Journal of New Technology and Materials (JNTM)
J. New Technol. Mater.
Vol. 08, N°01 (2018)139-143

OEB Univ. Publish. Co.

Preparation and characterization of CIS thin films obtained by electrodeposition onto ITO and Mo substrates

Bachir Bordji [a] and Souheil Mouetsi [b]

[a] *Laboratory of Materials and Structure of Electromechanical Systems and their Reliability, Larbi Ben MHidi University, Oum El Bouaghi 04000, Algeria.*
[b] *Laboratory of Active Components and Materials, Larbi Ben MHidi University, Oum El Bouaghi 04000, Algeria*

Email: bordji.bachir@univ-oeb.dz

Received date: June 01, 2018; revised date: June 22, 2018; accepted date: June 24, 2018

Abstract

In this study, thin films of copper and indium selenide ($CuInSe_2$) were electrochemically deposited on ITO glass substrates and Mo films. A three electrodes system is used for in-situ monitoring of the deposition process in which the working electrode voltage is kept at 0.7 V. Selenium oxide SeO_2, copper chloride $CuCl_2$ and indium $InCl_3$ were used as precursors. The thin films produced on two different substrates for different deposition time, were characterized by different analysis techniques. The UV-Visible characterization shows a total absorption of the incident light between 190 and 1100 nm for a film thickness greater than 2µm. On the other hand, optical microscopy and MEB illustrate good homogeneity in the texture of all surfaces of the films deposited. Spectral Raman and DRX analyzes confirm the formation of a dominant phase of $CuInSe_2$ chalcopyrite structure characterized by a dominant peak at 1.77 cm^{-1}.

Keywords: *Electrodeposition, Copper and indium selenide ($CuInSe_2$), Solar cell absorber.*

1. Introduction

Solar energy represents an abundant and inexhaustible source of energy that could perfectly meet our energy needs and represents a real alternative to fossil fuels. The photovoltaic industry is undergoing accelerated development aimed at increasing the efficiency of energy conversions and reducing the cost of production in order to make this energy increasingly competitive. Mono or polycrystalline silicon is considered as the base material for the photovoltaic solar cells. For this purpose, direct gap materials are generally recommended, whereas a new generation of cells, based on thin layer materials, having a high optical absorption coefficient with respect to crystalline silicon have been developed [7; 8].

Copper and indium selenides are chalcopyrite ternary compounds I-III-VI_2 considered among the promising conductive seedlings used in the fabrication of thin films for photovoltaic applications [6]. These absorbent layers possess interesting optical properties, namely an energy gap of approximately 1.04 eV with an optical absorption coefficient of greater than 10^5 cm^{-1} allowing high convection efficiencies [1].

The copper and indium selenides of 1 µm thickness have an absorption coefficient of about 90% of the incident light [5] and exhibit long-term stability with respect to photo degradation with a better energy conversion which reaches 19.5% at laboratory scale (NREL) [2]. The development of CIS absorptive thin films is possible from semiconductors homos-junctions or heterojunctions [3,4].

The effectiveness of CIS-based solar cells is influenced by several factors such as: the elaboration technique, experimental parameters, preferred orientation (or phase) of the deposited CIS layers as well as the properties of the deposited substrates [4].

Among the techniques used for CIS-layers elaboration, there are, evaporation, sputtering, electroplating and chemical bath deposition (CBD) [8]. The choice of such deposition technique takes into account several advantages like the low cost, high production range, work at atmospheric pressure and ambient temperature. Electrodeposition is the most suitable technique for depositing $CuInSe_2$ thin film absorbers at low cost [5] and large-scale with good electrical quality of high absorption [2].

The first CIS-based thin films were developed in 1983 by Bhachattarya [3] from an aqueous solution containing copper, indium and selenium oxide chlorides. Since then, several research studies have been carried out in order to improve the properties of

CIS thin films [8]. Currently, several research studies insist on obtaining CIS by the electroplating technique using a three-electrode system [9].
In the scope of this study, we are interested to the development and characterization of CuInSe2 thin films by electrodeposition on conductive substrates. Two different substrate types were used: ITO glass substrate and Mo foil substrate. A three-electrode system (Potentiostat Voltalab PGP100) is used for deposition process control for variable deposition time durations. Indeed, the morphological, compositional and structural properties of deposited thin layers were characterized by three different analyzes: X-ray diffraction, UV-Visible spectroscopy and RAMAN spectroscopy. Optical microscopy and spectral analysis show the homogeneity and orientation towards the preferred phase <112> of deposited thin films.

