CHAPTER VII

ELLIPSOMETRIC STUDY OF THERMAL EFFECTS ON SILVER THIN FILM SURFACES

7.1 Introduction

In the study of the optical properties of thin films it is generally assumed that the boundaries between the media are perfectly flat planes. However, in practice, it is difficult to prepare perfectly smooth flat surfaces. Hence the interpretations of the experimental results, based on the above assumption, may be seriously affected (especially in the short wavelength region). It is therefore necessary to consider the influence of the surface roughness on the optical studies of thin films.

As stated in the earlier chapter, ellipsometry finds a unique place in this field. Of the two parameters \( \psi \) and \( \Delta \) in ellipsometry, the first one is directly affected by the surface roughness and the second one by the thickness factor in the case of films with thickness \(<100\text{Å}\) and for films of larger thickness, both these parameters are equally affected by the factors\(^1,^7\). Probably this may be the reason due to which this technique is widely used for this type of investigations. A brief review of earlier works gives an idea about the importance of this technique.
7.1a Brief review of earlier works

Mainly the works in this field can be divided under two subheadings; one based on the Maxwell Garnett theory\textsuperscript{2-4} and the other on Kirchhoff's theory of diffraction. The work by Fenstermaker et al\textsuperscript{5} can be taken to be the pioneering one in this field. In that they calculated the effects on the optical constants (mainly the refractive index) produced by the surface irregularities of known shapes like square ridges, triangular ridges and pyramidal shaped irregularity. They found large errors in the refractive index values even for a small value of roughness (≈50Å). Smith also used the same theory for the study of the surface of aluminium in different conditions\textsuperscript{1,6,7}. In the study of aluminium surface during fatigue cycling\textsuperscript{6}, he had described ellipsometry as a unique means of following the developments of submicroscopic cracks. In another work he studied the variations in ellipsometric parameters by using controlled surface roughness experiments on aluminium. In this work, he also used the scanning electron microscope, light scattering technique, photoelectron emission, surface potential difference and water
contact angle measurement along with ellipsometry. In another very elaborate study on aluminium surface it was found that the effect of 32 contaminants comprising of different types like, processing errors (like anodisation voltage or anodisation time) handling damages, human contamination (like finger prints or cigarette smoke) and constituents of smog (like stearic acid, Eruic acid, Brassidic acid, Benzoic acid, Amino-Benzoic acid etc.). In this ellipsometric technique alone was found to be capable of detecting the effect of 26 contaminants. The surface potential difference method was capable of detecting the effects of 17 contaminants while the water contact angle measurement could detect the effects of only 14.

Ohlidal et al8-12 through a series of publications developed a theory to deal with the variations of $\gamma$ and $\Delta$ due to surface roughness and is based on the Kirchhoff's theory of diffraction. In their earlier works8,9 they developed the theory by which they analysed the variations in $\gamma$ and $\Delta$ caused by rough surfaces of isotropic materials. Later in another publication10 the effect of randomly rough surface was studied which was based on Stratton-Chu-Silver integral and compared it with earlier results.
obtained using Kirchhoff's theory. They also showed that the theoretically calculated value of the ellipsometric parameters for a randomly rough surface correspond to the experimental values measured with ideal ellipsometers. Brudzewski\textsuperscript{13} used this technique to measure the variations in polarisation of He-Ne laser light reflected from silicon and germanium surfaces. In this a rough surface is taken to be equivalent to a thin rough layer over a smooth surface and the theoretically calculated values of polarisation are compared with those measured in experiment for different samples of rms roughness in the range 2-20nm. The author used the same theory for the study of tungsten-tungsten oxide system\textsuperscript{14} also to calculate the variation of ellipsometric parameters due to surface roughness. Here the rough surface is considered as a transitional layer between the bulk substrate and the surrounding medium. Maris et al\textsuperscript{15} studied the surface of gold film on glass substrate and showed that $\psi$ and $\Delta$ depend not only on surface roughness, but also on the root mean slope of the irregular height. Chan\textsuperscript{16} analysed the free surface as well as the metal-glass interface of rough metallic films sputtered onto smooth pyrex
substrate. The work was based on Maxwell Garnett theory\textsuperscript{2-4} and the study was performed on platinum, molybdenum and vacuum annealed molybdenum. Scanning electron microscopy was also used along with ellipsometry. Marten\textsuperscript{17} also elucidated the capability of Maxwell Garnett theory for the study of roughness of silicon surfaces. Svilashov et al\textsuperscript{18} studied the surface of silicon and germanium at different stages of etching. They considered the roughness as a transition layer with optical constants that change continuously from those of the bulk material (which forms the lower layer) to those corresponding to air. They pointed out that the changes in the values of the optical constants are due to the variations in the polarisation angles caused by the roughness. Vorburger et al\textsuperscript{19} also noted the effect of roughness on ellipsometric parameters. They found that, due to roughness, the values of $\Psi$ and $\Delta$ varied much rapidly with the angle of incidence.

