4. 1 Introduction

Vast majority of important technological applications of thin films are in their polycrystalline form. Polycrystalline metal thin films are used in wide range of applications like VLSI and ULSI metallization and protective coatings. However, all common thin film deposition techniques utilize vacuum deposition processes. These deposition processes inherently introduce residual stress in the deposited thin films that merit investigation [1]. This stored mechanical stress can have deleterious effects on the film-substrate system. It can either cause cracking of the film in case of tensile stress ‘or’ buckling in case of a compressive stress [2]. It also plays an important role in the evolution microstructure and thus affects the mechanical and other associated properties of the film like for example, change in superconducting transition temperature $T_c$ of Mo films with residual stress [3]. As such, evaluation of residual stress in vacuum deposited polycrystalline metal thin films is technologically important from both application and the related deposition process optimization point of view and as well as for understanding the nature of thin film growth characteristics. Among the two commonly used non-destructive techniques, residual stress analysis using X-ray diffraction has found wide acceptance as it allows the determination of
complete stress tensor for all crystallite phases present and can also provide other additional information like texture and crystallite size [4]. The other method is substrate curvature measurement method based on Stoney’s formalism [5]. However, the classical \( \sin^2\psi \) method (\( d \) Vs \( \sin^2\psi \)) for stress analysis which relies on the measurement of peak shifts of a high angle reflection as a function of specimen tilt \( \psi \) often fails when applied to thin films [6], the limiting factors being the thickness of films and the occurrence of crystallographic texture. The highly penetrating symmetric Bragg Brentano (BB) geometry used in the \( \sin^2\psi \) method and the resulting low diffraction volume therein result in a signal too weak to be measurable with good peak to noise ratio. The elastic anisotropy introduced due to texture often limits the number of measurable reflections at high angle [7-8]. Hence, an asymmetric geometry employing low grazing incidence is generally used for the residual stress analysis of thin film specimens, because of its inherent advantage in limiting the penetration of X-ray beam and maximizing the diffraction volume within the films. Indeed, several authors have proposed and employed different modified \( \sin^2\psi \) methods using a small fixed grazing incidence either in the Seemann-Bohlin (SB) or GIXRD geometry [9-10] for thin films. These modifications are possible when assumptions with regard to lattice symmetry, elastic properties and stress state are considered[11]. While some authors measure the peak shift of a single reflection, some of them combines the peak shifts from multiple reflections to find out the stress [4,7,12]. But both or all the approaches are same in a way because stress is calculated from the slope of a straight line fitting obtained through a linear regression of some function of the inter-planar spacing \( d \) and the specimen tilt angle \( \psi \) as in the traditional \( \sin^2\psi \) method. A comparison is given in most cases. It is also noteworthy to mention that while a multiple \( hkl \) method gives a stress value averaged over all crystallographic planes, a
single $hkl$ method provides stress for a selected family of planes. These two values can differ.

In this chapter, the effect of substrate temperature ($T_s$) on the in-plane biaxial residual stress in polycrystalline Mo thin films is investigated. The residual stresses are estimated using both multi $hkl$ reflection peak shifts as well as single $hkl$ reflection peak shift methods in a parallel beam geometry. These estimates were used to study the evolution of residual stress as a function of $T_s$ and the results are compared. The deposited films exhibit a compressive stress at low deposition temperature which reverses to a tensile one at high deposition temperature. The origin and evolution of the residual stress as a function of $T_s$ is elucidated in this chapter.

4.2 Mathematical Formalism

Hooke’s law relating the stress to the strain forms the basis of X-ray stress analysis in materials. Hooke’s law in its generalized form [13] is given by

$$\varepsilon_{ij} = \frac{1}{E} \sigma_{ij} - \frac{\nu}{E} \delta_{ij} \sum_k \sigma_{kk}$$  \hspace{1cm} (4.1)

where $\varepsilon_{ij}$ and $\sigma_{ij}$ are the $ij^{th}$ component of the strain and stress tensors, respectively; $E$ and $\nu$ represent elastic modulus and Poisson ratio, respectively.

