

Effect of electrodeposition potential on the composition and morphology of CIGS absorber thin film

Pham Hong Quang, Ngo Dinh Sang, Le Tuan Tu, Dang Thi Bich Hop and Nguyen Thanh Nghi

Hanoi University of Science, 334 Nguyen Trai, Thanh Xuan, Hanoi, Vietnam

Introduction

The Cu(In_{1-x}Ga_x)Se₂ (CIGS) thin film has potential as an absorber materials for solar cell application because it has a large optical absorption coefficient ($5 \times 10^5 \text{ cm}^{-1}$) which results from the direct band gap [1-2]. Recently, a number of works have done on the growth of CIGS thin film using one-step electrodeposition technique [3-8] which provides all constituents from the same electrolyte in a single step. However, one-step electrodeposition of CIGS films is rather difficult due to the large difference in the values of equilibrium reduction potential for each constituent. In this investigation, we study the deposition mechanism of the constituents by using the cyclic voltammetry technique. We also grow the CuInGaSe (CIGS) thin films on Mo/soda-lime glass substrates by electrodeposition at different potentials ranging from -0.3 to -1.1 V vs. Ag/AgCl. The aim of this work is not to find out the best concentration of electrolyte for obtaining the stoichiometry but to find out the appropriate deposition potential in one-step electrodeposition of CIGS layer.

Experiments

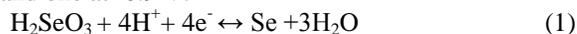
The cyclic voltammetry studies and the potentiostatically electrodeposition process were carried out using a potentiostat/galvanostat model Autolab 3020 N in a three-electrode configuration where the reference electrode was Ag/AgCl, the counter electrode was a Pt spiral wire and the working electrode was a Mo/soda-lime glass substrate with an area of 2 cm². The electrolyte bath contained 120 ml deionized water with 20 mM CuCl₂, 40 mM Ga(NO₃)₃, 30 mM InCl₃, 20 mM H₂SeO₃, 350 mM LiCl was used as the supporting agent. A combination of 25 mM KHP (Potassium Hydrogen Phthalate) and 20 mM H₃SNO₃ (sulphamic acids) was used as a complexing agent. The cyclic voltammetry was carried out in the range of potentials from -1.2 V to 0.0 V vs. Ag/AgCl at the scan rate of 20 mV/s. The electrodepositions (ED) were processed at the potentials ranged from -0.3 V to -1.1 V vs. Ag/AgCl for 20 minutes. The annealing process was carried out in Ar at 550°C for 60 minutes. The concentration of the films grown by ED was determined by EDS, the surface morphology was examined by SEM and the crystallinity was examined by XRD.

Results and discussion

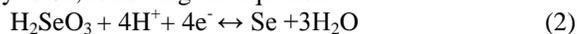
1. Voltammograms of unitary Cu, In, Ga and Se systems

The voltammogram of the unitary Cu system shows one weak peak at about 0.15 V and one peak at about -0.4 V,

corresponding to the reductions of Cu²⁺ to Cu⁻ and Cu⁰, respectively. The reduction peaks of In and Ga ions were observed at -0.8 V and -0.9 V, respectively. The voltammogram of H₂SeO₃ shows two strong peaks, one at -0.3 V and one at -0.9 V.



The first peak is likely relate to the reduction of H₂SeO₃ directly to Se, following the equation:



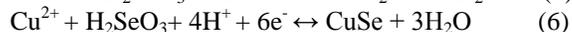
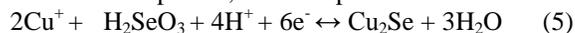
We suggest the second peak corresponding to the complex process described by the equations:



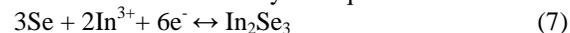
This suggestion is similar to those reported by S. Massaccesi et al. [9] and K. K. Mishra et al. [10].

2. Voltammogram of binary Cu-Se, Ga-Se and In-Se

There are some differences between the voltammogram of Cu-In binary system and voltammograms of Cu and Se unitary systems. These difference can be explained by the formations of Cu-Se phases, for examples:



In binary In-Se system, we can observe one peak at -0.57 V which may relate to an underpotential deposition of indium as indium selenides described by the equation:



The underpotential deposition of gallium as gallium selenides do not occur in this system.

3. Voltammogram of quaternary Cu-In- Ga-Se

The most notable feature in this voltammogram is a strong peak at -0.5 V. This peak may relate to an underpotential depositions process to form Cu-Se and/or In-Se phases. This voltammogram also reveals that deposition of Ga still needs a highly negative potential.

4. Potential dependence of composition

The EDS composition of the CIGS films deposited at various potentials is listed in Table 1. The concentration of Cu increases as the deposition potential decreasing to -0.5 V then decreases as the deposition potential decreasing continuously. We can see that Ga concentration has very low value in the samples deposited at the negative potential above -0.7 V, then rises rapidly as the potential decreasing and reaches to maximum value of 18.14 % at the potential of -1.0 V. In the case of In, the insertion of In can be achieved at -0.5 V, that is more positive than the desired deposition potential for Ga. The Se concentration is high in all samples and depends mainly on the concentration of the other

constituents. It is interesting to note that there is a range of potential from -0.8 V to -1.0 V where the concentration of all constituents is quite unaffected by potential. This potential range is also where we can obtain the highest concentration of In and Ga. It means that this potential range is the best choice for obtaining films with desired and stable stoichiometry. Our observation about the suitable potential range is in agreement with that reported by Y. Lai et al. [11].

