



Cyclic Voltammetry Investigation of the Mechanism of CuInSe₂ and CuIn(Al)Se₂ Electrodeposition from Aqueous Solution

Y. Ganjkanlou, T. Ebadzadeh*, M. Kazemzad, A. Maghsoudipour, M. Keyanpour-Rad

Department of Ceramic, Materials and Energy Research Center, Karaj, Iran

PAPER INFO

Paper history:

Received 17 February 2015

Accepted in revised form 29 May 2015

Keywords:

Cyclic Voltammetry

Scan Rate

Electrodeposition

CuInAlSe₂

Mechanism Study

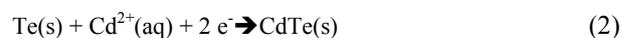
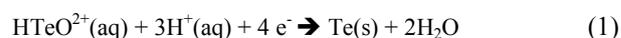
ABSTRACT

Electrodeposition of CuInSe₂ (CIS) and CuInAlSe₂ (CIAS) from aqueous solution is systematically investigated by cyclic voltammetry implemented at different scan rates. It is shown that electrodeposited CIS and CIAS layers are formed on the substrate through electrochemical-chemical interactions of the reduced species on the substrate. The results confirm that the induced electrodeposition is the main mechanism of incorporating Aluminum and Indium in the deposited layer. Effect of electrodeposition potential on composition of the prepared film is also studied which confirms that at potential of -0.7 V, composition close to CIAS solar cells desired stoichiometry is obtained. X-ray Diffraction Analysis (XRD) also indicates that in potential range of -0.7-0.8 V almost the single phase of chalcopyrite is deposited while additional binary selenide phases are formed at more positive potentials and the metallic indium phase is formed at negative potentials.

1. INTRODUCTION

Solar cells based on CuInSe₂ (CIS) absorber layer with chalcopyrite structure possess the highest reported efficiency among the various thin film solar cells and they are one of the most important candidates to compete with Silicon based solar cells [1, 2]. The main drawback of using such cells is the high cost of vacuum techniques conventionally utilized for their preparation [3]. Electrochemical deposition of CIS based layers offers a low cost method for fabricating thin film solar cells [3]. Although the electrodeposition of CIS has been reported since 1983 [4], there is still debate on the mechanisms involved in the process of single step electrodeposition ternary and quaternary semiconductors with chalcopyrite structure [3]. Moreover, some researchers recently tried to incorporate Aluminum in the CIS phase instead of Gallium in order to enhance the band gap. Due to greater band gap of CuAlSe₂ (2.7 eV) in comparison to CuGaSe₂ (1.8 eV), incorporating low amount of Aluminum could tune the band gap of CIS phase toward the desired value of 1.4 eV with effects similar to that of Gallium [5, 6]. Utilizing Al instead of Ga not only reduces the cost but also introduces less distortion in the structure. Fabricating efficient CIAS based solar cell with efficiency more than 16.9% is reported by Marsillac et al. [7]. The CuIn(Al)Se₂

(CIAS) electrodeposition is also recently reported by different research groups but the mechanism involved in CIAS electrodeposition is rarely investigated [8, 9]. Induced electrodeposition is one of the reported mechanisms which describes the incorporation of active elements in electrodeposited binary semiconductors at potentials less negative than their actual reduction potentials [10]. The formation energy of binary semiconductors provides enough energy to reduce active species at less negative voltages than their actual reduction potentials, in the other word noble species are reduced first and then they interact with ions of active species and induce their reduction. This mechanism which is also well known as Under Potential Electrodeposition and also Induced Co-Deposition is initially reported by Kroger in 1973 for electrodeposition of CdTe [11, 12]. Kroger and coworkers observed that the more noble ion (HTeO²⁺ in the case of CdTe) that is reduced at less negative potential is deposited first on the electrode surface (Eq. 1) and induces the reduction of the less noble ion (Cd²⁺) and formation of CdTe (Eq. 2) at less negative potentials than the condition in which the reduction of Cd²⁺ to metallic Cd (Eq. 3) would take place.