2. Experimental study

The $CuInSe_2$ thin films were deposited electrochemically using a three electrode system. Two types of substrates are used, covered glass ITO and Mo sheet of 2.5 cm x 2.5 cm. The conductive substrate Mo or ITO (99.9% -Aldrich) serves as the working electrode and the platinum grid (2 cm x 2 cm) is used as an auxiliary electrode (anode) and the saturated calomel electrode (SCE) is used as an electrode of reference (Fig. 1). The voltage of the working electrode is kept constant (at 0.7 V) during the electro-deposition process by means of a galvanostat (Voltalab PGP 100) which monitors the current-voltage characteristic.

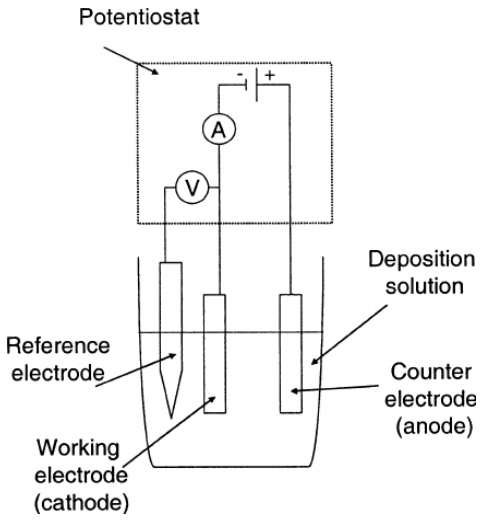

Figure1. Schematic view of the three-electrode setup used in electrodeposition. [7]

An acidic aqueous solution is used whose pH is carefully adjusted to about 2 by adding a few drops of concentrated chloric acid (HCl). In a volume of 80 ml of doubly distilled water, copper $CuCl_2$ and indium $InCl_3$ chlorides and selenium oxide SeO_2 were dissolved in adequate amounts and the following concentrations of each compound ($CuCl_2$: 10 mM, $InCl_3$: 40mM and SeO_2: 20mM) [4]. The solution is stirred for a few seconds before use.

Tableau 1. Values of the parameters used to deposit the CIS films

Reference	Substrate	PH	Tension (mV)	Average Courant (mA)
ITO-30	ITO	2	700	31.4
ITO-45	ITO	2	700	29.5
ITO-60	ITO	2	700	29.5
Mo-20	Mo	2	700	33.6
Mo-30	Mo	2	700	34.4
Mo-45	Mo	2	700	30

Before each experiment, the substrates are well cleaned and rinsed with double distilled water, and then deposited since 30, 45 to 60 minutes at room temperature in order to follow the evolution of the layers deposited on two types of substrates. The thin layers obtained have different thicknesses. The morphology of the films obtained is observed by optical microscopy (A100 model of APER), SEM microscopy as well as X-ray diffraction (PHILIPS X'pert with a Cu-tube) characterizes the structural and crystalline properties of deposited thin layers. The Raman spectra were obtained by a Raman spectrometer (Renishaw inVia – Laser excitation wavelength 633nm).
Transmittance analysis is carried out by a JASCO 630 spectrophotometer which allows the study of the optical properties of deposit thin films.

3. Results and discussion

3.1. Optical microscopy

The characterization of thin layers of $CuInSe_2$ electrodeposited by optical microscopy (Euro Max ME2660 microscope x1000 magnification) reveals on a profile of irregular and rough surfaces. As time went on, the layers formed became uniform and denser. (fig 2)

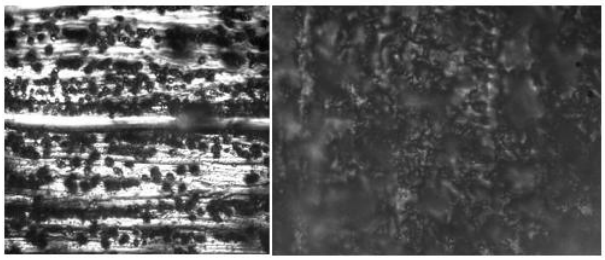

Figure 2 . Image shows formation of *CuInSe₂* thin films grown by electrodeposition in aqueous solution. in different regions of the substrate.

The SEM images taken on the same CIS samples deposited on an ITO-covered glass substrate (FIG. 3) reveal the formation of clusters of non-uniform grain of variable dimensions, this texturing of the surface is favourable for the absorption of the incident light. In fact, the reflection on a textured surface is considerably reduced compared with a smooth surface.

