Deposition and characterization of molybdenum thin films using DC-plasma magnetron sputtering

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Molebdenum (Mo) thin films were deposited on well-cleaned soda-lime glass substrates using DC-plasma magnetron sputtering. In the design of experiment, deposition was optimized for maximum beneficial characteristics by monitoring effect of process variables such as deposition power (100−200 W). Their electrical, structural and morphological properties were analyzed to study the effect of these variables. The electrical resistivity of Mo thin films could be reduced by increasing deposition power. Within the range of analyzed deposition power, Mo thin films showed a monocrystalline nature and the crystallites were found to have an orientation along [110] direction. The surface morphology of thin films showed that a highly dense microstructure has been obtained. The surface roughness of films increased with deposition power. Adhesion of Mo thin films could be improved by increasing the deposition power. Atomic force microscopy was used for the topographical study of the films and to determine the roughness of the films. X-ray diffractrometer and scanning electron microscopy analysis were used to investigate the crystallinity and surface morphology of the films. Hall effect measurement system was used to find resistivity, carrier mobility and carrier density of deposited films. The adhesion test was performed using scotch hatch tape adhesion test. Mo thin films prepared at deposition power of 200 W, substrate temperature of 23°C and Ar pressure of 0.0123 mbar exhibited a monocrystalline structure with an orientation along (110) plane, thickness of $\sim$ 550 nm and electrical resistivity value of $0.57 \cdot 10^{-4}\ \Omega \cdot$ cm.

1. Introduction

Molybdenum (Mo) is the contact material commonly used in high efficiency solar cells. Thin films of Mo play an important role in the formation of copper-indium-galliun-selenide (CIGS) based thin film solar cells. The main properties of the Mo thin films which make it an proper back contact material for CIGS solar cells are: inertness during deposition of the CIGS absorber lauer foration of an ohmic contact, low recombination rate for minority carriers, relative stability at the processing temperature, low contact resistance to CIS and its alloys, resistance to alloying with Cu and In [1–8]. Mo has been reported by Scofield et al. [1] as a prevalent back contact material and leading choice for the CIS and CIGS solar cells. Like other refractory metals deposited through physical vapor deposition techniques, Mo thin films were deposited through DC-magnetron sputtering [9]. Argon pressure and deposition power an process parameters. It was reported that the lowest possible sheet resistance for back contact of the solar cell was obtained at the lowest Ar pressure [9]. Films deposited at higher pressure passed the adhesion test. Metals deposited through DC-magnetron sputtering possess a correlation between the sputter gas pressure and the stress of the as-deposited film [1]. Film deposition at high pressure leads the film to be under tensile stress and whereas film grow that low Ar pressure [9] leads the film to be under compressive stress.

Martinez and Guillen [6] studied the electrical, structural and morphological properties of Mo thin films prepared using RF-magnetron sputtering for various deposition parameters. They determined that all the samples have comparable electrical properties but to obtain densely packed structure and to have minimum stresses, it is necessary to have low RF-power densities.

As the properties of Mo play a critical role in performance of CIGS solar cells, our objective in this work was to study the effect applied DC power on the crystal structure, adhesion, morphology and resistivity of Mo thin films.

2. Experimental Details

2.1. Substrate Preparation

Soda lime glass (SLG) slides (SLG, Cat. No 7105) were used as substrates for the deposition of molybdenum thin films through DC-magnetron sputtering. The SLG substrates were cut down to the size of 1 cm × 1 cm × 1 mm. Substrates were cleaned using methanol, soap, chromic acid and distilled water. Initially the substrates were cleaned using methanol in an ultrasonic bath for 20 min. After scrubbing with soap, the substrates were dipped in chromic acid for 10 min. Finally the substrates were washed with distilled water using an ultrasonic bath for 30 min in order to remove impurities and contaminants from the surface of the substrate. Immediatly after drying, the clean substrates were transferred to the deposition chamber.

