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12.4% Efficient $Cu(In,Ga)Se_2$ solar cell prepared from one step electrodeposited Cu–In–Ga oxide precursor layer

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ABSTRACT

This paper presents new advances on an atmospheric-based deposition process for $Cu(In,Ga)Se_2$ synthesis, consisting of the electrodeposition of a Cu–In–Ga mixed oxide/hydroxide layer from an aqueous solution, at room temperature, followed by a thermochemical reduction and selenization. This process enables the one-step co-deposition of the three elements, from a simple aqueous electrolyte containing nitrate ions as oxygen precursor, with fast growing rates and precise control of composition. The reduction process is carried out thermally in pure hydrogen atmosphere and leads to Cu–In–Ga metallic alloys. After selenization, $Cu(In,Ga)Se_2$ phase was obtained and completed solar devices reach a 12.4% maximal power conversion efficiency.

1. Introduction

The photovoltaic market is currently dominated by crystalline silicon solar cells, with a market share of almost 90% in 2012 [1,2]. Besides this technology, a growing interest shifts towards thin-film solar cells. Among the different thin film technologies, $Cu(In,Ga)Se_2$ (CIGS) solar cells have so far demonstrated the highest efficiency beyond 20% [3] and is now at an early industrialization stage [4].

Following the brutal collapse of silicon solar cell price, the reduction of production costs represents more than ever a major issue for the CIGS technology. Both the increase in conversion efficiency and the use of low-cost and easy scalable technologies are of particular interest. Atmospheric deposition methods, based on screen printing and electrodeposition, are considered as the main candidates to drive the costs of the CIGS technology further down. This field has been reviewed in Refs. [5,6].

In the case of screen printing, one strategy is to prepare oxide particulate films, which are then reduced into metallic films and selenized to reach a maximal conversion efficiency of 13.6% [7]. This process involves multiple steps, such as nanoparticules synthesis, ink formulation and ink printing.

Electrodeposition represents the other major technology to respond to the challenge of cost reduction and has already demonstrated its feasibility for large scale production of CIGS. Excellent results are also obtained with electrodeposition at the industrial level by Solopower, with a 14.2% best cell efficiency and 13% best module aperture area efficiency [8], and also by Nexcis with a best record cell efficiency value of 15.9% recently released (module efficiency of 12.2%) [9]. In the latter case the deposition proceeds through the multiple electrodeposition of stacked metallic layers. Such process is also more than likely used by Solopower [8]. As a consequence the use of metallic precursor layers appears as a very promising route toward industrial development. Research studies published in this area confirm the aforementioned appeals of this approach, and give more details on the involved processes. For example, Bhattacharya et al. reported a best conversion efficiency of 11.7% for a CIGS prepared by selenization of electrodeposited stacked Cu/In/Ga layers [10]. Nevertheless, further improvement could be anticipated by using direct co-deposition in a single bath, instead of separate individual baths. Direct co-deposition of the three metallic elements has been already studied, but it is difficult to carry out due to the highly negative deposition potential of metallic Ga. In basic electrolytes, the use of a complex mixture of additional ligands is necessary to solubilize copper, indium and gallium ions [8]. On the other hand, In acidic media, the deposition comes along a large production of hydrogen and results in dendritic morphology [11,12], and uneasy difficult control of the Ga content in the film. Nevertheless, conversion efficiencies up to 9.3% have been demonstrated in acidic media by our group, showing the potential of one-step deposition of the three metallic elements [12].

An alternative method developed in our laboratory to produce metallic precursor layers, consists of a one-step electrodeposition of Cu–In–Ga mixed oxide/hydroxide precursor followed by a thermochemical reduction [13]. This method possesses similar features to the ink-process, but has the great advantage of using a single-step solution-based deposition process, without the need

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for a complex ink formulation and its production. This electrodeposition process takes advantage of the strong affinity of indium and gallium for oxygen, due to the large free energy of formation of the corresponding oxides or hydroxides. Therefore, it enables to deposit simultaneously the three elements at a much less negative potential than for the metallic alloy [14]. First cell results showed conversion efficiency up to 9.4% [14].

In this paper, we are reporting recent developments in synthesis and annealing steps leading to a best cell efficiency of 12.4%. The whole process is recalled and the major evolutions leading to improved material quality are presented.

2. Material and methods

Co-electrodeposition of Cu–In–Ga mixed oxide/hydroxide layer was performed in an electrolyte containing 100 mM $NaNO_3$, 13.4 mM $Cu(NO_3)_2$, 15 mM $In(NO_3)_3$ and 7.5 mM $Ga(NO_3)_3$ dissolved in deionized water (18.2 MΩ cm resistive water), and final pH was adjusted at 1.8 by addition of concentrated HNO_3 (under proprietary process [13]). A conventional three-electrode setup was used and electrodes were placed vertically in the solution. The reference electrode was a saturated mercurous sulfate electrode (MSE), an IrO_2-covered Ti grid was used as counter electrode and the working electrode was Mo-coated soda-lime glass (Mo/SLG). The Mo film was 900 nm thick and was deposited by DC sputtering. Prior to each experiment, Mo substrates were cleaned in 25% ammonia solution for 5 min in order to remove superficial molybdenum oxide, and rinsed with deionized water. The deposition experiments were performed in potentiostatic mode, using a Biologic VSP potentiostat, at room temperature and without stirring, on a (5×5) cm^2 Mo/SLG substrate.

