



European Materials Research Society Conference
Symp. Advanced Inorganic Materials and Concepts for Photovoltaics

Electrodeposition of In_2S_3 buffer layer for $\text{Cu}(\text{In,Ga})\text{Se}_2$ solar cells

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Abstract

The electrochemical deposition of In_2S_3 thin films was carried out from an aqueous solution of InCl_3 and $\text{Na}_2\text{S}_2\text{O}_3$. The effect of the potential of deposition was studied on the cell parameters of CIGSe based solar cells. The obtained films depending on the deposition potential and thickness exhibited complete substrate coverage or nanocolumnar layers. XPS measurements detected the presence of indium sulphide and hydroxide depending on the deposition parameters. Maximum photoelectric conversion efficiency of 10.2% was obtained, limited mainly by a low fill factor (56%). Further process optimization is expected to lead to efficiencies comparable to CdS buffer layers.

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Selection and/or peer-review under responsibility of Organizers of European Materials Research Society (EMRS) Conference: Symposium on Advanced Inorganic Materials and Concepts for Photovoltaics.

Keywords : Indium sulfide; buffer layer; CIGSe solar cells; electrodeposition

1. Introduction

Solar cells based on $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGSe) chalcopyrite absorbers have reached 20.3% conversion efficiencies at the laboratory scale, using high vacuum processes [1]. However, due to the toxicity of cadmium and the possible gain in current associated with the use of a wider bandgap material, many works are carried out with the aim of developing alternative buffer layers [2]. The In_2S_3 -based material is among the most relevant alternatives [2]. Several

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techniques, such as sputtering, atomic layer deposition (ALD), ion layer gas reaction (ILGAR), evaporation and chemical bath deposition (CBD) [2] have been used to synthesize In_2S_3 thin films on CIGSe. However it seems that soft chemical based deposition techniques such as ALCVD or CBD which do not damage the surface of the absorbers and can provide highly conformal coating are more suitable to get high efficiency Cd-free CIGS solar cells [3].

Electrodeposition is a soft technique widely used in industrial processes for large area coating, both in batch and inline systems [4]. This method, more recently applied to semi-conductor synthesis, may allow to control the width of the bandgap and the doping level by monitoring solution composition, applied potential, pH and temperature [5,6]. Moreover it provides conformal growth with controlled thickness layers. All these advantages yield the method attractive for the synthesis of the absorber, the buffer layers as well as the transparent conductive oxide layer in CIGSe-based solar cells.

Even if important works have been done on the electrodeposition of the CIGSe-based absorbers, very few attempts have been carried out so far to electrodeposit In_2S_3 buffer layers [7-10]. The best results reported up to now are obtained on CuInS_2 absorbers leading to maximum conversion efficiencies of 7.1 %. [10]. In this paper we investigate the optimisation of In_2S_3 buffer layers prepared by electrodeposition in aqueous solution.

2. Experimental

The electrodeposition of In-S based buffer layers was carried out using an aqueous solution containing indium chloride (5 mM), sodium thiosulfate (20 mM) as sulfur source and potassium chloride as supporting electrolyte (0.1M). A standard three-electrode setup was used. The reference electrode was a saturated mercurous sulfate electrode (MSE, $E^\circ = 0.64\text{V/NHE}$) and platinum was used as the counter electrode. The deposition was carried out at 60°C .

A preliminary investigation was carried out on molybdenum-coated glass substrates to determine the optimal deposition conditions. In-S layers were then deposited on Cu(In,Ga)Se_2 absorbers, co-evaporated on Mo-coated glass substrate provided by Würth Solar. The solar cell structure was completed with classical $i\text{-ZnO/ZnO:Al}$ top-window layer deposited by radio-frequency (RF) sputtering.

The surface morphology of the samples was investigated by scanning electron microscopy (SEM) using a Leo Supra 35 field emission gun (FEG). XPS surface chemical analysis are achieved with a Thermo Electron K-Alpha spectrometer using a monochromatic $\text{Al-K}\alpha$ X-Ray source (1486.6 eV). The electrical properties of cells were characterized by current voltage measurements at 25°C under illumination (AM1.5 global spectrum). Absolute spectral response measurements were made with a monochromator (Spectral Products CM110) under chopped illumination and a lock-in technique. Thermal annealing at 200°C for 10 min in air and light soaking for 60 minutes under AM 1.5 solar-type spectrum were typical post treatments.

