Physical and electrical properties of molybdenum thin films grown by DC magnetron sputtering for photovoltaic application

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ABSTRACT

DC magnetron sputtering was utilized to grow thin layers of molybdenum (Mo) on top of soda lime glass substrates. Deposition power was varied for suitable characteristics of films grown at various DC powers, i.e. 100 W, 150 W and 200 W. Thin Mo film of approximately 580 nm thickness was successfully grown at DC power of 100 W at room temperature. Structural, morphological, electrical and optical properties of Mo thin films were analyzed. XRD patterns revealed Mo films to be monocrystalline in nature and only one peak was observed corresponding to the (1 1 0) plane reflection at 2θ = 40.5°. Exceptionally dense microstructure was found for surface morphology observation by AFM and FESEM. Increasing deposition power resulted in coarser surface of the grown films. The minimum average surface roughness was found to be around 0.995 nm. Scotch tape adhesion test was performed to validate adhesion. Grown Mo films were found metallic in nature with electrical resistivity of 2.64 × 10⁻⁵ Ω-cm. Furthermore, it was found that by increasing deposition power, the electrical resistivity could further be reduced.

Introduction

Highly efficient solar cells have been using molybdenum (Mo) as the successful contact material. For instance, a thin layer of Mo plays a significant role in the formation of Copper–Indium–Gallium–(di)–Selenide (CIGS) solar cells. Mo thin films possesses several favorable properties as a suitable back contact material for CIGS based solar cell, which significantly improves the fill factor [1–12]. Scofield et al. reported Mo as a prevalent back contact material and leading choice for the CIS and CIGS solar cells [1]. The most important requirements of a good back contact material are: it should form a low-resistance contact with the absorber layer, the contact should be non-rectifying, and the contact should be stable under low term worst-case use conditions [5]. Other requirements include good adhesion with the substrate and the absorber, low film stress, high optical reflectance and high stability during high temperature absorber growth process [11,13].

Alike other refractory metals deposited through physical vapor deposition (PVD) techniques, such as; RF magnetron sputtering [14], high impulse magnetron sputtering [15] and DC magnetron sputtering etc [16–21], Mo thin films are grown by DC magnetron sputtering under Argon (Ar) atmosphere and deposition power as process parameters [3]. It is reported that the lowest possible sheet resistance for back contact of the solar cell is obtained at the lowest Ar pressure [16,21,22]. Metals deposited through DC magnetron sputtering have a correlation between the stress and sputtering gas pressure [1]. Film deposition at high pressure leads the film to be under tensile stress whereas film growth at low Ar pressure leads the film to be under compressive stress [16,20].

Sputtering is a broadly utilized technique to deposit thin films on substrates [23]. The method is based upon ion bombardment from a
source material. Ion bombardment effects in a vapor due to a merely physical manner. The benefits of sputtering are lower substrate temperatures as compared to thermally activated deposition strategies, excessive chemical reactivity of the species because of plasma-assisted excitation, ideal for the deposition of compounds and alloys, compact and dense, nicely-adhering films may be prepared [24]. Furthermore, sputtering is a properly established huge-vicinity deposition method which allows uniform deposition to any size of substrates. Hence, this method is a part of the elegance of PVD techniques.

Martinez and Guillen studied the electrical, morphological and structural properties of Mo thin films grown by using RF magnetron sputtering for various deposition parameters [6]. They determined that all the films have equivalent electrical properties. Nevertheless, to obtain densely packed structure and minimum stresses, it is necessary to have low RF power densities. Shou-Yi Kuo et al. investigated various growth parameters of Mo by RF magnetron sputtering and found that working pressures strongly influence the physical, electrical and structural properties of thin films [7]. Bansal et al. reported a bilayer structure of Mo film deposited by DC magnetron sputtering and found that higher pressure followed by low pressure produces improved electrical conductivity and adhesion [25]. Zhu et al. investigated the influence of working pressure and target to substrate distance on Mo films grown by DC and RF magnetron sputtering and found that DC sputtered thin films have higher conversion efficiency of CIGS solar cells compared to RF sputtered electrodes [26]. Though many studies already been conducted to examine the impact of sputtering parameters [1,6,7,14,16,20] but few studies have highlighted on impact of DC power on sputtered Mo films. As the Mo properties play a critical role in the performance of CIGS based solar cells, deposition parameters like DC affects of applied DC powers on the crystal structure, morphology, resistivity, reflectance and adhesion of Mo thin films.