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Table 1. Summary of the deposition parameters for the preparation of Mo thin films

ID	Power (W)	Pressure (mbar)	Flow rate (sccm)	Substrate temperature (°C)	Time (min)
1	100	0.0123	18	RT	14
3	200	0.0123	18	RT	8

Table 2. Physical, electrical and adhesion properties of DC-plasma sputtered Mo films

Deposition power (W)	Thickness (nm)	Rate (nm/s)	Crystallite size (nm)	Strain %	Resistivity $\Omega \cdot$ cm	Tape Test
100	562	0.67	15.6	0.684	$4.85 \cdot 10^{-4}$	Pass
200	545	1.13	21.1	0.564	$0.57 \cdot 10^{-4}$	Pass

2.2. Film Fabrication

Molybdenum thin films were prepared on $1\,\text{cm} \times 1\,\text{cm} \times 1\,\text{mm}$ SLG substrates by means of a DC-magnetron sputtering system (Alliance Concept DP650). Mo was used as a target material. Substrates were subsequently introduced into the chamber. Before depositon of the thin film, target was pre-sputtered in an Argon atmosphere for about 15 min so that any oxide layer remains on the surface of the target can be removed. For this purpose the shutter was kept closed. The procedure for depositing all the films is as under

1. The chamber was evacuated to a base pressure of $7.49 \cdot 10^{-6}$ mbar.

2. Pure Argon (99.99%) flow was introduced into the chamber. The flow rate of Argon was 18 sccm and the working gas pressure was 0.0123 mbar.

3. The DC-power supply was then turned on. The DC-power was varied from 100 to 200 W. The experimental details are summarized in Table 1.

3. Results & Discussion

In this study, molybdenum (Mo) thin films were deposited using DC-plasma magnetron sputtering. Deposition power was analyzed using characterization tools in order to find optimum deposition conditions to obtain thin films of back contact material with high electrical conductivity for Cu (In, Ga)Se_2 based thin films solar cells.

The results obtained from different characterization tools and related discussions on each of these results are as under.

3.1. Structural Analysis

The X-ray diffraction patterns of Mo films produced at applied DC power of 100 or 200 W are presented in Fig. 1. The corresponding crystallite size and percent strain values calculated using XRD data are listed in Table 2. It can be seen that the crystallites of Mo films maintain the cubic crystal ctructure (JCPDS Card No 3-065-7442). From Fig. 1 it is clear that single main peak was observed with preferred crystallographic orientation along (110) plane. The average particle size or crystallite size was calculated from the broadening of the (110) peak using Scherrer with equation:

$$L = \frac{K\lambda}{B\cos\theta},$$

where $K(K = 0.94)$ is the Scherrer constant, L is the crystallite size, λ ($\text{Cu}K_\alpha = 1.5404$ Å) is the wavelength of the incident monochromatic X-ray bean and B is the FWHM of diffraction peak at θ. The crystallite size was found to increase as the deposition power increases

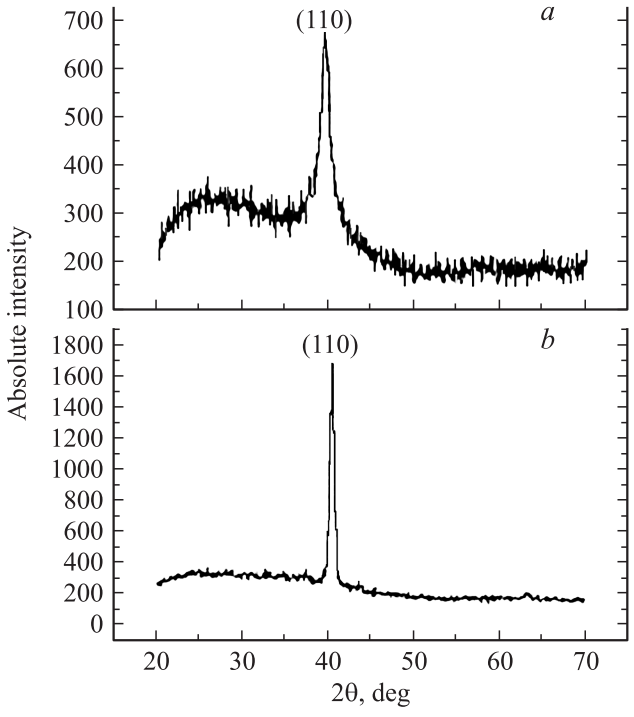

Figure 1. XRD patterns of Mo films produced at DC power of (a) 100 W and (b) 200 W.