*Corresponding Author's Email: t.ebadzadeh@merc.ac.ir (T. Ebadzadeh)

The reason for under-potential reduction of the less noble ion (Cd^{2+}) is the energy released in the compound formation. In the cases of CIS and CIGS, it was also reported that In and Ga could be incorporated in the deposited layer by induced co-deposition while Cu incorporation should be controlled by balancing the diffusion fluxes [3, 13]. Cyclic Voltammetry (CV) is the well known and powerful electrochemical technique which can be utilized to study kinetics and thermodynamics of various electrochemical reactions [14]. In the present work, different scan rates and deposition times are applied for CIAS and CIS electrodeposition from aqueous solution to determine the mechanism of CIAS electrodeposition on the substrate. Moreover, the electrodeposited CIAS layers at different potentials are also investigated by various techniques to find out the proper potential for electrodeposition of CIAS from aqueous solution.

2. EXPERIMENTAL

Stainless steel (SS) foils were applied as substrate for electrodeposition of CIS and CIAS compounds. Prior to electrodeposition, the metallic foils were polished with alumina paste followed by washing with acetone and deionized water several times. The solution employed for electrodeposition was prepared by dissolving sulfate salts of Cu (5 mM), In (20 mM) and Al (20 mM) and also 10 mM of SeO_2 in MilliQ water (18 M Ω). For CIS electrodeposition, the same electrolyte without Al precursor was prepared.

Electrodeposition was carried out by electrochemical work station (IviumStat Instruments) in three electrodes system using a 20 mL beaker as the reaction cell. The stainless steel substrate, a graphite rod and an Ag/AgCl (saturated with KCl) electrode were employed as working, counter and reference electrodes, respectively. Before electrodeposition, CV measurement was performed several times with different scan rates to study the mechanism of CIAS and CIS electrodeposition. Then, the co-deposition was carried out in chronoamperometry configuration in fixed potential for 30 min. The resulting samples were then characterized by Field Emission Scanning Electron Microscopy (FE-SEM) and Energy-Dispersive X-ray Spectroscopy (EDS). FE-SEM and EDS analyses were carried out using a ZEISS electron microscope (EVO50) occupied with EDS (Oxford INCA Energy 200). The X-ray Diffraction (XRD) patterns were recorded by Philips PANalytical PW3040/60 instrument using Cu $K\alpha$ radiation operating at 50 kV and 250 mA in the 2θ range of 15-120 $^\circ$.

3. RESULT AND DISCUSSION

Figure 1a. shows the effect of scan rates on the cyclic voltammograms of the ternary electrolyte which is

consisted of Cu, In and Se. The single cathodic peak could be almost observed at low scan rates (e.g. 0.02 and 0.04 V/S), while with increasing the scan rates the cathodic peak separated into two peaks which shifted toward negative potentials with scan rate amplification. The electrochemical reaction proceeds at higher rate compared to conventional chemical reaction, because diffusion of ions under electrical field and the followed electron transfer in electrochemical reaction could be happened faster than the arbitrary diffusion of two different species involved in chemical reactions. The observed trend in Figure 1a. indicates that at low scan rates, the electrochemical-chemical reaction occurs for electrodeposition of CIS and as active Indium ions reduced in less negative potential (due to induced reduction by selenium). Therefore, its reduction peak could not be observed while measuring the CV, but with increasing the scan rates when there is not enough time for induced reduction of indium ions (the chemical reaction between reduced Selenium and Indium ions could not be completed), reduction potential of indium ions could separately be observed during the CV measurements. The small negative shifts of reduction peaks could be attributed to the higher polarization at higher scan rates (limited diffusion time).

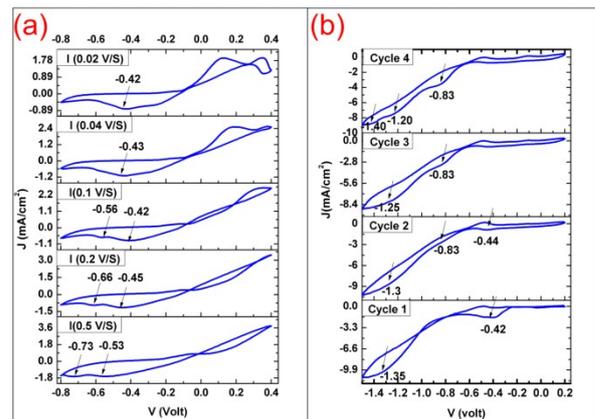


Figure 1. a) Effect of scan rates (0.02, 0.04, 0.1, 0.2 and 0.5 V/S) on the CV curves measured in ternary solution containing Cu (5 mM), In (20 mM) and Se (10 mM). b) Effect of CV measurement cycle on the CV curves obtained from quaternary solution containing Cu (5mM), In (20 mM), Al (20 mM) and Se (10 mM).

