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Innovative solution to avoid glass substrate bending in a chalcopyrite solar cell fabrication process

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ABSTRACT

Considering the chalcopyrite solar cell fabrication process, the commonly reported substrate bending effect that is observed after thermal process, in a front side halogen lamp-based annealing configuration (Rapid Thermal Annealing –RTA- equipment), has been investigated. We first proposed a simple model explaining the substrate bending shape dependence on the initial stress state within the molybdenum (Mo) layer (free, tensile or compressive). Then, we showed that it is possible to overcome this issue by simply using a reactive (oxygen based) sputtering process for the deposition of the Mo layer. Finally, we showed that using a bilayer structure Mo(O)/Mo allows a more precise control of the flatness of the annealed samples. To understand the mechanisms governing such changes in substrate bending, structural and morphological material changes as a function of oxygen flow have been investigated by using X-ray diffraction and scanning electron microscope imaging, respectively. The elemental distribution throughout the Mo(O)/Mo bilayer structure thickness was also investigated.

1. Introduction

After over more than four decades of chalcopyrite (namely CIGS, copper-indium-gallium-diselenide) solar cells development, molybdenum (Mo) is always used as a reference back contact material thanks to its low cost, abundance, excellent mechanical and electrical properties, low reactivity with and diffusivity into the CIGS layer, ability to conserve its properties at/after the high temperature deposition/annealing process of CIGS, and its ability to form an ohmic contact with the CIGS absorber layer [1–5].

Furthermore, sputtering deposition technique is commonly used for the deposition of Mo back contact of CIGS solar cells; the use of sputtering offers the possibility to manage the stresses within the Mo layer by tuning its deposition parameters [1,6]. Moreover, sputtered Mo layer density, which is also easily controlled by changing the deposition conditions, is known to play a very important role in controlling the out-diffusion of alkaline elements from the soda lime glass (SLG) substrate [7,8], when this one is used.

All these advantages and others, related to both Mo material and sputtering deposition technique, make the sputtered Mo layer a back contact of choice for CIGS solar cells in standard configuration (substrate configuration with about 2.5 µm thick CIGS absorber layer).

During the full solar cell fabrication process, high temperature (between 500 °C and 600 °C depending of process) annealing is used and, regardless of all the previously mentioned advantages of Mo back contacts, SLG substrates are commonly and unfortunately reported to bend due to mechanical stresses produced by the Mo layer. Researchers from Saint-Gobain Glass group have investigated this phenomenon and have concluded that the inhomogeneous temperature distribution over the substrate thickness during rapid thermal processing (RTP) (since the coated side is heated more than the uncoated side) is the main cause of substrate bending [9]. However, we have to introduce a somewhat discordant note into their explanation since it excludes the possibility of getting convex substrates at the end of the cooling down and we observed such a behaviour in some of our experiments.

As a solution, they have proposed the use of a dual side heating system and the joint deposition of an “auxiliary” layer on the uncoated side of the substrate in order to ensure a symmetrization of the temperature gradient in the substrate. In other words, this auxiliary layer is used to counterbalance the stress effects existing on both sides of the substrate [9].

Despite the predicted increase in production cost resulting from the use of an additional layer and of a dual side annealing system, the suitability of this suggested solution could be questioned, more especially for the development of particular applications such as photovoltaic windows with controlled transparency.

Firstly, we will hereby present a more complete explanation of substrate bending in case of a front side halogen lamps-based RTP. Both

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the temperature distribution throughout the substrate thickness and the stress state within the Mo layer, whatever it is related to native (tensile or compressive) stress resulting from the deposition technique or generated stress during the heating up due to the different thermal coefficients, are taken in consideration. Then, we will present an innovative solution for overcoming this substrate bending issue, which is far simpler than the one reported above [9].

2. Experimental

SLG substrates were first chemically cleaned by acetone, ethanol and DI-water in an ultrasonic bath for 10 min, each step, and then dried under N_2 flow. An Alliance Concept CT200 sputtering machine was used as deposition equipment. The deposition chamber was initially pumped down to 2.9×10^{-4} Pa in order to prevent any contamination of the thin films, caused by residual gas.

A rather usual bi-layer structure was used for the deposition of 500 nm-thick Mo thin films using the DC-magnetron mode and a constant Ar flow of 10sccm. An adhesion layer (100 nm) and a conductive layer (400 nm) were successively deposited, respectively under high and low pressure (a butterfly valve was used for pressure control).

The same layer structure has been reactively sputtered using a mixture of Ar and O_2 gas resulting in Mo(O) films. The Ar flow was kept unchanged while an O_2 flow was added and varied from 0.2 sccm to 0.8 sccm.

For the Mo(O)/Mo stacks, the O_2 flow was turned off during the last part of the deposition process. The corresponding “pure” Mo layer thickness is about 150 nm.

Following the film deposition, an annealing process was carried out, using a RTA furnace (JetFirst JIPELEC 200). It has been performed at atmospheric pressure under N_2 atmosphere at about 540 °C using the same set of parameters (temperature, profile) that is used for re-crystallising the CIGS absorber layer in our solar cell fabrication process.