Experimentally, X-ray stress analysis relies upon the measurement of strain induced in the lattice by the residual stress. The direction of the measured strain is defined by the rotation of the azimuth angle $\phi$ and inclination of the specimen tilt angle $\psi$, respectively, in a laboratory frame of reference. The lattice spacing $d^{hkl}$ is related to the diffraction angle $2\theta^{hkl}$ by Bragg’s law

$$2d^{hkl} \sin \theta^{hkl} = \lambda$$  \hspace{1cm} (4.2)
where \( \lambda \) is the wavelength of the X-ray used.

The strain is then given by

\[
\varepsilon_{\phi \psi}^{hkl} = \frac{d_{hkl} - d_{0}^{hkl}}{d_{0}^{hkl}}
\]  
(4.3)

where \( d_{0}^{hkl} \) is the strain free lattice spacing of the \( hkl \) lattice planes. Stress is then derived from the measured strain by inserting a reliable proportionality constant. Fig. 4.1(a) shows the relation between laboratory and specimen frames of references and Fig. 4.1(b) shows the various angles with their axes.

The strain tensor in the laboratory frame is related to the strain in the specimen reference frame by a tensor transformation which is given by

\[
\varepsilon_{\phi \psi}^{hkl} = \varepsilon_{33}^{L} = m_{i}^{s} \varepsilon_{ij}^{s} m_{j}^{s}
\]  
(4.4)

where \( m^{s} = \begin{pmatrix} \sin \Psi \cos \phi \\ \sin \Psi \sin \phi \\ \cos \Psi \end{pmatrix} \)  
(4.5)

is a unit vector along the direction of diffraction vector as expressed in the specimen frame of reference.

Upon substituting the equation (4.1) into equation (4.3), the fundamental equation for X-ray stress analysis is obtained as:-

\[
\varepsilon_{\phi \psi}^{hkl} = \frac{1}{2} S_{2}[\left( \sigma_{11}^{s} \cos^{2} \phi + \sigma_{22}^{s} \sin^{2} \phi + \sigma_{12}^{s} \sin 2\phi \right) \sin^{2} \Psi \\
+ (\sigma_{13}^{s} \cos \phi + \sigma_{23}^{s} \sin \phi) \sin 2\Psi + \sigma_{33}^{s} \cos^{2} \Psi]
\]  
+ \( S_{1} (\sigma_{11}^{s} + \sigma_{22}^{s} + \sigma_{33}^{s}) \)  
(4.6)
Fig. 4.1 (a) Relation between the specimen (S) and the laboratory (L) reference frames; (b) the ω, φ and χ axes that describe the orientation of the specimen with respect to the laboratory frame of reference.
where $S_1$ and $\frac{1}{2}S_2$ are the elastic constants of the material. For isotropic materials, these are related to $E$ and $\nu$ of the material by the following relations

$$S_1 = -\frac{\nu}{E} \quad (4.7)$$

and

$$\frac{1}{2}S_2 = \frac{(1 + \nu)}{E} \quad (4.8)$$

---

**Fig. 4.2 (a)** Relation between the specimen tilt angle $\Psi$, the incident angle $\alpha$ and the Bragg angle $\theta_{hkl}$ for a set of $\{hkl\}$ planes in the asymmetric diffraction geometry.
In the biaxial stress model, all off diagonal components of the stress tensor vanish along with the out-of-plane component (i.e. $\sigma_{33}^S = 0$) and the only non-vanishing components are the in-plane component $\sigma_{11}^S = \sigma_{22}^S = \sigma_{\parallel}$ such that the stress tensor transform to

$$
\sigma_{ij}^S = \begin{pmatrix}
\sigma_{\parallel} & 0 & 0 \\
0 & \sigma_{\parallel} & 0 \\
0 & 0 & 0
\end{pmatrix}
$$

(4.9)

Considering the specimen to have rotational symmetry, the fundamental equation (4.6) reduces to

$$
\varepsilon_\psi = \frac{1 + \nu}{E} \sigma_{\parallel} \sin^2 \psi - \frac{2\nu}{E} \sigma_{\parallel}
$$

