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Full Length Article

DC and RF sputtered molybdenum electrodes for $Cu(In,Ga)Se_2$ thin film solar cells

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ABSTRACT

In this study, molybdenum (Mo) thin films are deposited at different working pressures and different target-substrate distances (D_{t-s}) (8 cm and 10 cm) under the excitation of the radio frequency (RF) or direct current (DC) power supply for applications in $Cu(In,Ga)Se_2$ (CIGS) thin film solar cells. The various material properties including dynamic deposition rate, electrical and optical properties, crystal structure and morphology are systematically investigated and compared for these RF and DC sputtered Mo thin films. Mo bilayer, i.e. bottom Mo layer prepared at a high working pressure and top Mo thin film sputtered at a low working pressure are employed as back electrodes in CIGS thin film solar cells. CIGS thin film solar cells with DC Mo/DC Mo bilayer have relatively higher efficiency as compared to the others with RF Mo layers, which might be related to a relatively easy migration of sodium (Na) passing through the DC Mo layers and entering into the CIGS absorbers. A high efficiency CIGS thin film solar cell of 16.2% has been achieved in this work.

1. Introduction

Molybdenum (Mo) thin film is usually used as back electrode in high efficiency Cu(In, Ga)Se_2 (CIGS) thin film solar cells due to its good electrical property as well as a high thermal stability and a strong chemical stability [1,2]. Normally, the Mo thin film is prepared by magnetron sputtering from Mo metallic target with the excitation of direct current (DC) or radio frequency (RF) discharge power supply [3,4]. The material properties of Mo thin films are often influenced by the process conditions like discharge power, working pressure, substrate temperature and etc. It was reported that high discharge power and low working pressure would lead to a good conductivity and a high light reflection [3,5]. However, a low working pressure might cause a large stress and lead to the peel-off of Mo thin film from the substrate when it is used in CIGS thin film solar cells as back electrode. Thus, prior to it another Mo buffer is first sputtered at a high working pressure (> 2 Pa) for good adhesion. Combined the bottom high pressure Mo buffer and top Mo thin film with good electrical and optical properties, the double Mo layers are a good option for back electrode in CIGS thin film solar cells. In addition to the electrode role, it could be a barrier hindering the migrations of some elements such as the sodium (Na) from glass substrate and ion (Fe) from stainless-steel (SS) foil substrate [6] into CIGS absorbers. Even though a small amount of Na impurities are good to the performance of CIGS thin film solar cells whereas a large content of Na impurities in CIGS absorber are detrimental. Differently, the ion (Fe) impurities in CIGS thin film from SS foil are combination centers and would lead to a low photo-generated current and low open circuit voltage [7]. Furthermore, the excitation type from DC or RF discharge power supply and substrate-target distance are also important factors to affect the material properties and device performance as well, which are significant to be investigated. For sputtering deposition technology, the substrate is normally put in Faraday dark space of the plasma, which is also important to sputtering deposition of thin films. Thus proper distance from substrate to target (cathode) might be optimal to specific properties of functional thin films. Different excitation types would form the different plasma statements, so as to effect the film growth and corresponding material properties as well as the performances of the optoelectronic devices.

In this study, the Mo thin films were prepared by magnetron sputtering from a Mo metallic target under the excitation of DC or RF discharge power supply. The various material properties of Mo thin films including optical and electrical properties related to the deposition rate, morphology and crystal structure were systematically investigated. In addition, the Mo thin films were applied in CIGS thin film solar cells as back contacts and the corresponding performances of solar cells were also studied.

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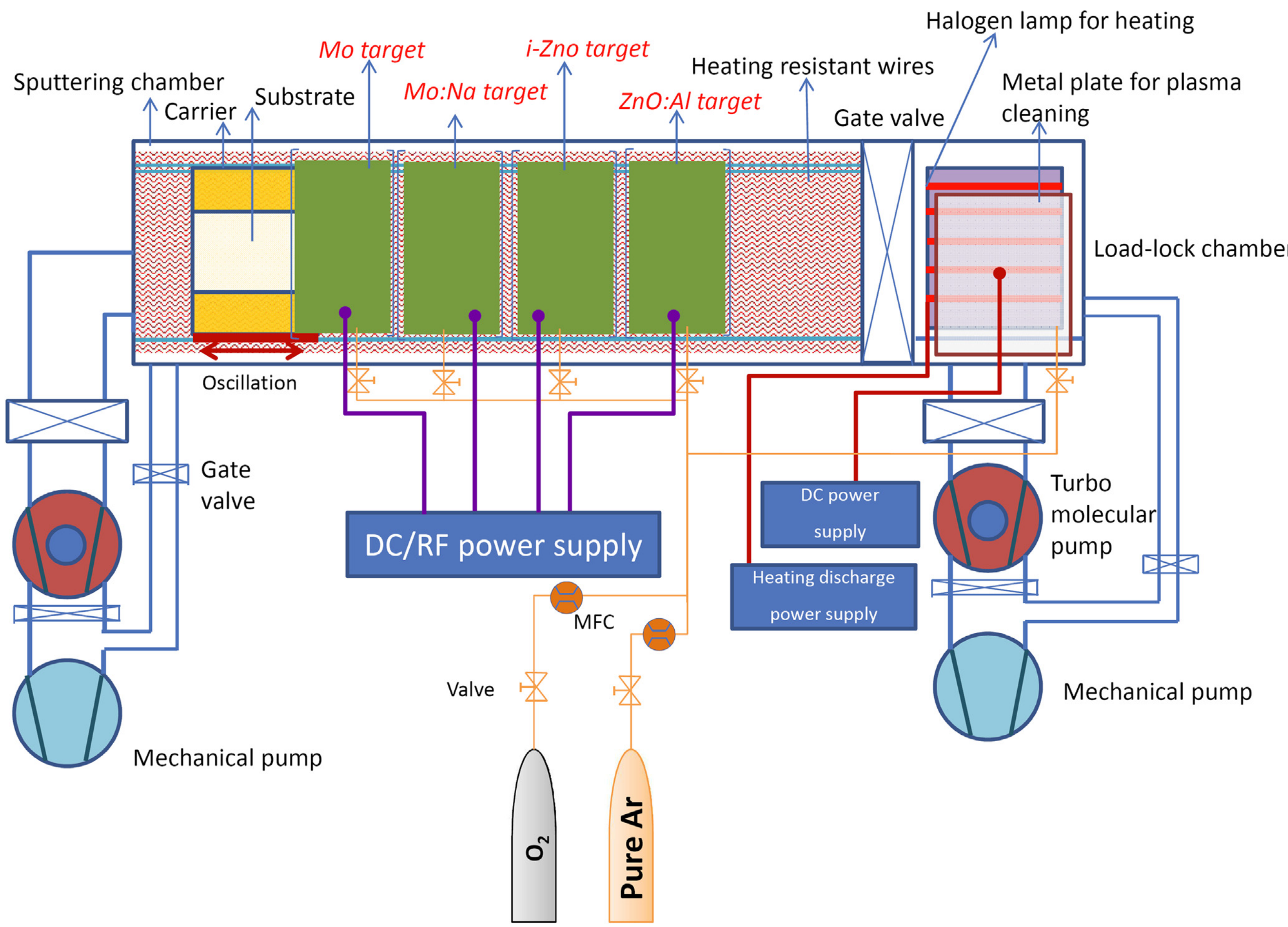

