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Sputtered Mo-bilayer thin films with reduced thickness and improved electrical resistivity

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**Abstract**

In this study, Mo-bilayer film, the thickness of which was reduced to approximately 270 nm with a very low resistivity of 14 μΩ.cm, was successfully grown by DC magnetron sputter. The Mo-bilayer, whose bottom and top layers were obtained by high pressure sputter (HPS) and low pressure sputter (LPS) respectively, demonstrates good adhesivity and crystalline properties, together with high reflectance. In order to obtain Mo-bilayer with these improved properties, we first determined the optimal growth temperature and pressure parameters by checking the structural and electrical properties respectively of Mo-single layers. As a result, we achieved a deposit of Mo-bilayer thin film that can be used as a good back contact layer in solar cell applications, both in terms of material cost saving and its superior properties, even at such low thickness.

**1. Introduction**

Due to its remarkable properties, such as high thermal stability at elevated temperatures, good adhesion property, remarkable electrical conductivity [1, 2], and high reflectivity [3], molybdenum (Mo) has been widely used as a back contact layer, especially in chalcopyrite (CuInGaSe2)-based thin film solar cells [4–6]. The superiority of Mo, which enables the Na out-diffusion from the soda-lime glass (SLG) substrate to the CIGS absorber layer due to its columnar microstructure, along with its role as back reflector for incoming light [3], results in improved solar cell efficiency. Therefore, demand for Mo has rapidly increased within the last decade, especially for use in the CIGS photovoltaic industry, with annual production currently reaching up to a quarter million metric tons [7, 8].

The most commonly used method for the deposition of the Mo layer is sputtering [6, 9–11], since a higher conversion efficiency can be achieved with a sputtered Mo back contact. A Mo layer with high reflectivity, low resistivity and good adhesivity is the most desirable for use in a CIGS solar cell. However, this is a challenging task, since it may not be possible to obtain the desired Mo film, even by carrying out the sputter deposition properly. For instance, reflectance decreases by applying gas pressure [4] and increases by plasma power [6]. Moreover, the increment in pressure improves adhesivity and reduces resistivity [5], while resistivity decreases when the temperature is applied [12]. In order to overcome the trade-off, particularly between resistivity and adhesivity (since these are the basic requirements), Scofield attempted to form a Mo-bilayer structure consisting of two deposition regimes starting with high pressure for good adhesion before continuing with low pressure in order to achieve high conductivity [13]. The relevant literature shows that the Mo-bilayer structure exhibits better adhesive properties, while its electrical properties still require improvement [14]. To obtain Mo-bilayer that meets all the requirements for a proper back contact, growth parameters—such as substrate temperature [15], working gas pressure [5] and power [16]—should be adjusted carefully. Many researchers have managed to obtain Mo-bilayer thin film with the desired properties at the approximate micron scale [5, 15]. However, thickness must be lowered as well, while also lowering material costs without sacrificing quality.
In this study, we examined ways of producing a more adhesive and thinner Mo–bilayer film with low resistivity and high reflectivity by firstly optimizing Mo–single layer properties. After varying the deposition temperature from room temperature (RT) to 400 °C in order to find the lowest resistivity, we investigated the effect of gas pressure, ranging from low to high, on the adhesivity of the Mo–single layer. Then we used the temperature and pressure information that we found from the Mo–single layer optimization to carry out the deposition of Mo–bilayer film with superior properties. As a result, we succeeded in obtaining a very thin Mo–bilayer, the resistivity and reflectivity of which was extremely low and high respectively, which also showed strong adhesion, crystallinity and surface morphology.

2. Experimental

Mo–single and bilayers were deposited on conventionally RCA cleaned soda–lime glass (SLG) substrates via DC magnetron sputtering, using the Mo target with a high purity level (99.95%). The distance between the target and substrate holder was fixed in all sputter depositions. The base pressure was set to approximately \( 2 \times 10^{-6} \) Torr, which is low enough to start the process. To remove the contaminants on the target surface, pre-sputtering was applied before the actual deposition. In all of the following depositions, ultra-pure Ar (99.9999%) gas was introduced into the chamber and the substrate was rotated at the speed of 8 rpm to achieve uniform film formation. Initially, the effect of substrate temperature and working gas pressure on the structural and electrical properties of the Mo–single layer was examined by separating growth procedures for optimization. First, the Mo film deposition was carried out under gas pressure of 12 mTorr at various substrate temperatures from RT to 400 °C. Gas pressure was varied from low to high by fixing the temperature at 300 °C. Then, in order to obtain Mo bi-layers, a bottom layer was initially deposited at a high pressure of 24 mTorr (HPS) followed by the deposition of the top layer at a low pressure of 3 mTorr (LPS) without any interruption during the process. The effect of the substrate temperature on the crystal features of both the Mo–single and bilayer films were examined through x-ray diffraction (Rigaku Smartlab) with CuKα radiation. The surface morphology and microstructure of the samples were then observed with the use of a scanning electron microscope (Nova nanoSEM 430). The electrical parameters of the samples were examined using both the four probe and contactless methods to verify the validity of the results. The reflectance measurement was carried out by using a UV–vis–NIR spectrometer (Jasco V–670 model) at the range of 300nm–1800nm. The scotch tape trial was then employed to check the adhesivity of the films onto the substrates.

