Communications in Physics, Vol. 21, No. 4 (2011), pp. 365-372

ELECTRODEPOSITION OF $CuGaSe_2$ LAYER FROM SOLUTIONS WITH DIFFERENT COMPLEXING AGENTS

NGO DINH SANG
National University of Civil Engineering
PHAM HONG QUANG AND LE TUAN TU
Hanoi University of Science, Vietnam National University, Hanoi

Abstract. *$CuGaSe_2$ (CGS) thin films were deposited on ITO substrates by electrodeposition from the solutions with different acidic agents, namely hydrochloric, sulphamic and citric acids. Cyclic voltammetry (CV) studies of unitary Cu, Ga, and Se systems and ternary Cu-Ga-Se systems were carried out to determine the reduction potentials, the mechanism of deposition and the ability to deposit of each constituent. The reduction peaks were observed in all unitary systems except the case of Ga from solution with non-acid and citric acid. For the ternary systems, the voltammograms only show the peaks relating to the reduction of Cu^{2+} and Se^{4+}, indicating the difficulty in deposition of Ga. The electrodepositions have been processed at - 0.6 V and - 0.95 V vs. SCE. The concentration of the films was determined by EDS. For all complexing agents, the concentration of Ga has been found to depend strongly on the deposition potential and has reached to the value of about 16% at. at potential of -0.95 V from the solutions with hydrochloric and sulphamic acids.*

I. INTRODUCTION

$Cu(In_{1-x}Ga_x)Se_2$ (CIGS) is one of the most promising absorber materials for solar cell application. CIGS has a large optical absorption coefficient ($5x10^5 cm^{-1}$) which results from the direct band gap [1]. The CIGS base-thin film solar cell has reached a conversion efficient of 20.3 % for laboratory-size devices fabricated from a physical vapor deposition process (PVD) [2]. Additionally, CIGS modules have shown a long-term stability [1]. In order to make the CIGS-based solar cell become more realizable, an alternative low cost process has to be developed for the growth of the high quality CIGS absorber layer. Electrodeposition technique is potentially suitable to satisfy this requirement. The formation of high quality CIGS and CGS compounds by electrodeposition is always followed by an annealing step [3-5]. A conversion efficient as high as 15.4 % has been achieved in the devices with CIGS film grown by electrodeposition and adjusted the composition by PVD [6]. In CIGS materials, the value of band gap ranges from 1.0 eV to 1.7 eV, depending on the ratio between Ga and In. The optimum value of band gap is about 1.3 eV corresponding to the Ga/(Ga+In) ratio of 0.3 [7].

There are two different electrochemical approaches to form CIGS films: one-step electrodeposition [8] that provides all constituents from the same electrolyte in a single step and multi-step electrodeposition that deposits sequentially each constituent from different electrolytes [9]. However, one-step electrodeposition of CIGS films is rather difficult due to the large difference in the reduction potential for each constituent. Among four elements, Ga is the most difficult one to deposit since it has very negative reduction potential. One of the most useful method to solve this problem is to add a complexing agent into the bath. This may shift the reductions of the elements closer together and/or improve the film quality. Recently, Muthuraj et al. has described the complexation of $Cu^{2+}$by thiocyanate for $CuGaSe_2$codeposition [10]. In present work we studied the effect of complexing agents on the deposition of Cu, Ga and Se. Hydrochloric, sulphamic and citric acids were chosen as the complexing agents because they are most popular. The aim of this work is to find the best complexing agent for achieving high concentration of Ga in one-step electrodeposition of CIGS.

II. EXPERIMENTAL

The cyclic voltammetry (CV) studies and the potentiostatically electrodeposition process (ED) were carried out in a three-electrode configuration consisting of a saturated calomel electrode (SCE) as a reference electrode, a Pt spiral wire as a counter electrode and an ITO substrate as a working electrode. The electrolyte bath contained 120 ml deionized water with 15 mM $CuCl_2$, 24 mM $Ga(NO_3)_3$, 20 mM H_2SeO_3. 350 mM LiCl was used as the supporting agent.

A combination of 25 mM KHP (Potassium Hydrogen Phthalate) and 10 mM one of hydrochloric (HCl), sulphamic (H_3SNO_3) and citric ($C_6H_8O_7$) acids provided the different complexing agents. The pH of the solution was adjusted to 2.0 by adding drops of concentrated hydrochloric acid. In order to see more clearly the effect of acidic agent, the CV study of solution with non-acid has also been carried out. The CV was carried out in the range of potential from -1.2 V to 0.0 V vs. SCE at the scan rate of 20 mV/s. The first scan was in negative direction. The electrodepositions were processed at -0.6 V and -0.95 V vs. SCE for 20 minutes. The concentration of the films grown by ED was determined by EDS, the surface morphology was examined by SEM and crystalline structure was characterized by XRD.

