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# Effect of the Negative Substrate Bias on Properties of Sputtered Molybdenum Thin Films as a Back Contact for $Cu(In,Ga)Se_2$ Solar Cells

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***Abstract***- **Molybdenum (Mo) back contact in CIGS solar cells have been deposited using rf-magnetron sputtering. Properties of thin films were based on the deposition parameters. The influence of working gas pressure on the electrical resistivity and the residual stress of Mo thin films have been widely studied. Therefore, we propose to study the effect of the substrate bias of soda- lime glass (SLG) on film properties of molybdenum back contact. The structural, electrical and morphological properties of these films were investigated. Indeed, by biasing negatively the substrate holder, layers with electrical resistivity less 100µΩcm than were obtained with an elevated working argon pressure of 5 $10^{-2}$ mbar. The effect of negative substrate bias on structural properties was studied by X-ray diffraction (XRD). The electrical resistivity of Mo thin films and their surface morphology were estimated by measurements of sheet resistance and scanning electron microscope (SEM), respectively. The main contribution of this work was to obtain Mo thin films using only a single argon pressure and with adequate properties to be used as back contact for CIGS based solar cells**.

***Keywords***: **Thin films, CIGS Solar cells, Molybdenum back-contact, rf- magnetron sputtering.**

## I. INTRODUCTION

In Cu $(In,Ga)Se_2$ (CIGS) based cells, the highest conversion efficiency has yielded 20.3 % using Molybdenum (Mo) as back contact [1]. Molybdenum is the most suitable material compared to W, Ta and Nb, because of its outstanding properties [2]. It is a refractory metal largely used for high temperature applications [3]. Mo thin films are distinguished by their low resistivity and their inertia to Se corrosive atmosphere during the growth of CIGS layers at high temperature. Moreover, the emergence of $MoSe_2$ layer at the interface (Mo/CIGS) promotes the formation of an ohmic contact [4,5]. Similarly, molybdenum is an excellent barrier to the migration of impurities from the substrate soda Lime Glass (SLG) to the CIGS absorber. Nevertheless, it helps the diffusion control of Na atoms from the substrate SLG, which is a special glass that contains 15.6% wt of sodium in oxide $Na_2O$ form [6]. Na atoms slow the growing of CIGS by the creating Na-Se component, thus allowing better Se incorporation into CIGS films and improve p conductivity of the absorber [7,8]. Low resistivity ( $\rho < 100 \mu\Omega cm$ ) Mo thin films prepared by rf sputtering have a very bad adhesion to SLG substrate. They are mainly obtained at low argon pressure. Films with good adhesion can be obtained with high argon pressure, but they are inadequate for Back contact application. The Mo back-contact is developed in two steps. First, an intermediate high resistivity film elaborated at high argon pressure followed by another film of low resistivity elaborated at low argon pressure [4, 9]. In this paper, we focused on the effect of holder substrate negatively biased on structural, electrical and morphological proprieties of Mo thin films. We showed that it is possible to obtain Mo thin films with low resistivity in high argon pressure, allowing the elaboration of back-contact in a single and high argon pressure.

## II. EXPERIMENTAL

Molybdenum thin films are obtained by diode magnetron rf sputtering 13.56 MHz**.** The target is a disc of 75 mm diameter, 6 mm thickness with 99, 95% purity. The holder is equipped by a magnetron system. The stainless steel reactor is connected to a pumping system consisting of a primary pump and a diffusion pump to reach $10^{-6}$ mbar residual vacuum. The substrate holder is made of stainless steel too, connected to a DC voltage generator allowing putting the substrate holder at required negative bias. Films are deposited in same conditions on soda-lime glass (SLG) substrates. The substrate was fixed at a distance of 5 cm from the target and was not heated during film deposition. Before introduction into the reactor, the SLG substrates were cleaned thoroughly in the ultrasonic bath of trichloroethylene for two minutes and were immersed in acetone followed by deionized water and dried under a nitrogen flux. After reaching a residual pressure of $10^{-6}$ mbar, we introduce argon gas at desired working pressure. Mo target is first submitted to a pre-sputtering period of 5 minutes with a power of 200 watt before deposition process. In order to investigate the effect of deposition pressure and negative bias value on deposited film proprieties. Two series of films of Mo were prepared. In the first series, the working pressure was varied from 0.5 $10^{-2}$ mbar to $5.10^{-2}$ mbar for 40 minutes of deposition time and without substrate bias. In the second series, the working pressure was fixed at 5 $10^{-2}$ mbar and at 0V, -10V and -40V of substrate bias. The structural proprieties of thin films have been characterized by X-ray diffraction (XRD Bruker D8 Advance) using $CuK_{\alpha}$ radiation ($\lambda$=1.54 Å). The resistivity of Mo films has been obtained by four- point probe (JIPELEC SRM 200) method and their morphological properties have been studied by scanning electron microscope (PHILIPS SEM 505).