3. Results and discussion

3.1. Voltammetric investigation on Mo and CIGSe substrate

In order to define the optimal deposition potential range of the In-S thin films and the role of S, a voltammetric investigation was carried out both on Mo and CIGSe substrates. Figure 1 shows cyclic voltammograms recorded at 60°C on Mo and CIGSe layers.

As is observed on this figure, on both substrates, the deposition starts at potentials lower than -0.8V/MSE . the deposition process is more significantly inhibited on CIGSe absorber. On CIGSe a plateau is observed corresponding to a low current density between -0.8 and -1.2V , which might indicate that a different nucleation and/or deposition process occurs on this substrate compared to Mo.

When sodium thiosulfate is added to the In(III) solution, a whitish colloid solution is formed. This is due to the formation of elemental sulfur which is favoured at low pH values [11] where the $\text{Na}_2\text{S}_2\text{O}_3$ is decomposed according to the disproportionation reaction:



For solutions with the mixture of sodium thiosulfate and In(III), no oxidation peak of the In-S layer on the reverse scan is observed, whatever the substrate used, indicating the formation of a passive layer during the oxidation process.

Based on these observations, when InCl_3 and $\text{Na}_2\text{S}_2\text{O}_3$ are mixed in acidic solutions and for potential lower than -0.9 V/MSE, In-S compound can be formed, thanks to In_2S_3 energy formation ($\Delta G^\circ = -413 \text{ kJ mol}^{-1}$), based on the overall reaction:

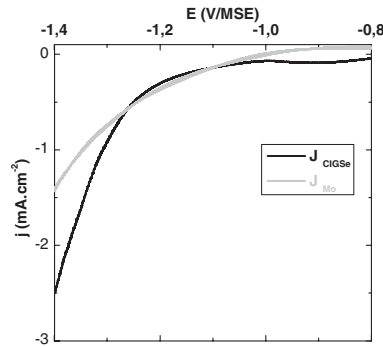


Fig. 1: Voltammetric curves recorded at 5 mVs^{-1} , 60°C . for 0.1 M KCl , 5mM InCl_3 and $20 \text{ mM Na}_2\text{S}_2\text{O}_3$ solution on Mo and CIGSe substrates.

which may involve an intermediate step related to the formation of elemental sulfur by disproportionation.

Moreover it is important to note that, based on literature [12], the precipitation of $\text{In}(\text{OH})_3$ and/or In_2O_3 occurs at pH value higher than 3.9 based on the following reactions



which means that during the ED- In_2S_3 depositions these reactions remain in competition with reaction 2 and so the In-S layers may contain oxygen and/or hydroxide [8-10].

3.2. Compositional analysis and morphology of the films

In-S layers were deposited at various potentials on Mo and CIGSe substrates for different electrical charges between -1.0 and -1.3 V/MSE under potentiostatic conditions. The evolution of the film morphology is presented in Figure 2. SEM observations point out that the substrate nature has a marked influence on the morphology of the buffer layer.

For films deposited on a Mo substrate (Fig. 2 upper part) we can observe that, whatever the potential of deposition, films remain dense and homogenous and for the same deposition time, the electrical charge and the thickness of the buffer layer increase by decreasing the potential of deposition from -1.0V , to -1.3 V/MSE.

In parallel, In_2S_3 deposited films on CIGSe absorbers are dense, homogenous, and provide a conformal covering of the absorbers for films deposited at low potential <-1.1 V/MSE. However, as soon as the potential and the thickness of the layer increases, a transition in the morphology is observed and more or less disordered nanorods are growing (Fig. 2 downer part).

To analyse the surface composition of our films, XPS measurements are also performed on the surface of films deposited on CIGSe absorbers at various potentials between -1.0 V/MSE and -1.3 V/MSE. These analysis show the presence of indium and sulfur but also of oxygen on the surface of the films, whatever the deposition potential. An average of 10% sulfur amount is measured whatever the applied potential. The global film stoichiometry can be estimated by correcting the total O % measured from a C/4 quantity corresponding to a classical ratio of O involved in the carbonaceous contaminant layer. The $\text{In}/(\text{S}+\text{O}-\text{C}/4)$ ratios obtained are close to 0.7 for deposition at -1.3 V and -1.2 V and close to 1.0 when proceeding at -1.0 V. These values approach the one expected for an $\text{In}_2\text{S}_x\text{O}_y$ compound (with $x+y = 3$), which is 0.66. The O 1s spectra (figure 3) show structured peak shape with at least two main components at 530 eV and 532 eV and consequently two distinct chemical environments. The relative proportion of these two main contributions evolves with the applied potential. In the literature, the peak at 530 eV was assigned to In_2O_3 [8, 10] and the additional peak close to 532 eV was attributed to the presence of hydroxide [10]. This means