Figure 1b. illustrates that during CV measurement in quaternary solution containing Cu, In, Al and Se, shapes of cathodic peaks and their locations are changed with CV measurement cycle. In the first cycle, as the deposited layer formed on stainless steel substrate, induced electrodeposition could not be occurred while in the next cycles (for instance 4th cycle of measurement which is illustrated in Figure 1b.) due to existence of reduced Se, reduction of Indium and Aluminum ions could be induced. Changes in peak shapes with scan rates and CV measurement cycles

clearly state that induced electrodeposition was the main mechanism for CIS and CIAS deposition. In fact, when single unitary cathodic peak observed in CV curves it could be anticipated that induced electrodeposition is the main mechanism of deposition which could be elucidated by cycle and scan rate changes according to the results obtained in current work. The following equations summarize the obtained results. Selenium and Copper are initially reduced (Equations (4) and (5)) at comparatively positive potentials (peaks around the -0.42 V in Figures 1a, b). Then induced reduction of In^{3+} by Se (Equation 6) happens at less negative potentials (peak around -0.43 V at low scan rate [Figure 1a]) instead of reduction of In^{3+} (Equation 7) at relatively negative potential (peaks around the -0.73 V at high scan rate [Figure 1a]). The same reactions could be taken place in the case of Aluminum containing solution (Equation 6) and intensity of the peak related to the reduction of Al (peak around -1.3 V) is diminished (Figure 1b) in 4th cycle of CV measurement.

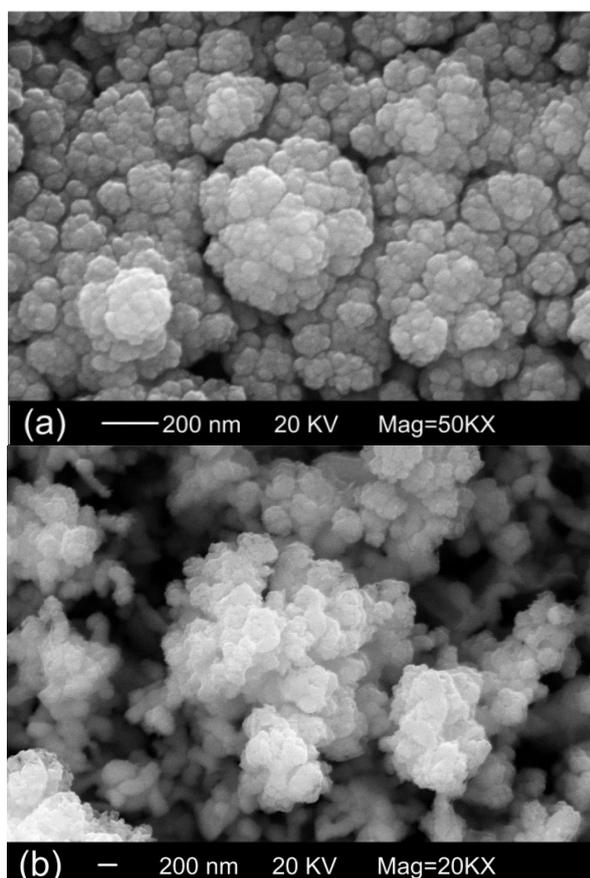
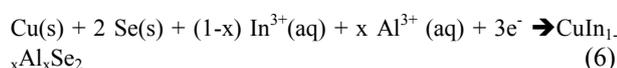


Figure 2. SEM images of electrodeposited layers at potentials of (a) -0.7 V and (b) -1.2 V



Following the CV studies, the CIAS layer was deposited in potentiostatic condition at different potentials. Figure 2. shows the SEM images of electrodeposited CIAS layers at two different potentials. It can be seen in Figure 2. and the EDS results (Table 1) that the morphology of the deposited films and also their compositions were function of electrodeposition potential. Density of cracks in the electrodeposited films increased at more negative potentials and therefore -0.7 V was the suitable potential for electrodeposition. The changes of composition also verify this conclusion as listed in Table 1. It could be seen that at a negative electrodeposition potential (-1.2 V), the amount of Indium in the deposited layer was considerably increased. Formation of the cracks at negative potential can be attributed to H_2 gas formation on working electrode, because electrolyte contains aqueous base and over-potential of H_2 formation on stainless steel and selenide phases was reported to be in this range [8]. The calculated particles size distributions based on SEM images are shown in Figure 3. It could be seen that the particles sizes are increased at the negative potentials. This observation may be due to fact that at the negative potentials, the nucleation is limited and therefore growing of the grain is enhanced at negative potentials. It should be also considered that formation of some of the grains could be related to the presence of metallic Indium.

