Cd-FREE HETEROSTRUCTURES BASED ON CIS AND CIGS THIN FILMS FOR PHOTOVOLTAIC APPLICATIONS

M. Nya[1], A. Ihlal[1*], K. Bouabid[1], and X. Portier[2]

[1] *Laboratoire Matériaux et Energies Renouvelables, Département de physique, Faculté des Sciences B.P 8106 hay dakhla, , Agadir, Maroc.*

[2] *Centre de recherche sur les Ions, les Matériaux et la Photonoque (CIMAP), Ensicaen, B[d] Maréchal Juin, 14050 Caen, France.*

[*] *ihlal_ahmed@yahoo.fr*

Abstract: Copper Indium diselenide and disulphide (CIS) and their alloys with Ga based thin film solar cells have achieved efficiencies approaching 20%. The best results were obtained with chemical bath deposition CdS buffer layers. However, cadmium is harmful for health and environmentally unfriendly. Then, the replacement of toxic CdS buffer layer is a challenge in photovoltaic research development. A variety of alternative Cd-free buffer layers were studied. The most efficient were Zn- and In –based compounds. In this paper, we present some results concerned with high absorbing layers and high transmitting buffer layers prepared by cheap and simple methods. Good quality CIS and CIGS absorber layers prepared by one step electrodeposition. The films were polycristalline and exhibited an optical band gap varying between 1.01 to 1.26 eV by increasing the Ga content in the films. The absorption coefficient is higher than 10^5 cm^{-1}. In_2S_3 buffer layers were obtained by flash evaporation. The films exhibited high transmission coefficient, 80-90% and a gap varying between 2.5 and 2.65 eV depending on the thickness and the heat treatments. Finally, In_2S_3/(CIS,CIGS)/Mo/Glass heterostructures has been successfully obtained and has shown a rectifying effect and could be used to low energy production.

I. Introduction

Copper Indium diselenide and disulphide (CIS) and their alloys with Ga based thin film solar cells have achieved efficiencies approaching 20% [1,2].CIS and CIGS thin films have been prepared using a variety of processes including coevaporation of the elements in different ways, two or three stage process consisting in sequentially sputtered Cu and In thin layers and a subsequent chalcogenisation by selenisation and electrodeposition. The best results were obtained with a high vacuum method (Coevaporation of the elements) for the absorber CIS and CIGS layers and a chemical bath deposition of CdS buffer layers. However, cadmium is harmful for health and environmentally unfriendly. Then, the replacement of toxic CdS buffer layer is a challenge in photovoltaic research development. A variety of alternative Cd-free buffer layers were studied. The most efficient were Zn- and In –based compounds [3-10].

In this work we present some results concerned with CIS and CIGS absorber layers obtained by a non vacuum method (electrodeposition) and the preparation of In_2S_3 buffer layer obtained by flash evaporation. Finally, some results concerned with the preparation of Mo/(CIS,CIGS)/In_2S_3 heterostructures are presented.

II. Experimental

$CuInSe_2$ (CISe) were obtained by one step electrodeposition of Cu, In and Se from an electrolyte bath consisting in $CuSO_4$ (2.5 – 3.5 mM), $In_2(SO_4)3$ (2 - 3.5 mM) and SeO_2 (5 mM). For CuIn(Ga)Se_2 (CIGSe) thin film deposition, $Ga_2(SO_4)3$ (0-2.5 mM) was used for Ga grading. Citric acid ($C_6H_8O_7$, H_2O), with a concentration between 0.1 and 0.3 M, was used as the complexing agent. ITO and Mo substrates were thoroughly degreased with isopropanol, and cleaned ultrasonically in distilled water and finally dried under nitrogen. The deposition was carried out at room temperature using three electrodes potensiostat system with a satured calomel electrode (SCE) as the reference electrode and platinum as the counter electrode. The polarization curves were investigated at a sweep rate of 10 mV/s. All the films were grown at potentials ranging from – 0.4 to -0.6 V (vs. SCE). The complete procedure was described in our previous work [11-13]. In_2S_3 thin films were obtained by flash evaporation of 99.99% In2S3 powder [14,15]. The samples obtained were heat treated and characterized by X ray diffraction (XRD) using a Philips PW 1840 diffractometer with CuKα source (λ = 15418 Å), scanning electron microscopy (SEM) with the help of a JEOL 5500 SEM, energy dispersive X-ray analysis (EDX). The optical properties were carried out with a spectrophotometer Cary 500 (Varian) and Shimadzu UV-3101 UV-visible-IR spectrophotometer operating in the wavelength range 320 to 3200 nm. Finally, J-V electrical measurements were performed on various In_2S_3/(CIS, CIGS)/Mo heterostructures

III.Results and discussion

Figure 1 shows a typical SEM micrograph of CIS and

CIGS thin film electrodeposited onto ITO substrate, after annealing under argon for one hour at 400°C. This figure suggests a good morphological aspect of the CIS film. It shows a good and uniform coverage of the surface of the substrate. The film consists of grains with a size of about 1 µm consisting on the well known multinuclear cauliflower-like grains. In fact, the grains consist on clusters of small particles. On the other hand, no pinholes are observed.

