect of anion composition in the electrolytic bath and the type of lithium salts, in order to manipulate the atomic concentration of CuGaSe₂ during the electrodeposition of thin films, yielding copper-rich, gallium-rich or stoichiometric thin films. We also present the results of a study on the morphology and structure obtained using two types of substrates both before and after performing a heat treatment

Key words: electrodeposition, thin films, chalcogenide compounds

1.- Introduction

Ternary compound semiconductors (I-III-VI₂), in particular CuGaSe₂, have attracted scientific interest as absorber materials in photovoltaic devices due to: i).- high optical absorption coefficient for visible light ($\alpha \approx 10^4 \text{ cm}^{-1}$), ii).- favorable direct electronic transition wide band gap, iii).- interesting physics of defects, iv).- A wide variety of growth processes for material synthesis. According to the Cu₂Se-Ga₂Se₃ phase diagram in the region of 50-58% mol. of Ga₂Se₃, homogeneous CuGaSe₂ phase exist [1]. Ga/Cu atomic ratio for the single phase lies between 1.0 and 1.38, however where the Ga/Cu ratio is greater than 1.38, the materials are expected to contain secondary phases of type CuGa₃Se₅ and CuGa₅Se₈. If the Ga/Cu atomic ratio is less than 1.0, mixtures of CuGaSe₂+(Cu₂Se)_{1-x} are predicted. It is well established that the CuGaSe₂ has a direct band gap of 1.68 eV at 300 K [2]. However, CuGaSe₂ single phase thin films have shown that the energy gap decrease with increasing temperatures, according with the Varshni's model [3].

CuGaSe₂ obtained with different growth techniques has invariably resulted in p-type conductivity regardless of its composition. Nevertheless, Schön *et. al.* [4] successfully achieved n-type CuGaSe₂ after doping the material by Ge and annealing in Zn atmosphere to remove the compensating acceptor.

Marsen *et. al.* [5] reported the fabrication of semitransparent photocathodes for photoelectrochemical hydrogen production with high photocurrents based on vacuum-deposited p-type CGS thin films. In general terms there are a lot of efforts to optimize the device performance of CGS films.

The electrodeposition technique is a process to synthesize thin film absorbers such as CGS. The major drawback to the electrodeposition of Cu–In–Ga precursors is the difficulty in electrodeposition of gallium from aqueous media. The standard reduction potential of Ga is -0.53 V vs. SHE, meaning that the hydrogen evolution reaction (HER) is conducted in parallel with Ga electrodeposition, leading to low plating efficiencies. There are different strategies to overcome these difficulties, among which can be mentioned: (i) extremely basic plating bath conditions to reduce the HER [6,7], (ii) use of hydrogen suppressants, brighteners and complexing agents [8–11] and (iii) co-deposition with other elements to reduce the deposition potential [8,12], (iv) use of different salts in the chemical baths.

In this study, we have examined the electrodeposition process of CGS which makes use of the co-deposition mechanism in obtaining good control of the film composition. The effects of the type of ions in the bath composition, and also the type of substrate were examined. The CGS films were deposited on two types of substrate, tin oxide doped with fluorine (FTO) and Mo films, and examined with inductively coupled plasma-optical emission spectroscopy (ICP-OES), x-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis methods verifying the film composition

2. Experimental section

The electrodeposition was carried out potentiostatically in a three-electrode cell configuration. The reference electrode was an Ag/AgCl electrode or platinum gauze, the counter electrode was platinum gauze, and two types of substrate were used, one was

Mo glass film of 1 μm thickness deposited by DC magnetron sputtering and resistivity of $4 \times 10^{-4} \Omega \text{ cm}$. The other substrate was SnO_2 -coated doped with fluorine doped tin oxide (FTO) coated glass 100-TEC-8, made by Hartford Glass Company Inc. with a 6-9 $\Omega/\square$. All substrates were ultrasonically cleaned with acetone and rinsed with deionized (DI) water, and subsequently dried. In order to study the effect of the type of metallic salt and the LiNO_3 or LiCl on the atomic composition of the CGS films, different electrolytic baths were prepared using: 1.5-2.6 mM of $\text{Cu}(\text{NO}_3)_2$ or CuCl_2 , 10 mM of $\text{Ga}(\text{NO}_3)_3$ or GaCl_3 , and 8 mM of H_2SeO_3 . The LiNO_3 or LiCl concentration varies from 0.25 M to 1 M. All the reagents are puratronic and were dissolved in DI-water with 18 M Ω -cm.

