SURFACE STUDIES OF SOME METALLIC THIN FILMS BY OPTICAL METHODS

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DECLARATION

Certified that the work presented in this thesis is based on the original work done by me under the guidance of Dr.C.Purushothaman, Professor, Department of Physics, University of Cochin and has not been included in any other thesis submitted previously for the award of any degree.

Cochin 682022
May 28, 1984

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CERTIFICATE

Certified that the work presented in the present thesis is based on bona fide work done by Mr.K.P.Vijayakumar, Research Scholar, under my guidance in the Department of Physics, University of Cochin and has not been included in any other thesis submitted previously for the award of any degree.

Cochin 682022
May 28, 1984

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PREFACE

Optical properties of thin films are well-known due to the practical applications of thin films in different fields. The main limitation in experimental as well as theoretical aspects of the same was the difficult calculations involved and this has been removed by the introduction of high speed computers. But the factors affecting the surface and structure of films, causing variations in their optical properties, are enormous in number. In this work, the effects of some among them are studied in detail.

The thesis aims to present the results of experimental investigations on the changes of optical properties of metallic thin films due to heating. The parameters which are measured are reflectivity, refractive indices and the ellipsometric quantities ψ and Δ. The materials used in the studies are metals like Silver, Aluminium and Copper. By applying the optical method the interdiffusion taking place in multilayer films of Aluminium and Silver has also been studied. Special interest has been taken to reveal the mechanisms of the hillock growth and surface roughness caused by heating and their relation with the stress in the film.

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The thesis contains nine chapters which are generally self-contained with separate abstracts; however there exist many cross references among chapters. Chapter I is of an introductory nature. It contains some general considerations regarding the scope and importance of the present work. It also gives a brief description of the different features affecting the optical properties of films and a summary of different methods for its analysis. A brief survey of the earlier works is also included in this chapter. The present status and some aspects of the application of the optical studies are presented in the second half of this chapter.

The next chapter gives the details of the experimental procedure. It contains the description of method of preparation of the samples and the thickness measuring technique. The experimental set up for annealing and optical measurements are also included in the chapter.

The changes in the reflectivity of Silver films due to annealing in the temperature range $30^{\circ}C$ to $300^{\circ}C$ are discussed in chapter III. Here the results of annealing in air and vacuum are considered separately. The explanation of these changes is given on the basis

of the relationship between the internal stress and the surface energy of the film.

In the chapter IV, the study of interdiffusion in multilayer films by using reflectivity measurements is presented. Here the materials are Aluminium and Silver with the former always forming the lower layer. The changes of reflectivity of both surfaces of the film are studied as a function of temperature. The effect of different thickness ratios of the two layers is also considered.

The chapter V contains the results of the studies on Copper films. Here the temperature variation is from $50^{\circ}C$ to $200^{\circ}C$ and the thickness of the samples varies from $500\overset{o}{A}$ to $3000\overset{o}{A}$. From these results an attempt is made to calculate the intrinsic stress values of Copper films of different thickness.

A brief description of ellipsometry, including the basic theory, is presented in the next chapter. It also contains the details of the ellipsometric set up used for the investigation. In the second half of this chapter, the different uses of ellipsometry are included.

In chapter VII, the results of ellipsometric measurements of thermally induced surface roughness (hillock growth) of silver films are presented along with the required theory for the measurement of surface roughness by using ellipsometry. The variation of the hillock growth with thickness of the film is also brought under discussion. This chapter also contains the calculated values of intrinsic stress in Silver films of different thicknesses.

The light scattering measurements can give a lot of information regarding the roughness of film surfaces. Hence the surfaces of the samples analysed by using the ellipsometric method have been again examined by using light scattering technique and this is presented in the next chapter. These confirm the results of ellipsometric measurements mentioned in earlier chapter.

All these observations are summarised in chapter IX. This also points out the importance of the low temperature annealing.

A theoretical study of the lattice dynamics of ZnS crystal is also included as an appendix in the thesis. In this, the phonon frequencies for [100],[110]

and [111] wave vector directions are calculated for both normal crystal and the isotope substituted one $(Zn^{34}S)$. From these two values the eigenvector magnitude is computed for the three wavevector directions.

Part of the investigations presented in the thesis has been published/communicated in the form of following papers:

1. Effect of annealing on the reflectivity of Silver film
   K.P.Vijayakumar and C.Purushothaman
   Thin Solid Films 82, 225 (1981).

2. Temperature variations of reflectivity of Al-Ag double layer films
   K.P.Vijayakumar and C.Purushothaman
   Proceedings of Nuclear Physics and Solid State Physics Symposium held at Banaras Hindu University, Varanasi, Vol.25C, p.8JB5 (1982).