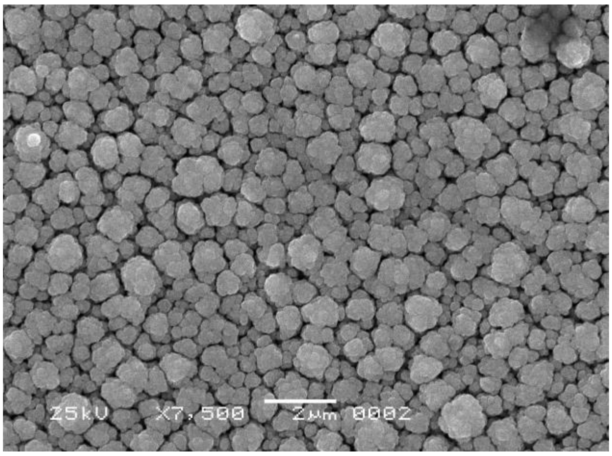

Figure 1: SEM micrograph of CIS thin film after annealing at 400°C under argon for 1 hour.

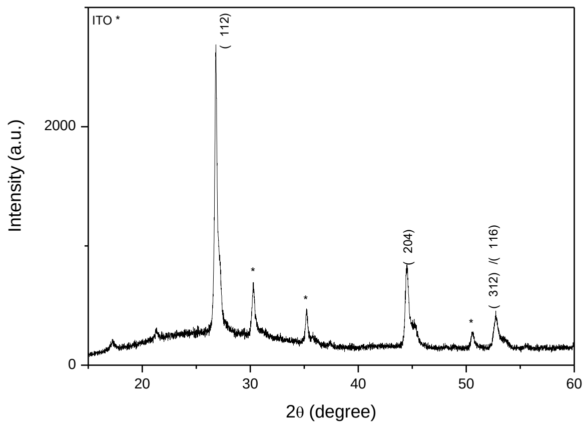

Figure 2: XRD spectrum of CISe thin film annealed under Ar at 400°C for 1 hour.

The as deposited films are almost amorphous. Annealing in Ar has lead to the formation of the well known chalcopyrite structure of $CuInSe_2$ with the preferential orientation in the (112) plane as illustrated in fig. 2. The sharpness of the peak at 2teta = 27.6 ° suggests a good crystalline quality of the film. The crystallite size as determined using Sherrer's formula from the half width of the (112) peak is about 40 nm [17].

The results concerning the preparation of In_2S_3 thin films were already published [14,15]. The optical transmission of the films was very high, 80 to 90 %, for wavelengths higher than 500 nm and their optical band gap scaled between 2.5 and 2.65 eV depending on the film thickness and annealing temperature. These values correspond to the optimum range for solar energy conversion.

In order to test the aptitude of our materials for photovoltaic conversion, different heterostructures were prepared. The multilayer structure used in this work is sketched in figure 3.

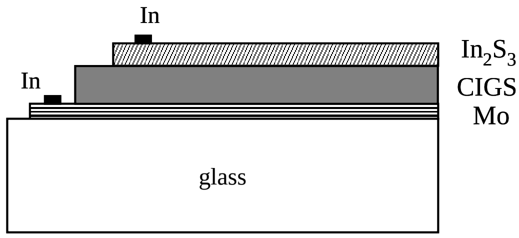

Figure 3: Schematic of the In2S3/(CIS, CIGS)/Mo heterostructures.

Typical dark I-V characteristic is shown in figure 4. Only structures with glass/Mo substrates exhibit a rectifying effect.

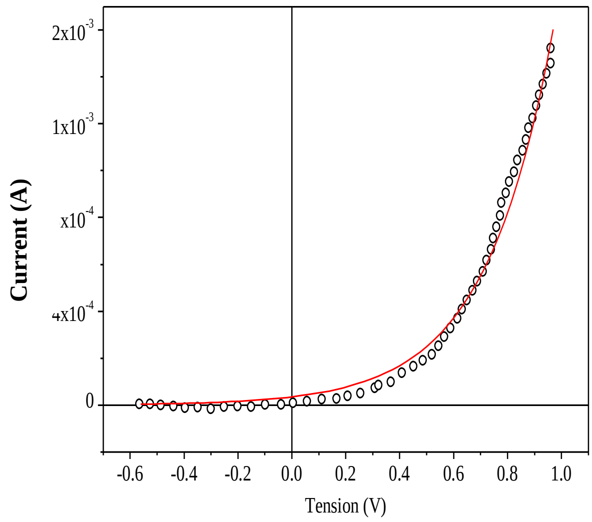

Figure 4: Dark I-Vcharacteristic of CIGS/ In_2S_3 /Mo heterostructure.