Experimental setup

Substrate preparation

Soda Lime Glass (SLG) was used as the substrate for the growth of Mo thin films by the means of DC magnetron sputtering. Initially, the substrates were mechanically scrubbed in the presence of distilled water to remove any dust particles from the surface and then ultrasonically cleaned by using methanol for 15 min, acetone for 15 min and again methanol for 15 min. Methanol is known as powerful solvent and it works better than 2-propanol because it can dissolve most of the organic sediments. 2-propanol though a good solvent but it is viscous and things dissolve slowly in it. Methanol evaporates faster than 2-propanol and methanol is comparatively inexpensive than 2-propanol. Therefore, methanol was utilized for glass cleaning process. Afterwards, all the substrates were cleaned with deionized (DI) water for 20 min in an ultrasonic bath in order to assure removal of impurities and contaminations from the surface. Finally, the substrates were dried with industrial grade nitrogen (N₂) gas and transferred to the sputtering chamber for deposition.

Deposition process

Mo was used as a target material. Before deposition of thin films, Mo target was pre-sputtered in Ar atmosphere for approximately 20 min to ensure oxide free environment in the chamber. Table 1 shows the summary of deposition parameters of Mo thin films grown by DC sputtering system. Before the deposition, the sputtering chamber was evacuated to a base pressure of 1.5 × 10⁻⁵ Torr. Pure Ar (99.99%) was introduced into the chamber with the flow rate of 2.0 SCCM. In order to obtain suitable structural and morphological properties of Mo as a back-contact material for thin film solar cells, deposition parameters like DC power was varied from 100 W to 200 W. Deposition conditions were strictly maintained throughout the yield process.

Thin films characterization

The structural properties of grown Mo thin films were obtained from the X-ray diffraction (XRD) of BRUKER aXs-D8 Advance Cu-Kα diffractometer. The XRD patterns were extracted in the range of 2θ, from 20° to 70° with 0.02 step size using Cu-Kα radiation of wavelength, λ = 1.5408 Å. CARL ZEISS EVO and SEISS SUPRA 55VP model of Field Emission Scanning Electron Microscopy (FESEM) was used to analyze the morphological properties of deposited thin films including layer thickness. The surface topography and roughness of the films were found by NANOSURF EASYSCAN 2 AFM system. Elemental compositional analysis of grown films was determined by EDX of Oxford Instruments INCA Penta FETx3. The electrical properties such as carrier concentration, mobility, resistivity and hall coefficient were measured by Hall Effect Measurement system of Ecopia HMS 3000 with a magnetic field of 0.57 T. The optical properties were studied by the Perkin Elmer Lambda 900 UV–VIS-NIR Spectrophotometer within the wavelength range of 200–1500 nm. All the measurements were taken at room temperature.

Results and discussion

Structural properties

XRD patterns of Mo thin films grown at different DC powers are shown in Fig. 1. It is found that the crystallites of Mo films maintain the cubic crystal structure. Also, it is observed that all the films possess a single peak at 2θ = 40.5° with an orientation along (1 1 0) direction. The average grain size or crystallite size is calculated from the broadening of the (1 1 0)_{sub} peak using Scherrer equation.

\[ L = \frac{Kλ}{Bcosθ} \]

Fig. 1. XRD pattern of Mo thin films grown at various DC powers.
where $K$, $L$, $\lambda$, $B$, $\theta$ are the Scherrer constant, crystallite size, wavelength of the X-ray source, full width half maximum and diffraction angle, respectively. It is found that the crystallite size increases with the increment of deposition power. Fig. 1 demonstrates that the intensity of the $(1 1 0)_{\text{lab}}$ peak rises slightly as the deposition power increases. It is also observed that for the films grown at high deposition power, the kinetic energy of the species enhances resulting in 3D Volmer–Weber growth. The films grown at high deposition power are found to have highly dense microstructure resulting the crystallization with big grains while the films grown at low deposition power are essentially more random and disoriented in nature [7].

The dislocation density ($\delta$) gives more information about the amount of defect in the films which can be calculated from Williamson–Smallman relation:

$$\delta = \frac{1}{L^2}$$

where $L$ is the crystallite size in nm. Higher $\delta$ values indicate lower crystallinity levels for the films and the amount of defects in the structure [27]. The number of crystallites per unit area $N$ can be calculated from the given formula:

$$N = \frac{t}{L^3}$$

where $N$ is the number of crystallites per unit area and $t$ is the thickness of concerned film. The higher $N$ values indicates abundance of crystallization [28,29]. The structural parameters calculated from XRD data are presented in Table 2.

