Morphological, electrical and optical properties of sputtered Mo thin films on flexible substrates

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1 Introduction

The photovoltaic market has increased dramatically during recent years and the main effort is focused at the moment in increasing the performance of the solar cells together with reducing the associated costs. An improved efficiency, in combination with a higher stability and the perspective of a decreased cost, has made of solar cells based on polycrystalline thin films an interesting alternative to the widely used silicon based cells. The structure of this type of cells from bottom to top is basically constituted, in its simplest configuration and naming in brackets commonly used materials, by a substrate (typically glass), a back contact layer (molybdenum), an absorber film (Cu(In1-xGa)xSe2 termed in the following as CIGS), a window layer (CdS, In2S3, …) and a front contact layer (ZnO) [1–3]. The device is usually finished with an anti-reflection coating (MgF2). CIGS-based solar cells show record total-area efficiencies as high as 19.9%, recently obtained on surface modified CIGS films [1]. Considering that CIGS is a direct semiconductor, solar cells with a total thickness of just a few micrometres are enough to ensure an optimum performance of the photovoltaic device.

The list of materials with potential to be used as back contact layer in these cells is relatively wide: Mo, Au, Ag, Cu, … [3–5]. From an electrical point of view, the film used as a back contact should have a very low sheet resistance in order to guarantee a contribution as small as possible to the total resistance of the cell. Furthermore the film should be stable enough against possible diffusion effects with Cu and In during preparation of the CIGS absorber film [6–10]. According to this, molybdenum (Mo) is the material with the best combination of properties among the different candidates for the back contact layer in CIGS solar cells [3, 11].

The potential applications of the solar cells are highly influenced by their efficiency, thickness, weight, flexibility, lifetime, and all the costs directly involved in the production process, installation and maintenance. Architectural applications give special importance to long lifetime solar cells while automotive, space and aeronautical applications do not precise such long-lasting cells; they require mainly thin, light and, in many cases, flexible cells to save expenses on fuel and, additionally, to offer the possibility of new and smaller designs [12, 13]. The use of glass substrates restricts strongly the possible application fields since they are very thick in comparison to the total thickness of the polycrystalline film structure of the solar cells. Furthermore, their fragility increases with decreasing their thickness which limits the possibility of achieving a significant weight reduction. The use of flexible substrates
may help to overcome these limitations. Different types of flexible substrates have been studied with special emphasis on metals and polymers. In this regard, basic requirements which comprise high thermal stability, chemical inertness, adequate thermal expansion, low surface roughness, lightweight and low manufacture costs, among others, make of certain polymers (polyimides, in particular) the best alternative. Commerically available Upilex® S and Kapton® fulfill the main requirements and, despite of having a relatively high coefficient of thermal expansion (CTE), this is lower than for other polyimides [12]. This is a fundamental point because a suitable CTE of the flexible substrate avoids adhesion problems and cracking of the Mo back contact [14], in addition to the associated adhesion problems of the CIGS layer to the latter.

Polyimides substrates make possible the use of a roll-to-roll process for the production of flexible solar cells which already results in significantly decreased fabrication costs compared with rigid solar cells [15]. This is due to a continuously running deposition process and the use of compact and less expensive equipment [13]. An important issue to be considered, however, is the limitation in the maximal temperature to be used during the preparation of the cell structure which should be well below 500 °C to avoid degradation of the polyimide [12]. Thus a suitable fabrication temperature of the solar cell must be achieved to avoid substrate degradation at expenses of a poorer crystallinity of the CIGS film, i.e., a poorer performance of the cell. Additionally, the back contact Mo layer deposited prior to the CIGS film should have a good adhesion to the substrate and a smooth surface, without forgetting the low resistivity requirement.

In this study, Kapton® foils of different thickness have been used as flexible substrates for the preparation of Mo thin films instead of the well-established soda-lime glass (SLG) substrate. The influence that the choice of the Kapton® substrate thickness, in addition to the selected working gas (Ar) pressure, may have on the morphological, optical and electrical properties of the Mo layer is analyzed. Furthermore, the correlation between the microstructure and the optoelectronic properties of the films is investigated in detail.