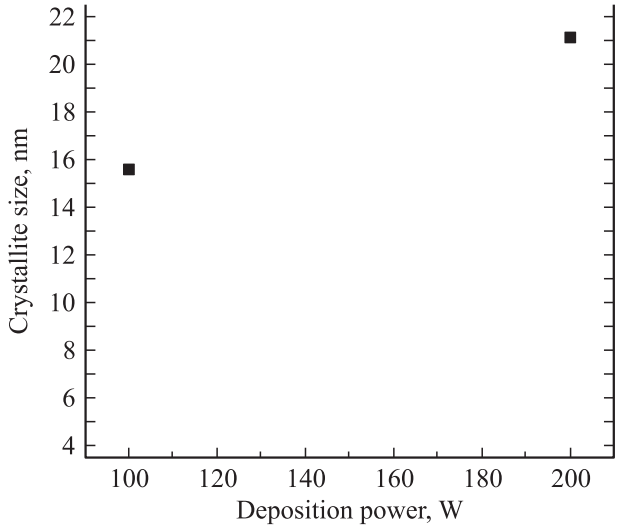

Figure 2. Crystallite size of Mo thin films as a function of deposition power.

(Fig. 2). Fig. 1 shows that the intensity of the (110) peak increases significantly as the deposition power increases. It was observed that in case the films produced at high deposition power, the kinetic energy of the species increases resulting in 3D Volmer–Weber growth. The films prepared at high deposition power were found to have highly dense microstructure with relatively higher degree of crystallinity and large crystallite size, whereas the films deposited at low deposition power are essentially more random and disoriented in nature [7].

The shift of the (110) peak along 2θ allowed us to calculate strain in thin films. The residual stress calculations were made from XRD-data by strain equation. Using Bragg's formula the inter-planar spacing d_{110} was calculated. The % strain in the films was then calculated by the following equation:

$$\text{Strain}(\%) = \frac{\Delta_a}{a}\,100\%,$$

where a is the lattice constant (for undeformed Mo lattice, $a = 0.31472$ nm). It is the main parameter for Mo films to determine whether the strain is compressive or tensile [1].

All the films showed tensile strain. It has been suggested that voids, crystallographic flaws, oxygen or argon impurities could be responsible for the stress in the sputtered Mo films [8]. It is argued that these effects are related to the frequencey of gas phase collisions in the sputtering system which alters the kinetic energy of both Argon and Mo atoms.

3.2. Electrical and Morphological Properties

Scanning electron micrographs of Mo thin films shown in Fig. 3 divulge the surface morphologies of the sputtered Mo thin films at different deposition powers. Literature review indicates that films sputtered at lower deposition power

