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Optimization of molybdenum thin films for electrodeposited CIGS solar cells

M. Jubault *, L. Ribeaucourt, E. Chassaing, G. Renou, D. Lincot, F. Donsanti

Institut de Recherche et Developpement sur l'Energie Photovoltaïque (IRDEP), UMR 7174, EDF-CNRS-Chimie Paristech, 6 quai Watier, 78401 Chatou, France

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ABSTRACT

Molybdenum thin films are widely used as back contact for CIGS-based solar cells. In this paper, the properties of Mo layers deposited by DC and RF sputtering are investigated in view of a specific optimization of electrodeposited CIGS solar cells. In the first part of the paper RF and DC films are grown on soda lime glass, in a pressure range from 2 to 20 mTorr, and for various RF power and DC current. They are then characterized by optical, electrical and structural methods. It appears that the films deposited by RF mode sputtering are more reflective, conductive and adherent than those obtained by DC mode. Structurally, they present different behaviors with respect to nucleation and growth of CIGS precursor layers by electrodeposition. A large difference is observed in the photovoltaic properties of completed cells, with much better performances obtained with DC Mo layers.

1. Introduction

$Cu(In_{1-x}Ga_x)Se_2$ (CIGS) thin film solar cells usually use molybdenum back electrodes. Substrates of Mo-coated soda lime glass can be purchased from commercial sources. However, it has been shown that the properties of the molybdenum thin films can strongly affect the performances of the solar cell.

Indeed, many studies point out the role of molybdenum as the main transport gate for Na diffusion during the annealing of CIGS, on the enhancement of the solar cell performances [1–3]. The reaction of Mo with Se to form a thin $MoSe_2$ layer also plays a positive role for promoting the ohmicity of the back contact. Former studies of our laboratory have shown the close dependence between molybdenum properties and electrodeposited CIGS growth. The purpose of our study is to investigate the effect of the Mo coating conditions over the overall properties of the CIGS-based solar cell. The objective is to adapt the Mo back contact for our CIGS electrodeposition method [4].

In comparison to the molybdenum substrate commonly used in PVD deposition processes of CIGS, the one needed for electrochemical processes requires a stronger chemical and physical resistance. To obtain the more suitable molybdenum for our process, we optimized the sputtering deposition by varying the different parameters (pressure, excitation mode, power, etc.).

In order to compare more accurately the influence of the Mo morphology on the growth of CIGS, a study of the nucleation at different steps of the electrochemical deposition process was carried out.

2. Experimental

2.1. Molybdenum deposition

Molybdenum thin films were deposited by a RF (13.56 MHz) or DC magnetron sputtering device using rectangular Mo target (purity, 99.95%). The soda lime glass substrates were positioned onto a substrate-holder moving parallel to the target surface at a distance of 55 mm, with fixed scan rate. Prior to molybdenum deposition, an argon plasma treatment was performed in order to remove contaminations and activate the surface. The pressure was varied between 2 and 20 mTorr by adjusting the argon flow (purity, 99.9997%), keeping RF power to 600 W, or DC current at 1.0 A. Then pressure was fixed to 2 mTorr whereas RF power was varied between 450 and 900 W or DC current from 0.5 to 1.5 A.

2.2. Films characterization

The thickness was obtained by X-ray fluorescence measurements. A four-point probe was used to determine the resistivity of the film. SEM-FEG and X-ray diffraction analysis were performed to characterize morphological modifications of the Mo thin films. The optical reflectance was measured with unpolarized light in the wavelength range of 250–2000 nm. The adhesion of the Mo was then tested by ultrasonic bath at 50 °C in presence of RBS 25 (alkaline detergent) diluted at 2% v/v in deionized water.

2.3. Solar cells elaboration and characterization

Copper indium gallium diselenide precursor films are deposited on the molybdenum substrates by electrodeposition from acidic aqueous solutions containing dissolved salts. Nucleation processes

* Corresponding author.
E-mail address: marie.jubault@edf.fr (M. Jubault).

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have been studied using a procedure described in [5] in presence of Cu, In and Se elements.

Precursor films for cell completion have been made by electrodeposition of a mixed copper indium gallium alloy. Then a first annealing is performed to strengthen the film, followed by a second annealing in the presence of selenium vapor as described in [6]. After etching the surface in KCN, the cell is completed by the deposition of 50 nm CdS interfacial buffer layer by chemical bath deposition and a iZnO, ZnO:Al double layer as a front contact electrode by RF sputtering. The photovoltaic properties are determined under simulated AM1.5 (100 mW/cm^2) solar spectrum.

3. Results and discussion

3.1. Preliminary study of Mo thin films properties

The first step of the optimization of the molybdenum layer was to correlate the sputtering parameters to its overall properties. As reported in other studies [7,8], we confirmed the major effect of working pressure on resistivity and adhesion of molybdenum thin films deposited by DC mode sputtering.