III. RESULTS AND DICUSSION

III.1. Voltammogram of unitary Cu, Ga, and Se systems

Figures 1, 2 and 3 present the voltammogram of unitary Cu, Ga, and Se systems, respectively.

In Fig. 1, voltammograms of $CuCl_2$ in different solutions are quite similar with one weak peak at about -0.2 V and a strong peak at about -0.45 V vs SCE.

We suggest that the strong peak relates to the process:

$$Cu^{2+} + 2e^- \leftrightarrow Cu^0 \tag{1}$$

According to Abrantes et al. [11], the weak peak may be attributed to the process:

$$Cu^{2+} + 2Cl^- + e^- \leftrightarrow CuCl_2^- \tag{2}$$

In Fig. 2, the very weak reduction peaks at about -0.8 V vs. SCE, corresponding to the reduction of $Ga^{3+}$to Ga, can be observed in the voltammograms of $Ga(NO_3)_3$ in solutions with hydrochloric and sulphamic acids but not with non-acid and citric acid. This is the evidence that among three elements Ga has the most negative reduction potential

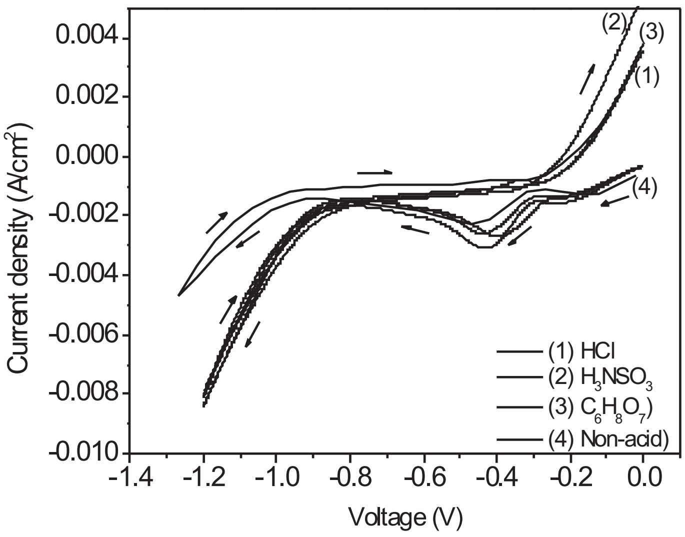


Fig. 1. Voltammogram of $CuCl_2$ in different solutions.

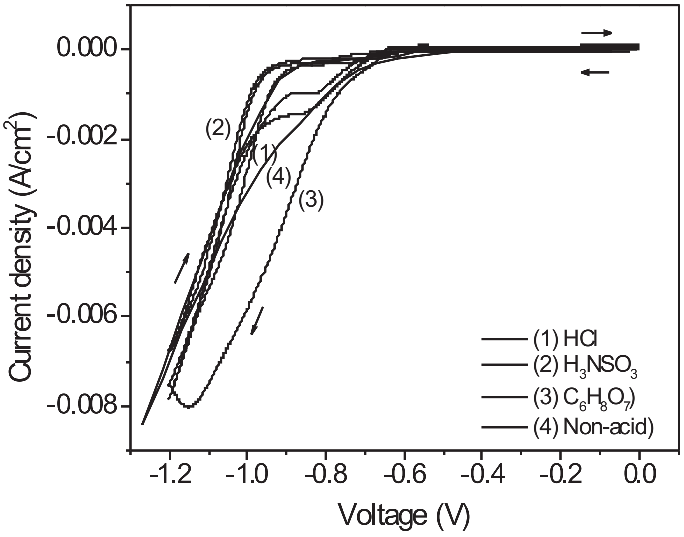


Fig. 2. Voltammogram of $Ga(NO_3)_3$ in different solutions.

and therefore is the most difficult element to deposit. It also indicates that among three acids, citric acid is not suitable to use as complexing agent.