Fig. 1. Schematic of in-line vertical magnetron sputtering system, where the Mo target is installed on the cathode position on the left side. The substrate on the holder of the carrier oscillates forwards and backwards in the front of the targets during sputtering process. The back plate with heating wires is installed inside for heating substrate. Before the sputtering, the substrate is often degassed by heating with the halogen lamps and cleaned the dusts by negative oxygen plasma.

2. Experimental details

Mo thin films were prepared by DC or RF magnetron sputtering technology on 2.0 mm thick soda lime glass (SLG) substrates (15.6 × 15.6 cm^2) from a Mo metallic target (99.99%) on a left cathode position in our home-made in-line vertical magnetron sputtering system as shown in Fig. 1. In the sputtering chamber there were four rectangular cathodes with the same sizes of 24 × 8 cm^2 that can be mounted different target materials for preparations of various thin films. Thus, in addition to the left cathode position for Mo metallic target here, a rectangle Mo:Na, an intrinsic ZnO (i-ZnO) and a ZnO:Al_2O_3 (97.5:2.0 wt %) planar ceramic targets were also mounted on other three cathode positions in the deposition chamber. Pure argon (Ar) gas from a pipe line was used as sputtering gas and other gases like oxygen or nitrogen could be inputted into the chamber as reactive gas when the metallic oxide or metallic nitride was prepared by reactive sputtering. The substrate on the holder of the carrier oscillates forwards and backwards parallel to the targets during sputtering process. The back plate with heating wires was installed inside for heating substrate. Prior to the sputtering, the substrate was often degassed by heating with the halogen lamps and also cleaned the dusts by negative oxygen plasma in the load-lock chamber. The DC discharge power was kept constant at 200 W under the constant discharge power mode while a RF discharge power of 390 W was employed for deposition of Mo thin films. The working pressure was changed from 0.5 Pa to 4 Pa by adjusting the inputted Ar gas flux. The target-substrate distance ($D_{t\text{-}s}$) could be adjusted and chosen at 8 cm and 10 cm in this work.

The sputtered double molybdenum (Mo) were prepared with bottom and top Mo layers, which were prepared by DC sputtering or by RF sputtering under the working pressures of 4 Pa and 0.5 Pa, respectively. The CIGS absorbers were co-evaporated on the Mo electrodes by a 3-stage co-evaporation process. More details about the co-evaporation system could be referred in reference [7]. Cadmium sulfide (CdS) buffer layers were grown on CIGS absorbers with the chemical bath deposition (CBD) method. After growth of CdS buffer, an intrinsic zinc oxide (i-ZnO) thin films of about 80 nm and an aluminum doped zinc oxide (ZnO:Al) thin films of about 300 nm were prepared by RF non-reactive magnetron sputtering, which were employed in CIGS thin film solar cells as window layers. More details about this could be referred to our previous study [8]. Finally, the Ni(~50 nm)/Al(~1000 nm)/Ni (~50 nm) grids were prepared on ZnO:Al/window layers by electron beam evaporations with a mask. The CIGS thin film solar cells with the structure of SLG/Mo/CIGS absorber/CdS/i-ZnO/n-ZnO:Al/Ni/Al/Ni grid were fabricated. In order to enhance the photo-generated current of CIGS thin film solar cells, the anti-reflection MgF_2 thin films of 105 nm were prepared by electron beam evaporation.

The thicknesses for all thin films here were measured with a surface profiler (Bruker Dektak XT). The crystal structure of Mo thin films was characterized by a Bragg-Brentano X-ray diffraction (XRD) measurement using the x-ray of Cu $K_{\alpha 1}$(1.54056 Å) radiation at a small incidence angle of 7° (Bruker D8 Advance). The sheet resistance of Mo thin films was measured by four point probe and corresponding resistivity was calculated based on the measured sheet resistance and thickness. The optical property i.e. light reflection here of Mo thin films