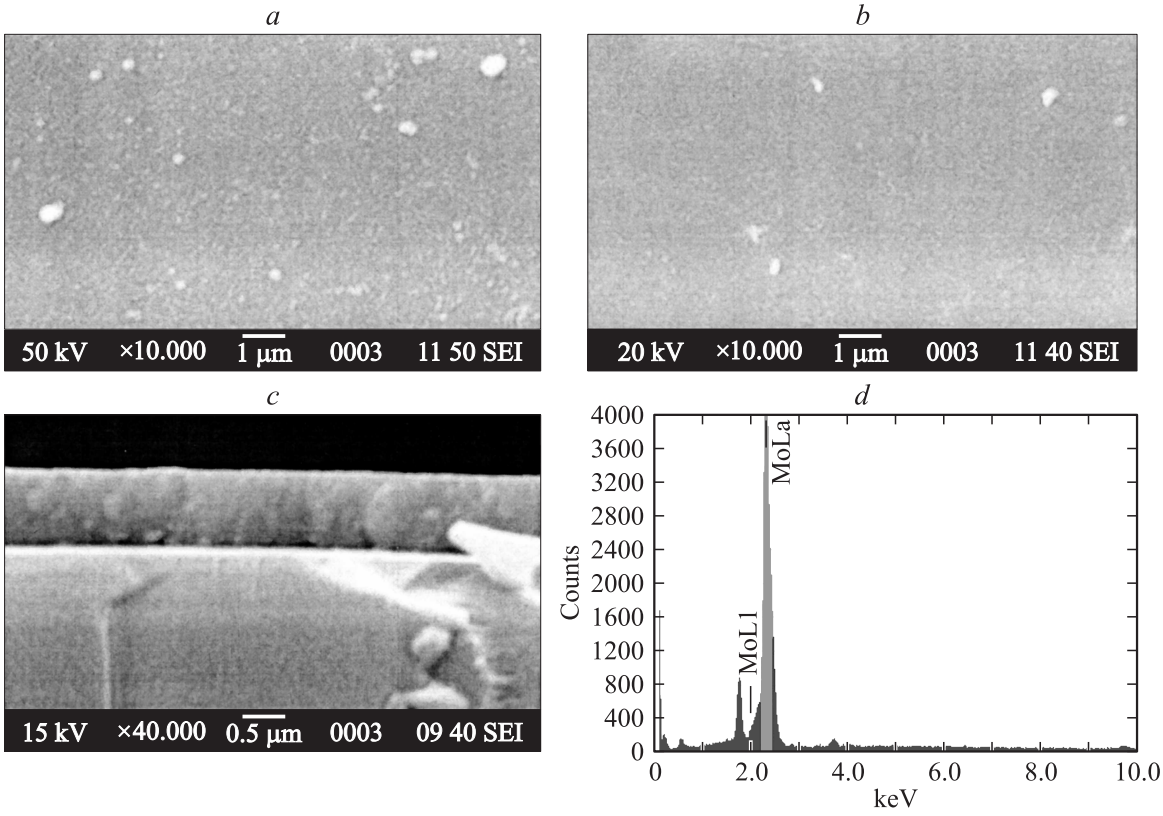

Figure 3. SEM micrographs of Mo thin films at (*a*) 100 and (*b*) 200 W (*c*) SEM cross-section (*d*) EDS analysis.