(4.10)

This is the well known classical $\sin^2 \psi$ formalism

4.3 Sample preparation and experiments

4.3.1 Thin film deposition

For the present study, polycrystalline Mo thin films were sputter deposited onto clean $p$-Si (111) substrates from a pure 2” Mo target using a radio frequency magnetron sputtering unit. The substrate temperature $T_s$ was systematically varied from room temperature (RT) to 800 °C in steps of 100 °C. The base pressure and the argon partial pressure in the deposition chamber during deposition were $\sim 10^{-6}$ mbar and $4 \times 10^{-3}$ mbar, respectively. The sputter power and deposition times were maintained at constant values of 130 watt and 7 minutes, respectively for all the depositions. In addition, a pre-deposition sputtering for about 5-10 min was maintained to achieve both sputtering equilibrium as well as to remove any surface
oxide present on the Mo target. The thickness of the films thus deposited ranges from 183 – 215 nm as measured by a surface profiler.

4.3.2 Stress measurement using GIXRD

All the XRD measurements in the present study were performed on a Bruker D8 diffractometer with parallel beam Cu kα; λ = 1.5406 Å. The diffractometer is equipped with a rotating anode (Cu) generator and it is operated at 4.5 kW and 100 mA current. Two methods were used:

(a) multi hkl method

Using a low angle of incidence α = 0.7°, the 2θ-detector scan was performed for an extended range of 2θ from 30° to 145° to record all measurable reflections in the GIXRD geometry. This extended 2θ scan was used to study the phase characteristics of the deposited films. It further formed the basis for residual stress analysis using multiple hkl reflections. It is because in the asymmetric geometry, each diffraction vector of different hkl reflection makes different angles with the specimen surface normal. These angles are uniquely related to the specimen tilt angle ψ. As can be seen in Fig. 4.2, the angle ψ for a set of {hkl} planes is given by

\[
ψ = θ^{hkl} – α
\]  

(4.11)

where ‘\(θ^{hkl}\)’ is the Bragg angle for a corresponding hkl plane.

Rotational symmetry of the stress state was checked by measuring the strain at three different azimuth angles φ = 0, 45 and 90° ‘or’ by doing φ – scans.
(b) Single hkl method

For thin films, it is important to select a ‘strong’ rather than a ‘high’ hkl reflection which can be measured with reliable peak-to-noise ratio for an extended range of $\psi$. Hence in the single hkl reflection method, the angle of incidence was fixed at a low value $\alpha = 0.7^\circ$ and the detector scanned the 20 range from 37.5$^\circ$ to 43.5$^\circ$ to measure the Mo (110) peak – the 100% peak for Mo. The measurement was repeated for various values of the specimen tilt angle $\psi$. The set of $\psi$ values† were chosen so as to obtain an equidistant net of $d$ values in the $\sin^2 \Psi$ plots. The $\chi$-mode (Fig. 4.1b) was used to vary the specimen tilt angle $\psi$ in the range from 0$^\circ$ to 71.57$^\circ$ in a way similar to the traditional $\sin^2 \psi$ method, but in the asymmetric parallel beam geometry. The angle $\alpha$ was kept constant for each $\chi \neq 0$ (i.e. each $\psi$) value by adjusting the angle $\omega$ as per the condition given in reference no. 4 which is

$$\sin \alpha = \sin \omega \cos \chi$$

(4.12)

4.3.3 Other experimental details

The compositional distributions of the impurities in the films were probed by using a CAMECA IMS-7F Secondary Ion Mass Spectrometer (SIMS). The parameters used for acquiring the depth profiles were 10 nA Cs$^+$ primary ion beam current, 45$^\circ$ angle of incidence, 5 keV impact energy, 250 $\mu$m raster size and 33 $\mu$m analyzed area. The species of interest were sampled as molecular Cs-complex ions viz., (CsM)$^+$, where $M$ is a metal. The SIMS crater depths were determined using a DEKTAK surface profiler. The peak positions (centroid) of all the measured XRD peaks presented in this chapter were determined by line profile analysis using a pseudo-Voigt function fitting.