3. An optical study of the thermal effects on Cu films
   K.P.Vijayakumar and C.Purushothaman
   Thin Solid Films, 112, 71 (1984).

4. Optical study of surface diffusion in Silver films

   K.P.Vijayakumar and C.Purushothaman

   Proceedings of Nuclear Physics and Solid State

   Physics Symposium held at University of Mysore,

   Mysore, Vol.26c, p. SAB8 (1983).

5. Lattice vibrations and eigenvector magnitudes in ZnS

   K.P.Vijayakumar and C.Purushothaman

   Indian Journal of Pure and Applied Physics,

   19, 749 (1981).

6. Ellipsometric study of thermal effects on Silver films

   K.P.Vijayakumar and C.Purushothaman

   (Communicated to Surface Science).

7. Hillock growth measurement by light scattering

   technique

   (Communicated to Applied Optics).

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CONTENTS
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CHAPTER I

OPTICAL PROPERTIES OF SINGLE AND MULTILAYER FILMS : GENERAL INTRODUCTION

1.1 Introduction

Thin films are used in a wide variety of scientific, engineering and industrial appliances. For example, their use is pervassive in integrated circuits; metal films are used for electrical connections and on the gate regions of the field-effect transistors; oxide or nitride films form insulating barriers between films; and layers of semiconductors are unavoidable parts of all structures. The latest application of thin film technology is in circuits based on films made from superconductors forming Josephson junctions. Similarly, thin films are familiar in optics as antireflection coatings on video screens, camera lenses etc. The ingenious exploitation of the interference phenomena in thin films has led to the development of sophisticated multilayer systems with nearly ideal reflection, antireflection polarisation, narrow and wide band

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reflection transmission and filtering, absorptance
and emittance properties. These optical coatings are
indispensable for several optical instruments.

Thin films also play an important role in
the field of material studies when optical methods
are employed. This is because they provide clean
and smooth surfaces which can be used for the optical
experiments like the determination of the optical
constants of materials. Again studies on absorption
in infrared and ultraviolet and photoemission have
yielded valuable information on the basic electronic
parameters of materials. The surface modes in an
ionic lattice can be excited in thin films and this
affects the plasma radiation emission and absorption
in metals. Studies of these absorption phenomena
give information about the lattice dynamics of the
materials.

The phenomenal growth of thin film research
and development owes much to the stimulus provided
by the early utilitarian interest in the application
of optical films in mirrors and interferometers.
The theoretical and experimental investigations on
the optical behaviour of thin films mainly deals with

optical reflection, transmission and absorption

properties and their relation to the optical constants

of the films. These elaborate studies have led to

the development of complex multilayer optical systems

with remarkable reflection, antireflection, inter-

ference and polarisation properties for both industrial

and laboratory applications. Moreover, using the

reflection, transmission and interference properties

of thin films new methods have been developed to

determine the optical constants conveniently which

will be discussed later.

1.2 Theory of thin film optics

In order to understand different optical

experiments one has to see the theoretical aspects

regarding the interaction of electromagnetic waves

with a multilayered system. In many of the optical

experiments on thin films, one is mainly concerned

with reflection and transmission and hence the theory

is also oriented in that direction. For convenience,

this section is divided into two parts; the first

part deals with ambient-film-substrate system and

the second part gives the more complicated case of

ambient-multilayer film-substrate system. A very

much simplified version of the first part is included
in chapter VI to show the relation of ellipsometric
parameters with reflectivity and transmission
coefficients.

1.2a   Single layer film

The system consists of ambient (medium-O),
the film (medium-1) and the substrate (medium-2) as in
fig.1.1. All these layers are considered to be
homogeneous optically isotropic with their surfaces
smooth and flat. They are having indices of refraction
N_o, N_1 and N_2 respectively of which most probably, N_o
is real (since ambient may be air) and the rest may
be complex. In this section, the complex index of
refraction is denoted as