In the present work, the surface roughness created by heating on silver films is analysed by using ellipsometry. It has been stated (in chapter III) that heating (annealing) of silver films results in the hillock growth on the surface of the films. This
growth is found to be strongly dependent on the stress in the film. Hence the low temperature annealing (i.e., upto ~250°C) produces very interesting result of minimisation of hillock growth at a particular temperature. In order to get a clear picture of this phenomenon (for example, to have an idea regarding the relation between the temperature and thickness of the film or the variation of the temperature in different ambient conditions) ellipsometric technique was selected for the elaborate investigation. A two layer model consisting of rough upper layer and a smooth lower layer, is considered for this study. The theory for this investigation is given briefly in the next section.

7.2 Theory of roughness measurement

In the last chapter, it was shown that for any plane polarised light, there can have two components; one in the plane of incidence (p-component). Due to reflection from a surface, in general, there is a relative phase change $\Delta$ and a relative amplitude reduction $\psi$ of these two components. These are the parameters directly measured in ellipsometric technique and used for the calculation of the refractive index.
of the material. But in the derivation of the equations connecting the refractive index and ellipsometric parameters the most important assumption is that the surface is perfectly smooth (see fig.7.1a). Hence, when the surface is rough, the calculated value of refractive index may not be correct and can have large deviations from the actual value.

Representing the rough surface as equivalent to a homogeneous film for reflection may not appear to be correct. In terms of ray optics, reflection occurs from the sides and top of the 'irregularity'. Then the multiple reflected beam can be combined together to get the total reflected light beam. However, in almost all the cases, the dimensions of the roughness will be always much smaller than the wavelength of the visible light and hence the ray optics cannot be used here. On the other hand, the light 'sees' an average effective refractive index \( N_e \) for the rough surface. Optically this has the effect of replacing the 'roughened surface layer' by an equivalent film with refractive index \( N_e \) and having plane parallel boundaries (see fig.7.1b). The thickness
Fig. 7.1a Smooth surface of an ideal film as conceived in the theory.
Fig. 7.1b(i) Actual film surface with irregularities.
Fig. 7.1b(ii) Replacement of the roughened surface by an equivalent film with parallel boundaries.
of the 'equivalent film' is equal to the characteristic roughness height parameter (eg. the rms value). The relation between the effective refractive index \(N_e\) and the actual refractive index of the material of the film \(N_f\) is given by the relation (according to Maxwell Garnett theory\(^2\!-\!^4\))

\[
\frac{N_e^2 - N_a^2}{N_e^2 + 2N_a^2} = Q \frac{N_f^2 - N_a^2}{N_f^2 + 2N_a^2}
\]  

(7.1)

where \(N_a\) is the refractive index of the ambient and \(Q\) is the volume factor occupied by the irregularities. Hence any change in the size of the irregularities will be represented by a corresponding change in the \(Q\)-factor value. In the present work the ambient is air so that \(N_a = 1\). Using ellipsometry one can calculate the value of \(N_e\) and for silver \(N_f\) is easily obtained. Thus \(Q\) becomes the only unknown which can be calculated from eqn.(7.1).

7.3 Experimental

Silver films for the present work, were prepared by using the vacuum evaporation technique which is described elsewhere\(^20\). All the thin films
were prepared under identical conditions. The samples were of two types which differed in thickness only; the first type was having a thickness of 1500Å while the second type was 3000Å thick. The wide difference in thickness was kept in order to have the variations due to thickness difference more pronounced (Here also the required thickness for the films was obtained by evaporating calculated mass of the evaporant which was obtained using the relation given in chapter III. Later the thickness was verified by using the multiple beam interferometric technique and the difference from the calculated value was not greater than ±50Å).

