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Photo-assisted electrodeposition of a ZnO front contact on a p/n junction

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ABSTRACT

Electrodeposition is an atmospheric and low temperature technique and consequently one of the most interesting way to grow transparent conductive materials at low cost. In this paper the electrodeposition of ZnO films as front contact of a $Cu(In,Ga)(Se,S)_2$ based solar cell is investigated. The electrodeposited ZnO can reach suitable conductivity and transparency for this application. One of the main challenges is to optimize its growth on the p-n junction formed by the $Cu(In,Ga)(Se,S)_2$/CdS stack. Indeed, due to the blocking behavior of this diode in dark conditions, the electrodeposition has to be photo-assisted with an appropriate incident flux. Moreover the growth of a compact film is tricky because of the poor nucleation of ZnO on the CdS surface. As this type of morphology is needed to ensure a sufficient lateral conductivity, we have adapted the electrochemical parameters in order to create a seed layer and improve the density of the nuclei in the first steps of the growth. As a result, with optimized parameters, a contact layer showing a high compactness is reproducibly deposited, leading to a 14.7% efficiency for a $Cu(In,Ga)(Se,S)_2$ based solar cell terminated with an electrodeposited front contact, which is close to the efficiency of the corresponding reference cell with a magnetron sputtered front electrode.

1. Introduction

Zinc oxide has received much attention over the past years due to its numerous applications in such fields as piezoelectric and optoelectronic devices, chemical sensors, photovoltaic applications [1–3]. This work focuses on the application of this transparent conductive oxide (TCO) as the front contact of $Cu(In,Ga)(Se,S)_2$ (CIGS) based solar cell [4,5]. We showed in previous studies that ZnO layers exhibiting high doping levels and intragrain mobilities can be grown by electrodeposition (ED) [6,7]. Two main challenges emerge in transferring the electrodeposition of ZnO from a metallic substrate to a solar cell stack, in our case glass/Molybdenum/CIGS/CdS. The first one is the blocking behavior of the CIGS/CdS diode in dark conditions for cathodic reactions. Therefore this type of substrate has to be illuminated during the growth phase to produce a photocurrent that will be consumed by the electrochemical reaction [8,9]. The second problem is the variation of the compactness of the layer observed as a function of the chemical nature of the substrate. Unfortunately, in the case of a direct deposition on the CdS surface, isolated nuclei are created leading to a three dimensional growth which results in the non-compactness of the deposited layer composed of large sized and disjoint grains. An activation of the CdS surface is then needed to promote the ZnO nucleation. In this paper we present the optimization of the photo-assisted growth by the control of the illumination flux power and the introduction of a seed layer. We apply optimized ED ZnO layers as front contact for CIGS-based solar cells and demonstrate conversion efficiencies close to the efficiency of reference cells with a sputtered ZnO front electrode.

2. Material and methods

The electrodeposition was performed at a low temperature set at 80 °C in a solution containing zinc chloride and potassium chloride with a concentration of 5×10^{-3} M and 0.15 M respectively. The solution was saturated by bubbling oxygen gas used as oxygen precursor [10]. Electrodeposition was performed in a transparent reactor with a three-electrode set-up, using a SP-150

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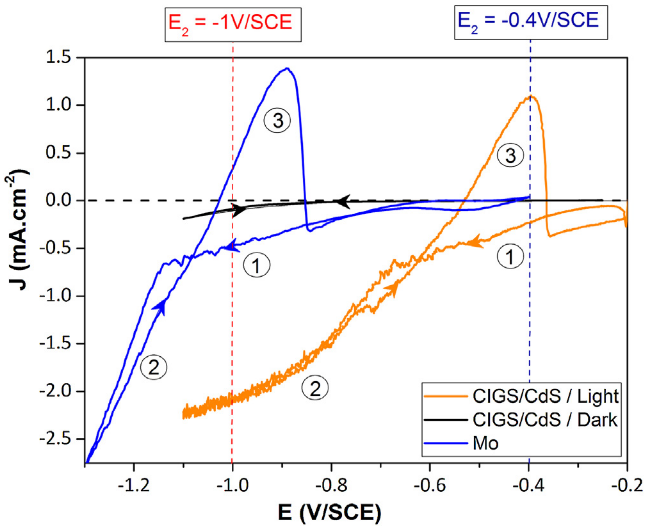

Fig. 1. a) Cyclic voltammetry carried out on a metallic substrate (blue), and on a Cu (In,Ga)(Se,S)$_2$/CdS stack in the dark (black) or under illumination (orange), please refer to the text for the corresponding reactions.

potentiostat from Bio-Logic Science Instruments and the EC-Lab software. The reference electrode was a saturated calomel electrode (SCE +0.248 V vs. normal hydrogen electrode (NHE)). A zinc foil was used as the counter electrode. The CIGS/CdS substrates were grown and provided by ZSW. The two micrometer thick CIGS layer was deposited by coevaporation and covered by a 50 nanometer thick CdS buffer layer deposited by chemical bath deposition.

