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MOLYBDENUM BACK-CONTACT OPTIMIZATION FOR CIGS THIN FILM SOLAR CELL

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*Molybdenum (Mo) thin films are most widely used as an ohmic back-contact in the copper indium diselenide (CIS) and its alloy copper indium gallium diselenide (CIGS) based thin film solar cell. Radio frequency (RF) magnetron sputtering system used to deposit Mo thin films on soda lime glass substrate. The deposition was carried out using argon (Ar) gas at different Ar controlled (working) pressures (*1 *mTorr to* 10 *mTorr) and at different RF powers (*60 *W to* 100 *W). The influence of both the working pressure and the RF power on the Mo thin films was studied by investigating its structural, morphological, electrical, and optical measurements. The results reveal that a stress-free, low-sheet-resistance (~*1 *Ω/□), and reflecting (~* 55 *%) Mo thin film was observed at* 1 *mTorr working pressure and* 100 *W RF power.*

Keywords: *RF MAGNETRON SPUTTERING, MOLYBDENUM THIN FILM, STRUCTURAL, MORPHOLOGICAL, ELECTRICAL, OPTICAL CHARACTERIZATION.*

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1. INTRODUCTION

Molybdenum (Mo) is the most important material used as a back-ohmic contact in copper indium diselenide (CIS) and its alloy copper indium gallium diselenide (CIGS) thin film solar cells. The metallic back-contact, Mo, serves as substrate on which the absorber layer i.e., CIS/CIGS is deposited. Mo is more favorable as a back-contact layer in CIS and CIGS thin film solar cells because its diffusion into the absorber starts above 600 °C [1] and, in addition, it offer a resistance to alloying with copper and indium [2]. Studies on the deposition of the Mo thin films by radio frequency (RF) magnetron sputtering have been reported in the literature [3, 4] and, recently, about 20 % energy conversion efficiency [5] has been reported for CIGS thin film solar cell. The adhesion property of the Mo thin film, which has direct impact on the film resistance, was depends on the deposition parameters like RF power, working pressure, etc. Studies on the correlation between the working gas pressure and growth of the film have been reported in the literature [3, 4].

In the present work, the emphasis was to deposit Mo thin films using the RF magnetron sputtering to achieve a low resistive and a well adherent Mo thin film. In order to achieve the above requirements the RF power was varied from 60 W to 100 W and the working pressure was varied from 1 mTorr to 10 mTorr. The structural, morphological, electrical, and optical properties of the Mo thin films were studied as a function of RF power and working pressure.

2. EXPERIMENTAL DETAILS

2.1 Film preparation

Mo thin films were prepared on organically cleaned soda lime glass substrate (50 mm × 50 mm) by using the circular RF magnetron sputtering system, (Huttinger Elektronik 600W, U.S.A.), at different working pressures and different RF powers. The distance between Mo target (2 - inch diameter, 5 mm thick) and the substrate was 90 mm and the substrate's rotation was kept at ~40 RPM for obtain uniform film. The thickness was kept constant at 1000 nm for all deposition and it is measured in-situ by using a quartz crystal thickness monitor. The argon (Ar) gas was used as a sputtering gas, whose flow was controlled by the needle valve. The deposition of Mo thin films was carries out in vacuum coating unit (model - 15F6 HINDHIVAC, Bangalore, India).

The following process was used for the deposition of all Mo thin films. Initially, the chamber was evacuated to a base pressure close to 1×10^{-5} mbar. Then the Ar gas was introduced into the chamber using a needle valve. Using the Ar flow, we set the chamber pressure at a desired working pressure and, subsequently, by throttling the high vacuum valve the pressure was maintained at the desired value during the deposition process. Before initiating the actual deposition of Mo layer on soda lime glass substrate, the target was pre-sputtered for 5 minutes to remove the surface contamination if any. We have first grown Mo thin films by varying the working pressure from 1 mTorr to 10 mTorr and keeping the RF power constant at 100 W. Subsequently, the films were characterized to find out the optimum pressure; thereafter, the films were prepared at this optimum pressure by varying the RF power from 60 W to 100 W.