Potential V vs. Ag/AgCl	Atomic percent (%)				Stoichiometry
	Cu	In	Ga	Se	
-0.3	23.9	03.3	01.9	70.9	$\text{CuIn}_{0.14}\text{Ga}_{0.08}\text{Se}_{2.96}$
-0.4	25.7	04.6	02.0	67.7	$\text{CuIn}_{0.18}\text{Ga}_{0.08}\text{Se}_{2.63}$
-0.5	27.0	10.2	02.3	60.5	$\text{CuIn}_{0.37}\text{Ga}_{0.08}\text{Se}_{2.24}$
-0.6	22.7	16.5	02.9	57.9	$\text{CuIn}_{0.73}\text{Ga}_{0.13}\text{Se}_{2.56}$
-0.7	19.8	19.5	06.0	54.7	$\text{CuIn}_{0.98}\text{Ga}_{0.30}\text{Se}_{2.76}$
-0.8	18.2	23.7	08.7	49.4	$\text{CuIn}_{1.30}\text{Ga}_{0.47}\text{Se}_{2.70}$
-0.9	18.0	22.4	13.4	46.2	$\text{CuIn}_{1.24}\text{Ga}_{0.74}\text{Se}_{2.56}$
-1.0	17.5	22.1	14.1	46.3	$\text{CuIn}_{1.26}\text{Ga}_{0.80}\text{Se}_{2.64}$
-1.1	17.0	21.8	13.2	48.0	$\text{CuIn}_{1.28}\text{Ga}_{0.77}\text{Se}_{2.81}$

Tab. 1 The EDS composition of the CIGS films deposited at various potentials.

5. The morphology and crystallinity

The evolution of morphology and crystallinity under the variation of applied potential and the annealing process can be seen from the XRD patterns which are shown in Fig. 1.

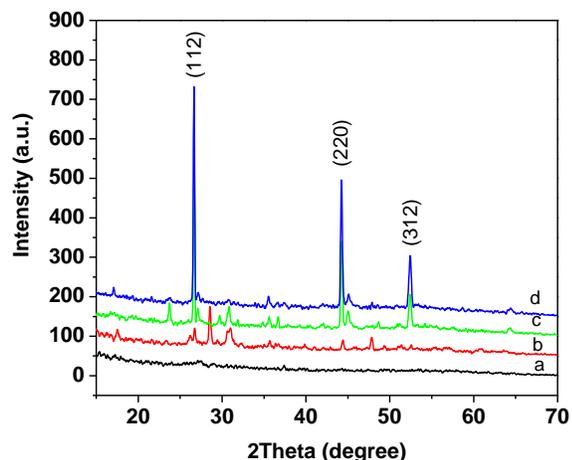


Fig. 1. XRD patterns of the typical CIGS films with plane indices corresponding to the chalcopyrite structure: (a) as-deposited, post-annealing films grown at (b) -0.3 V, (c) -0.5 V, and (d) -0.9 V vs. Ag/AgCl.

In all case of as-deposited samples, the XRD patterns exhibit a nanocrystalline and/or amorphous structure. For that reason, we show only one pattern of a typical as-deposited sample. The XRD patterns of the post-annealing samples reveal that these films have a better crystalline structure. The typical peaks of the chalcopyrite structure, namely (112),

(220) and (312), start occurring in the XRD pattern of the samples deposited at -0.5 V, increase as changing the applied potential toward negative direction and then become dominant in the film deposited at -0.9 V.

Conclusion

In this work, we have studied the deposition mechanism of the CIGS layer by using the cyclic voltammetry technique. We have also studied the dependence of composition on the deposition potential. The variation of concentration of each constituent has been found to be in good agreement with CV data. The underpotential deposition mechanism of Cu-Se and In-Se phases has been observed in voltammograms of binary and quaternary systems. A suitable potential range from -0.8 V to -1.0 V has been found for obtaining films with desired and stable stoichiometry.

References

1. A. M. Hermann, R. Wesfall, R. Wind, Sol. Energy Mater. Cells 52 (1998) 355.
2. R.N. Bhattacharya, W. Batchelor, J.E. Grannata, H. Hasoon, H. Wiensner, K. Ramanathan, J. Keane, R. N. Noufi, Sol. Energy Matter. Sol. Cells 55 (1998) 83.
3. J. Zank, M. Mehlin, H.P. Fritz, Thin Solid Film 286 (1996) 259.
4. M. Ganchev, J. Kois, M. Kaelin, S. Bereznev, E. Tzvetkova, O. Volubuzeva, N. Stratieva, A. Tiwari, Thin Solid Films 511-512 (2006) 325.
5. A. Kampmann, V. Sittinger, J. Rechid, R. Reineke-Koch, Thin Solid Films 361-362 (2000) 309.
6. L. Zhang, F. D. Jiang, J. Y. Feng, Sol. Energy Mater. Cells 80 (2003) 483-490.
7. A. M. Fernandez, R.N. Bhattacharya, Thin Solid Films 474 (2005) 10-13.
8. F. Kang, J. Ao, G. Sun, Q. He, Y. Sun, Current Appl. Phys. 10 (2010) 886-888.
9. S. Massaccesi, S. Sanchez, J. Vedel, Electroanal. Chem. 412 (1996) 95.
10. K. K. Mishra, K. Rajeshwar, Electroanal. Chem. 271 (1989) 279.
11. Y. Lai, F. Liu, Z. Zhang, J. Liu, Y. Li, S. Kuang, J. Li, Y. Liu, Electrochim. Acta 54 (2009) 3004-3010.