A Solartron Electrochemical Interface potentiostat/galvanostat (Model 1286) was used to grow CGS thin film depositions and to make cyclic voltammetry studies. The CorrWare software from Scribner Associates Inc. was used in both cases. The cyclic voltammograms were measured at a scan rate of 10 mV/s and were first scanned in the negative direction.

All film depositions and cyclic voltammetry measurements were performed in a stagnant (unstirred) bath at room temperature. The films were electrodeposited by applying a constant potential over 30 minutes. The solution was not stirred during the film deposition. The CGS film thickness was approximately 1.5 μm

The film morphology was observed with SU1500 Scanning Electron Microscope (SEM) and the atomic composition was measured using an ICP-OES system. The structure was evaluated by an X-ray diffractometer Rigaku DMAX2200 with Cu-K α radiation at 40 kV.

3. Results and Discussion

3.1 Cyclic voltammetry studies

In Figure 1 is the cyclic voltammetry for Cu-Se binary system, using two types of salts of the electrolytic baths, CuCl_2 and $\text{Cu}(\text{NO}_3)_2$. From these figures the B1 (0.15V) peak is associated with pre-deposition of Se and peak close to -0.1 V (B2) is identified as the reduction of Cu^{+2} to Cu^+ , most probably occurring as Cu_2Se formation by the following reaction:

However at more negative potentials, -0.7 V (B3) Cu_2Se formations occur under the following reaction:

Current density changes [13], if the type of anion changes, as it can be seen in Figure 1(a) or Figure 1(b).

Cyclic voltammetry for the Cu-Ga-Se system, on a FTO substrate is shown in Figure 2. From these figures it is possible to observe that the change of Cu^{+2} ion concentration, using nitrate electrolytic baths, shifts the peak C1 (Figure 2(a)) to more positive potentials. However, when a chloride electrolytic bath is used (Figure 2(b)), the same peak C1 keeps almost constant despite different copper chloride concentrations. This effect is also found using Mo substrates, as observe in Figure 2(c) and Figure 2(d), respectively.

As discussed previously [14,15] the presence of a reduction peak at -0.6 V is key in the synthesis of Ga_2Se_3 , because at this potential may occur the reaction (6) which generates the precursor H_2Se , which react with Ga^{+3} by the following reaction:

The formation of the Ga_2Se_3 binary compound is essential because it can react with the previously grown Cu_2Se compound, by the following reaction:

It is important to note that the formation of Ga-Se binary, and thus, the growth of CGS are favored when nitrate compounds are used. Figure 3 (a) and (b), show the atomic composition values of samples made with nitrate and chloride compounds at different applied potentials. Comparing both figures it can be seen that the films made with nitrate compounds are Ga-rich using either FTO or Mo substrates. The $[\text{Cu}]/[\text{Ga}]$ ratio goes from 0.86 to 0.61, when FTO substrate is used, as it can see in the table insert in Figure 3(a), but with Mo substrate the same ratio goes from 0.95 to 0.70. (see the table insert in Figure 3(b)). As it was mention, the thin films are Ga-rich and the $[\text{Se}]/[\text{Cu}+\text{Ga}]$ ratio, in most of the cases goes around 1.0. However the thin films made with chloride compounds gives Cu-rich films, as it seen in Figure 4(c-d), also either on FTO or Mo substrate. The $[\text{Cu}]/[\text{Ga}]$ ratio for nitrate baths goes from 0.86 to 0.61, when FTO substrate is used, as it can see in the Table insert in Figure 3(c), in the applied potential range of -0.5 to -0.9 V, but the same ratio goes from 3 to 6 with Mo substrate over the same applied potential. Using nitrate electrolytic baths leads to a $[\text{Cu}]/[\text{Ga}]$ ratio less than 1 on a FTO substrate with similar results on Mo substrates. The $[\text{Se}]/[\text{Cu}+\text{Ga}]$ ratio

indicates how far the composition of the films is from the ideal stoichiometry of CuGaSe_2 . The best case it is when this ratio is 1, it was found that the thin films made with nitrates electrolytic baths this ratio is around 1 for both types of substrates, but for chloride baths the same ratio, in most of the cases these values are more than 1.5, which it is an indication that the thin films most probably have more Se and then the possibility to grown Cu-Se phases. As mentioned before, the formation of Ga_2Se_3 binary compound is important in order to prepare CGS compound and the use of the nitrate salts improves its formation.