2 Experimental Kapton® films were supplied by Goodfellow in four different thicknesses, namely 25 µm, 50 µm, 75 µm and 125 µm. Molybdenum films were deposited at room temperature onto Kapton® films using a planar DC magnetron sputtering system Leybold type Z400. The base pressure was about $2 \times 10^{-5}$ Pa and the distance between the Mo target (75 mm diameter, 99.9% purity) and the substrate was 35 mm. Different batches of films were prepared by maintaining an unchanged DC power value of 70 W and a constant Ar gas pressure ranging from 0.6 Pa to 1.5 Pa. All the prepared Mo films had a thickness of 0.8 – 0.9 µm. The film thickness was determined by means of a Dektak 8 surface profilometer.

3 Results and discussion A comparison of the XRD patterns corresponding to the Kapton® films with different thickness used in this study and that of a commonly used soda-lime glass substrate showed important microstructural differences. SLG is an amorphous material whereas Kapton® films exhibit a semi-crystalline structure with the degree of crystallinity depending on their thickness. The root mean square (rms) surface roughness of the Kapton®

Film surface images were obtained by using an optical microscope, at a 100× magnification, equipped with a digital camera for images acquisition. The crystalline structure of the films was analyzed by X-ray diffraction (XRD) using a Phillips X’Pert diffractometer with nickel-filtered Cu Kα radiation. Calculation of the in-plane stress, $\sigma$, for selected films was done from surface-normal XRD measurements. The film resistivity, $\rho$, was measured with a four point probe system, Veeeco model FPP5000; four measurements were taken in different locations of the films and averaged. Microstructural characterization and roughness analysis were done by using a VEECO nanoscope IV multimode atomic force microscope (AFM). The public domain open source ImageJ (NIH, USA) platform [16] was used to analyze the mean grain size of the films from the resulting AFM images in addition to the average circularity of the grains. The total optical reflectance, $R$, was measured with unpolarized light at normal incidence in the wavelength range from 300 nm to 2300 nm, with a double beam Perkin–Elmer Lambda 9 spectrophotometer operating at room temperature.

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films, as determined by AFM, seemed to be independent of film thickness, obtaining values of about 1 nm in all cases.

Images obtained with the optical microscope (Fig. 1) show a continuous Mo layer independently of the Kapton® film thickness (25 µm and 125 µm) and the working gas pressure used during deposition (0.6 Pa, 0.9 Pa and 1.5 Pa). Important differences in the surface morphology arise with increasing the Ar pressure. As can be seen in Fig. 1, the films prepared at 0.6 Pa show some dots, while interconnected cracks appear on the surface of the films prepared at 0.9 Pa and 1.5 Pa. Several authors have attributed the appearance of cracks to a combination of high pressures with an open porous microstructure and/or residual stresses in the films [17–19]. The Mo/Kapton® structure showed some curvature which was more pronounced with decreasing the Ar pressure.

The degree of adhesion of the different films was qualitatively assessed by means of a single adhesive-tape test [3]. Only the films prepared at the lowest pressure, i.e., without cracks, passed the test while those with cracks were easily peeled off.

Figure 2a and b illustrate the XRD patterns of the Mo films prepared at the lowest (0.6 Pa) and highest (1.5 Pa) Ar gas pressures, respectively, on Kapton® substrates with different thickness. The reflection peaks measured in the range 2θ = 15°–30° are due to the Kapton® substrate. All the films show a strong (110) texture as commonly observed in sputtered Mo films [3, 11]. Small intensity peaks corresponding to the (200), (211) and (220) reflections can be additionally identified for both gas pressures, although the (200) reflection is practically absent at 0.6 Pa which might be due to the influence of the increased gas pressure on the transport direction in the sputtering [11, 20]. Insets of Fig. 2a and b show in detail the XRD profiles of the (110) reflection for the Mo films deposited onto Kapton® under two different Ar pressures (0.6 Pa and 1.5 Pa, respectively). Regardless the Ar pressure applied, a shift of the (110) peak to larger 2θ values is observed with increasing the Kapton® thickness which indicates a smaller interplanar spacing of the Mo film when using thicker Kapton® substrates.

