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Effects of RF magnetron sputtering deposition process parameters on the properties of molybdenum thin films

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ABSTRACT

RF-sputtered molybdenum (Mo) thin films have been deposited by varying operating pressure (0.88 to 2.66 Pa at 100 W) and RF power (50 W to 125 W at 1.33 Pa). The variation in process parameters studied herein primarily alters the kinetic energy of the sputtered particle during the Mo deposition process. Microstructural properties of the resulting Mo thin films such as crystal structure, orientation, surface morphology, microstrain, dislocation density and electrical properties were characterized and presented in this paper. The variation in the aforesaid growth parameters induced different growth rates in the range of 3.84–12.43 nm/min and subsequently Mo films with varying thickness in the range of 0.7–1.7 μm. All Mo films exhibited preferred crystallographic orientation of (110). Lowest operating pressure (0.88 Pa) resulted in Mo film with compressive stress and subsequently peeled off due poor adhesiveness on soda lime glass (SLG) substrates. The resistivity of Mo films was found to be in the range of 40–800 μΩ·cm and dependent on the thickness and structural imperfections such as microstrain and dislocation density.

1. Introduction

Cu(In,Ga)Se_2 (CIGSe) based thin film solar cells (TFSCs) have emerged from the promising photovoltaic material category to an established, proven, and marketable technology due to the rigorous research activities around globe in the past three decades. To date, the highest confirmed laboratory scale cell and module efficiencies for CIGSe TFSCs are 22.6% [1] and 17.5% [2], respectively. The generic structure of substrate type CIGSe TFSCs is shown in Fig. 1. One of the key components in the fabrication of highly efficient CIGSe TFSCs is the back contact layer. The preferred choice for the back contact layer in terms of deposition method and material is the sputtered molybdenum (Mo) either radio frequency (RF) or direct current (DC) [3–6]. The establishment of Mo thin film for the role of back contact in CIGSe TFSCs is essential due to several aspects, such as chemical and thermal stress stability towards the subsequent absorber layer deposition process, formation of ohmic contact with CIGSe via spontaneously induced beneficial p-$MoSe_2$ interfacial layer, and sodium (Na) migration from soda lime glass (SLG) substrate through the Mo layer into the CIGSe absorber layer, which is beneficial to the overall solar cells performance [7,8] etc. Furthermore, other upcoming thin film solar cells with novel absorber layer material such as Cu_2ZnSnS_4 (CZTS), Cu_2SnS_3 (CTS), and SnS are adapting the same structure as shown in Fig. 1 [9–11].

Revolutionary work of Scofield et al. on DC sputtered Mo films with bi-layer structure, which possesses low resistivity as well as good adhesion on the SLG substrate simultaneously, has further validated the Mo as the preferred back contact material [12]. The aforesaid key factors such as low resistivity, good adhesion to SLG substrates, p-$MoSe_2$ interfacial layer formation, and Na doping mechanism have shown a significant dependency on the Mo film microstructure property [12,13]. On the other hand, Mo film microstructural properties is strongly correlated to the sputtering deposition process variables, such as sputtering mode (RF or DC), operating pressure, deposition power, substrate temperature, throw distance etc.

In our previous work [14], electrical and structural properties of DC-sputtered Mo thin films with ex-situ thermal annealing were investigated. In this study, Mo films with varying thickness were deposited by RF magnetron sputtering method with the aim of elucidating the evolution of Mo electrical and microstructural properties. The Mo film thickness in this study was varied by deliberately inducing changes in the deposition

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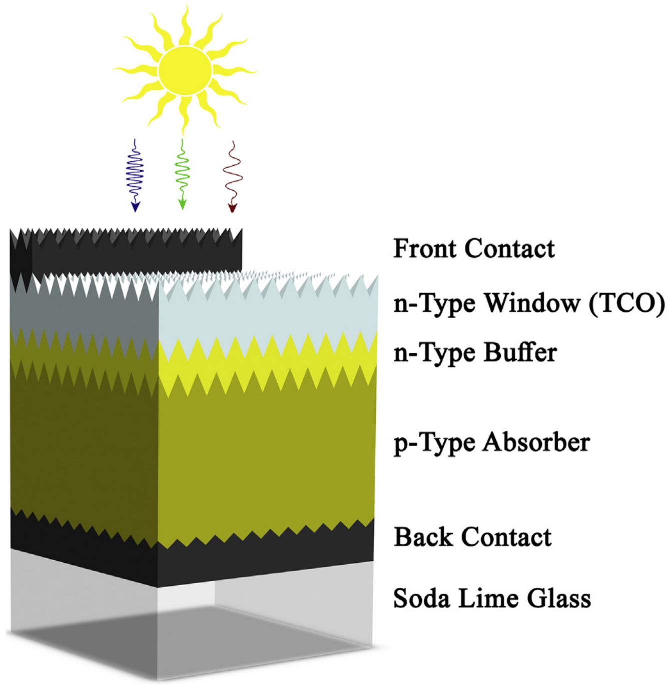

Fig. 1. Schematic of CIGSe thin film solar cell.

process parameters, namely operating pressure and RF power. These two process variables are known to alter the growth rate, microstructural, and electrical properties.