3.2 Effects of Lithium compounds on film characteristics

Several authors [16-25] suggested the use of different types of complexing agents in order to control the formation of Cu_{2-x}Se phase, and thus the formation of the ternary. They also propose that these compounds help to increase the atomic composition of Ga in films deposited in the presence of such chemicals. Some of these reports show in many cases the formation of copper rich layers [26]. Less attention has been given to the effect of the lithium salts compound to improve the gallium atomic composition in the films. It is reported that the addition of lithium salts can alter the pH of the solution, and thus can also help to control the pH in the electrolytic bath. However, the possibility that Li^+ can help modify the atomic concentration in these CGS films has never been mentioned. Figure 5 shows the effect of the increment of the lithium salt in the atomic ratio for CGS films at different applied potentials. As shown in Figure 4(a), the atomic ratio changes from the Cu-rich without lithium nitrite to Ga-rich with 1 M LiNO_3 concentration. In other words, the $[\text{Cu}]/[\text{Ga}]$ ratio values, which is an indication of either

Cu-rich or Ga-rich layer, goes from 16 to 3 without LiNO_3 and 0.86 to 0.61 with 1 M LiNO_3 . Also, the $[\text{Se}]/[\text{Cu}+\text{Ga}]$ ratio values may possible indicate the CGS formation (Figure 4(b) goes from 2.05 to 1.8 without LiNO_3 and 1.1 to 1.05 with 1 M of LiNO_3 . But in the case of chloride electrolytic baths, the Cu/Ga and Se/(Cu+Ga) ratios also reduce after adding LiCl to the electrolytic bath. The Cu/Ga ratio values go from 34.4 to 8.4 without LiCl and 3.08 to 2.1 with 1 M LiCl and Se/(Cu+Ga) goes from 1.89 to 1.1 without LiCl and 1.35 to 1.01 with 1 M LiCl, as can see in Figure 4(c-d). In this particular case, the effect of adding LiCl in the electrolytic bath reduces the Cu/Ga ratio values, but still keeping Cu-rich layer, however Ga-rich layer is improve by adding LiNO_3 , in particular with concentration close to 1 M. Also, the $[\text{Se}]/[\text{Cu}+\text{Ga}]$ ratio values close to 1 may possible indicate the CGS formation. Similar behavior was found when Mo was used as the substrate.

The surface morphologies of CGS films deposited on FTO and Mo substrates with 0.5 M of LiNO_3 in the electrolytic bath and with varying potential from -0.5 V to -0.9 V are shown in Figure 5(a-e). The surface morphology in Figure 5(a) exhibited dense morphology and cauliflower-like features on the surface, since the composition of film is Cu-rich layer with a Ga concentration of 18.32% at., made at -0.5 V. When the applied potential is increased to -0.9 V, the morphology changes and contains isolated small grains and voids on the surface, and the films change from Cu-rich to Ga-rich. However, when a Mo substrate is used the morphology changes dramatically, growing Cu-rich films with small and compact spherical particles and flake-like copper selenide as seen in the film deposited at -0.5 V in Figure 5(d). By increasing the applied potential (-0.9 V) the morphology and the composition change to Ga-rich films as observed in Figure 6(e).

The XRD patterns of CGS films fabricated at an applied potential of -0.5 V after annealing at 500 C for 20 min in N₂ atmosphere on either FTO or Mo substrates are shown in Figure 6(a) and (b), respectively. Two peaks can be seen corresponding to the (112) and (204) planes of CuGaSe₂ phase as confirmed in comparison to JCPDS diffraction JPCDS file no.75-0104. In addition to the diffraction peaks for the substrate, another peak was observed that corresponds to the main diffraction peak of CuSe₂ (JCPDS no.18-0453), indicative of a CuSe₂ phase.

