Rapid communication

Chemical resistance properties of molybdenum back electrodes used in non-vacuum Cu(In,Ga)Se₂ thin film solar cell

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ABSTRACT

The first step in fabricating copper-indium-gallium-diselenium solar cells (CIGS) is to deposit a thin film of molybdenum (to serve as the back electrode), on a glass substrate. Prior to depositing the absorption layer, the surface of the Mo back electrode is cleaned with acetone; however, this may cause the electrode to separate from the substrate. The aim of this study was to discover the specific cause of the separation, and arrive at a solution to correct this behavior. The result is a thin film comprising crystals of different sizes and orientations. Optimal results were obtained when the bi-layer Mo electrode was deposited on a substrate heated to a temperature of 373 K.

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Cu(In,Ga)Se₂ (CIGS) thin film solar cells are semiconductive compounds with a chalcopyrite structure I−III−VI. The CIGS absorption layer can be prepared by either vacuum [1−4] or non-vacuum [5−9] methods. Mo back electrodes used with CIGS solar cells are created using the non-vacuum method [10,11]. Although creating a bi-layer Mo back electrode improves adhesion to the CIGS absorption layer, a single-layer Mo back electrode enhances the electrical properties of the cells due to its incorporation of water vapor to supply the hydrogen bond at the electrode. This results in a thinner film, which reduces manufacturing costs [12]. Following deposition using the non-vacuum manufacturing method, oil and surface particles on the Mo back electrode must be cleaned with acetone. In single layer deposition, small acetone molecules diffuse along the columnar crystal structure through the grain boundary resulting in the Mo back electrode peeling away from the substrate, as shown in Fig. 1. To resolve this adhesion problem, the authors focused on two procedures aimed at improving chemical resistance to the acetone molecular diffusion: bi-layered deposition of the Mo and heating the substrate.

The experiments in this study used magnetron sputtering to prepare a bi-layer structure of molybdenum electrodes onto soda lime glass. The bi-layer Mo films were 1000 nm thick with a $R_{Mo}$% thickness ratio under conditions of low work pressure of 0.3 Pa/power of 100 W (lower layer, b) and high work pressure of 1.3 Pa/power of 200 W (upper layer, a) and the definition of these ratios as given by the Eq. (1).
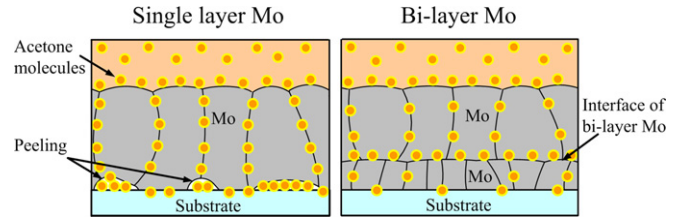
$$R_{Mo}\% = a/(a+b) \times 100\% \qquad (1)$$

where R_{Mo}% is the thickness ratio of Mo, a is the thickness of upper layer, b is the thicknesses of lower layer. Bi-layer samples with an R_{Mo} of 66% and 100% were deposited at normal substrate temperature, and bi-layer samples with an R_{Mo} of 66% were deposited on a substrate heated to 373 K. The samples were then soaked and ultrasonically cleaned in acetone (99.8%) for up to 10 min to observe their chemical resistance, peeling behavior, and the impact of acetone on bi-layer Mo back electrodes. A scanning electron microscope (SEM; JEOL TF-SEM JSM7000F) was used to observe the morphology in cross-section and analyze the chemical resistance of Mo back electrode. The crystal structure was analyzed using X-ray diffraction (XRD; CuKα, λ = 1.54052 Å) with an incident angle of 2°. The secondary ion mass spectrometry (SIMS, IMS-6f) was applied to identify the amount of residual carbon element after acetone cleaning. This implied that the residual acetone solution is the main factor to peel off Mo back electrode. The extraction voltages were 10 and 12.5 keV, respectively, and the O^{2+} ion current was 80 and 120 nA. These voltages yielded a sample surface energy of 5.5 and 8 kV.

This study used SIMS to analyze the depth of the carbon elements after being soaked in acetone for 4 min Fig. 2 shows that acetone molecules diffused along the columnar crystal structure of