that in our case, we probably do not deposit a pure In_2S_3 layer but a mixture of oxide, hydroxide and/or oxo-sulfide compound ($\text{In}(\text{S}, \text{O}, \text{OH})$). Such a mixed structure was already observed for In_2S_3 buffer layers deposited by electrodeposition [11]. More studies are in progress to have a better understanding of the evolution of composition of our films.

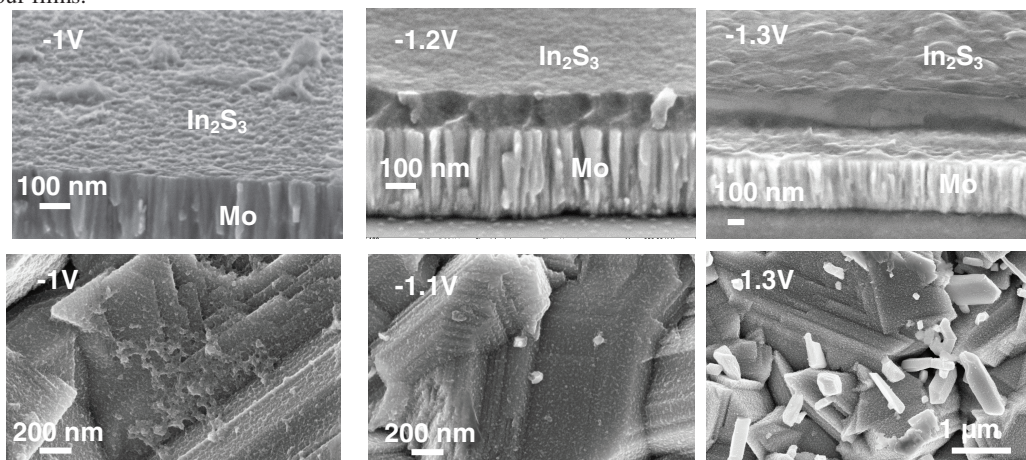


Fig. 2. Effect of the potential of deposition on film morphology deposited on (upper figures) molybdenum and (downer figures) CIGSe absorbers. The thickness of In_2S_3 on molybdenum as function of potential are : -1V : 16.5 nm, -1.2V : 124 nm and -1.3V : 178 nm.

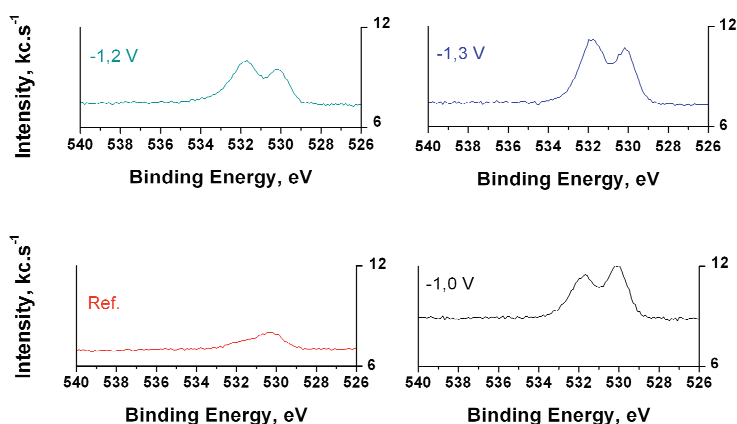


Fig. 3. O 1s XPS spectra recorded on In-S layers electrodeposited at -1.3V , -1.2V and -1.0V on CIGSe substrate and bare CIGSe substrate (labeled Ref.).