4. Conclusion

CuGaSe₂ thin films have been prepared by one-step electrodeposition by single-bath aqueous solution containing different concentrations of lithium compounds that serve to enhance the electrical conductivity of the solution. The effect of two lithium salts that had different anions was evaluated and it was found that that CGS films deposited in the presence of lithium nitrate had improved atomic composition compared to those made in electrolytes containing lithium chloride. With increased lithium nitrate concentration, the elemental ratios [Cu]/[Ga] and [Se]/[Cu+Ga] of the thin films are close to 1, which is an indication that the thin films have a stoichiometry similar of CuGaSe₂. It was found that the morphology of the as-deposited thin films was affected by the substrate. Using Mo substrates yielded a morphology that had isolated small grains and voids in comparison with FTO substrate. More studies are in progress in order to improve the morphology.

Acknowledgements

JAT and TGD acknowledge support from the U.S. Department of Energy (DOE) Fuel Cell Technology Office under contract No. DEAC36-08-GO28308 with NREL. A.M. Fernandez expressed his gratitude to the program PASPA-UNAM and CONACYT for the support received during the sabbatical grant. We would like to thank to Maria Luisa Ramon García for the XRD and Rogelio Morán Elvira for SEM measurements.

REFERENCES

- [1] O.M. Strok, I.D. Olekseyuk, O.F. Zmiy, I.A. Ivashchenko, and L.D. Gula, *Journal of Phase Equilibria and Diffusion* 34(2013)94-103.
- [2] S. B. Zhang, a) Su-Huai Wei, and Alex Zunger *J. Appl. Phys.*, 83(1998)3192-3196.
- [3] Y. P. Varshni, "Temperature dependence of the energy gap in semiconductors," *Physica (Utrecht)* 34(1967)149-154.
- [4] J. H. Schön, J. Oestreich, O. Schenker, H. Riazzi-Nejad, M. Klenk, N. Fabre, E. Arushanov, and E. Bucher, *Appl. Phys. Lett.* 75(1999)2969.
- [5] Bjorn Marsen*, Brian Cole, Susanne Dorn, Richard E. Rocheleau, Eric L. Miller, *Solar Hydrogen and Nanotechnology II*, edited by Jinghua Guo, *Proc. of SPIE Vol.* 6650(2007)665006-1.
- [6] M. Mehlin, J. Rimmasch, H.P. Fritz, *Zeitschrift Fur Naturforschung Section B-a Journal of Chemical Sciences* 49(1994)1597.
- [7] R. Friedfeld, R.P. Raffaele, J.G. Mantovani, *Solar Energy Materials and Solar Cells* 58(1999)375.
- [8] D. Lincot, J.F. Guillemoles, S. Taunier, D. Guimard, J. Sicx-Kurdi, A. Chaumont, O. Roussel, O. Ramdani, C. Hubert, J.P. Fauvarque, N. Bodereau, L. Parissi, P. Panheleux, P. Fanouillere, N. Naghavi, P.P. Grand, M. Benfarah, P. Mogensen, O. Kerrec, *Solar Energy* 77(2004)725.
- [9] J. Zank, M. Mehlin, H.P. Fritz, *Thin Solid Films* 286(1996)259.
- [10] J. Kois, M. Ganchev, M. Kaelin, S. Bereznev, E. Tzvetkova, O. Volobujeva, N. Stratieva, A.N. Tiwari, *Thin Solid Films* 516(2008)5948.
- [11] Y. Oda, T. Minemoto, H. Takakura, *J. Electrochem. Soc.* 155(2008)H292.
- [12] L. Thouin, S. Massaccesi, S. Sanchez, J. Vedel, *Journal of Electroanalytical Chemistry* 374(1994)81.
- [13] N. G. Romeo, G. Sberveglieri, and L. Tarricone, *Appl. Phys. Lett.* 30(1977)108.
- [14] Y. Lai, F Liu, Z. Zhang, j.Liu, S.Kuang, J. Li, Y. Liu, *Electrochimica Acta* 54(2009)3004-3010
- [15] H. Lee, J. Lee, Y. Hwang, Y. Kim, *Current Applied Physics* 14(2014)18-22.