## III. RESULTS AND DISCUSSION

### *A. Effect of working pressure on the electrical resistivity of Mo films*

The evolution of the resistivity of molybdenum (Mo) thin films as a function of the variation of working pressure is shown in Fig 1. When the working pressure increased from 0.005 to 0.05 mbar, the resistivity of Mo film rapidly increased from 10µΩcm to 100µΩcm. This increase in resistivity is mainly due to the creation of microcavities (porous structure) which do not allow good crystallization in the layers of Mo [10]. Note that the high resistivity layers inadequate for the application back contact (BC) in CIGS solar cells [7]. The low values of the resistivity layers of Mo obtained for the low pressure have poor adhesion with substrates of soda-lime glass (SLG). But, the adhesion is very good for the high resitivity layers obtained for high pressure.

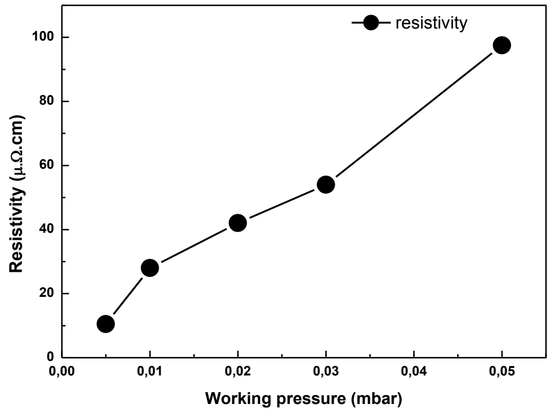


Fig. 1 Resistivity variation of the Mo films sputtered with different working pressures

### *B. Effect of substrate bias on the electrical resistivity*

The holder substrate is based to negative potential supplied by continue generator. The influence of negative substrate bias on the resistivity evolution of Mo thin films is shown in Fig.2**.** The experimental conditions in this series are the same as the first round except the working pressure was fixed at $5.10^{-2}$ mbar and the values of the polarization of the substrate holder are variable. We can see that the electronic resistivity was decreased with increasing the polarization of the substrate holder and this is probably due to the decreased amount of oxygen in these layers and to homogeneity, compactness and reducing the microporosity of the deposition surface [11].

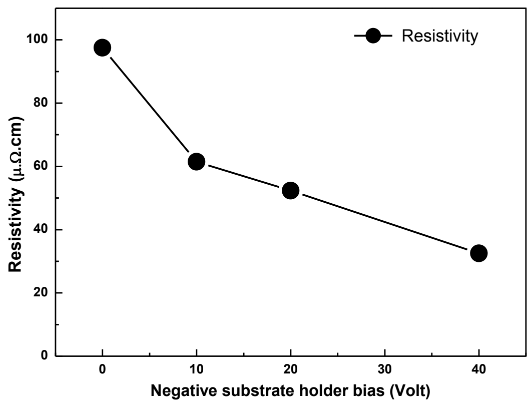


Fig 2 Resistivity variation of the Mo films sputtered with different substrate holder bias

### *C. Effect of substrate bias on the structural properties*

Fig.3 illustrates the XRD patterns of single thin layer of Mo elaborated at 0V, -10V and -40V of negative substrate bias for a fixed Ar gas pressure of $5.10^{-2}$ mbar. We can see in this figure, the films prepared without substrate bias show a small intensity of the (110) peak and practically absent for the peaks corresponding to the (200) and (211).

No great effect detected for peaks intensity with negative substrate bias of – 10V, while we note for -40V, all the peaks can be easily observed with the small line width of the peaks and thus an indication for good crystal quality. The relative intensity of the observed peaks is in good accordance with JCPDS standard spectra of Mo. Therefore, we can conclude that the application of a negative bias on the substrate holder causes densification of the layer and decrease its roughness [11].

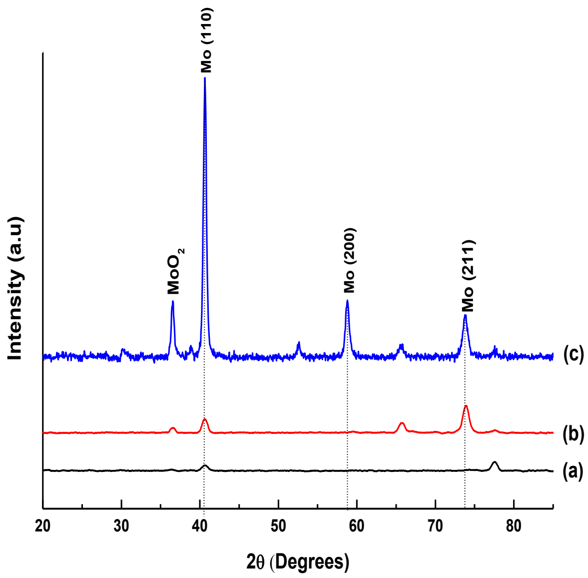


Fig. 3 XRD patterns of single thin layer of Mo obtained for different values of substrate bias: (a)= 0V, (b) = -10V, (c) = -40V