2. Experimental methods

Confocal RF magnetron sputtering system was used to deposit Mo thin films on 75 mm × 25 mm SLG. Preceding to deposition, all SLG substrates were ultrasonically cleaned in following sequence of methanol-acetone-methanol-deionized water and finally dried by jet stream of industrial N_2 gas. 50.8 mm diameter Mo (purity 99.99%) target purchased from Kurt J. Lesker, USA as a source material was placed at the angle and distance of 20° and about 14 cm from the substrates, respectively. The target was pre-sputtered prior to deposition to remove any possible contamination on its surface. Deposition chamber was vacuumed to 0.133 mPa roughly, and all runs were performed at room temperature (RT) with substrate rotation of 10 rpm. Argon gas flow rate and RF power were varied, which resulted in different operating pressure (0.88 Pa, 1.33 Pa, 1.99 Pa and 2.66 Pa at 100 W) and RF power (50 W, 75 W, 100 W and 125 W at 1.33 Pa). An averaged deposition time of 120 mins yielded sputtered Mo thickness in the range of 0.7 to 1.7 μm.

Structural properties such as the crystallographic orientation normal to the sample's surface was measured by BRUKER aXS-D8 Advance Cu-Kα diffractometer at RT. XRD patterns in the 2θ range were recorded from 10° to 60° with a step size of 0.02° via Cu Kα radiation wavelength of λ = 1.5408 Å. Surface morphological properties such as grain size and cross-sectional view were monitored by Carl Zeiss Merlin field emission scanning electron microscope (FESEM) at 3 kV. The mean crystallite sizes (D) of the films were calculated using Scherrer formula [15]:

$$D = (0.9 \times \lambda)/(\beta \times cos\theta) \quad (1)$$

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 micro-strain, ε and dislocation density, δ developed in the thin films were calculated from eq. (2) and (3), respectively:

$$\varepsilon = \beta/(4 \times tan\theta) \quad (2)$$

$$\delta = n/D^2 \quad (3)$$

whereby, n is a factor, which is almost equal to unity for minimum dislocation density and D is the grain size [16,17]. The electrical parameters such as mobility, carrier concentration, and resistivity were measured by HMS ECOPIA 3000 Hall Effect measurement system with a magnetic field of 0.57 T and probe current of 10 mA.

3. Results and discussion

3.1. Growth rates and structural properties

Table 1 shows the measured thickness and growth rate as well as the outcome of Scotch tape test, which was performed on the samples immediately after the sputtering deposition process. As shown, intentional variation in the growth parameters of RF power and operating pressure as in this study resulted in different growth rates. Higher growth rate is observed for increasing RF power due to the higher density and energy of charge carriers (electrons and ions), which results in higher ejection rate of Mo atoms from the target. These charge carriers can transfer their energy or a part on the total energy deposited onto the substrates [18,19]. If the ion energy is high, it may also result in re-sputtering of the deposited film, leading to a loss in energy [20], which might be a possible explanation for the saturating growth rate when the RF power is increased from 100 W to 125 W. Conventionally, RF sputtering deposition rate initially increases with increasing operating pressure up to a certain threshold rate before rapidly decreasing with further increase in operating pressure [21,22]. The initial increase in deposition rate is due to higher sputter yield and the subsequent decrease in deposition rate with increasing operating pressure is due to the pronounced collision between sputtered atoms and Ar atoms [23,24]. Interestingly, in this study, continuous higher growth rate trend has been observed as the operating pressure is increased from 0.88 Pa to 2.66 Pa. Hence, it is postulated that, the combination of sputtering system geometry (throw distance and confocal cathode alignment), and the range of operating pressure investigated in this study results in sputtering mechanism, which is operative in the higher sputter yield regime. This explain the absence of decreasing deposition rate trend with increasing operating pressure, which also has been previously reported [25]. All samples passed the tape test except for Mo films deposited at 0.88 Pa (shown in Fig. 2), which corresponds to the film deposited at the lowest operating pressure. The poor adhesion of Mo films deposited at 0.88 Pa is in good agreement with the outcome of Scofield et al. whereby the failure of Mo adhesion to the SLG substrates is linked with the build-up of internal compressive stress during the nucleation process [12]. Film with compressive stress tends to buckle up and detach from the

Table 1
Thickness, growth rate and outcome of Scotch tape test of Mo film deposited at different operating pressure and RF power.

Deposition parameters Pressure	power	Thickness (nm)	Growth rate (nm/min)	Scotch tape test
0.88 Pa	100 W	692	6.12	Fail
1.33 Pa	100 W	1150	9.42	Pass
1.99 Pa	100 W	1251	10.87	Pass
2.66 Pa	100 W	1641	12.43	Pass
1.33 Pa	50 W	876	3.84	Pass
1.33 Pa	75 W	993	6.51	Pass
1.33 Pa	100 W	1150	9.42	Pass
1.33 Pa	125 W	982	9.44	Pass