The dislocation density ($\delta$) value is found to be in the range of $1.71 \times 10^{15} \text{m}^{-2} - 3.54 \times 10^{15} \text{m}^{-2}$ while the number of crystallites per unit area ($N$) are calculated in the range of $4.10 \times 10^{16} \text{m}^{-2} - 12.24 \times 10^{16} \text{m}^{-2}$ with a decreasing trend in the numerical values as the deposition power increases from 100 W to 200 W. The higher value of $N$ is observed for films grown at 100 W DC power embarking the fact of abundance of crystallization. The strain in the thin films is calculated by the peak shift of $(1 1 0)_{\text{lab}}$ along $2\theta$. The residual stress calculations and inter-planar spacing $d_{110}$ are calculated using strain and Bragg's formulas. The strain percentage is calculated by the following equation:

$$\text{Strain} (%) = \frac{\Delta a}{a} \times 100\%$$

where $a$ is the lattice constant and determinant parameter to understand compressive or tensile types of strain [1]. It is revealed that the nature of films is found to be in tensile strains. Mo film grown at 200 W DC power is found to have least value of strain as $0.493\%$ whereas 100 W deposition power is computed with higher strain value as $0.695\%$. In general, the trend of strain can be noticed to decline with the increase in deposition power. Impurities from the process gases like argon and oxygen usually deteriorate the crystal orientation introducing defect states and voids. Hence, such effects are unlikely unavoidable in the sputtered Mo films [8]. Such effects are eventually related with the kinetic energy of the ions created by the collision of the inserted gas phase in the chamber [30].

### Morphological properties

The FESEM images presented in Fig. 2(a, c and d) divulge the surface morphologies of sputtered Mo thin films at various deposition powers. Literature review specifies that films sputtered at lower deposition power exhibited porous microstructures while films sputtered at higher deposition power exhibited dense microstructures [16]. At higher deposition power, deposition rate increases so that number of species received at the substrate enhances resulting in a denser microstructure. At low deposition power, deposition rate declines and the number of species arriving at the surface of the substrate becomes less resulting in a porous microstructure.

However, in this work, no porous microstructure is observed and pin-hole free films are obtained. Fig. 2 illustrates the smooth morphology and the dense microstructure. Nearly perpendicular thin ‘flake-like’ grains are observed at the surface of films. The size of ‘flake-like’ grains are found to be in the range of 30–130 nm long and it is observed that with the increase of deposition power, the grain size also increases, validating the trend obtained from XRD analysis. Morphology of sputtered films was observed growing from rough surface to compact and much smoother as the deposition power increases. The cross-sectional view of the grown Mo thin film at 100 W DC power is shown in Fig. 2(b). The thickness of the film is found to be 580.6 nm, visualizing the granular morphology.

Fig. 3(a–c) represents the AFM images of Mo thin films grown at various DC powers. The Root-Mean-Square (RMS) roughness ($R_q$) and Average Surface Roughness ($R_a$) calculations are essential to understand the surface topology of a film. RMS calculation usually considers the deviation between the standard and specified surfaces; whereas, $R_a$ calculation considers the expansion of mean roughness in 3D to measure the actual surface roughness. The identical surface roughness is found to be increased with the increase in sputtering power [31].

The $R_a$ for the films grown at 100 W, 150 W and 200 W are about 0.995 nm, 1.28 nm and 3.23 nm, respectively. The RMS roughness also increases as the deposition power increases. Though the visual analysis of FESEM results give an idea that roughness decreases with the increment of power but AFM analysis represents opposite outcome. This outcome is credited to the enormous increase in the number of sputtered Mo molecules arriving at the surface of the substrate.

### Electrical properties

Hall Effect measurement system with the magnetic field of 0.57 T and current source of 10 mA is used to investigate the electrical properties of Mo thin films at room temperature. The measured resistivity, mobility, carrier concentration and Hall coefficients of sputtered Mo films grown at various DC powers have been tabulated in Table 3.

In confirmation with the Gordillo et al. results, the resistivity decreases slightly by increasing the deposition power [3]. This decrease in resistivity is ascribed to the dense microstructure at high deposition power which enriches the swift growth of comparatively thick film.

### Elemental compositional analysis

Fig. 4 represents the elemental compositional analysis obtained from EDX spectroscopy for Mo thin films grown at various DC powers.

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**Table 2**

Structural parameters of Mo thin films deposited at various DC powers.

<table>
<thead>
<tr>
<th>Deposition power (DC)</th>
<th>Strain (%)</th>
<th>(hkl)</th>
<th>Thickness (nm)</th>
<th>Crystallite Size (nm)</th>
<th>$\delta$ (m$^{-2}$)</th>
<th>$N$ (m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 W</td>
<td>0.695</td>
<td>(1 1 0)</td>
<td>580.6</td>
<td>16.8</td>
<td>$3.54 \times 10^{15}$</td>
<td>12.24 $\times 10^{16}$</td>
</tr>
<tr>
<td>150 W</td>
<td>0.537</td>
<td>(1 1 0)</td>
<td>614.1</td>
<td>19.4</td>
<td>$2.66 \times 10^{15}$</td>
<td>7.95 $\times 10^{16}$</td>
</tr>
<tr>
<td>200 W</td>
<td>0.493</td>
<td>(1 1 0)</td>
<td>688.5</td>
<td>24.2</td>
<td>$1.71 \times 10^{15}$</td>
<td>4.10 $\times 10^{16}$</td>
</tr>
</tbody>
</table>
The scanning results reveal the presence of Si, C, O, Ca, Mg and Na beside Mo within the EDX spectrum of thin films. The obtained values in weight % are presented inside the table for each thin film grown at 100 W, 150 W and 200 W DC powers within the spectrum image. The presence of Si, C, O, Ca, Mg and Na elements is attributed to SLG substrate. It is observed from Fig. 4 that the weight % of Mo has an inverse function with deposition power. As the deposition power increases, the value of Mo weight % decreases. The film grown at 100 W is found to have the maximum value of weight % of Mo element as 71.2%.

