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Annealing effect in structural and electrical properties of sputtered Mo thin film

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ABSTRACT

In this study, the effects of vacuum annealing on the structural and electrical properties of DC-sputtered molybdenum (Mo) thin films have been investigated. Mo thin films were deposited by DC sputtering and subsequently subjected to vacuum annealing in a tube furnace from 350 to 500 °C. Films that were deposited with different temperatures showed good adhesion with soda lime glass substrate after "tape testing". X-ray diffraction (XRD) spectra have indicated existence of (1 1 0) and (2 1 1) orientations. However, $I(1\,1\,0)/I(2\,1\,1)$ peak intensity ratio decreased for all vacuum annealed Mo films compared to as-sputtered films indicating change of preferential orientation. This suggests vacuum annealing can be employed to tailor the Mo thin film atomic packing density of the plane parallel to the substrate. SEM images of surface morphology clearly show compact and dense triangular like grains for as-sputtered film, while annealed films at 350 °C, 400 °C and 450 °C indicate rice-like grains. Stony grains with less uniformity were detected for films annealed for 500 °C. Meanwhile, electrical resistivity is insensitive to the vacuum annealing condition as all films showed more or less same resistivity in the range of 3×10^{-5}–6×10^{-5} Ω cm.

1. Introduction

Sputter deposited molybdenum (Mo) thin film has been the primary choice as back contact material for thin film solar cells (TFSCs) especially for Cu(In,Ga)Se_2 (CIGSe) based solar cells since the early stage of research development and up to the current state-of-the art high efficiency CIGS device [1,2]. Thermal as well as chemical inertness of Mo during high temperature deposition of absorber layer and formation of ohmic contact with CIGSe via unintentionally induced adventitious p-$MoSe_2$ interfacial layer have rendered Mo advantage over other investigated metals [3–5]. In addition, pioneering work of Scofield et al. in depositing DC-sputtered Mo film on soda lime glass (SLG) substrates which is both adhesive and possesses low resistivity further cemented the role of Mo as an impeccable choice of back contact not only for the established CIGSe quaternary material but also has been an automatic back contact preference for upcoming novel selenium free absorber layers such as Cu_2ZnSnS_4 (CZTS), $CuSnS_3$ (CTS) and SnS [6–9]. However, further Mo thin film optimization is needed due to the expected different interfacial reaction kinetics of sulphur and molybdenum. Different Mo microstructural property is expected to influence the interface property of Mo and absorber layer [10,11].

Hence, in this study we have investigated the effects of thermal annealing at different temperatures in vacuum condition on the structural, surface morphology and electrical properties of DC-sputtered Mo thin film. Greater attention is given to the evolution of preferred orientation in the annealed films at different temperatures. Variation in preferred orientation is then correlated with planar packing density which is postulated to play crucial role in determining the interface properties of Mo and the subsequent photovoltaic absorber layer. Routine study of grain size and lattice parameter variation obtained from (XRD) analysis is also presented. Hall measurement was used to measure electrical resistivity of Mo films and the obtained values are correlated to the microstrain and dislocation density which dictates the electron scattering mechanism in thin film. Surface topology features are correlated to the sheet resistance of Mo film via spreading sheet resistance measurement (SSRM) technique.

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2. Experimental

2.1. Materials and methods

The thin film preparation in this study can be divided into two processes, direct current (DC) magnetron sputter deposition of Mo thin film and subsequent vacuum annealing in tube furnace. Soda lime glass substrates of 75 mm × 25 mm × 2 mm were pre-cleaned ultrasonically in methanol–acetone–methanol–deionised water sequence and dried with N_2 gas flow. A 50.8 mm diameter Mo (99.95%) sputtering target (Kurt. J. Lesker) was used as source material. Pre-sputtering was carried out for 20 min with 50 W power to remove the contamination on the target surface. Deposition chamber base pressure was brought down to 10^{-4} Pa by turbomolecular pump and the working pressure during all the deposition run was maintained at 1.33 Pa by flowing 2 sccm of purified Ar (99.99%) as the working gas into the chamber. DC power, substrate holder rotation and target to substrate distance (sputter down) were fixed at 100 W (≈5 W/cm^2), 10 rpm and 100 mm respectively. With these sputter deposition parameters, homogenous sputtered thin films were able to be reproduced with thickness variations across the SLG substrates not more than 6%. Sputter deposition process was carried at room temperature. However, increase in substrate temperature was observed due to non-intentional heating caused thermal energy transfer between highly energetic sputtered particles and substrate. Upon completion of Mo sputter deposition, the samples were left inside the chamber under vacuum environment for cooling process to avoid oxidation. A 500 nm thick Mo film was obtained for a deposition time of 60 minutes. Sputtered Mo thin films were then transferred into a tube furnace in an alumina crucible for annealing process. Base pressure of the tube furnace was brought down to 2.66 Pa by mechanical roughing pump and internal furnace temperature was increased from room temperature to the desired annealing temperature with a fixed ramp-up rate of 25 °C/min. Mo thin films were annealed at 4 different temperatures of 350 °C, 400 °C, 450 °C and 500 °C with constant holding time of 60 min. In situ temperature control and monitoring was carried out by a K-type thermocouple which was connected to a digital handheld temperature thermometer. The thermocouple was placed underneath the alumina crucible through a feed-through port. Real time temperature monitoring and control resulted in temperature deviation lesser than ±5%.