The ZnO growth is photo-assisted with a light flux produced by a LED (6 mW.cm^{-2}) panel and followed by an annealing at 150 °C for 30 minutes. This annealing step is carried out under low pressure conditions (15 mbar). For the reference cell, a bilayer i-ZnO (50 nm)/ZnO:Al (370 nm) was grown by sputtering on the top of the CIGS/CdS stack. Finally, a zinc metallic grid is electrodeposited according to the procedure described in Ref. [11]

The morphology, composition and thickness of the films were studied by Scanning Electron Microscopy (SEM) using a Zeiss Merlin VP compact microscope coupled with an EDS analyzer. The crystalline structure of the layers was examined by X-ray Diffraction (XRD) with a Panalytical Empyrean X-ray Diffractometer using Cu K$_{\alpha 1}$ radiation (1.5405 Å), in the classical Bragg–Brentano setup.

3. Results and discussion

3.1. Optimization of the incident flux

In order to illustrate the difference between a metallic and a semiconducting substrate, Fig. 1 compares voltamperograms carried out on a glass/molybdenum substrate and on a CIGS/CdS junction.

The current response obtained on the Molybdenum surface is composed by the two electrochemical waves [12] related to the deposition of ZnO (1) from the reduction of O_2 and to the reduction of Zinc ions into metallic Zinc (2). The deposition mechanism of ZnO has been widely studied and is commonly divided into three steps; the reduction of O_2 into hydroxide ions (1a) is followed by the precipitation of the zinc hydroxide (1b) that finally dehydrates as the temperature of the bath is high enough (1c). During the reverse scan, an anodic peak corresponding to the oxidation of the metallic zinc previously deposited (3a) is observed at a potential close to the redox potential of Zn(0)/Zn(II) in this electrolyte. As this electrochemical reaction takes place in a basic environment due to the concomitant reduction of oxygen into hydroxide ions (1a), the zinc ions produced precipitate and form ZnO nuclei at the working electrode according to (3).

$$\frac{1}{2}O_2 + Zn^{2+} + 2e^- \rightarrow ZnO \tag{1}$$

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \tag{1a}$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \tag{1b}$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \tag{1c}$$

$$Zn^{2+} + 2e^- \rightarrow Zn \tag{2}$$

$$Zn \rightarrow Zn^{2+} + 2e^- \tag{3a}$$

$$Zn + 2OH^- \rightarrow ZnO + 2e^- + H_2O \tag{3}$$

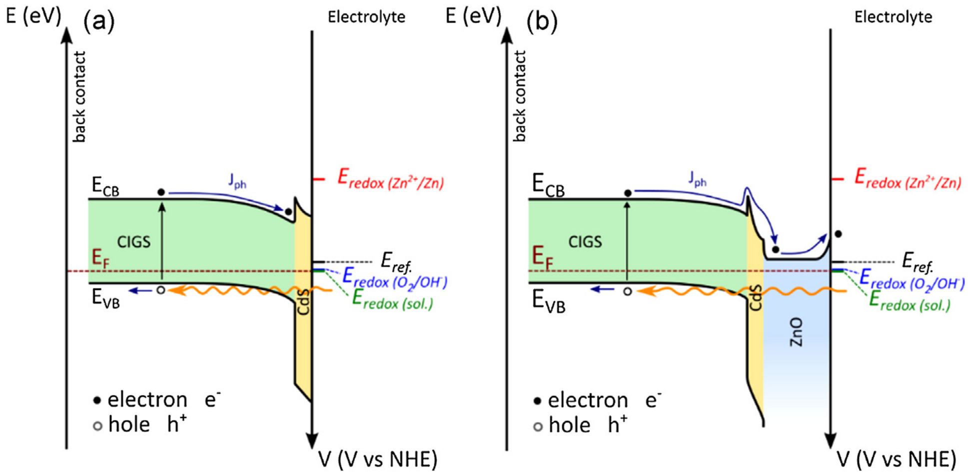

Fig. 2. (a) Band diagram of a CIGS/CdS p/n junction stack in contact with the electrolytic bath. (b) Band diagram of a Mo/CIGS/CdS/ZnO stack in contact with the electrolyte at open circuit potential.