Using the well known I = f(V) law:

$$I = I_S\left[\exp\left(\frac{V - IR_S}{nV_{th}}\right) - 1\right]$$

Where I_S is the saturation current, V_{th} is the thermal voltage ($V_{th} = \frac{K_B T}{q}$) and n is the ideality factor.

The different parameters deduced from the dark I-V characteristic, are reported in table1:

Table I: Parameters deduced from the dark I-V

characteristic.

Structure	*Is (A)*	*n*	*Vc (V)*
CIS/ In_2S_3 /Mo	1.7 10^{-7}	2	0.2

The ideality factor deduced approaches the ideal value ranging from 1 to 1.6. This suggests a good quality contact between the absorber and the buffer layers. However, some problems of stability and reproducibility of the structures were encountered. To elucidate the origin of such problems, complementary studies are being done. Especially, the study by HREM and XPS of the interface CIS- In_2S_3 are necessary.

IV. Conclusion

Good quality one step electrodeposited CIS and CIGS thin films were obtained. The well known chalcopyrite structure is observed upon annealing at 400°C. The films exhibit a high absorption coefficient suitable for PV conversion. The band gap value was increased by Ga grading. β- In_2S_3 thin films were obtained by flash evaporation and subsequent annealing in vacuum at 400°C. These thin films were used successfully as a buffer layer onto CIS and CIGS absorber thin films. (CIS,CIGS)/ In_2S_3/Mo have shown a rectifying effect. Therefore, such structures have a potential in solar energy conversion and should be used instead of CdS thin films.

Acknowledgments

This work was partially supported by the CNRST/CNRS cooperation program (SPM05/09, SPM05/10, SPM05/11).

References

[1] M. A. Contreras, B. Egaas, K..Ramanathan, G. Hiltner, A. Swartzlander, F. Hasoon, and R. Noufi, Prog. Photovoltaics, 7 (1999) 311.
[2] K..Ramanathan, M. A. Contreras, C. L. Perkins, S. Asher, F. S. Hasoon, J. Keane, D. Young, M. Romero, W. Metzger, R. Noufi, J. Ward and A. Duda, Prog. Photovolt.: Res. Appl. 11(2003) 225.
[3] M. A. Contreras, T. Nakada, M. Hongo, A. O. Pudov , and J. R. Sites, 3rd World. Conf. on Photovolt. Energy Conv., 2LNCO8, (2003).
[4] K. Kushiya, M. Tachiyuki, T. Kase, N. Nagoya, T. Miura, D. Okumura, M. Satoh, I. Sugiyama, and O. Yamase, Proc. 26th IEEE Photovolt. Spec. Conf. (IEEE, New York), (1997), 327.
[5] K. Kushiya, and O. Yamase, Jpn. J. Apll. Phys. 39 (2000), 2577.
[6] W. Eisele, A. Ennaoui, P. Shubert-Bischoff, M. Giersig, C. Pettenkofer, J. Kauser, M. Lux-Steiner, S. Zweigart and F. Karg, Solar Energy Mat. And Solar. Cells 17 (2003), 17.
[7] A. Ennaoui, W. Eisele, M. Lux-Steiner, T. P. Niesen, and F. Karg, Thin Solid Films, 431-432 (2003), 335.
[8] C. H. Huang, S. S. Li, W. N. Shafarman, C. H. Chang, E. S. Lambers, L. Rieth, J. W. Johnson, S. Kim, B. J. Stanbery, T. J. Anderson and P. H. Holloway, Solar Energy Mat. And Solar Cells, 69 (2001), 131.
[9] S. Spiering, D. Hariskos, M. Powalla and D. Lincot, Thin Solid Films, 431-432 (2003) 359.
[10] M. Konagai, Y. Ohtake and T. Okamoto, Mat. Res. Symp. Proc. 426 (1996) 153.
[11] K. Bouabid, A. Ihlal, A. Manar , A. Outzourhit, and E.L. Ameziane . Thin Solid Films 488, (2005), 62-67.
[12] K.Bouabid, A. Ihlal, A. Manar,A. Sdaq, A. Outzourhit and E. L .Ameziane, Journal Physique IV, 123 (2005) 47.
[13] K. Bouabid, A. Ihlal, A. Manar, A. Outzourhit and E. L .Ameziane, Journal de Physique IV, 123 (2005) 53.
[14] K. Bouabid , A. Ihlal, A. Outzourhit, E. L. Ameziane, . Active and Passive Electr. Compo. 27 (2004), 207.
[15] K. Bouabid , A. Ihlal, Y. Amira, A. Sdaq, A. Outzourhit, and G. Nouet, European Physical Journal : Applied Physics, 40, (2007), 149.
[16] L. L. Kamerski, M. Hallerdt, P. J. Irland, R. A. Hickelsen and W. S. Chen, J. Vac. Sci. Technol. A1 (1983) 395.
[17] A. Ihlal, K. Bouabid, D. Soubane, M. Nya, O. Ait-Taleb-Ali, Y. Amira, A. Outzourhit and G. Nouet, Thin Solid Films, 515 (2007), 5852-5856.