Optical properties

The optical properties of Mo thin films are premeditated by the reflectance spectrum obtained from UV–Vis-NIR analysis. It is observed that the grown films have around 53–60% reflectance in the UV range of light spectrum while 54–58% in the visible range and goes up to 88%
within the IR range. The reflectance spectra are presented in the Fig. 5(a).

Fig. 5(b) represents the refractive index \( n \) with respect to light spectrum in the range of 200–1500 nm calculated using the equation below for grown films of Mo at 100 W, 150 W and 200 W DC powers [32].

\[
R = \frac{1 + \sqrt{R}}{1 - R}
\]

where \( R \) is reflectance and \( n \) is refractive index. The mean refractive index in the UV range is calculated as 5.22 for Mo film grown at 100 W, 5.16 for 150 W and 5.10 for 200 W DC powers while in the visible range as 5.41, 5.46 and 5.53 for 100 W, 150 W and 200 W DC powers, respectively.

Adhesion of Mo thin films

The adhesion of Mo thin films is examined with scotch tape adhesion test by attaching the tape on the surface of the film and detaching it by applying force manually. The adhesion property worsens as the deposition power increases. It might be because of high power results in atom to bounce from substrate when bombardment occurs from target. Therefore, a noticeable amount of elemental Mo has been visually observed on the grown films. It is reported by Jubault et al. that deposition power highly influences the physical and electrical properties of Mo thin films grown by DC magnetron sputtering [33]. The films grown at lower deposition power have enhanced properties such as more adherent, conductive, denser and highly reflective than those grown at higher deposition power [33]. The effects of residual stress on thin film’s adhesion is demonstrated well by Wang et al. [34]. Also, the relationship between working pressure and residual stress is examined [31]. Increased deposition power results in residual stress to change from the compressive stress to the tensile stress. The intemperate compressive stress or tensile stress result in worse adhesion [35].

The results obtained from the structural analysis of deposited films shows a trend of slightly higher crystallinity in the film grown at lower deposition power i.e. 100 W which can also be noticed from the AFM analysis that the films have least roughness value. FESEM results embark the fact of a highly dense microstructured thin film growth and adhesion test results support the durable and robust structure of 100 W grown films. Higher deposition power results in coarser surface of the grown films. The elemental compositional value of 100 W grown Mo is found to be maximum with its weight % value obtained from EDX spectroscopy compared with other films. The results obtained from hall effect measurement are supportive and in the favour of low deposition DC power i.e. 100 W to be used for the growth of Mo as back contact material for possible implications in CIGS, CIS and CZTS based solar cells structures.

Conclusion

As a summary, Mo thin films are grown at various deposition powers by DC magnetron sputtering. The effects of deposition power on the structural, morphological, compositional, electrical and optical properties are investigated in this study for the use of Mo as back contact material with optimized parameters for thin film solar cells fabrication. Grown films are found to exhibit single diffraction peak corresponding to \((1 1 0)_{\text{sub}}\) plane. Surface morphology is found to be dense, smooth and a low average surface roughness of 0.995 nm is calculated. The combination of process parameters used in this study suggests growth of dense films due to high energy of species incident onto the substrate as well as greater degree of surface and volumetric diffusion during film growth. The electrical resistivity is found to be approximately \(2.64 \times 10^{-5} \, \Omega \cdot \text{cm}\). Film grown at 100 W power is found to be sturdily adhesive and the refractive index in the visible range is computed as 5.41. Thin films investigated here showed characteristics
in internal residual stresses and in tensile strains conditions. The number of crystallites per unit area is calculated as $12.24 \times 10^{16}$ m$^{-2}$ for lower deposition power film, indicating the abundance of crystallization in 580 nm thick layer of Mo. Finally, with the correlation of various parameters analyzed in this study, it is proposed that 100 W power is the optimized deposition power for DC sputtering to grow thin films of Mo on top of SLG as back contact material for possible fabrication of CIS, CIGS and CZTS based solar cell devices.

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