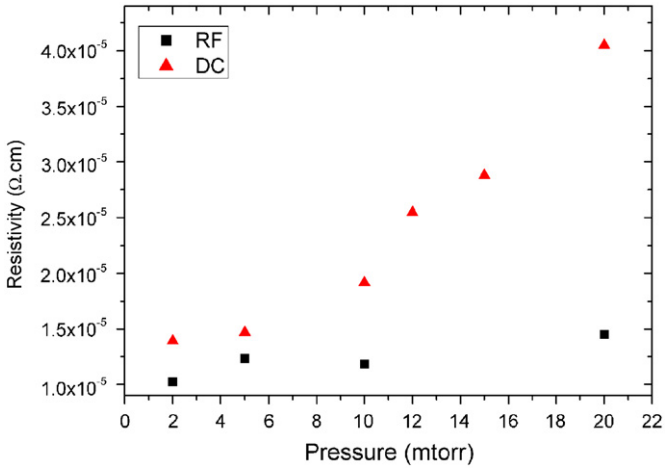

Fig. 1. Evolution of the Mo thin film resistivity over deposition pressure.

3.1.1. Influence of the working pressure

Fig. 1 shows the variation of molybdenum films electrical resistivity with respect to the working pressure, depending of the excitation mode of the discharge. For RF deposition mode, the power was fixed to 600 W. In DC mode, the sputter current was fixed to 1.0 A. In each series, the thickness was around 500 nm, depending on the scan number, and the deposition rate. At low pressure, under 5 mTorr, resistivity remains around $1.2 \times 10^{-5}\ \Omega$ cm (around 0.25 $\Omega/\square$) whatever the chosen excitation mode. This value is nearly twice the resistivity of the bulk material, which is $5.5 \times 10^{-6}\ \Omega$ cm. For pressure higher than 10 mTorr, the films deposited by the different excitation modes exhibit two behaviors. For RF mode, the resistivity stays around the same value of $1–1.5 \times 10^{-5}\ \Omega$ cm. In the case of the DC mode, the resistivity rises up to $4 \times 10^{-5}\ \Omega$ cm, at the maximum pressure reachable by our process. Compared to the literature [7–9], these values, especially for high pressure deposited films, are ten times lower.

An increase in resistivity with pressure can be explained by a decrease in atoms energy in the discharge. Species arriving on substrate surface has then a lower mobility, and the as-grown film exhibits a porous columnar grain growth with intergranular voids. Hall effect measurement confirmed the decrease in electron mobility from 8 to 1.8 cm^2 V^{-1} s^{-1}, when the pressure varies from 2 to 20 mTorr in DC mode sputtering. Fig. 2d shows clearly the presence of large voids between grains. One can also see that the large elongated grains observed at low pressure became pyramidal at high pressure. When RF excitation is used, pressure effect over morphology of the Mo films is less pronounced. Density slightly decreases with pressure, and grains become larger (Fig. 2a and c).

XRD measurements (Fig. 3) revealed that the films grown with a preferred orientation along the (1 1 0) plane, which is classically reported for Mo deposited by sputtering processes at room temperature [10]. However, it can be noted that an increase of this preferred orientation for high pressure in the case of DC mode, and an opposite effect for RF mode deposited films. X-ray reflectivity measurements provided us an accurate determination of the material density and roughness. It appears that for films deposited

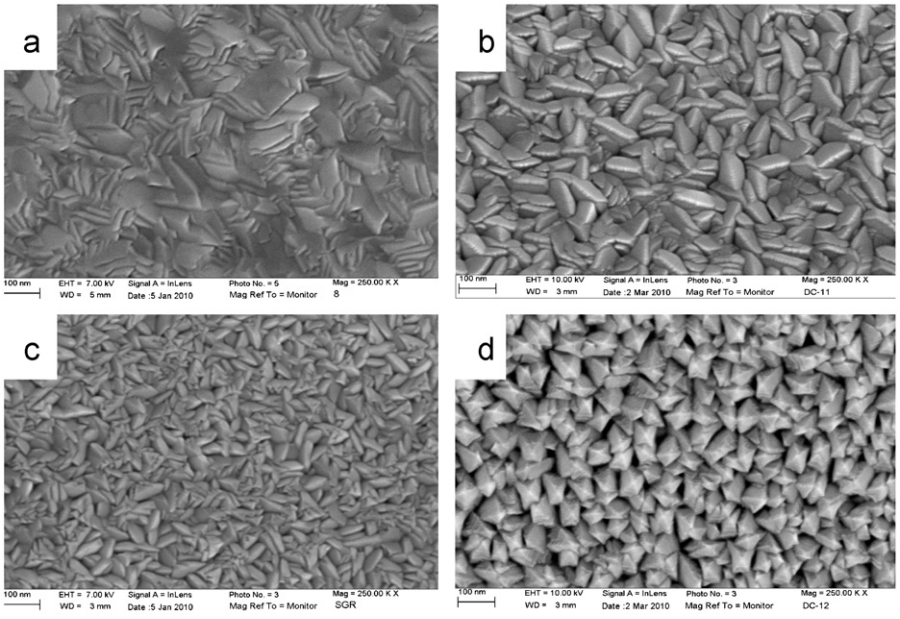

Fig. 2. SEM-FEG of molybdenum thin film deposited in: (a) and (b) RF and DC mode at 2 mTorr, (c) and (d) RF and DC mode at 20 mTorr.