2.2 Film characterization

The structural and morphological characterizations of Mo thin films grown at different working pressures and at different RF powers were carried out using the glancing incident X-ray diffractometer (GIXRD) (Bruker D8 ADVANCE), and atomic force microscopy (AFM), respectively. The four-point probe method is used for sheet-resistance measurement. We have used keithley 2420C source meter in four-point method. The optical reflectance of the Mo thin films was measured using the reflectivity setup, which consists of the apparatus like the monochromator (CM110), tungsten halogen lamp, silicon detector (818-SL), lock-in amplifier (SR 530), and a cube beam splitter. The whole reflectivity setup was automated by using the Lab-VIEW software (version 8.2).

3. RESULTS AND DISCUSSIONS

3.1 Different Working Pressures

3.1.1 Structural Characterization

The influence of the working pressure (1 mTorr to 10 mTorr) on the Mo thin films is observed from the XRD spectra shown in Fig. 1, by the means of the change in the full width half maxima (FWHM) and the shifting of the

2θ value from its bulk value i.e., 40.05°. Using the values of FWHM, the crystallite size (L), was calculated using the Scherrer's formula [6],

$$L = \frac{0.94\lambda}{\beta \cos\theta} \tag{1}$$

where λ is the X-ray wavelength (λ = 1.540 Å) and β is the FWHM of the (110) peak. The observed d-value of (110) plane for 1 mTorr is matched with the JCPDS data card 01-1208. By using the d-value and the (hkl) value of the peak, the lattice constant (a) was derived from the relation [6],

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \tag{2}$$

The variations in the value of a, and L is shown in Table 1. From the XRD spectra, shown in Fig. 1, the change in the FWHM of the (110) peak and the shifting of the 2θ value from its bulk value i.e., 40.05°, for the same peak are clearly noticed.

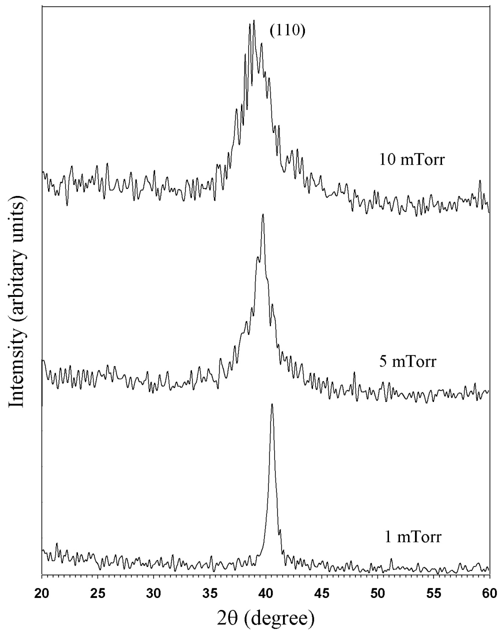

Fig. 1 *– The XRD spectra of the Mo thin films grown at different working pressures (from 1 mTorr to 10 mTorr) and a constant RF power (100 W) show that by increasing the working pressure the crystallinity of the Mo thin film degrades due to the decrease in the deposition rate*

The broadening of the FWHM and the shifting of 2θ value are both related to the structure defects in the films and so, indication of the stress present in the film. The stress is directly related to the lattice strain. The percentage of strain is determined from the lattice constant, a [7],

$$strain(\%) = \frac{\Delta a}{a_0} \times 100 \quad (3)$$

where a_0 = bulk lattice constant of Mo = 3.1469 Å, and Δa = difference between the lattice constant of observed Mo thin film and the bulk Mo. Knowing the strain, we can estimate the isotropic stress [8],

$$y = \frac{E}{2x_f} \times \frac{a_0 - a}{a_0} \quad (4)$$

where, E is the Young modulus and x_f is the Poisson ratio. For the calculation of the stress, we have used the bulk values of E and x_f viz. 3.36×10^{11} Nm^{-2} and 0.298, respectively [9]. The values of crystallite size L, lattice constant a, percentage strain, estimated stress, 2θ angle and its corresponding d-values for Mo thin films grown at different working pressures are tabulated in table 1. At lower working pressure (1 mTorr) the highest crystallite size, 143.4 Å was observed, which shows the improvement in the crystallization of the Mo thin films.