† Values of $\psi = 0^\circ, 18.43^\circ, 26.57^\circ, 33.21^\circ, 39.23^\circ, 45^\circ, 50.77^\circ, 56.79^\circ, 63.43^\circ$ and 71.57$^\circ$
4.4 Experimental Results

The GIXRD patterns for the as-deposited films are shown in Fig. 4.3. The peak patterns were indexed [14] to cubic-bcc structured polycrystalline Mo and these are in good agreement with JCPDS card no: 421120.

![GIXRD Pattern](image)

*Fig. 4.3 GIXRD pattern for the Mo thin films deposited at various substrate temperatures.*

For thin films with cubic symmetry, elastic isotropy and rotational symmetry, the residual stresses can be obtained from the slope of linear regressions performed on the strain distribution given by the fundamental equation for X-ray stress analysis in accordance with Eqn. (4.10) and the insertion of appropriate elastic constants. The value of Poisson ratio and elastic modulus used in the present study were: $\nu = 0.31$ and $E = 329$ GPa, respectively.
4.4.1 Single hkl method

For the single hkl peak shift analysis, the strongest reflection Mo (110) was selected as it can safely be measured with a reliable peak-to-noise ratio for the large angular range of tilt angles $\Psi$ from 0 to 71.57 °. The measured values of lattice spacing give the $d$-$\sin^2 \Psi$ distribution plot for each specimen. Some representative $d$-$\sin^2 \Psi$ plots are shown in Fig. 4.4. The unstrained lattice or $d$-spacing $d_0$ were determined from the $d$-distribution plot as the $d$-value corresponding to the strain free tilt angle $\Psi^*$ which is derived from Eqn (4.10) after setting $\varepsilon_\psi = 0$ as

$$\sin^2 \Psi^* = \frac{2\nu}{1 + \nu} = 0.4732$$  \hspace{1cm} (4.13)

for each film deposited at various temperatures. These $d_0$ values show good agreement with values lying within 2.223 ± 0.004 Å. The lower and upper bound of $d_0$ value observed in this study are shown in Fig. 4.4. The corresponding plots of lattice strain $\varepsilon_\psi$ Vs $\sin^2 \Psi$ obtained for all the specimens are shown in Fig. 4.5. The values of residual stresses obtained upon performing linear regression analyses of the plots shown in Fig. 4.5 are tabulated in Table 1. One can observe that high compressive stress results at low deposition temperature which gradually relaxes and then changes to a tensile one at high deposition temperature. However, unlike films deposited at other temperatures, the $d$-distribution plot of the films deposited at 400 °C and 500 °C shows an oscillatory behavior (Fig. 4.6) suggesting presence of strong textures/anisotropy in the deposited films. Moreover, there is no significant $\Psi$-splitting of the $d$-distribution plot for positive and negative tilts showing the absence of shear stress. Hence, the single hkl peak shift analysis fails for cases where anisotropy is introduced by grain texturing/grain interactions.
**Fig. 4.4** $d$-$\sin^2 \psi$ plots for (110) reflection of Mo films deposited at (a) room temperature and (b) 600 °C. $\Psi^*$ and $d_0$, respectively, are the stress free tilt angle and stress free lattice spacing in corresponding film.
Fig. 4.5 Lattice strain $\varepsilon_\psi$ Vs $\sin^2\psi$ plots from Mo (110) reflections of Mo thin films deposited at various substrate temperatures. The straight lines represent the corresponding linear regression lines.