The crystal structure of the thin films was analyzed by using X-ray diffraction equipment (Rigaku SMARTLAB) in Bragg-Brentano mode with Cu-Kα radiation. A FEG-SEM (Zeiss Ultra 55) was used to obtain surface and cross sectional images of the thin films. The elemental depth profile was obtained by the mean of a SIMS system (IMS 7f CAMECA) using Cs^+ ions as primary ions. The thickness of the different films was measured by surface profilometry (DektakXT stylus surface profiler). The electrical resistivity of the as deposited and annealed thin films was obtained by using a 4-probe system.

3. Results and discussion

3.1. Proposed model explaining substrate bending

The schematic sketches presented in Fig. 1 will drive the discussion about the possible scenarios that might occur during and after the RTP of Mo thin films at different stress states. First of all, one should point out that the initial stress state (σ_i) of the sputtered Mo thin films can be different from zero (internal or external stresses can be present) ($\sigma_i > 0$: tensile stress, $\sigma_i < 0$: compressive stress) (1). Furthermore, one should also point out the inhomogeneous temperature distribution throughout the substrate thickness that results from the single side configuration of the RTP (2).

Because the Mo layer has a lower expansion coefficient than the SLG substrate, the substrate surface is within compressive stress while the stress state within the molybdenum layer is changed by adding the contribution of the thermal component (σ_{th}) (2). Up to the softening temperature ($T_{softening}$) of the substrate, the system (substrate and Mo thin film) expansion is intuitively expected to be governed by the substrate behavior since the Mo film is at least four order of magnitude thinner than the substrate (3). One consequence of the inhomogeneity in temperature distribution throughout the substrate thickness is the different expansions of the top and the bottom of the substrate (3). At high temperature, this difference in expansion between the top and the bottom of the substrate is expected to induce a substrate deformation (4).

Once reaching the substrate softening temperature, the substrate changes its nature from rigid to viscous fluid-like and therefore the implied forces by Mo layer become dominant. At this stage, the Mo layer releases its stress -the initial stress (σ_i) plus the induced thermal stress (σ_{th})-, leading to a substrate deformation (bending). The shape of the induced deformation (bending) depends on both the nature and the intensity of the released stresses (5), (7) & (9).

If the initial stress within the Mo layer is tensile ($\sigma_i > 0$), then both initial and induced (thermal) stresses will pull on the substrate resulting in highly bended substrate with a concave-shape (5). Similarly, stress free Mo layer should result as well in a concave bended substrate. In this case, only the thermal component of stress will act and consequently less pronounced bending is expected (7). During the cooling down, the greater thermal contraction of the hotter side of the substrate will result in a more pronounced concave shape (6) (8).

On the contrary, Mo layer with highly compressive initial stress (higher than the induced thermal component) is expected to result in a pronounced convex shape bending after stresses relaxation (9). Depending on the initial compressive stress intensity and the annealing temperature, flat or less pronounced convex samples are achievable once cooling down is achieved (10) (11).

Based on this ascertainment of substrate bending, one can conclude that substrate flatness can be conserved by simply using as-deposited Mo thin films in adequate compressive stress level. This can be accomplished either by using low pressure deposition process or by introducing some impurities.

3.2. Reactively sputtered Mo(O) thin films

On the contrary to the commonly observed adhesion issues related to the use of low pressure sputtering processes [1,6], we found out that introducing oxygen during Mo sputtering (reactive process), previously proved by T. Yamaguchi et al. as an efficient process for stress engineering [10], does not affect the adhesion of the Mo(O) thin films. Furthermore, we were able to change the bending shape of annealed samples simply by tuning the oxygen flow during the sputtering process. The first obtained set of samples is presented in Fig. 2.

As can be seen, the concave bending radius was found to increase (so, the resulting bent aspect to decrease) when an oxygen flow of 0.4sccm is used, while an oxygen flow of 0.5sccm was found to be sufficient to change the bending shape from concave to very slightly convex. Furthermore, a more pronounced convex bending was observed for an oxygen flow of 0.6sccm, while higher oxygen flow led to a reduced convex bending.

The SEM surface and the corresponding cross sectional images of the reactively sputtered Mo(O) thin films using different oxygen flow are presented in Fig. 3. As can be clearly seen, Mo(O) thin film microstructure was found to be highly affected by the presence of oxygen during the deposition process. The thin film morphology was found to gradually change from regular grains surface with well-defined edges (for oxygen-free process) to grinded grains surface (for oxygen flow of 0.6 sccm). Correspondingly, the cross sectional feature was found to have a gradual change from a clear columnar structure to a fibrous structure.

This change in the microstructure can be simply explained by the knock-on linear cascade theory [11]: high energy particles penetrate the surface and randomly displace atoms from their equilibrium positions through a series of primary and recoil collisions, producing a volumetric distortion.

Consequently, and based on Davies' model [12], the stress state within the as-deposited Mo(O) layer is expected to change from tensile to highly compressive with the increase of partial O_2 flow during sputtering deposition process. Therefore, applying our paradigm for