Table 1 – *The 2θ value of the* (110) *plane, its corresponding d-value, crystallite size, L, and lattice constant, a, of Mo thin films grown at different working pressures by keeping the RF power constant at* 100 *W*

Working Pressure (mTorr)	d-value (Å)	2θ (degree)	Crystalline size, L (Å)	Lattice constant, a, (Å)	Strain (%)	Stress ($\times 10^9$ Nm^{-2})
1	2.22174	40.572	143.2	3.1420	0.1562	0.88
5	2.27067	39.661	56.7	3.2112	2.0427	-11.51
10	2.33142	38.586	37.7	3.2971	4.7728	-26.90

During the deposition of the thin films, the strain or stress arises from the incomplete process of structural ordering occurring during the film growth and may be due to the substrate contamination. The grain growth process in the film mainly depends on the deposition or condensation rate and the deposition temperature. By varying the working pressure, the deposition rate varies. At lower pressure, at 1 mTorr, the collisions of the sputtered particle with the gas will be reduced and therefore the deposition rate higher ~3.2 Å/s in our case. Owing to this, the sputtered particles with its improved energy reduce its arrival angle to the substrate. Thus, the possibility of the formation of inter-granule void reduces, which, in turn, results in the dense structure of the grains and hence the improvement in the crystallinity of the film [8]. The higher crystallite size, 143 Å, due to the dense microstructure of the film was observed at 1 mTorr working pressure shown in Eable 1.

On the other hand, at a higher pressure, greater than 5 mTorr in our case, due to the multiple collisions of the sputtered particle with the gas, the deposition rate is reduced, ~2.3 Å/s at 5 mTorr and ~1.5 Å /s at 10 mTorr. This leads to a reduction in the energy of the sputtered particle as well as an increase in the average angle of arrival at the substrate. This results in the formation of porous grain growth and inter-granule voids.

This deformation of the crystallinity of the film leads to an increase in the lattice constant and thus introduces strain in the film. In addition, the crystalline size reduces to 56.7 Å to 37.7 Å, as the working pressure is increases from 5 mTorr to 10 mTorr respectively.

The stress values, as obtained by solving equation (4), for different lattice constants of Mo thin films, which are grown at different pressures, is tabulated in Table 1. For pressures greater than 1 mTorr the value of lattice constant is lower than the bulk value, i.e. 3.1469 Å, due to which the grains of the film experience a tensile force between them. The negative and positive signs in table 1 indicate a compressive stress and a tensile stress, respectively. The stress in the film does not allow the grains to accumulate uniformly to the surface of the substrate. In our case, we experienced that at greater than 5 mTorr pressure, due to the considerably low deposition rate the grains were not conglomerate together, and formed a surface having pinholes or scratch-like morphology.

3.1.2 Morphological characterization

The study of the surface morphology of the RF magnetron sputtered Mo thin films was carried out using AFM. Fig. 2 shows the AFM images of Mo thin films grown at different working pressures (1 mTorr to10 mTorr) by keeping the RF power constant at 100 W. From the AFM images, we observe that the average grain size, and hence the surface roughness, decreases as the working pressure increases. As a result, the surface homogeneity is degraded and becomes porous. At 10 mTorr pressure, the 'scratch-like' appearance of the film surface having a surface roughness 1.87 nm was observed. This observation, as already analyzed in section 3.1.1, is due to the lower deposition rate. By lowering the working pressure, viz. ~ 1 mTorr, due to the higher deposition rate the uniform surface morphology observed which has a higher surface roughness viz. 7.78 nm.