4.4.1 Multi hkl method

The peak positions of the GIXRD pattern in Fig. 4.3 were used to perform the multi $hkl$ analysis for residual stress in the deposited films. For cubic system, the lattice spacing $d$ of each $hkl$ reflection is uniquely related to the lattice parameter $a$ by the relation

$$a = d\sqrt{h^2 + k^2 + l^2}$$  \hspace{1cm} (4.14)

And hence, the strain $\varepsilon$ can be expressed either as

$$\varepsilon = \left(\frac{d - d_0}{d_0}\right) \quad \text{or} \quad \varepsilon = \left(\frac{a - a_0}{a_0}\right)$$  \hspace{1cm} (4.15)

depending on the availability of either a reliable strain free lattice spacing $d_0$ or lattice
Table 4.1

Comparison of residual stress values obtained through single hkl and multiple hkl peak shifts analysis in Mo thin films.

| Substrate temperature (°C) | Residual stress $\sigma_{||}$ (GPa) |
|---------------------------|----------------------------------|
|                           | Single hkl method | Multi hkl method             |
|                           | $(d - d_0) \nu_s \sin^2 \psi$ | $(a - a_0) \nu_s \sin^2 \psi$ |
| 30                        | -1.858             | -2.526                       | -2.471                       |
| 200                       | -1.215             | -2.084                       | -2.029                       |
| 300                       | -0.507             | -0.853                       | -0.798                       |
| 400                       | anisotropic        | -0.288                       | -0.233                       |
| 500                       | anisotropic        | -0.222                       | -0.167                       |
| 600                       | 0.436              | 0.126                        | 0.181                        |
| 700                       | 0.705              | 0.658                        | 0.713                        |
| 800                       | 0.778              | 0.728                        | 0.801                        |

Parameter $a_0$. In the former case, as many $a_0^{\text{hkl}}$ values as the multiple hkl reflections are included in the analysis for the stress determination. In the present study, $a_0^{\text{hkl}}$ values from the standard Mo powder data (JCPDS card no: 421120) were used to find the corresponding strain in each hkl reflection of the measured pattern. In the latter approach, the recorded lattice spacing $d$ of each hkl reflection is converted into equivalent lattice parameters $a$ (through Eqn. 4.14) [15] and the strain is determined using the well known bulk lattice parameter of Mo ($a_0 = 3.147$ Å). Subsequently, residual stress is determined by fitting the measured strain as a function of $\sin^2 \psi$ using
Fig. 4.6 Oscillatory behaviour in $d$ Vs $\sin^2\psi$ plots obtained from (110) reflection of Mo films deposited at (a) 400 °C and (b) 500 °C.
Equation (4.10). Representative plots showing both the multi \( hkl \) approaches are illustrated in Fig. 4.7. Although the latter approach have been claimed to be beneficial [12], no significant difference in the values of the residual stresses were observed in the present study. The values of residual stresses obtained using both these multiple \( hkl \) approaches are given in Table 1. While both the multi \( hkl \) methods show comparable values of residual stress, the averaging effect of the stresses over all crystallographic planes in the multiple \( hkl \) method makes it slightly different from the values estimated using single \( hkl \) reflection. However, unlike in the single \( hkl \) method, texture seems to have little effect on the measurement of stress in the multi \( hkl \) approach as can be seen from \( \varepsilon \) Vs \( \sin^2\psi \) plots for 400 °C and 500 °C in Fig. 4.8. This is indicative of the fact that the multi \( hkl \) approach has distinct advantages over the single \( hkl \) approach.

Both the single and multi \( hkl \) approaches clearly demonstrate the general evolutionary trend of residual stress in Mo films as a function of substrate temperature. Low temperature deposited films contain high compressive residual stress. The stress is so high (~ 2.5 GPa) for RT deposited films that blister buckling delamination that is common in compressively stressed film [16-17] is seen in the form of formation of telephone cord structures on aging. Though this kind of delamination may be driven by the wetting of the substrate prior to deposition of the film from the residual water vapour in the deposition chamber, the magnitude of strain energy that is stored in the films deposited at such low temperature compounded the process of delamination into a physical manifested pattern as shown in Fig. 4.9.
Fig. 4.7 Lattice strain $\varepsilon_\psi$ Vs $\sin^2 \psi$ plots for the multi hkl approach (a) $(d - d_0)/d_0$ Vs $\sin^2 \Psi$ for RT and (b) $(a - a_0)/a_0$ Vs $\sin^2 \Psi$ for 800 °C. The straight lines represent linear regression lines.
Fig. 4.8 Lattice strain $\varepsilon_\Psi$Vs $\sin^2\Psi$ plots for the multi hkl approach: (a) $(a - a_0)/a_0$ Vs $\sin^2\Psi$ for 400 °C and (b) $(d - d_0)/d_0$ Vs $\sin^2\Psi$ for 500 °C. The straight lines represent linear regression lines.
Fig. 4.9 Telephone cord structure assisted buckling in Mo films deposited at room temperature indicating presence of large amount of compressive stress stored in the film.