2.2. Film characterization

Structural and crystallinity properties as well as the crystal orientation along the film's surface normal were examined by BRUKER aXS-D8 Advance Cu Kα diffractometer at room temperature. XRD patterns were recorded in the 2θ range from 10° to 80° with a step size of 0.02° using Cu Kα radiation wavelength, λ = 1.5408 Å. Grain size, surface morphology and cross-sectional view were observed by using Carl Zeiss Merlin field emission scanning electron microscope (FESEM) which was operated at 3 kV while surface topography and roughness were analyzed by using Integra Prima, NT-MDT Scanning Probe Microscope (SPM) with non-contact mode settings. Spreading sheet resistance measurement (SSRM) was conducted by using the same SPM setup in contact mode with a conductive tip. DC bias voltage of 1 V was applied to the tip while the sample was grounded and the resulting current flow was recorded and plotted as a function of probed surface area. The mean crystallite sizes (D) of the films was calculated using Scherrer formula [12]

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

Table 1
Sample identification nomenclature and corresponding film thickness and adhesion test outcome.

Sample identification	Annealing temperature (°C)	Film thickness (nm)	Scotch tape test
Mo-AS	None (as-sputtered)	517.3	Pass
Mo-350	350	517.3	Pass
Mo-400	400	517.3	Pass
Mo-450	450	509.9	Pass
Mo-500	500	539.6	Pass

whereby λ is the X-ray wavelength (0.15406 nm), and β is the full width at half maximum [FWHM] of the film diffraction peak at 2θ in radian and θ is the Bragg diffraction angle in degree. The microstrain, ε and dislocation density, δ developed in the thin films are calculated from Eqs. (2) and (3) respectively [13,14]

$$\varepsilon = \frac{\beta}{4\tan\theta} \quad (2)$$

$$\delta = \frac{n}{D^2} \quad (3)$$

whereby n is a factor, which is almost equal to unity for minimum dislocation density and D is the grain size. The electrical parameters such as carrier concentration, mobility, and resistivity were measured by Hall Effect measurement system, HMS ECOPIA 3000 with a magnetic field of 0.57 T and probe current of 10 mA for all the samples.

3. Results and discussion

3.1. Structural properties of Mo films

Cross-sectional image viewing by using FESEM was used as a method to determine the Mo film thickness. Table 1 shows the measured thickness as well as the outcome of Scotch tape test in which all the films had shown good adherence to the SLG substrates.

Scotch tape test was performed on samples immediately after sputter deposition process for as-sputtered films and after the completion of natural cooling in tube furnace following the thermal annealing process for annealed films. No signs peeling off or cracking were observed for all Mo films even after 6 months of deposition. Fig. 1 shows the XRD pattern for as-sputtered and annealed Mo films from 10° to 80°. All films exhibited only two primary peaks of (1 1 0) and (2 1 1) orientations indicating polycrystalline

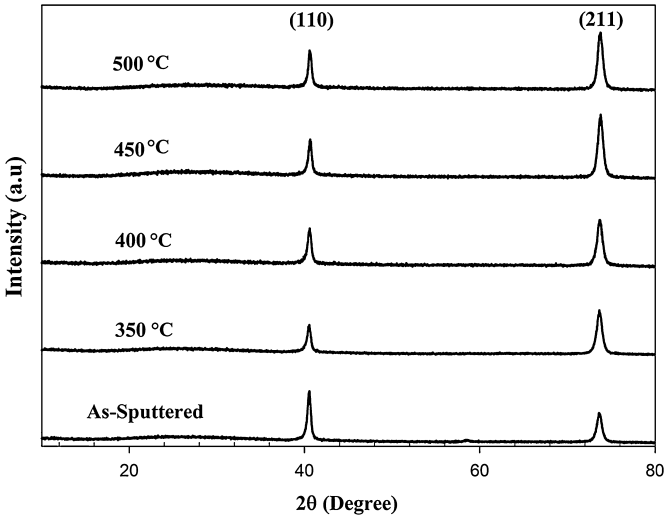

Fig. 1. XRD patterns of as-sputtered and annealed Mo thin films.

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