3.3. Cells performances

Cells with electrodeposited In_2S_3 buffer layer at different deposition potentials were prepared using co-evaporated CIGSe absorbers. Cells were then completed by sputtered $\text{i-ZnO}/\text{ZnO}:\text{Al}$ windows. Finally, a post annealing of the completed cells in air at 200°C for 10 min and a light-soaking at room temperature for 1 h were made. Figure 4 shows the dependence of the efficiency of the CIGSe cells with

In-S buffer layers prepared at different potential (-0.9V, -1.1V, -1.2V) and different electrical charges used for the buffer layer deposition.

As shown, for very low electrical charge values (<20 mQ/cm²) corresponding to low thickness of In₂S₃ buffer layers, similar conversion efficiencies are obtained for layers deposited between -1.0 and -1.2 V. However the conversion efficiency for cells deposited at -1.2V decreases markedly when the electrical charge used for the buffer layer deposition increases. On the contrary, for buffer layers deposited at -0.9 V the efficiency of solar cells increases with the increase of electrical charge. Best results are obtained for a potential of -0.9 V and an electrical charge between 10 and 20 mQ/cm² with a maximum efficiency of 10.2%. Although this value remains lower than that of the CdS buffer layer or In₂S₃ prepared by ALD, it is higher than what was reported up to now in the literature [10].

Figure 5 shows the current voltage curve of one of the best cell prepared at -0.9 V compared to that with CdS (Figure 5b). An improvement of Jsc for cells with In₂S₃ buffer is observed compared to cells with CdS. For comparison the spectral responses of the cell obtained with In₂S₃ and that of a cell with a classical CdS/i-ZnO buffer layer are shown in Figure 5b. The spectral response displays external quantum efficiencies of about 80% between 350 and 900 nm. Towards short wavelengths, for CdS buffer layers, the quantum efficiency drops from about 500 nm, while for In₂S₃ buffer layers the drop of the quantum efficiency occurs only at about 380 nm. Such a result confirms the higher value of the apparent bandgap of the In₂S₃ buffer layers. However for instance the V_{oc} and FF of the solar cells remains lower than the one with CdS buffer layers indicating the non optimized interface between CIGSe and the ED-In₂S₃.

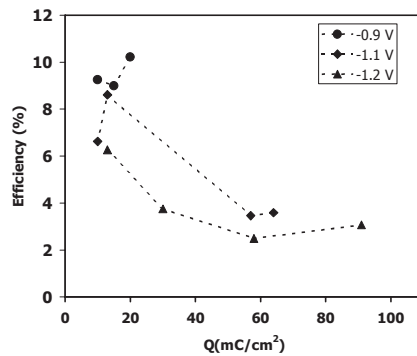


Fig. 4. Efficiency of CIGSe/In₂S₃-based solar cell as a function of deposition potential and electrical quantity of deposition measured under simulated AM1.5–100 mW/cm² illumination

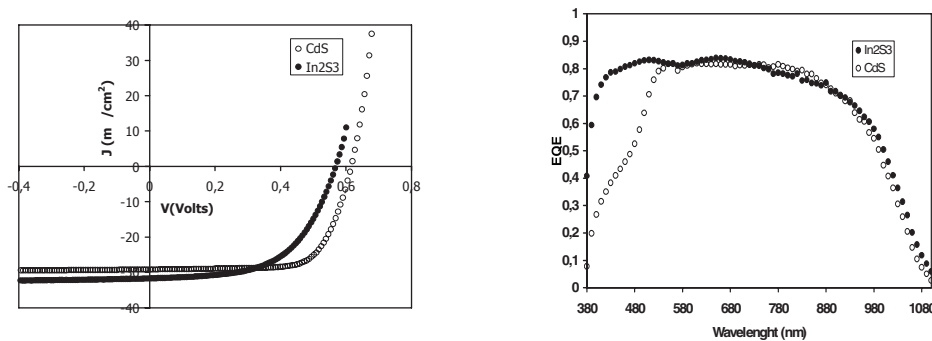


Fig. 5. (a) Current–voltage curves for best CIGSe cells under simulated AM1.5–100mWcm⁻²-illumination with a CdS/i-ZnO (η =13.3%, Voc=631mV, Jsc=29.7 mA/cm², FF=71%) buffer layer and In₂S₃/i-ZnO, (η =10.2%, Voc=569mV, Jsc=32 mA/cm², FF=56%) buffer layer. (b) Spectral responses measured under short-circuit conditions with a In₂S₃/i-ZnO buffer layer compared to a cell with CdS/i-ZnO buffer layer