Heating of the films was done in a glass cell both in air and vacuum (the pressure being maintained at 10⁻² torr for the latter case) and the set up is described in chapter II. The films were kept pressed against an aluminium block which was electrically heated and temperature was measured by using a thermocouple. The heating rate for all the films was 1°C/minute.

The ellipsometric set up used for the measurements was a static photometric type and consisted of polarised-system-analyser arrangement.
Its detailed description is given in chapter II and the theoretical aspects are included in chapter VI. Using this set up $\psi$ and $\Delta$ values were measured at different values of angle of incidence (in the range $60^\circ-75^\circ$). The Q-factor value was computed from the values of the ellipsometric parameters at the angle of incidence $60^\circ$ for all the films. A mini computer (Micro-78) was used for this purpose.

7.4 Results

Figs.7.2 and 7.3 represent the variations of the Q-factor with temperature for the films of thickness 1500Å and 3000Å respectively. Figs.7.4a and 7.4b give the $\Delta$ values at different temperatures $^\circ$ for the films of thickness 1500Å when annealed in vacuum and air respectively while Figs.7.5a and 7.5b give the corresponding values for the other type of films with thickness 3000Å.

7.4a For films with thickness 1500Å

In the case of this film, the Q-factor shows a steady increase with temperature when annealed in air. But when the films are annealed in vacuum, the Q-factor value at first shows a very slight decrease
Fig. 7.2 Variation in Q-factor with annealing temperature for silver films of thickness 1500A.
- o-o when annealed in vacuum;
- - - when annealed in air.
Fig. 7.3 Variation in Q-factor with annealing temperature for silver films of thickness 3000A.
- - - when annealed in vacuum,
- - - when annealed in air.
upto \( \sim 70^\circ C \) and then increases. As the temperature value reaches \( \sim 160^\circ C \) the increase in Q-value is almost stopped and it tends to remain a constant.

The variations in A values are also of the same nature (Figs. 7.4a and 7.4b). Due to annealing in air, A value is reduced and this reduction is more or less uniform. On the other hand, when the films are annealed in vacuum, there is a very sharp decrease in A value upto \( 109^\circ C \). But as the annealing temperature increases, the reduction is rather retarded showing a tendency to remain constant.

The variations of the Q-factor and A values with annealing temperature lead to the same conclusion. When these are annealed in vacuum, upto \( \sim 70^\circ C \) there is no hillock growth and thereafter the growth takes place upto \( \sim 160^\circ C \). As the temperature increases above \( 160^\circ C \) the growth is stopped. But when annealing is done in air, the hillock growth starts from the beginning of heating and continues with no retardation.

7.4b For films with thickness 3000A

As the thickness is doubled, there is marked variations in the nature of the changes of the film surface. Here also, annealing in air causes increase
Fig. 7.4a  Variation in $\Delta$ values with angle of incidence for silver films (of thickness 1500Å) at different annealing temperatures (annealing in vacuum): $\Delta_1$, before annealing; $\Delta_2$, after annealing at 109°C, $\Delta_3$, after annealing at 180°C.

Fig. 7.4b  Variation in $\Delta$ values with angle of incidence for silver films of same thickness at different annealing temperatures (annealing in air): $\Delta_1$, before annealing; $\Delta_2$, after annealing at 109°C, $\Delta_3$, after annealing at 180°C.
Fig. 7.5a Variation in $\Delta$ values with angle of incidence for silver films (thickness - 3000A) at different temperatures (annealing in vacuum)

- $\Delta-\Delta$, before annealing;
- $\Delta-\Delta$, after annealing at 105°C,
- $\circ-\circ$, after annealing at 143°C;
- $\bullet-\bullet$, after annealing at 180°C.

Fig. 7.5b Variation in $\Delta$ values with angle of incidence for silver films of same thickness at different temperatures (annealing in air)

- $\Delta-\Delta$, before annealing;
- $\Delta-\Delta$, after annealing at 67°C;
- $\circ-\circ$, after annealing at 105°C;
- $\bullet-\bullet$, after annealing at 143°C;
- $\bullet-\bullet$, after annealing at 180°C.
in Q-factor value. But this happens up to \( \sim 120^\circ C \) only. Beyond that temperature the Q-factor is constant up to \( \sim 150^\circ C \). As the temperature increases further, there is a sharp increase in its value also. But when annealing is performed in vacuum there is slight reduction at first (upto \( \sim 70^\circ C \)) after which it increases till about 100°C. Beyond that temperature, the Q-factor value shows a slight decrease.