3. Results and discussion

3.1. Growth temperature effect on Mo–single layer formation

The morphology of the Mo layers grown at 12 mTorr and elevated growth temperatures starting from RT seen in the SEM images (not shown) does not differ significantly, as the temperature has a greater effect on the crystalline properties rather than their morphologies. The XRD spectra demonstrate that all thin films have the (110) orientation, which proves the crystalline formation [14] regardless of growth temperature as shown in figure 1. Structural parameters calculated by using the shift of the main (110) XRD peak (inset of figure 1) are summarized in table 1. The FWHM value decreases proportionally by the temperature increment up to 300 °C, becoming the lowest at this point. As a consequence, the crystalline size calculated by Scherrer’s formula [17] is the largest, while dislocation density and strain is the lowest accordingly at this growth temperature. Therefore, it can be concluded from these findings that Mo thin film grown at 300 °C has the best structural properties and that slight deterioration begins to show up with further growth temperature increments, as shown in table 1.

Variations in the sheet resistance of Mo thin films can be seen in figure 2. The graphs acquired by using both the contactless and four-point probe methods are extremely similar to each other, confirming the validity of the measurements. The lowest sheet resistance was recorded at a 300 °C growth temperature, standing at 1.44 ohm sq⁻¹ and 1.22 ohm sq⁻¹ with the use of the contactless and four-point probe methods respectively. The healing of sheet resistance by the elevated growth temperature leads to a significant drop at 300 °C, which can be explained by the enhanced adatom mobility of charge carriers. These carriers gain the excess kinetic energy due to the heating, resulting in their enhanced mobility [15, 18]. The reverse behavior (seen in the graphs in figure 2) after the minima points is possibly due to the deterioration of the crystalline properties at the growth temperature near 400 °C.

3.2. Working gas pressure effect on Mo–single layer formation

After putting the best growth temperature at 300 °C by examining structural and electrical properties, the pressure dependency of the Mo thin films was examined by keeping the temperature constant and varying growth pressure.
The film structure is transformed from a continuous to a porous aspect by pressure increment, as seen in figure 3. The resulting film is too dense when it is grown at low pressure (figure 3(a)). At medium pressure, it begins to show granular-like formations on its surface (figure 3(b)). Finally, at high pressure, the size of the granules increases and elongated shapes are formed (figure 3(c)). This change in structure formation by applying different pressures is typical, and has been widely reported in the relevant literature [5]. The incident deposition atoms obtain enough kinetic energy to achieve mobility, due to fewer collisions between working gas ions, and thus form dense and flat film at low pressures. On the other hand, the incident target species are subject to heavy collisions during HPS, so they reach the substrate with lowered kinetic energies and higher incident angles [19]. The adatoms then start to settle onto the nearest clusters and formed porous microstructure since they do not have excess energy to diffuse further. The 3D-like formations seen in HPS can be attributed to the shadowing affect [20], as the former clusters shadow the deposition onto lower areas. The working pressure not only affects morphology, but also electrical and adhesion properties as summarized in table 2.

Figure 1. XRD spectra of Mo thin films with various growth temperatures. The inset shows the enlarged image of the main peak belonging to (110) orientation.

| Temperature (°C) | FWHM (degrees) | Crystalline size (nm) | Dislocation density*10^14 | Strain (ε) |
|------------------|----------------|-----------------------|---------------------------|------------|
| RT               | 0.78           | 10.86                 | 84.79                     | 0.0034     |
| 100              | 0.37           | 22.89                 | 19.08                     | 0.0016     |
| 200              | 0.31           | 27.59                 | 13.13                     | 0.0013     |
| 300              | 0.26           | 33.22                 | 9.06                      | 0.0011     |
| 400              | 0.37           | 23.02                 | 18.87                     | 0.0016     |

Figure 2. Sheet resistance of Mo thin films as a function of growth temperature.

Table 1. Structural properties of Mo thin films calculated from the main peak using the XRD spectra.
The sheet resistance of all pressure-dependent Mo thin films is quite low when compared to their counterparts grown at room temperature (not shown) due to the positive effect of temperature. The negligible difference in the sheet resistance of the films, especially between MPS-Mo and HPS-Mo, can be explained by the improved structural properties, since temperature has the ability to heal imperfections and defects in crystalline structure.