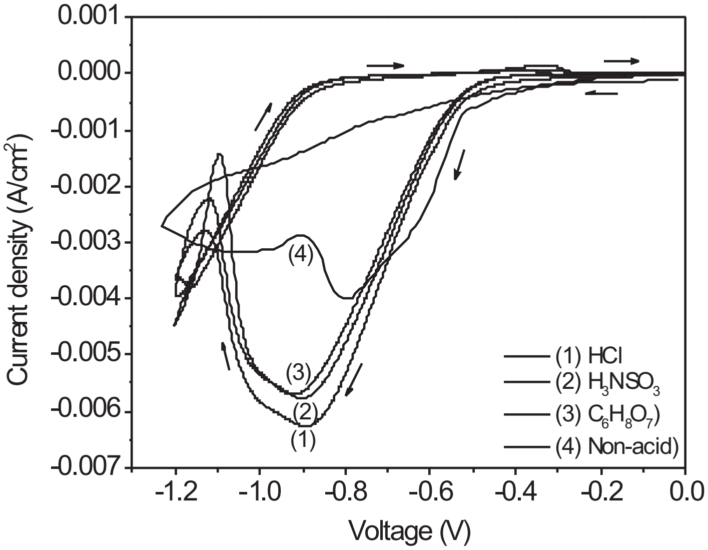


Fig. 3. Voltammogram of H_2SeO_3 in different solutions.

The voltammograms of H_2SeO_3 in different complexing agents are almost the same. The peaks obtained in these voltammograms seem to be doublet with a major peak at -0.9 V and a minor one at -1.0 V. The peak at -0.9 V is not likely relate to the reduction of H_2SeO_3directly to Se which takes place at about -0.4 V vs. SCE, following the equation:

$$H_2SeO_3 + 4H^+ + 4e^- \leftrightarrow Se + 3H_2O \tag{3}$$

We suggest this peak corresponding to the complex process described by the equations:

$$H_2SeO_3 + 6H^+ \leftrightarrow H_2Se + 3\ H_2O \tag{4}$$

$$H_2SeO_3 + 2H_2Se + 6e^- \leftrightarrow Se + 3H_2O \tag{5}$$

Our suggestion is in agreement with those of Massaccesi *et al.* [12] and Mishra et al. [13]. It is worth to note that we have observed the peaks of both direct and complex process in the voltammogram of the same chemical system but on Mo coated substrate. In that case, the intensity of two reduction mechanisms are equal. The domination of complex process in the present work may be due to the effect of ITO substrate, that is, the direct deposition of Se on ITO substrate is diminished. The minor peak at -1.0 V should relate to the hydrogen evolution. By comparing the voltammograms of solutions with and without acidic agents, we can see that acidic agents have promoted the reduction of H_2SeO_3but inhibited the H^+ reduction to H_2.

III.2. Voltammogram of ternary Cu-Ga-Se systems

Fig. 4 illustrates the voltammogram of ternary Cu-Ga-Se systems in different solutions with different acids. We can observe three peaks corresponding to the reduction processes of $Cu^{2+}$and Se^{4+}.

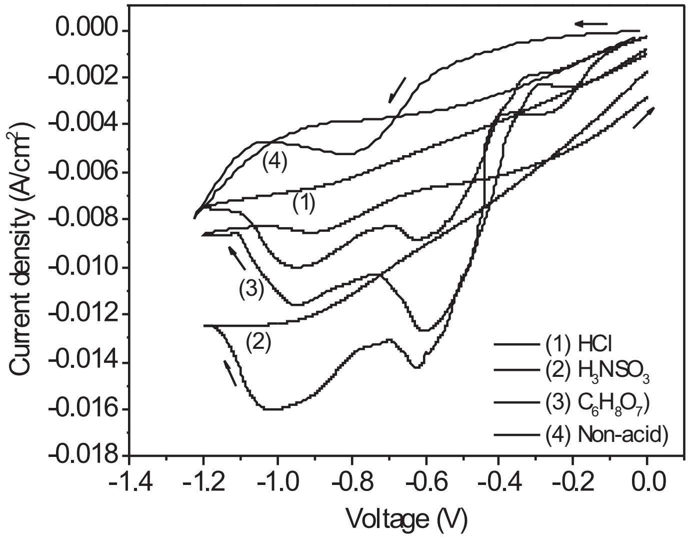


Fig. 4. Voltammogram of $CuCl_2$, $Ga(NO_3)_3$, H_2SeO_3 in different solutions.