TABLE 1. Atomic percentages (in parentheses) and weights of different elements in layers deposited at different potentials.

Potential	Cu%	Se%	In%	Al%	Composition
-0.7 V	16.3 (20.8)	44.2 (45.5)	37 (26.2)	2.5 (7.5)	$\text{Cu}_{0.91}\text{In}_{1.15}\text{Al}_{0.33}\text{Se}_2$
-1.2 V	11 (17.5)	10.7 (13.7)	78.3 (68.8)	0 (0)	$\text{Cu}_{2.55}\text{In}_{10}\text{Se}_2$

Figure 4. shows the XRD patterns of the layers deposited from the quaternary solution of Cu, In, Al and Se at different potentials. The peaks related to the stainless steel (Fe) substrate and chalcopyrite CIAS phase could be distinguished in all of the patterns. In some patterns, other additional diffraction lines are presented which could be assigned to the binary selenide phases (mainly CuSe and Cu_2Se) or metallic Indium phase. At potentials of -0.5 and -0.6 V, some binary selenide phases were observed and at negative potentials of -1.2, -1.0 and -0.9 V, the diffraction lines of elemental Indium are noticed. At potentials of -0.7 and -0.8 V, almost single phase of CIAS could be obtained (intensities of diffraction lines relating to other phases are very weak). Formation of elemental Indium phase at potential of -1.2 V was in agreement with the EDS results which indicate high indium percentage in this sample (Table 1).

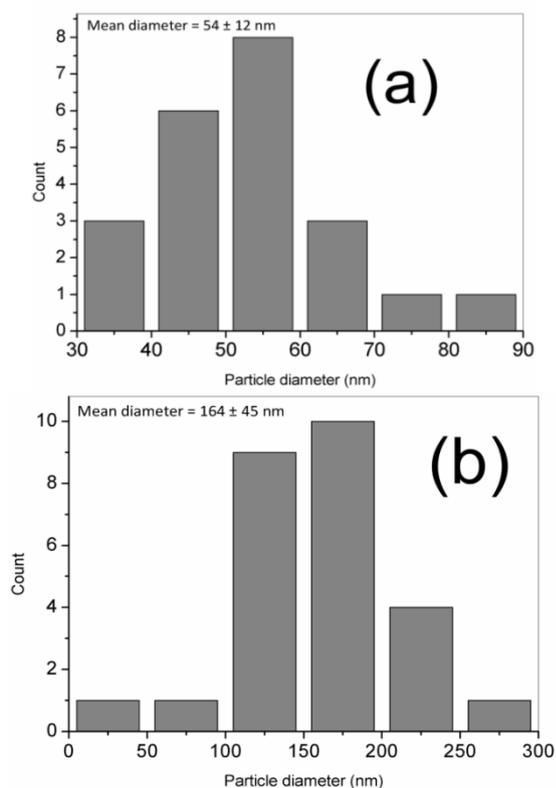


Figure 3. Particles size distribution of the deposited layers at potentials of (a) -0.7 V and (b) -1.2 V

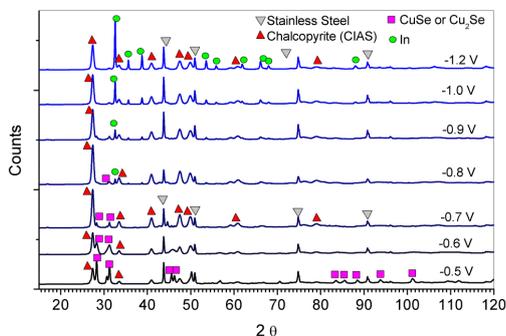


Figure 4. XRD patterns of the layers deposited from quaternary solution of Cu, In, Al and Se at different potentials.