The well-known Scotch-tape method \cite{21} was used to examine the films’ respective adhesion properties. Only the Mo film grown at the lowest pressure failed, while the others passed the adhesion test and also yielded relatively low sheet resistance values, as summarized in table 2.

### Table 2. The sheet resistance and adhesion properties of Mo thin films grown under different working gas pressures.

| Pressure (mT) | Sheet Resistance (ohm sq$^{-1}$) | Adhesion Test |
|---------------|----------------------------------|---------------|
| 3 (LPS)       | 0.48                             | Fail          |
| 12 (MPS)      | 1.51                             | Pass          |
| 24 (HPS)      | 1.31                             | Pass          |

3.3. Mo-bilayer formation

It is commonly preferred to combine the HPS-Mo and LPS-Mo as the bottom and top layers respectively to obtain a bilayer Mo thin film with good adhesion property and low sheet resistance. The surfaces of both bilayer Mo thin films appears quite smooth, as shown in figures 4(a) and (b), since the top dense layer covers the bottom columnar microstructure like a blanket. The film grown at 300 °C is thinner (~270 nm) than the RT-grown film (~335 nm), as can be seen from the cross-sectional SEM images. The crystalline size of the first film is approximately three times larger than that of the latter film (see table 1).

In contrast to the conventional way of producing Mo-bilayer by keeping the bottom HPS layer too thin \cite{15, 22}, we used a thicker HPS-Mo bottom layer (see the cross-sectional SEM images) to strengthen adhesivity,
since we could already achieve very low sheet resistance, even for HPS-Mo. For the Mo-bilayer thin films, sheet resistance decreases from $\sim 0.67$ ohm sq$^{-1}$ to $\sim 0.5$ ohm sq$^{-1}$ when the growth temperature is raised from RT to 300 °C, as summarized in table 3. Resistivity for the temperature used for Mo thin film is calculated as 14 $\mu\Omega$.cm, which is quite low when compared to that found in the relevant literature [2]. The inverse behavior between crystalline size and sheet resistance (table 3) is not a coincidence: larger crystalline size results in lowered grain boundaries, which in turn lead to enhanced electron mobility and lowered sheet resistance.

The reflectance of both RT-grown and temperature-applied Mo-bilayer thin films and the Mo-single layer with the lowest growth pressure are almost the same or quite higher than the two other Mo-single layers (figure 5). On the other hand, the lowest reflectance was recorded by the Mo-single layer grown by HPS, while the MPS-Mo shows medium reflectance. As is well known, reflectance is identified by the surface properties and material density of the front layer, regardless of its microstructure. Therefore, the conclusion is drawn that the highest and lowest reflectance are from the samples whose front layers were grown using LPS and HPS respectively, since LPS-grown film would have a high material density and a smoother surface, while a porous surface, along with a lowered material density, are obtained by using HPS [23].

### 4. Conclusions

In conclusion, we put the optimum temperature at 300 °C, which yields the best crystalline and lowest sheet resistance of the Mo-single layer by maintaining pressure at 12 mTorr. We also observed that not only the surface properties, but also electrical and adhesivity properties, are affected by varying the growth pressure while keeping a constant temperature of 300 °C. Notably, the HPS-Mo demonstrates good adhesivity but reduced sheet resistance, while the LPS-Mo behaves in a contrary manner, leading to a trade-off to obtain a proper Mo-single back contact layer. We therefore deposited a Mo-bilayer thin film whose bottom HPS layer was made thicker than the top LPS layer in order to strengthen adhesivity. Despite the enlarged thickness of the HPS layer, we were able to achieve a resistivity of approximately 14 $\mu\Omega$.cm for the Mo-bilayer thin film grown under 300 °C. To our knowledge, this is one of the lowest resistivity values to be seen in the relevant literature for a very thin film ($\sim$270 nm). Additionally, we were able to improve crystallinity as well. Finally, the reflectivity of Mo-bilayer films grown at both RT and 300 °C is high enough for use of a good back reflector. As a result, we could successfully grow an adherent Mo-bilayer thin film whose thickness is very low when compared to a conventional Mo back contact layer with good crystallinity, high reflectivity and extremely low resistivity, making our Mo-bilayer quite unique in this regard.

**Table 3. Sheet resistance and crystalline size of Mo-bilayer thin films grown at different growth temperatures.**

| Temperature (°C) | Sheet Resistance (ohm sq$^{-1}$) | Crystalline Size (nm) |
|-----------------|---------------------------------|----------------------|
| RT              | 0.67                            | 25.67                |
| 300             | 0.50                            | 37.82                |

**Figure 5.** The reflectance graph of Mo-single and Mo-bilayer thin films.
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