Table 2 – *The variation of the surface roughness as a function of working gas pressure suggests that as the pressure decreases from 10 mTorr to 1 mTorr, at 100 W RF power, and thus the increase in the deposition rate, a dense structure of the grains is observed and so, the roughness is improved.*

Working pressure (mT)	1	5	10
Surface roughness (nm)	7.78	2.43	1.87

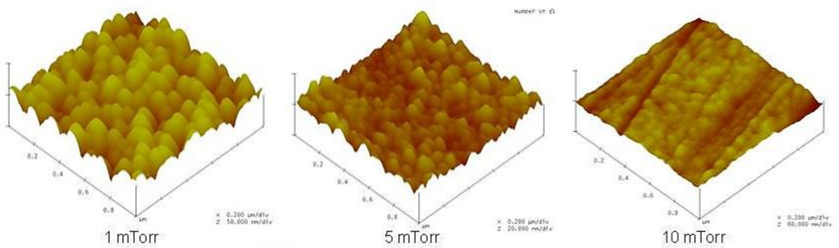

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Fig. 2 – *The AFM images of Mo thin film at different working pressures from 1 to 10 mTorr shows that by reducing the working pressure from 10 to 1 mTorr, the uniformity in the grain coalescence improves significantly*

3.1.3. Electrical and optical characterization

The sheet-resistance is a crucial parameter in the application of the solar cell. Minimum sheet-resistance of Mo thin film gives minimum series resistance of the solar cell and that, in turn, improves the final efficiency of the solar cell. Fig. 3 shows the sheet-resistance, using the four-probe technique, of the Mo thin films deposited at different working pressures.

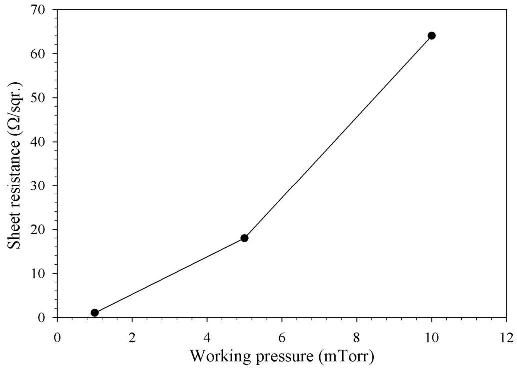

Fig. 3 *– The sheet-resistance of Mo thin films at different working pressures by keeping the RF power constant at 100 W, which shows that at lower working pressure viz. 1 mTorr, the sheet-resistance is lowest*

The observed increase in the sheet-resistance as shown in Fig. 3, at higher sputtering pressure is a direct result of the sputtering induced porous structure that has the greater number of grain boundary [10], observed from the AFM results, compared to the lower working pressure Mo thin film. As we move towards the lower pressure, the porosity reduces and hence the sheet-resistance decreases. The sheet-resistance at 1 mTorr working pressure and 100 RF power was ~ 1 Ω/□.

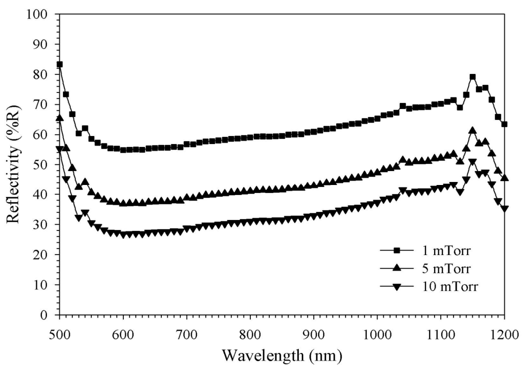

Fig. 4 *– The optical reflectivity of Mo thin films at different working pressures indicates that due to the improvement in the surface uniformity at lower working pressure viz. 1 mTorr, the surface scattering reduces and the reflectivity improves*

In the optical study, we have measured the optical reflectivity of the Mo thin film, shown in Fig. 4, grown at different working pressures by keeping the RF power constant at 100 W. The optical reflectivity plays an important role in the solar cell application. Highly reflective back-contact improves the absorption in the absorber layer. At 1 mTorr working pressure we observed highly reflective silvery white Mo thin films. By increasing the working pressure the isolates columnar crystallites, can be observed from the AFM images, reduces the optical reflectance. J.A. Thornton et al. [11] observed a similar kind of response of Mo thin film deposited at different working pressure.