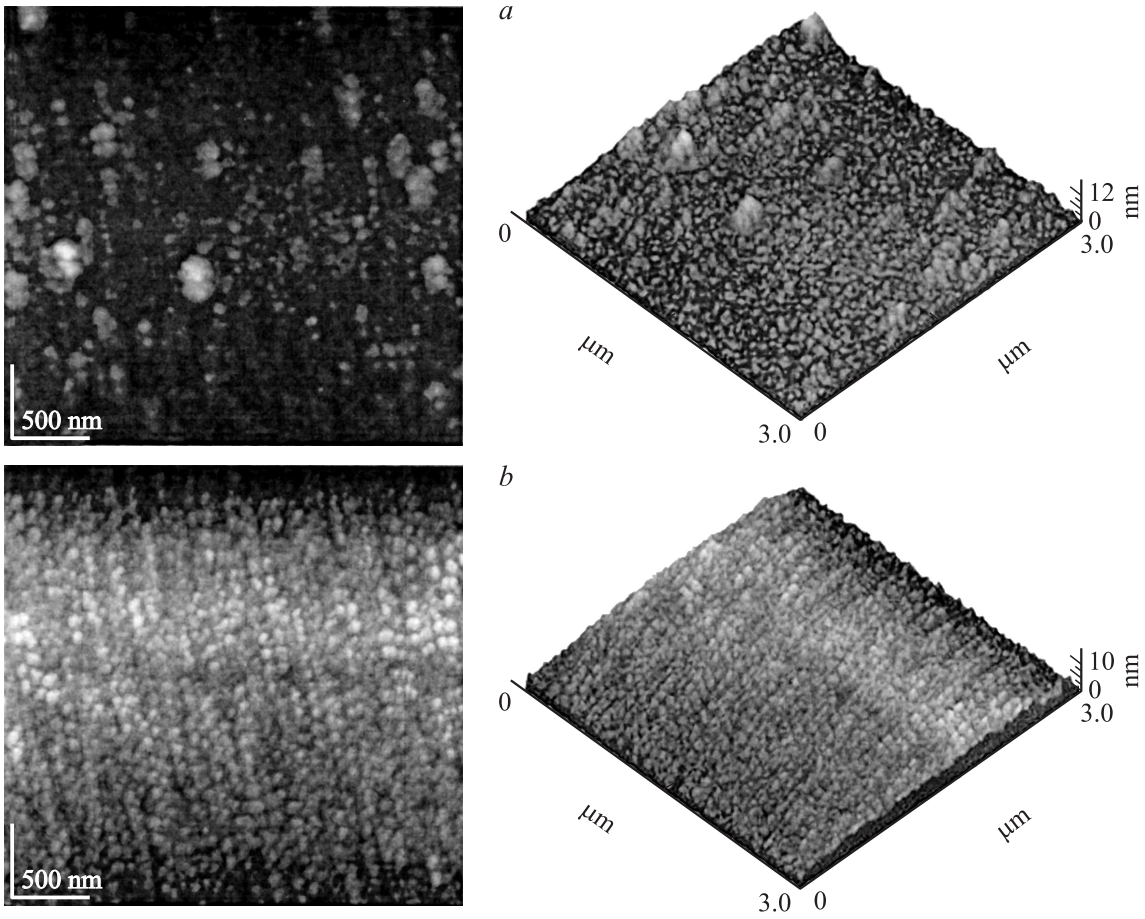

Figure 4. AFM morphologies of Mo thin films for deposition powers of (*a*) 100 and (*b*) 200 W.

exhibited porous microstructures while films sputtered at higher deposition power exhibited dense microstructures [9]. At higher deposition power, deposition rate increases so that number of species arriving at the substrate increases resulting in a denser microstructure while at low deposition power, deposition rate decreases and the number of species arriving at the surface of the substrate becomes less resulting in a porous microstructure. However, in our case no porous microstructure was observed. Fig. 3, *a, b* show film surfaces with smooth morphologies and dense microstructures. Fig. 3, *a* shows that the surface of the film is rough and less dense. As the deposition power increases, the surface becomes more smooth and compact, as shown in the Fig. 3, *b*. The cross-sectional view of the Mo film presented in Fig. 3, *c* also revealed morphology. The EDS analysis confirms that 100% Mo thin films was deposited.

Fig. 4 shows AFM images of Mo thin films sputtered at deposition power of 100 and 200 W. To study the surface features of Mo films, it is necessary to measure the main surface roughness parameters of these films, namely root mean square (RMS) and roughness average (R_a) Generally, the surface roughness at a certain area is determined by the height differences of all the distinct points at this area. RMS roughness is the mean of the root for the deviation from the standard surface to the indicated surface. R_a represents the 3D expansion of the center line mean roughness so that it is applicable to the measurement surface. The surface roughness of the films increased as

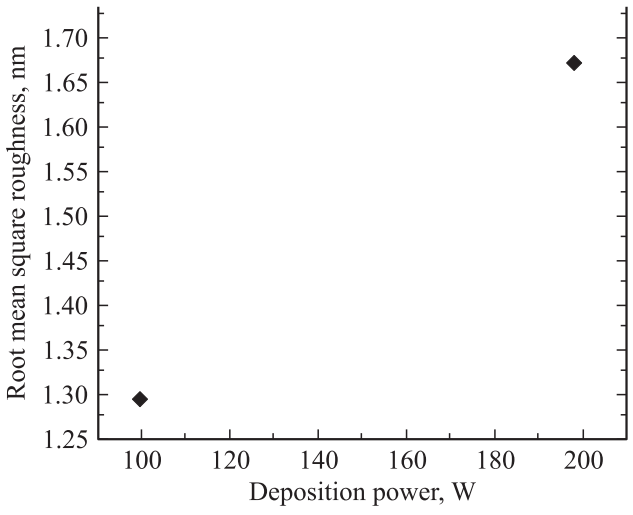

Figure 5. Root mean square roughness of Mo films as function of deposition power.

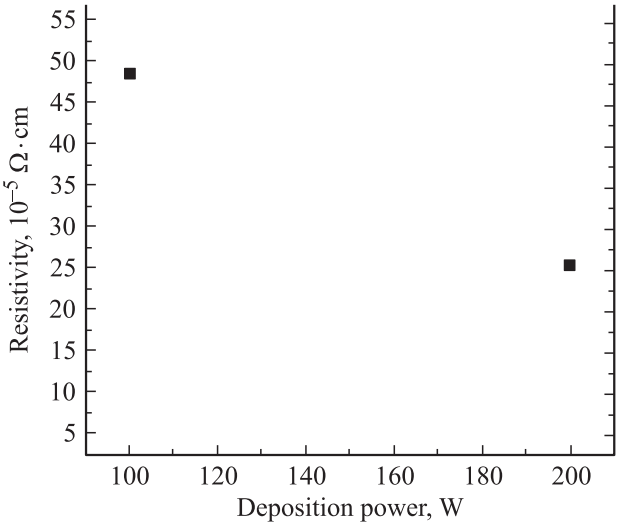

Figure 6. Resistivity of Mo films as a function of deposition power.