4. CONCLUSION

Mechanism of CIAS layer electrodeposition is studied using different electrochemical techniques. It is found that Electrochemical-Chemical (EC) reaction occurs at low scan rates while the sole electrochemical reaction proceeds at high scan rates in ternary solution containing In, Cu and Se. Similarly, shapes of the peaks in CV curves are function of measurement cycles in the quaternary solution containing Cu, In, Al and Se. The results reveal that Al and In are incorporated in electrodeposited layer through the induced electrodeposition mechanism. In addition, different CIAS thin films were electrodeposited at different potentials and the best

potential in respect to morphology, structure and composition of the layer for CIAS electrodeposition is determined to be -0.7 V.

5. ACKNOWLEDGMENTS

The authors would like to acknowledge the financial support of Materials & Energy Research Center of Iran for this research.

REFERENCES

- Chirilq, A., Reinhard, P., Pianezzi, F., Bloesch, P., Uhl, A.R., Fella, C., Kranz, L., Keller, D., Gretener, C., Hagendorfer, H., Jaeger, D., Erni, R., Nishiwaki, S., Buecheler, S. and Tiwari A.N., "Potassium-induced surface modification of Cu(In,Ga)Se₂ thin films for high-efficiency solar cells", *Nature Materials*, Vol. 12, (2013), 1107-1111.
- Contreras, M.A., Egaas, B., Ramanathan, K., Hiltner, J., Swartzlander, A., Hasoon, F. and Noufi, R., "Progress toward 20% efficiency in Cu(In,Ga)Se₂ polycrystalline thin-film solar cells", *Progress in Photovoltaics: Research and Applications*, Vol. 7, (1999), 311-316.
- Saji, V.S., Choi, I.-H. and Lee, C.-W., "Progress in electrodeposited absorber layer for CuIn_(1-x)Ga_xSe₂ (CIGS) solar cells", *Solar Energy*, Vol. 85, (2011), 2666-2678.
- Bhattacharya, R.N., "Solution growth and electrodeposited CuInSe₂ thin films", *Journal of The Electrochemical Society*, Vol. 130, (1983), 2040-2042.
- Zhou, L., Wu, S. and Yu, J., "Study on the thin films of CuIn_{1-x}Al_xSe₂ prepared by selenization process", *Surface and Coatings Technology*, Vol. 228, (2013), S214-S218.
- Peng, D.-C., Chen, J.-W. and Wu, C.-J., "Formation of CuInAlSe₂ film with double graded bandgap using Mo(Al) back contact", *Solar Energy Materials and Solar Cells*, Vol. 95, (2011), 257-260.
- Marsillac, S., Paulson, P.D., Haimbodi, M.W., Birkmire, R.W. and Shafarman, W.N., "High-efficiency solar cells based on CuInAlSe₂ thin films", *Applied Physics Letters*, Vol. 81, (2002), 1350-1352.
- Deepa, K.G., Shruthi, N.L., Sunil, M.A. and Nagaraju, J., "Cu(In,Al)Se₂ thin films by one-step electrodeposition for photovoltaics", *Thin Solid Films*, Vol. 551, (2014), 1-7.
- Prasher, D., Sharma, R., Sharma, A.K. and Rajaram, P., "CuIn_{1-x}Al_xSe₂ Thin Films Grown By Electrodeposition", *AIP Conference Proceedings*, Vol. 1349, (2011), 597-598.
- Kemell, M., Ritala, M. and Leskela, M., "Effects of post-deposition treatments on the photoactivity of CuInSe₂ thin films deposited by the induced co-deposition mechanism", *Journal of Materials Chemistry*, Vol. 11, (2001), 668-672.
- Kröger, F.A., "Cathodic Deposition and Characterization of Metallic or Semiconducting Binary Alloys or Compounds", *Journal of The Electrochemical Society*, Vol. 125, (1978), 2028-2034.
- Panicker, M.P.R., Knaster, M. and Kroger, F.A., "Cathodic Deposition of CdTe from Aqueous Electrolytes", *Journal of The Electrochemical Society*, Vol. 125, (1978), 566-572.
- Lincot, D., "Electrodeposition of semiconductors", *Thin Solid Films*, Vol. 487, (2005), 40-48.
- Huang, K.-C., Liu, C.-L., Hung, P.-K. and Hounz, M.-P., "Cyclic Voltammetric Study and Nucleation of Electrodeposited Cu(In,Al)Se₂ Thin Films with Sodium Dodecyl Sulfate Additive", *Journal of The Electrochemical Society*, Vol. 160, (2013), 125-131.