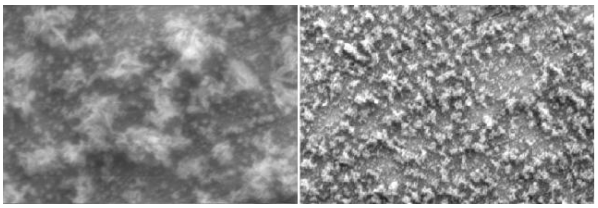

Figure 3 . MEB Images shows Mechanism of *formation* of $CuInSe_2$ thin films grown by electrodeposition in aqueous solution [14].

3.2. Raman Spectroscopy

Raman spectroscopic analysis of the surfaces is carried out by a multi-channel spectroscope (Dilor XY800). The Raman spectra shown in figure 4 show that for a large deposition time (40 min), there is the presence of the *CuInSe₂* chalcopyrite structure having the direction (112) characterized by a clear peak at 177 Cm^{-1}.

3.3. DRX Spectroscopy

On the DRX diffraction spectra of CuInSe2 films on ITO coated glass substrates, a strong peak of the phase (112) at 2θ=25 ° (Fig.5) and two less intense peaks corresponding to the (204)/(220) at 44.3° and (116) / (312) at 52.5°. These peaks are the most intense given by the file JCPDS No. 40-1487 [10] for the chalcopyrite structure of the *CuInSe₂* phase. These results confirm the formation of a dominant phase of CuInSe2 and assert the crystallinity of the CIS electrodeposited films.

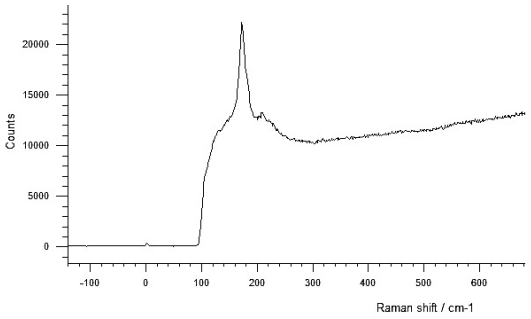

Figure 4. Raman spectra of $CuInSe_2$ thin films grown by electrodeposition in aqueous solution.

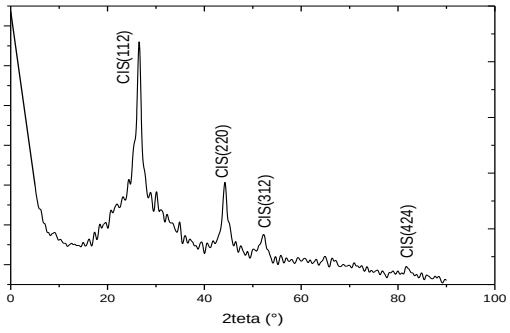

Figure 5. XRD spectra of CuInSe2 thin films grown by electrodeposition in aqueous solution.

3.4. Optical Spectroscopy

In order to obtain structural information on the absorbent aspect of our CIS layers, to determine their gap and to estimate the deposited thicknesses, ultraviolet, visible and near infrared optical absorption spectra were recorded on three deposited samples on ITO glass.

The optical band gap value obtained from transmittance measurements can be concluded that the $CuInSe_2$ thin films shown an Eg value of 1.01 eV, which in good agreement with reported values that of $CuInSe_2$ published in the literature [11, 12, 14]. The optical band gap Eg was determined from the linear extrapolation of $(\alpha.h\nu)^2$ vs. $(h\nu)$ using the following relationship[13].

$$\alpha = \frac{C}{h\nu}\left(h\nu - E_g\right)^{\frac{1}{2}}$$

Where α is the absorption coefficient, h is Plank constant (h= 6.62 x 10-34 J s), *ν* is the frequency and C is constant.

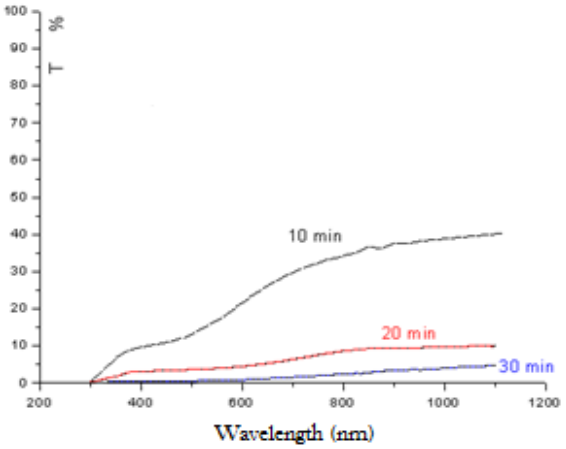

Figure 6. Transmittance (T) spectra of CIS films measured in the range 200-1100 nm for different deposition times (10 min, 20 min, 30 min)

4. Conclusion

This paper presents the development and characterization of CuInSe2 thin films by electrodeposition on conductive substrates using two different substrate types (ITO glass substrate and Mo foil).