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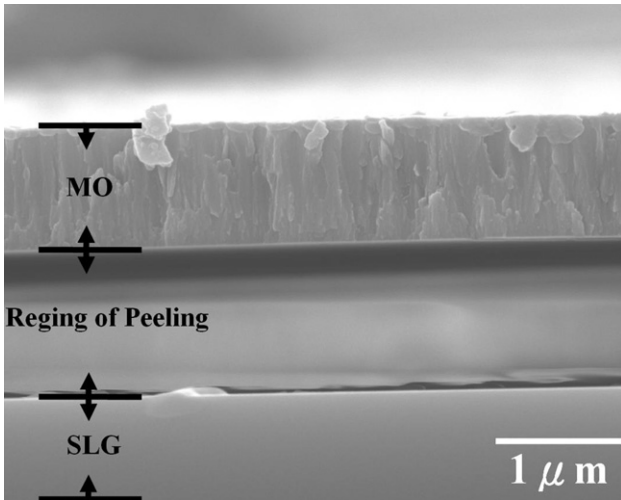
Fig. 1. Mo electrode peeling is observed at a working pressure of 0.3 Pa, at 200 W after soaking with acetone for 10 min.
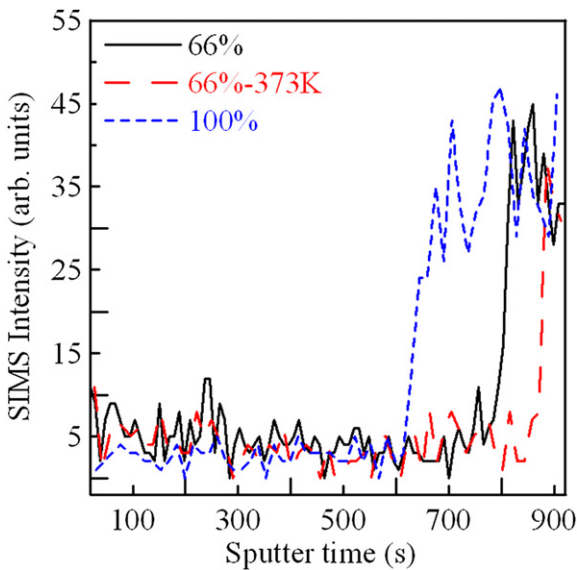

Fig. 3. A schematic diagram of acetone diffusion paths.

solution and the depth of the carbon in Mo back electrodes are the main causes of the separation between the Mo back electrode and substrate.

Fig. 4(a) illustrates patterns in the XRD thickness ratio for film deposited under a low work pressure of 0.3 Pa at 200 W. This illustrates the correlation between the XRD patterns of the Mo back electrodes when the R_{Mo}% range was between 66% and 100% with

the films with a thickness ratio of 100% reaching the bottom and eroding the bond between the Mo back electrode and the glass substrate due to the excessive thickness of the carbon composition. When the thickness ratio was reduced to 66%, the interface of bi-layer Mo introduce more mismatch between upper and lower layers Mo film which will block the acetone diffusion path by sub-grain of Mo [13]. These results illustrate the acetone diffusion model to compare the possible diffusion paths with different crystallization and texture, as show in Fig. 3.

Depositing films to a thickness ratio of 66% at a temperature of 373 K using glancing angle deposition resulted in the growth of Mo grains which increased the columnar crystal structure and inhibited the diffusion of acetone all the way to the bottom. This approach also enhanced the electrical properties of the Mo electrode and inhibited the damage caused by acetone molecular diffusion. Furthermore, SIMS measurements indicate that residual acetone

Fig. 2. Mo electrode carbon composition depth profiles at a working pressure of 0.3 Pa, at 200 W and thickness ratios of 66% / 100%; and 66% at 373 K after soaking with acetone for 4 min.
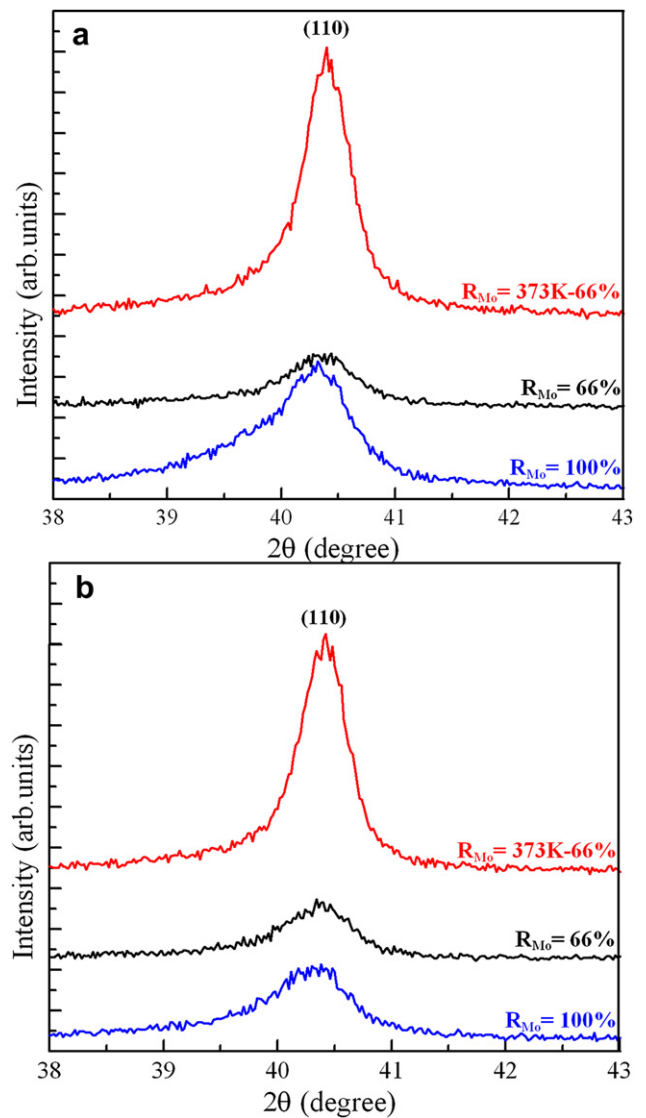
Fig. 4. Mo electrode XRD patterns at a working pressure of 0.3 Pa, at 200 W and thickness ratios of 66% / 100%; and 66% at 373 K, (a) Without acetone; (b) after soaking with acetone for 4 min.