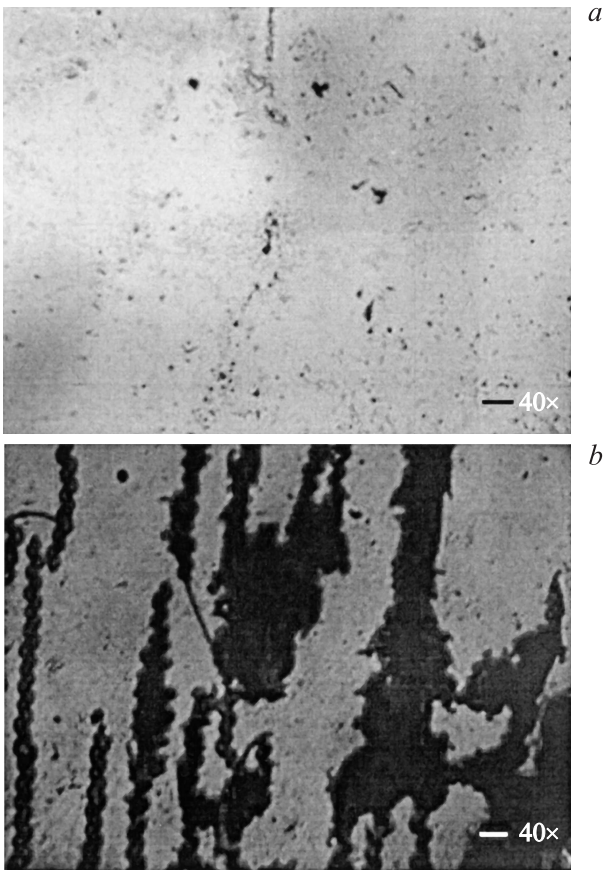

Figure 7. Optical images of Mo thin films after the scotch tape test at deposition power 100 (a) and 200 W (b)

applied DC power was increased [10]. The average surface roughness R_a for the films deposited at 100 and 200 W was about 0.962 and 1.34 nm respectively. The root mean square roughness R_q (RMS) also increases as the deposition power increases as shown in the Fig. 5. This result is attributed to a significant increase in the flux of sputtered Mo species incident initially at the substrate surfe, and later, at tthe growing film.

The electrical resistivity of the Mo thin films was determined using van der Pauw method. In agreement with Gardillo et al. [3], the resistivity value was found to drop upon increasing DC power to 200 W. The resistivity data is graphically presented as a function of applied DC power in Fig. 6, while chamber pressure and substrate temperature were maintained at their respective values of 0.0123 mbar and 298 K. Since both films are of approximately same thickness, this decrease in electrical resistivity maybe attributed to a more dense, crystalline structure with low defect density obtained in case of film growth at 200 W.

3.3. Adhesion of Mo Thin Films

The adhesion of the films was investigated with scotch tape adhesion test by gluing the tape on the surface of the film and it by applying manual force. The adhesion property worsens as the deposition power increases (Fig. 7). The delamination of the film from the substrate at high deposition power can be attributed to a fast deposition rate of Mo on the substrate. Consequently, the successive deposited Mo layers lack the appropriate time to strongly adhere to the substrate.

4. Conclusions

Thin films of molybdenum were prepared on soda lime glass substrates using DC-magnetron sputtering system. The effect of deposition power on film microstructure, resistivity and interfacial strength of the Mo thin films have been investigated. The following conclusions were drawn from this work.

For the range of synthesis conditions investigated, deposited films were found to exhibit single diffraction peak corresponding to (100) plane. This finding is in agreement with reported literature. Film morphology was found to be very smooth with a low average surface roughness value.

Minimum value of electrical resistivity, as measured using Hall effect apparatus, was $\sim 0.57 \cdot 10^{-4}\,\Omega \cdot \mathrm{cm}$ for films produced at 200 W. This combination of processing parameters 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.

Thin films investigated showed characteristics internal residual stresses. Within the range of deposition parameters studied, Mo thin films were under tensile stresses.

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