The reduction peak of $Ga^{3+}$to Ga is too weak to discern in this voltammogram. We still observe the peak at about -0.2 V which corresponds to the reduction of $Cu^{2+}$to Cu^+. The notable difference of the voltammograms of ternary systems compared with those of unitary systems is the present of a strong peak at -0.6 V instead of the Cu^{2+}reduction peak at -0.45 V. According to Lai et al. [14], this phenomena corresponds to the reduction of $Cu^{2+}$to Cu via a formation of a copper selenide compound, in this case might be Cu_3Se_2, following equations:

$$2H_2SeO_3 + 3Cu^{2+} + 8H^+ + 14\ e^- \quad \leftrightarrow Cu_3Se_{2+} + 6H_2O \tag{6}$$

$$Cu_3Se_2 + 4H^+ + 4e^- \leftrightarrow 3Cu + 2H_2Se \tag{7}$$

Unfortunately, because the as-deposited samples are amorphous, it is impossible to use XRD to determine the actual copper selenide stoichiometry.

The reduction peaks of H_2SeO_3 described by Eq. 4 and 5 are still observed with a slightly negative shift when the complexing agent going from HCl to $C_6H_8O_7$. This is due to the difference in the effect of Cu^{2+} and Ga^{3+} on reduction of H_2SeO_3 in different solutions. In these voltammograms, we can see more clearly that acidic agent promotes the deposition of CGS layer.

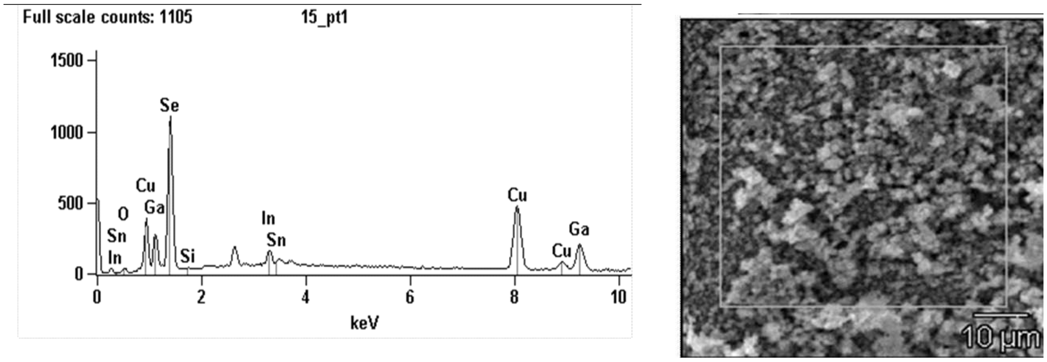
III.3. Results of electrodeposition of CGS films

The composition of the CGS films determined by EDS are listed in Table 1.

Table 1. The composition of the CGS films determined by EDS

Solutions with	Potential V vs. SCE	Atom %		
		Cu	Ga	Se
HCl	-0.60	35.8	2.8	65.4
HCl	-0.95	23.8	16.3	59.9
H_3SNO_3	-0.60	38.5	0.9	60.6
H_3SNO_3	-0.95	29.2	16.2	54.6
$C_6H_8O_7$	-0.60	35.8	0.2	63.9
$C_6H_8O_7$	-0.95	61.2	2.3	36.5

Fig. 5 illustrates the typical EDS spectra and SEM morphology of the CGS film deposited at -0.95 V vs. SCE in solution with HCl. The data listed in Tab.1 are in accordance with the CV results. First of all, these data indicate the difficulty in deposition of Ga. However, we can see a possibility for deposition of Ga at a quite negative potential in solution with HCl and H_3SNO_3. At the potential of -0.95 V, we have obtained the Ga concentration up to about 75 % of stoichiometry. The concentration of Cu in the samples deposited at -0.60 V is higher than those of the samples deposited at -0.95 V because of the lower concentration of Ga in the former samples compared to the later ones. This result is also probably caused by an underpotential process relating to the formation of Cu-Se phases. Since the reduction process of Se^{4+} in all solutions starts from -0.5 V, a high concentration of Se has been obtained in both systems of samples grown at -0.6 V and -0.95 V.



(a) (b)

Fig. 5. Typical EDS spectra and SEM imagine of the CGS film deposited at -0.95 V vs. SCE from the solution with different complexing agents.

The slightly lower concentration of Se in the samples deposited at -0.95 V is mainly due to the increase of Ga concentration. For the samples deposited in solution with $C_6H_8O_7$, the concentration of Ga is very small. It suggests that $C_6H_8O_7$ is not suitable to be a complexing agent. As an attempt, we have increased the concentration of $Ga(NO_3)_3$ up to 40 mM in solution with sulphamic acids and have obtained the sample with Ga concentration of 27 at. %.