Figure 3 shows the evolution of the in-plane stress, σ, with the Kapton® thickness for two different pressures (0.6 Pa and 1.5 Pa). Calculation of σ has been done according to

\[ \sigma = -\frac{E}{2\nu}\left(1 - \nu\right)\left(d - d_0\right) \]

where \( E = 3.36 \times 10^{11} \text{ Nm}^{-2} \) and \( \nu = 0.298 \) are the Young’s modulus and the Poisson ratio of bulk Mo in the (110) lattice direction, respectively [18]; \( d \) and \( d_0 \) are the out-of-plane lattice spacing and the “relaxed” lattice spacing, respectively. The determined σ values must be understood as an average magnitude of the stresses existing in the films [18]. A general trend which may be observed in Fig. 3 is an enlarged stress with increasing the
Kapton® substrate thickness. This might explain the more pronounced curvature which was observed for the latter. And, additionally, it agrees with the increased density of features (dots and cracks) observed in Fig. 1 with increasing the Kapton® thickness. Interestingly, in the case of substrates with 25 μm, 75 μm and 125 μm in thickness, the stress values obtained for 0.6 Pa and 1.5 Pa differ very little. This is in contrast with the optical microscope images from Fig. 1 which suggest that the density of cracks increases significantly with increasing the Ar gas pressure. An explanation for this apparent discrepancy might be the effect due to the tension exerted by the substrate holder on the Kapton® film; this external tension would be released after removal of the sample from the holder and would affect to the Mo layer deposited onto it. This would be in accordance with previous observations done by Jensen et al. [19] on tensioned molybdenum-coated polyimide. Returning to Fig. 3, we observe a significant difference between the σ values corresponding to the two represented pressures only for the case of a Kapton® substrate with a thickness of 50 μm. The stress for the Mo layer prepared at 1.5 Pa is significantly reduced. This may be understood studying the influence of the working gas pressure on the microstructure of the Mo film.

Figure 4a and b show SEM images of the microstructure and a cross-sectional view, respectively, for a Mo film grown onto 50 μm Kapton® at a working gas pressure of 0.6 Pa. The film surface is uniform with observable grains ranging in size between 70–100 nm (Fig. 4a). The cross-sectional view of the film (Fig. 4b) shows a dense film without visible porosity.

AFM was used to obtain detailed images of the surface topography. Due to the difficulty of obtaining quality AFM images of films prepared on flexible substrates, Mo films prepared onto 50 μm Kapton® were selected to study the influence of the working gas pressure on the microstruc-
Figure 6 Evolution of (a) the mean grain size (full symbols) and circularity of the grains (empty symbols) and (b) rms-roughness, with the working gas pressure for Mo films deposited onto a 50 µm Kapton® substrate. Insets to (b): Three dimensional reconstructions of the AFM images shown in Fig. 5b (Mo/Kapton® – 50 µm at 0.9 Pa) and 5c (Mo/Kapton® – 50 µm at 1.5 Pa) with a scanned area of 2 × 2 µm and a selected z-scale of 100 nm/div.

Figure 7 Evolution of the electrical resistivity, ρ, in dependence on the Ar gas pressure used during deposition of the Mo films onto Kapton® substrates with thickness of 25 µm, 50 µm, 75 µm and 125 µm. Inset: Evolution of ρ with the mean grain size determined from AFM images for a Mo film on a 50 µm Kapton® substrate.
films with larger grains (low Ar pressures) exhibit lower resistivities than those with a finer microstructure (high Ar pressures). Gordillo et al. [21] explained this behavior in terms of a reduction of the grain boundary potential barrier height, in addition to a reduced number of grain boundaries and/or a smoother surface show decreased resistivities by comparison with those with a finer microstructure and a rougher surface. This latter characteristic leads to a decreased reflectance as a consequence of a stronger light scattering effect.

4 Conclusions

The effect of the morphology and the microstructure on the optoelectronic properties of sputtered Molybdenum films onto Kapton® substrates has been analyzed in dependence on the working gas pressure and the substrate thickness. The increased pressure and/or substrate thickness may result in a high density of cracks on the Mo film which may be avoided by using sufficiently low pressures. Mo films deposited onto thick Kapton® substrates, at a fixed Ar pressure, are more prone to suffer stress effects than those prepared on thin substrates. Furthermore, the effect of increasing the Ar pressure is a poorer crystallinity of the Mo films, consisting of significantly smaller grains and an increased surface roughness compared to those at low pressures. The electrical resistivity and the reflectance of the films are strongly correlated with the microstructure and morphology. Mo films consisting of larger grains and/or a smoother surface show decreased resistivities by comparison with those with a finer microstructure and a rougher surface. This latter characteristic leads to a decreased reflectance as a consequence of a stronger light scattering effect.

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References


Figure 8 Representation of the reflectance, R, vs. the wavelength, λ, for Mo films deposited onto Kapton® substrates with thicknesses of 25 µm, 50 µm, 75 µm and 125 µm and prepared at 0.6 Pa and 1.5 Pa.