The variations of \( \Delta \) values are also indicating the same result. In the fig.7.5a (which gives the variations due to vacuum annealing) it can be seen that the \( \Delta \) values at 105°C and 143°C are the same for all angles of incidence, which indicates that the size of the irregularities is remaining constant in this temperature range. But at 180°C, the values show an increase hinting that the size of the irregularities is slightly reduced which is also clear from the Q-factor values in fig.7.3. In the case of the films annealed in air also, the \( \Delta \) value variations support the Q-value variations. Here, the \( \Delta \) values show a slight decrease at 67°C while at 105°C the decrease is considerably large and steep. (Compare this with the sharp increase in Q-value at 105°C in fig.7.3). At the angle
of incidence $60^\circ$, there is no change in its value for $105^\circ C$ and $143^\circ C$, (which can be compared with the constant value of $Q$ in the same range of temperature in fig.7.2). On further increasing the temperature, $\Delta$ is found to be decreasing again.

Thus here the observations lead one to the following conclusions. When thickness of the film is increased, the vacuum annealing results in the retardation of hillock growth at a lower temperature. Annealing in air also has a no-hillock growth region (or a constant $Q$-value region) between $120^\circ C$ and $150^\circ C$ which is not observed in the case of films with thickness $1500\AA$.

7.5 Discussion

In this case also, the relationship between the hillock growth and the stress in the film should be considered for the explanation and this theory has been described in detail in chapter III. The most important point in the theory, put forward by Presland et al\textsuperscript{23}, is the condition for hillock growth to take place and that can be written as

$$\gamma \ll \frac{\sigma r_0}{2}$$  \hspace{1cm} (7.2)
where $\gamma$, $\sigma$ and $r_0$ represent the same parameters as stated in chapter III. For convenience, the discussion part may be divided into two; one part deals with the results of annealing in vacuum while the other deals with those of annealing in air.

7.5a Annealing in vacuum

On heating a metallic film coated over glass substrate, beyond its deposition temperature, thermal stress develops in the film which will be compressive in nature. The intrinsic stress formed in the film during deposition itself is tensile in nature. Hence due to heating, the net effect will be to reduce the resultant stress in the film because these components of stress are opposite to each other. When the stress in the film is reduced to such a low value that the condition in eqn.(7.2) is not satisfied the hillock growth stops. When this happens the Q-factor in eqn.(7.1) remains constant. This is exactly taking place here. Due to vacuum annealing, for the films with thickness 1500Å this happens at $\sim 160^\circ\text{C}$ (fig.7.2) and for the other type of films (3000Å thick) it occurs at $\sim 100^\circ\text{C}$ (fig.7.3). These observations are again supported by $\Delta$ values in figs.7.4a and 7.5a.
But there is a striking difference between the temperature values at which the hillock growth stops (at which Q-value becomes constant) for the two types of films. It can be very easily seen from the figs. 7.2 and 7.3 that for the thinner films this takes place at a higher temperature while in the case of thicker films this happens at a lower temperature. In order to understand its reason one has to see fig. 7.6 which shows the variation of intrinsic stress with thickness \(^{24,25}\) (of silver films). It is quite clear from the figure that silver films, with thickness \(\sim 1500\text{Å}\), have maximum intrinsic stress and as the thickness increases further, the intrinsic stress decreases. Hence for the films with thickness \(1500\text{Å}\), the thermal stress has to be increased to a very high value in order to reduce the resultant stress in the film to such a low value that eqn. (7.2) is not satisfied and thereby the hillock growth is retarded. On the other hand for the thicker film, this phenomenon can take place at a low temperature because of the low intrinsic stress.

For both types of films, no appreciable change in Q-value is noted up to \(\sim 70\degree\text{C}\). This may be due to the 'induction time effect' observed by
Fig. 7.6 Variation of intrinsic stress in silver films with thickness.
Presland et al\textsuperscript{23} on silver films annealed in vacuum. During the annealing process of silver film they observed that there was no appreciable change for the film for a particular period of time in the initial stage of annealing and this period of time was called the 'induction time' ($t_i$). They also found that $t_i$ is very much reduced in presence of oxygen and the variation is governed by the relation

$$t_i = 11.5 - 3.8 \log_{10} P_{O_2}$$  \hspace{1cm} (7.3)

where $P_{O_2}$ is the pressure of oxygen. In the present work also no such variation in Q-factor is observed for annealing in air. Hence it is concluded that this effect may be due to induction time.