The delamination is absent in rest of the thin film specimen deposited at higher substrate temperature. This is due to the fact that the magnitudes of stress are comparatively less and also because a heated substrate assembly serves to desorb any absorbed water vapour. The magnitudes of compressive residual stress slowly decrease with increasing $T_s$ and it turns into a tensile stress at high $T_s$. 
4.5 Discussion

The evolution of stress as a function of $T_s$ can be understood as below. The total macroscopic residual stress in a thin film system is basically composed of two components – (a) intrinsic and (b) thermal components [18]. Intrinsic stress is the component of stress that results from the cumulative effects of crystallographic defects that occur due to the non-equilibrium nature of the growth process. Thermal stress is the component that results because of the mismatch in thermal expansion coefficient of the film and the substrate; it is generally observed when the film-substrate system is cooled down to RT after deposition. Generally, intrinsic stress dominates at low $T_s$ and is important for films with low ad-atom mobility, but thermal stress gains importance and dominates at high $T_s$. For films whose thickness is small in comparison with the substrate’s thickness and assuming that the plastic flow in the substrate is negligible, the thermal stress in the film is given by [18]:

$$\sigma_{th} = \frac{E_f}{(1-v)} \left( \alpha_f - \alpha_s \right) (T_s - T_a)$$  \hspace{1cm} (4.14)

where $E_f$ is the young’s modulus of the film, $\alpha_f$ and $\alpha_s$ are the average thermal expansion co-efficient for the film and substrate, respectively. $T_a$ is the temperature at which stress measurement is carried out (usually RT).

A positive value of $\sigma_{th}$ indicates a tensile stress while a negative value that of compressive stress. As $T_s$ almost invariably exceeds RT ($T_a$) in all practical cases, a tensile stress is generally expected for films having higher thermal expansion co-efficient than the substrate. Accordingly, from Equation (4.14), a tensile stress is
expected when Mo is deposited on Si substrate because of the higher thermal expansion co-efficient of Mo than Si at all range of temperatures [19-20]. The calculated values of thermal stresses that are expected to be generated in Mo films deposited at different elevated temperatures upon cooling down to RT are given in Table 2. There is a good agreement between these calculated values and the values estimated from X-ray stress analysis at high $T_s$ as shown in Fig. 4.10. Hence, the observed tensile stress in films deposited at high $T_s$ is attributed to the thermal stress generated in the Mo films upon being cooled down to RT. However, such an observation is overshadowed by the dominance of intrinsic stress at low $T_s$. At low $T_s$, the ad-atoms mobility is quite low and intrinsic stresses that are compressive in nature results, the reason for which is analyzed and deliberated in the following.

**Table 4.2**

*Values of thermal stress expected in Mo films deposited on Si substrate at various elevated temperatures from Equation (4.14) with data from Ref. 19 and 20.*

<table>
<thead>
<tr>
<th>Substrate temperature (°C)</th>
<th>Thermal stress $\sigma_{th}$(GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>0.16</td>
</tr>
<tr>
<td>300</td>
<td>0.237</td>
</tr>
<tr>
<td>400</td>
<td>0.313</td>
</tr>
<tr>
<td>500</td>
<td>0.40</td>
</tr>
<tr>
<td>600</td>
<td>0.51</td>
</tr>
<tr>
<td>700</td>
<td>0.638</td>
</tr>
<tr>
<td>800</td>
<td>0.795</td>
</tr>
</tbody>
</table>
Fig. 4.10 Evolution of residual stress in sputter deposited Mo thin films as a function of substrate temperature.