3.2 Different RF power

3.2.1 Structural characterization

After observing better structural, optical, and electrical properties of the Mo thin film grown at 1 mTorr working pressure, the RF power was varied from 60 W to 100W by keeping the working pressure constant at 1 mTorr. The XRD spectra of Mo thin films grown at different powers keeping the Working pressure at 1 mTorr are shown in Fig. 5.

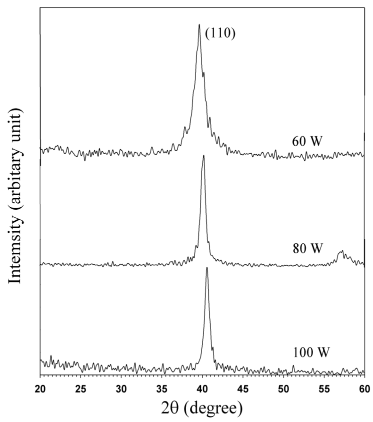

Fig. 5 *– The XRD analysis of the Mo thin films grown at different RF power by keeping the working pressure constant at* 1 *mTorr. At* 100 *W RF power and* 1 *mTorr working pressure, the negligible shift in the* 2θ *angle from its bulk value,* 40.05°, *this shows that a minimum strain is present in the Mo thin film*

The XRD spectra shown in Fig. 5 indicate a preferred orientation along the (110) plane and observed d-values matches with the JCPDS data card 01-1208. There was the 2θ angle shifts to a lower angle with the decrease in the RF power indicates this indicates the strain, and therefore, the stress introduced in the film. In addition, by reducing the RF power, the FWHM increases, which indicates that the crystalline size reduces to 84.7 Å due to the lower kinetic energy of the sputtered particles hence lower deposition rate. Table 3 shows the 2θ value of the (110) plane, its corresponding d-value, crystalline size, lattice constant, percentage of strain, and the estimated stress of Mo thin films grown at different RF power by keeping the Working pressure constant at 1 mTorr.

Table 3 – *The 2θ value of the* (110) *plane, its corresponding d-value, crystalline size, lattice constant, strain, estimated stress of Mo thin films grown at different RF power by keeping the Working pressure constant at 1 mTorr*

RF power (W)	d-value (Å)	2θ (degree)	Crystalline size, L (Å)	Lattice constant, a, (Å)	Strain (%)	Stress ($\times 10^{-9}$ Nm^{-2})
100	2.22174	40.572	143.2	3.1420	0.1562	0.88
80	2.24344	40.163	140.6	3.1727	0.8100	– 4.5
60	2.27387	39.603	84.7	3.2157	2.1800	– 12.29

By reducing the RF power from 100 W to 60 W, the deposition rate decreases from ~ 3.2 Å/s to ~ 2.8 Å/s respectively. Due to the reduced scattering of the sputtered atoms at lower power, at 60 W, with the gas atoms, the crystallinity degrades. Thus, the strain in the Mo film increases. At higher RF power (100 W) due to the increase in the deposition rate, ~ 3.2 Å/s, the crystallinity improvement reduces the strain in the film.

3.2.2 Morphological characterization

The AFM morphology of Mo thin films grown at 1 mTorr working pressure and different RF powers viz. from 60 W to 100 W is shown in Fig. 6. At lower RF power, viz. 60 W, due to the lower deposition rate the grain growth is not uniform. The surface roughness, shown in Table 4, of Mo thin films is 3.45 nm for 60 W RF power. As the RF power increases from 60 W to 100 W, the deposition rate increases, which leads to the improvement in the uniform grain growth and so, the surface roughness improves.