4. Conclusion

Through a systematic study of the deposition parameters of In_2S_3 buffer layers on Mo and CIGSe solar cells as a function of potential of deposition we have achieved a high efficiency of about 10.2%. These studies demonstrate the potential in the fabrication of cadmium-free CIGSe thin-film solar cells without the CBD method and using electrodeposition of indium sulfide buffer layers. We observed that, to obtain good efficiencies, the two key parameters are potential of deposition and the thickness of the films. The morphology of films are highly substrate dependent and for higher deposition potential (higher than -1.1V) and low thicknesses films exhibited good substrate coverage. Solar cells with ED- In_2S_3 buffer layers present very good photo current densities, but cell performance was limited by the low Voc and fill factor. The low values of the open-circuit voltage and the fill factor of the best cells show that the interface quality between CIGSe and In_2S_3 can be more improved.

Based on these results and given the strong dependence of film thickness, morphology and bath composition on cell parameters, these can be further optimized and the conversion efficiency improved.

Acknowledgements

The authors wish to thank S. Borensztajn and C. Cossange for the SEM observations and Wurth solar for CIGSe providing.

References

- [1] Jackson P, Hariskos D, Lotter E, Paetel S, Wuerz R, Menner R, Wischmann W, Powalla M, New world record efficiency for $\text{Cu}(\text{In,Ga})\text{Se}_2$ thin-film solar cells beyond 20%. *Prog. Photovolt: Res. Appl.* 2011 ; DOI: **10.1002/pip.1078**.
- [2] Naghavi N, Abou-Ras D, Allsop N, Barreau N, Bücheler S, Ennaoui A, Fischer CH, Guillen C, Hariskos D, Herrero J, Klenk R, Kushiya K, Lincot D, Menner R, Nakada T, Platzer-Björkman C, Spiering S, Tiwari AN, Törndahl T. Buffer layers and transparent conducting oxides for chalcopyrite $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ based thin film photovoltaics: present status and current developments. *Prog. Photovolt. Res. Appl.* 2010;**18**:411-433.
- [3] Naghavi N, Renou G, Bockelee V, Donsanti F, Genevee P, Jubault M, Guillemoles JF, Lincot D. Chemical deposition methods for Cd-free buffer layers in $\text{CI}(\text{G})\text{S}$ solar cells : role of windows layers. *Thin Solid Films.* 2011; **DIO :10.1016/j.tsf.2011.01.091**.
- [4] Datta M, Landolt D, Fundamental aspects and applications of electrochemical microfabrication. *Electrochimica Acta.* 2000;**45 (15-16)**:2535-2558.
- [5] Pandey RK, Sahu SN, Chandra S, Handbook of Semiconductor Electrodeposition, New York, Basel, Hong Kong: Marcel Dekker Inc. 1996.
- [6] Lincot D. Electrodeposition of semiconductors. *Thin Solid Films.* 2005;**487(1-2)**:40-48.
- [7] Hibberd CJ, Chassaing E, Liu W, Mitzi DB, Lincot D, Tiwari AN, Non-vacuum methods for formation of $\text{Cu}(\text{In, Ga})(\text{Se, S})_2$ thin film photovoltaic absorbers. *Progress in Photovoltaics: Research and Applications.* 2010;**18(6)**:434-452.
- [8] Asenjo B, Chaparro AM., Gutierrez MT, Heffero J, Maffiotte C, Study of the electrodeposition of In_2S_3 thin films. *Thin Solid Films.* 2005;**480**:151-156.
- [9] Abdel Haleem A, Ichimura M. Electrochemical deposition of indium sulfide thin films using two-step pulse biasing. *Thin Solid Films.* 2008;**516**:7783-7789.
- [10] Todorov T, Carda J, Escribano P, Grimm A, Klaer J, Klenk R. Electro deposited In_2S_3 buffer layers for CuInS_2 solar cells. *Solar Energy Mat. and Solar Cells.* 2008;**92**:1274-1278.
- [11] Zhdanov SI, *Standard potentials in aqueous solution*, ed. R.P. A. J. Bard, J. Jordan., New York and Basel: Marcel Dekker, Inc. 1985.
- [12] Pourbaix M. *Atlas of electrochemical equilibria in aqueous solutions*. 2nd ed. Texas: NACE International Cebelcor; 1974.