Atomic peening from reflected neutral argon atoms had been long considered as the cause of compressive stress in sputter deposited thin films [21-23]. However, it is more so for cylindrical magnetron and forms small to negligible contribution for planar magnetron geometries [24]. In cases where such peening process is profound, the amount of trapped working gas (Ar) in the films will serve to indicate the extent of such peening effect. Fig. 4.11 shows the SIMS compositional depth profiles of Ar and O impurities in the deposited films. It is observed that the Ar intensity and hence the amount of atomic peening thereby ascribable to it, are constantly low in all the thin film specimen, revealing that peening is indeed negligible for the planar magnetron geometry used in the present study. On the other hand, the presence of oxygen
impurities can be observed in the films deposited at low $T_s$ below 500 °C, while films deposited at high $T_s$ and above 500 °C are free of oxygen impurities. It has been recently reported that the origin of compressive stress in polycrystalline thin films can be traced to diffusion of ad-atoms into the grain boundaries because of higher than equilibrium condition that raise the surface chemical potential during growth [25-26]. And since the O impurities get completely desorbed from the growing film at high temperature $T_s > 500$ °C, it is less likely that it occupies a substitutional impurity site. With less thermal energy for desorption at low $T_s$, the most probable place for O atoms to get absorbed into the growing film are the grain boundaries. These O atoms may also play a decisive role in the evolution of the film’s microstructure as a function of substrate temperature (which mainly influences the ad-atom mobility). The cross sectional SEM micrographs of Fig. 4.12 illustrate the micro-structural evolution of the Mo films deposited at different substrate temperatures. Features ranging from wavy crystalline to fibrous grains that are characteristics of zone I in Thornton’s structure zone model (SZM) scheme [27], and Zone Ia, Ib and Ic of the extended SZM scheme of Mahieu [28] can be seen in low temperature deposited films. The growth of these fibrous grainy features through diffusion is limited by both the oxygen impurities and ad-atoms mobilities at relativity low $T_s$. This fact is further supported by the observation of T. Yamaguchi et al. where they investigated the role of O in decreasing the width of the fibrous grains with increasing oxygen and the associated compressive stress it generates [29]. Hence, the compressive nature of the intrinsic stress prevailing at low deposition temperature is attributed to the oxygen impurities that are incorporated into the growing film along with other defects associated with low ad-atom mobility. And as $T_s$ increases, thermal desorption of O atoms increases and correspondingly ad-atom mobility also increases leading to grain
Fig. 4.11 SIMS depth profiles of (a) Argon and (b) Oxygen, in Mo films deposited at various substrate temperatures.
Fig. 4.12 Cross sectional micrographs of Mo films deposited at various substrate temperatures.
restructuring in terms of grain growth and finally leading to re-crystallization at higher temperature which aids the expulsion of O from the growing films. While facet poly-crystals with distinct columnar structure that are characteristics of inter grain diffusion of ad-atoms expected in the zone $T$ of the SZM were observed for films deposited above 600 °C, re-crystallization were observed for higher $T_s$ at 800 °C (Fig. 4.12). The subsequent attractive interaction along the boundaries of the compactly packed columnar grains at higher $T_s$ along with the mismatch in thermal expansion co-efficient between the Mo films and Si substrate result in a tensile stress at high $T_s$.

**Conclusion:**

The effects of substrate temperature on the resulting residual stresses in sputtered deposited polycrystalline Mo thin films deposited on Si were investigated using X-ray diffraction studies employing both single $hkl$ as well as multiple $hkl$ methods. High compressive stress (as high as 2.5 GPa for RT deposited film) were observed at low deposition temperature while the stress was tensile at high deposition temperature. While the compressive stress results from the intrinsic component of stress introduced by O impurities during growth at low $T_s$, thermal stress due to mismatch in average thermal expansion co-efficient of the film and substrate reverses it to tensile stress at high $T_s$. 
References