Table 4 – *The surface roughness of the Mo thin films deposited at different RF power. The values suggest that at higher RF power, due to the higher deposition rate, a dense grain growth is obtained and thus the surface roughness is improved*

RF Power (Watt)	100	80	60
Surface roughness (nm)	7.78	4.93	3.45

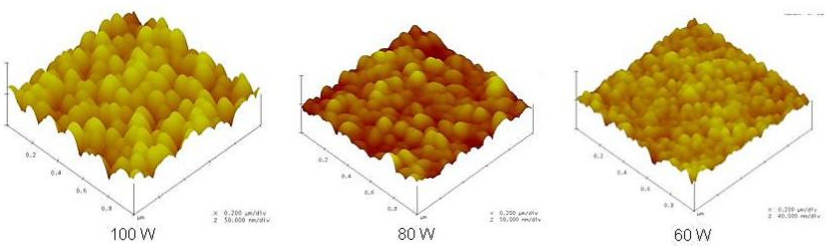

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Fig. 6 – *The AFM images of Mo thin film at different RF power, by keeping the working pressure* 1 *mTorr, indicate that by increasing the RF power the film surface becomes dense and relatively uniform due to the increase in the deposition rate*

3.2.3 Electrical and Optical Characterization

The sheet-resistance of Mo thin film decreases as the RF power decreases. The sheet-resistance mainly depends on the surface morphology of the film. The AFM results confirm that the porosity increases as the RF power reduces from 100 W to 60 W, which increases the sheet-resistance of the Mo thin film shown in Fig. 7. At 1 mTorr working pressure and 100 W RF power we got the minimum sheet-resistance viz. ~1 Ω/□.

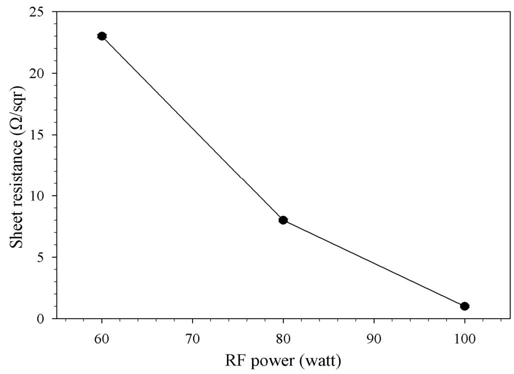

Fig. 7 *– The sheet-resistance of Mo thin films deposited at different RF power by keeping the working pressure constant at 1 mTorr. At higher power the films shows a lower sheet-resistance because of the dense grain structure of the film*

In the optical reflectivity, here, by reducing the RF power, the columnar crystallites isolates, observed from the AFM images, which reduces the optical reflectance shown in Fig. 8. Owing to a uniform distribution in the grains, the Mo thin film grown at 100 W RF power shows a higher reflectance (~ 55 %).

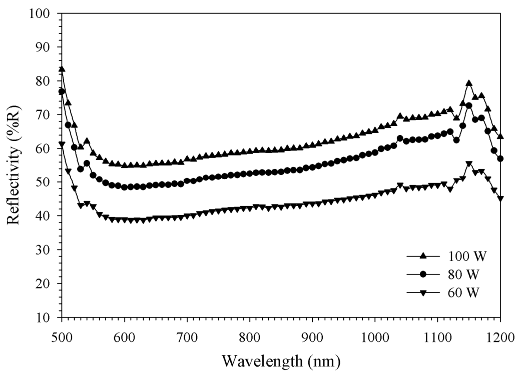

Fig. 8 *– The optical reflectivity of Mo thin films grown at different RF power, by keeping a constant Working pressure at 1 mTorr, suggests that at a relatively higher RF power, due to a uniform surface structure, the reflectivity is higher compared with that at other RF power*

4. CONCLUSIONS

The Mo thin films were grown on soda lime glass substrate using RF magnetron sputtering system for its use as a back-contact in the CIGS thin film solar cell. The significant influence of Working pressure and the RF power was observed by the structural, morphological, electrical, and optical studies. The observations indicate that the metallic Mo thin films showed a better crystallinity, morphology, conductivity, and reflectivity at a lower working pressure (1 mTorr) and a higher RF power (100 W). The Mo thin film grown at 100 W RF power and 1 mTorr working pressure shows a sheet-resistance of ~ 1 Ω/□ surface roughness of 7.78 nm and near to 55 % reflectivity in the visible region.

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