The reduction of the electrodeposited precursor films was carried out by annealing at 500–550 °C under flowing pure hydrogen. The selenization of the reduced precursor films was performed at 550–600 °C using elemental selenium powder.

At each step, samples were characterized by X-ray fluorescence (XRF), to determine the composition, and by X-ray diffraction (XRD) using Cu-Kα_1 radiation (λ=1.5406 Å), to identify the crystalline phases. The cross sectional morphology was examined by field-emission gun scanning electron microscope (FE-SEM, Zeiss Supra), coupled with an energy-dispersive spectroscopy (EDS) detector.

The photovoltaic devices were completed by a 50 nm CdS buffer layer by chemical bath deposition (CBD), and a window layer composed of 80 nm intrinsic ZnO and 400 nm Al doped ZnO was deposited by RF sputtering. Optoelectronic properties of the devices were determined by current–voltage (*I*–*V*) characteristic measured under standard under AM1.5G spectrum using a class AAA solar simulator, and spectral response was used to determine the gap of the CIGS layers.

3. Results and discussion

The electrodeposition of Cu–In–Ga mixed oxide/hydroxide film is carried out in nitrate based electrolyte, without any complexing agent. The pH of the electrolyte is fixed at 1.8 to avoid precipitation of copper, indium and gallium oxides/hydroxides in the solution [15].

This process is based on the nitrate reduction and the so-called “electrogeneration of base”, applied for oxides electrodeposition [16]. The reduction of nitrate consumes protons, which leads to a pH increase at the cathode surface, subsequently causing the precipitation of Cu, In and Ga hydroxides precipitation. One can propose the following reactions to describe this process:

$$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O$$

$$Cu^{2+} + NO_3^- + H_2O + 2e^- \rightarrow Cu(OH)_2 + NO_2^-$$

$$In^{3+} + 3/2NO_3^- + 3/2H_2O + 3e^- \rightarrow In(OH)_3 + 3/2NO_2^-$$

$$Ga^{3+} + 3/2NO_3^- + 1/2H_2O + 3e^- \rightarrow GaOOH + 3/2NO_2^-$$

Previous experiments indicated that the co-deposition of copper, indium and gallium oxides/hydroxides starts at −0.7 V/MSE [14]. When the deposition potential decreases, the deposition becomes mass transfer controlled and the composition of the layer is constant in the potential range −0.95 to −1.2 V/MSE. Consequently, the overall composition of the layer can be easily controlled by the concentration of Cu(II), In(III) and Ga(III) species in solution. The precursor growth rate reaches approximately 500 nm min^{-1}, and the thickness can be easily tuned with the duration of deposition. However the precursor after electrodeposition appears in the form of an oxide made of nanoparticles with some porosity, which makes difficult the quantitative determination of the materials growth rate. A better evaluation can be done by considering the thickness of the compact metallic layer obtained after the reduction step. Doing so, we estimate the growth rate to be around 700 nm after 10 min electrodeposition. Converting to CIGS, this indicates that a 1.5–2 µm thick layer could be prepared from a 10 min electrodeposition step.

The precise amount of Cu, In and Ga electrodeposited on a (2.5×2.5) cm^2 sample was determined after dissolution and Inductively Coupled Plasma measurement. From these values and Faraday's law, we found that the faradaic efficiency is about 50% in the given conditions. This value is related to the parallel reduction of nitrate with protons, which lowers the faradaic efficiency. A slight increase of the initial pH, below the precipitation of indium or gallium oxide/hydroxide, will significantly reduce this reaction, and maximizes the faradaic efficiency.

After 10 min electrodeposition at −1.2 V/MSE, the overall composition was estimated by XRF. From the resulting atomic concentration, we calculate the atomic ratio Cu/(In+Ga) and Ga/(In+Ga), which were estimated to be 0.87 and 0.22, respectively, which corresponds to the optimal composition for high efficiency CIGS solar cells.

Fig. 1a presents SEM cross-sectional view of the as-deposited Cu–In–Ga mixed oxide/hydroxide layer. It exhibits a porous structure made of aggregated particles with diameters of about 20–50 nm. These particles are not crystallized as shown by the absence of diffraction peak on the corresponding XRD pattern (Fig. 2a, pattern A). It can be noticed that the film thickness is homogeneous with a flat outer surface.

Before selenization, Cu–In–Ga mixed hydroxide has to be reduced into metallic alloy. Different reducing agents can be used, such as hydrogen or alcohol vapor (ethanol or methanol). In the present work, the reduction was carried out under pure hydrogen atmosphere, preventing any contamination from carbon species.

Fig. 1b shows a cross-sectional view of the layer after thermal treatment under pure hydrogen gas at 500–550 °C during 30 min. A spectacular structural transformation takes place with the complete disappearance of the particulate morphology leading to dense metallic layer, as shown by composition and structural characterizations as described below. The morphology of the layer results from a melting process as shown by the rounded shapes. As a consequence of the reduction process and the formation of a dense metallic layer, the total thickness of the layer is reduced by a factor of 8–10. The induced roughening effect is probably detrimental to the properties of the cells by creating local fluctuations of the photovoltaic properties and possibly shunting paths. The corresponding XRD pattern is presented in Fig. 2a, pattern C. It shows the formation of the Ga-rich phase $Cu_9(In,Ga)_4$ in addition to In.