Homogeneous films of $CuInSe_2$ were successfully deposited on ITO glass and molybdenum foil by an electrochemical way.

A three-electrode system (Potentiostat Voltalab PGP100) is used for deposition process control for variable deposition time durations.

The morphological, compositional and structural properties of deposited thin layers were characterized by three different analyzes: X-ray diffraction, UV-Visible spectroscopy and RAMAN spectroscopy.

In the light of what has been presented in this work, the following conclusions can be drawn:

- The $CuInSe_2$ thin films having good characteristics were deposited on ITO glass substrates and Mo foil by electrochemical means.
- The electrodeposition parameters are chosen to better control the growth and composition of the films deposited.
- The results of the DRX analysis show that the crystalline properties of the thin films have been improved over time (duration of 40 minutes).
- Raman analysis asserts the stoichiometry of the $CuInSe_2$ electrodeposited phase with a chalcopyrite structure is mainly oriented <112>, which is in agreement with the results published in the literature [7].
- The CIS layers obtained are uniform and sufficient to be good absorbers.
- The optical gap obtained is close to that published in the literature.

In perspective, we plan to improve the quality of our layers with an annealing under an inert atmosphere.

Acknowledgments

This work is supported by the Algerian Ministry of High Education and Scientific Research through the PNR (project code 8/u04/4673 (2011), *www.mesrs.dz*, and *www.univ-oeb.dz*. We thank the PNR project members.

References

[1] M. A. Contreras, B. Egaas, K. Ramanathan, G. Hiltner, A. A. Swartzlander, F. Hasoon, R. Noufi, Prog. Photovoltaics, 7, (1999)311.

[2] L. Kaupmees, M. Altosaar, and O. Volubujeva, "Study of composition reproducibility of electrochemically co-deposited CuInSe2 films onto ITO", Thin Solid Films, 515, (2007)5891.

[3] R. N. Bhattacharya, J. Electrochem. Soc., 130, (1983)2040

[4] A. Bouraiou, M. S. Aida, E. Tomasella, J. Mater. Sci. Mater. Electron, 44, (2009)1241

[5] M. E. Calixto, P. J. Sebastian, R. N. Bhattacharya, R. Noufi, Sol Energy Mater Sol Cells, 59, (1999)75

[6] S. Agilan, D. Mangalaraj, S. A. .K. Narayandass, G. Mohen Rao, S. Velumani, "Structure and temperature dependence of conduction mechanisms in hot wall deposited CuInSe2 thin films and effect of back contact layer in CuInSe2 based solar cells.",Vacuum, 84(10), (2010)1220-1225

[7] Marianna Kemell, Mikko Ritala, and Markku Leskela, Critical Reviews in Solid State and Materials Sciences, 30, (2005)1–31

[8] Gaëtan Masson, Marie Latour, Manoël Rekinger, Ioannis-Thomas Theologitis, and Myrto Papoutsi. Global Market Outlook for photovoltaics. Technical report, EPIA, 2013.

[9] I. M. Dharmadasa, R. P. Burton, M. Simmonds, Sol Energy Mater Sol Cells, 90, (2006)2191

[10] I. V. Dubrovin, L. D. Budennaya, I. B. Mizetskaya, E. V. Sharkina, Inorg. Mater., 19, (1983)1603-8.

[11] Antonio Luque, Steven Hegedus, Hanbook of Photovoltaic Science & Engineering Wiley, 2003.

[12] F. Kang, J.P. Ao, G.Z. Sun, Q. He, Y. Sun, Materials Chemistry and Physics, 115(2-3), (2009)516

[13] A. Han, Y. Zhang, W. Song, B. Li, W. Liu, and Y. Sun. Structure, morphology and properties of thinned Cu(In,Ga)Se2 films and solar cells. Semicond. Sci. Technol., 27, (2012)35022

[14] A. Mahdjoub, L. Remache, H. Moualkia, B. Bordji, A. Hafid Chalcogenide Letters, 12(2), (2015)59-66

[15] J. Tauc, Amorphous and Liquid Semiconductors, Plenum, New York, 1976