*D. Effect of substrate bias on the morphological properties*

The effect of negative substrate bias on microstructure of the Mo films is illustrated by the plan-view SEM images. Without negative substrate bias, Fig.4a reveals that this film had a small grains microstructure and it was easier to find the presence of voids and porous structures in the Mo films because the sputtered Mo particles have a longer free pathway and a higher kinetic energy [12]. It is presumable that such presence of voids and porous structures also result in the increasing resistivity of Mo thin film. However, the surface of the Mo films elaborated with negative substrate bias of -10V had the porous and fibrous grains with fine valleys (see Fig. 4b). The morphology consisted of elongated grains with open grain boundary structure of tapered crystallites, while that the surface of Fig.4c reveals that the Mo films have a larger, densely packed grain microstructure with closed boundaries and no voids were obtained. Increasing the substrate bias from 0V to -40V promotes compactness films. This change in morphology is attributed to the effects of a more intense bombardment of the growing layer. Indeed, this intense bombardment causes an increase of kinetic energies of incident Mo particles on this layer which will tend to eliminate the porous structure by implanting atoms and filling voids. This process conducts to a much denser structure, subjected to intrinsic compressive stresses [13].

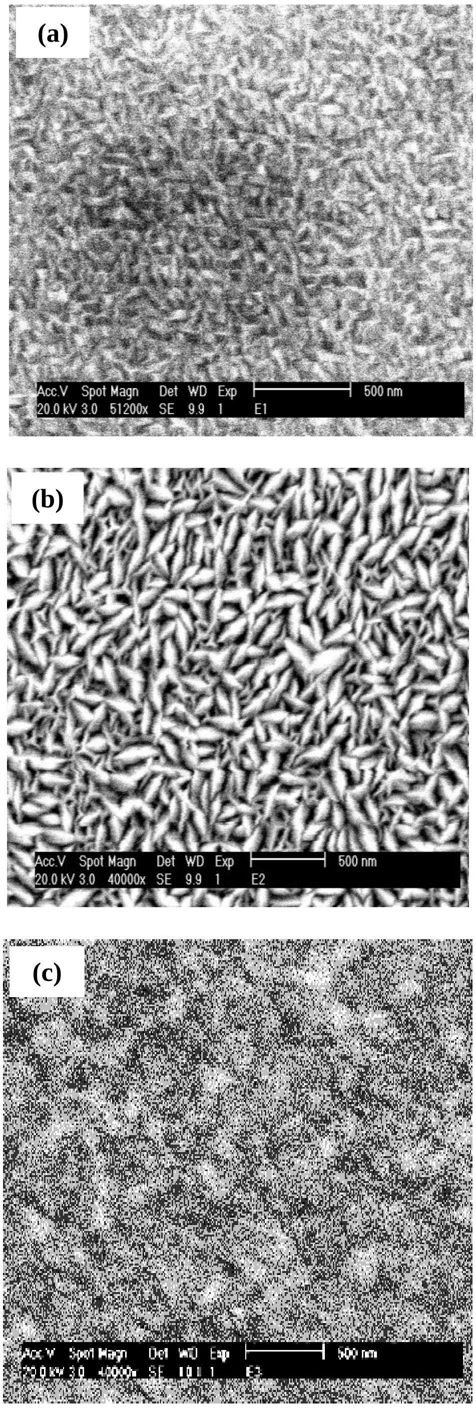


Fig. 4 SEM images of the Mo films elaborated with different value of substrate bias: (a) 0V, (b) -10V, (c) -40V

## IV. CONCLUSIONS

In this experiment, we analyzed the effect of negative substrate bias on the properties of Mo films prepared using rf magnetron sputtering system. The experimental results showed that both working pressure and negative substrate bias were important parameters for the deposition of Mo film. The resistivity of Mo film decreased when the values negative substrate bias increased. The crystallinity was improved with the negative substrate bias increasing from 0V to -40V. Moreover, the negative substrate bias not only affected the resistivity and the crystallinity but also directly affected on the surface morphology of Mo film. From these results, it is possible to obtain Mo thin films with adequate properties using only a single working pressure and with optimal substrate bias to be used as back contact for CIGS solar cells.

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