- [16] Yanqing Lai, Fangyang Liu, z Sanshuang Kuang, Jun Liu, Zhian Zhang, Jie Li, and Yexiang Liu, *Electrochemical and Solid-State Letters* 12(2009)D65-D67
- [17] K. Bouabid, A. Ihlala, A. Manar, A. Outzourhit, E.L. Ameziane, *Thin Solid Films* 488 (2005) 62–67.
- [18] F. Chraïbi, M. Fahoume, A. Ennaoui, J.L. Delplancke, *Phys. Stat. Sol.* 186(2001)373–381.
- [19] R.N. Bhattacharya, *J. Electrochem. Soc.* 130(1983)2040–2042.
- [20] T.J. Whang, M.T. Hsieh, Y.Ch. Kao, Sh.J. Lee, *Appl. Surf. Sci.* 255(2009)4600–4605.
- [21] F.J. Pern, J. Goral, R.J. Matson, *Sol. Cells* 24(1988)81–90.
- [22] M. Ganchev, J. Koïs, M. Kaelin, S. Bereznev, E. Tzvetkova, O. Volobujeva, N. Stratieva, A. Tiwari, *Thin Solid Films* 511–512(2006)325–327.
- [23] M. Kemell, M. Ritala, H. Saloniemi, M. Leskela, T. Sajavaara, E. Rauhala, *J. Electrochem. Soc.* 147(2000) 1080–1087.
- [24] R. Ugarte, R. Schrebler, R. Cordova, E.A. Dalchiele, H. Gomez, *Thin Solid Films* 340(1999)117–124.
- [25] S. Beyhan, S. Suzer, F. Kadirgan, *Sol. Energy Mater. Sol. Cells* 91(2007)1922–1926.
- [26] F. Liu, J. Yang, J. Zhou, Y. Lai, M. Jia, J. Li, Y Liu , *Thin solid Films* 520(2012)2781-2784

Figure captions

Figure 1.- Cyclic voltammograms of 2.6 mM of CuCl_2 (dashed line) and 2.6 mM of $\text{Cu}(\text{NO}_3)_3$ (solid line) with 8 mM of H_2SeO_3 using (a) FTO substrate, and (b) Mo films.

Figure 2.- Cyclic voltammograms of 10 mM of GaCl_3 and 8 mM of H_2SeO_3 varying concentration of CuCl_2 on (a) FTO substrate and (b) Mo substrate and 10 mM of $\text{Ga}(\text{NO}_3)_3$ and 8 mM of H_2SeO_3 varying concentration of $\text{Cu}(\text{NO}_3)_2$ on (c) FTO substrate and (d) Mo substrate.

Figure 3. ICP-OES determined film composition of Cu-Ga-Se as-deposited films as a function of applied potential, using (a) FTO substrate and LiNO_3 ; (b) Mo substrate and LiNO_3 ; (c) FTO substrate and LiCl ; (d) Mo substrate and LiCl . All depositions were made at room temperature (25 C) and 1200 seconds as deposition time.

Figure 4.- (a) $[\text{Cu}]/[\text{Ga}]$ ratio and (b) $[\text{Se}]/[\text{Cu}+\text{Ga}]$ ratio as a function of applied voltage at different lithium nitrate concentrations, (c) $[\text{Cu}]/[\text{Ga}]$ ratio and (d) $[\text{Se}]/[\text{Cu}+\text{Ga}]$ ratio as a function of applied voltage at different lithium chloride concentrations. FTO substrate was used in all cases.

Figure 5.- SEM images of the surface morphology of CGS film prepared at (a) $E = -0.5\text{V}$ vs Pt and 0.5 M of LiNO_3 on FTO substrate; (b) -0.6 V vs Pt and 0.5 M of LiNO_3 on FTO substrate; (c) -0.9 V vs. Pt and 1 M of LiNO_3 on FTO substrate; (d) -0.5 V vs Pt and 0.5 M LiNO_3 on Mo substrate; (e) -0.9 V vs. Pt and 1 M LiNO_3 on Mo substrate.

Figure 6.- An XRD pattern of CGS pattern of CGS films annealed at 550 in Se for 1 hr. (a) on FTO substrate and (b) Mo substrate.

(a)

(b)

(a)

(b)

(c)

(d)

(a)

(b)

(c)

(d)

(a)

(b)

(c)

(d)

(a)

(b)

(c)

(d)

(e)

(a)

(b)