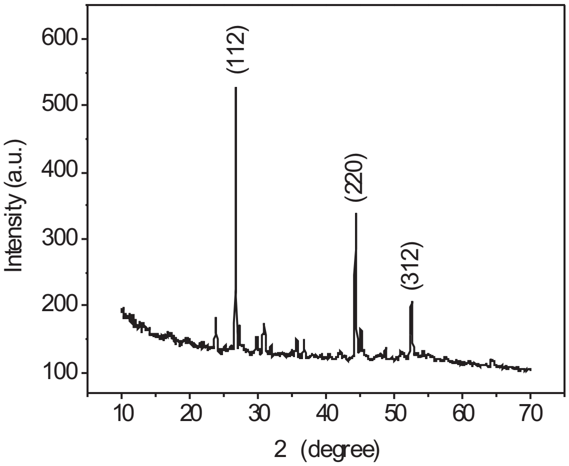


Fig. 6. XRD pattern for a post-annnealing sample grown from sulfamic acid solution at -0.95 V.

As mentioned above, it is impossible to use XRD patterns of as-deposition samples to show the phase structure of deposited layer because they exhibit a nanocrystalline and/or amorphous structure. For that reason, we show in Fig. 6 only one typical XRD pattern for a post-annnealing sample which was grown from sulfamic acid solution at -0.95 V. In this figure we can see the domination of the chalcopyryte structure with the typical peaks, namely (112), (220) and (312). Beside that, we can see also some peaks relating to the existence of secondary phases such as elemental selenium and Cu-Se compounds. This observation can be expected because the obtained samples are not well stoichiometry.

IV. CONCLUSION

One step electrodeposition of CuGaSe absorber layers has been studied by cyclic voltammetry and the potentiostatically electrodeposition. The positive shift of the reduction peaks caused by the induced reaction has not been observed. The reduction mechanism of $Cu^{2+}$and Se^{4+} is a complex process and takes play in a wide range of potential. For all complexing agents, the concentration of Ga has been found to depend strongly on the deposition potential and has reached to the value of about 16% at. (equal to 75 % of stoichiometry) at potential of -0.95 V from the solutions with hydrochloric and sulphamic acids. The stoichiometry composition of Ga can be achieved by increasing the concentration of $Ga(NO_3)_3$ in solution with hydrochloric and sulphamic acids.

ACKNOWLEGMENTS

This work was supported by the Vietnam National Foundation for Science and Technology Development (NAFOSTED) in the period 2010 – 2011 (Project Code: 103.02.59.09).

REFERENCES

[1] R.N. Bhatacharya, W. Batchelor, J.E. Grannata, H. Hasoon, H, Wiensner, K. Ramanathan, J. Keane, R. N. Noufi, *Sol. Energy Matter. Sol. Cells* **55** (1998) 83.
[2] M.A. Green, K. Emery, Y. Hishikawa, W. Warta, *Prog. Photovolt: Res. Appl.* **17** (2009) 32.
[3] 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.
[4] E. Chassaing, P. P. Grand, A. Etcheberry, and D. Lincot, *ESC Transactions* **19** (2009) 149.
[5] R.N. Bhatacharya, *J. Electrochem. Soc.* **157** (2010) D 406.
[6] R.N. Bhatacharya, J. F. Hiltner, W. Batchelor, M. A. Contreras, R. N. Noufi, J. R. Sites, *Thin Solid Film* **361** (2000) 396.
[7] M. Marudachalam, R. W. Birkmire, H. Hichri, *J. Appl. Phys.* **82** (1997) 2896.
[8] J. Zank, M. Mehlin, H.P. Fritz, *Thin Solid Film* **286** (1996) 259.
[9] A. Kampmann, J. Rechid, A. Raitzig, S. Wulff, M. Mihhalova, R. Thyen, K. Kaberlah, *Matter. Res. Soc. Symp. Proc.* **763** (2003) 323.
[10] J. J. J. Muthuraj, D. H. Rasmussen, and I. I. Sunia, *J. Electrochem. Soc.* **158** (2011) D 54-D56.
[11] I. M. Abrantes, L.V. Araujo, D. Veli, *Minerals Engineering* **8**, No 12 (1995) 1467.
[12] S. Massaccesi, S, Sanchez, J. Vedel, *Electroanal. Chem.* **412** (1996) 95.
[13] K. K. Mishra, K. Rajeshwar, *Electroanal. Chem.* **271** (1989) 279.
[14] Y. Lai, F. Liu, Z. Zhang, J. Liu, Y. Li, S. Kuang, J. Li, Y. Liu, *Electrochim. Acta* **54** (2009) 3004.

Received 26 July 2011.