7.5b Calculation of intrinsic stress

As a support to the above argument, the intrinsic stress in the silver films (for the two thickness) has been calculated. For this calculation, the value of the thermal stress, at the temperature at which the Q-factor becomes a constant, is assumed to be (approximately) equal to the intrinsic stress. But the thermal stress can be easily calculated using
the expression,

\[ \sigma_{\text{thermal}} = \frac{\alpha_t - \alpha_s}{1 - \nu} E(\Delta T) \]  

(7.4)

where \( \alpha_f \) and \( \alpha_s \) are linear thermal expansion coefficients of film and substrate, \( E \) is the Young's modulus of the film material, \( \nu \) is Poisson's ratio of the film and \( \Delta T \) is the temperature difference. The values obtained in the present work and those obtained by earlier workers\(^{24}\) are given in table 7.1.

Table 7.1

<table>
<thead>
<tr>
<th>Thickness ( \AA )</th>
<th>( \sigma_{\text{intrinsic}} ) (from earlier works) ( \times 10^9 ) dynes cm(^{-2} )</th>
<th>( \sigma_{\text{intrinsic}} ) (present work) ( \times 10^9 ) dynes cm(^{-2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>1.25</td>
<td>1.5</td>
</tr>
<tr>
<td>3000</td>
<td>0.75</td>
<td>0.82</td>
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It can be seen that they are in good agreement in spite of the approximation that both the intrinsic and thermal stresses are taken to be equal at the temperature for which Q-factors becomes constant.
7.5c Annealing in air

When silver films are kept in air, the only change to be taken into account is that of the surface energy ($\gamma$). It will be considerably reduced in presence of oxygen in air and the variation is given by the relation (ref.24 of chapter III)

$$\gamma = 228 - 188 \log_{10} P_{O_2}$$

(7.5)

where $P_{O_2}$ is the pressure of oxygen. Hence, when the annealing is in air, $\gamma$ will have a very low value. But to stop the hillock growth one should have,

$$\gamma > \frac{\sigma f_0}{2}$$

(7.6)

When annealing is in air, to satisfy the above condition $\sigma$ (the resultant stress in the film) must be reduced to a very low value for which the thermal stress must be increased very much (i.e., the temperature at which the difference between the thermal stress and intrinsic stress becomes less than $\gamma$, is very high when compared with the corresponding temperature value in the case of vacuum annealing). This is clearly indicated by the Q-factor variations with temperature in figs.7.2 and 7.3.
In the case of films with thickness 1500Å, due to vacuum annealing, the Q-values become constant at \( \sim 160^\circ C \). But when similar films are annealed in air, no such variations are taking place even up to 180°C. Similarly for the other type of films (3000Å thick) the vacuum annealing results in a constant Q value at \( \sim 100^\circ C \) while due to annealing in air the Q-factor becomes constant at about 120°C. Here also for the thinner films, this phenomenon occurs at higher temperature due to reasons stated in section 7.5a while discussing the results of vacuum annealing.

The second increase in Q-factor after 150°C (in fig.7.3) is due to the action of the thermal stress alone. Even after making the resultant stress in the film a minimum, the thermal stress is increasing along with the temperature. Now as the intrinsic stress is completely overcome, the resultant stress starts increasing along with the thermal stress component. Hence the condition in eqn.(7.2) is again satisfied whereby the hillock growth resumes. This is the reason behind the second increase of the Q-factor.

7.6 Conclusion

The relation between hillock growth and the stress distribution in silver films is studied in the
present work using ellipsometry. Here the conclusions are drawn from the variations of two factors viz., the Q-factor and $\Delta$. It has been found that due to annealing in low temperature range (i.e., $< 200^\circ$C) the stress in the films can be minimised. The temperature at which this occurs depends upon the thickness of the film and the ambient in which annealing is performed. As stress is minimised the hillock growth (surface roughness due to thermal effects) on the film surface is also stopped.
REFERENCES