$$N = n - ik \tag{1.1}$$

where n is the index of refraction and k is the
extinction coefficient (n and k may also be called
as real and imaginary parts of the complex index
of refraction N). The film is having a thickness 'd'.
A plane wave is incident on the interface between
the medium-O and medium-1 (the O-1 interface) at an
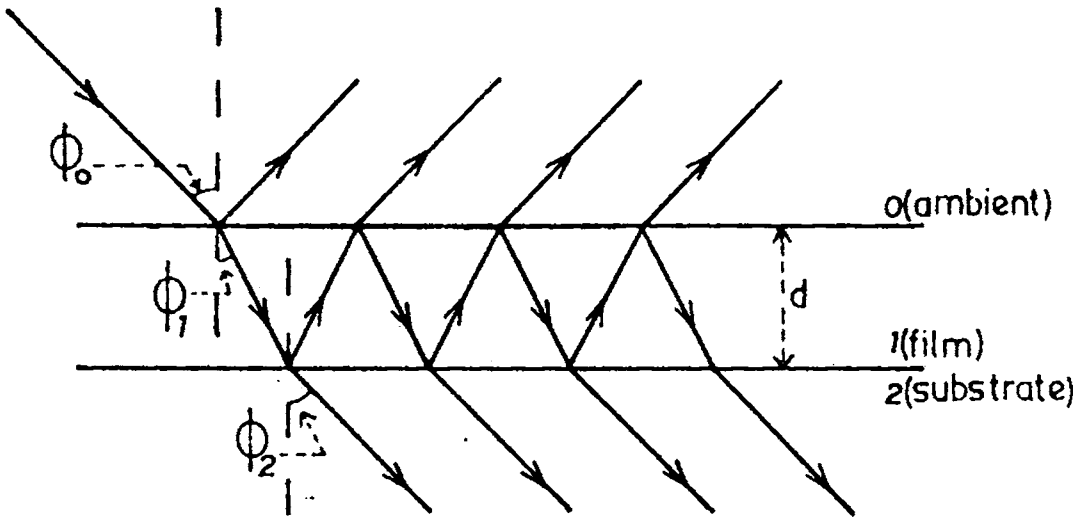
Fig.1.1 Oblique reflection and transmission of a
         plane wave by an ambient (O)-film(1)-
         substrate(2) system with parallel plane
         boundaries.

an angle of incidence ϕ_o. This wave gives rise to a 'resultant reflected wave' in the same medium and a 'resultant transmitted wave' in the medium-2 at an angle ϕ_2. Here the aim is to relate the complex amplitudes of the resultant reflected and transmitted waves to the amplitude of the incident wave when the latter is linearly polarised parallel (p) and perpendicular (s) to the plane of incidence. Fresnel reflection and transmission coefficients are necessary for this part and the derivation of the coefficients are given in all text books on optics[1]. As an example, if one has E_{ip} and E_{rp} to be the complex amplitudes of components of electric vectors (parallel to the plane of incidence) of incident and reflected waves respectively then r_{oip} the Fresnel reflection coefficient at 0-1 interface can be obtained from the expression,

$$E_{rp}/E_{ip} = r_{olp} = \frac{N_1 \cos \phi_o - N_o \cos \phi_1}{N_1 \cos \phi_o + N_o \cos \phi_1} \quad (1.2)$$

Similarly one can get coefficients for other component (s-component) and for other interfaces also.

$$r_{ols} = \frac{N_o \cos \phi_o - N_1 \cos \phi_1}{N_o \cos \phi_o + N_1 \cos \phi_1} \quad (1.3)$$

$$r_{12p} = \frac{N_2\cos\phi_1 - N_1\cos\phi_2}{N_2\cos\phi_1 + N_1\cos\phi_2} \qquad (1.4)$$

$$r_{12s} = \frac{N_1\cos\phi_1 - N_2\cos\phi_2}{N_1\cos\phi_1 + N_2\cos\phi_2} \qquad (1.5)$$

$$t_{o1s} = \frac{2N_o\cos\phi_o}{N_o\cos\phi_o + N_1\cos\phi_1} \qquad (1.6)$$

$$t_{o1p} = \frac{2N_o\cos\phi_o}{N_1\cos\phi_o + N_o\cos\phi_1} \qquad (1.7)$$

$$t_{12s} = \frac{2N_1\cos\phi_1}{N_1\cos\phi_1 + N_2\cos\phi_2} \qquad (1.8)$$

$$t_{12p} = \frac{2N_1\cos\phi_1}{N_2\cos\phi_1 + N_1\cos\phi_2} \qquad (1.9)$$

To determine the relation between the reflected, transmitted and incident amplitudes here, the procedure originally due to Drude[2] is followed. (For simplicity the suffix p or s is omitted in following steps. When the coefficient of a particular component alone is

required, the specified suffix is to be added and this will be shown at the end of the derivation). According to this theory, as the incident wave first meets the 0-1 interface, a part of it is reflected into the medium-0 and another part is refracted in the film (medium-1) strictly following the Fresnel reflection and transmission coefficients in eqns (1.2)-(1.9). The refracted wave inside the film subsequently undergoes multiple internal reflections at 1-2 and 1-0 film bounding interfaces which are in general, not perfectly reflecting. Hence each time the multiply reflected wave strikes the 1-0 or 1-2 interface a component (partial) wave is leaked (refracted) into the ambient or substrate medium respectively. If the Fresnel reflection and transmission coefficients at 0-1 (1-0) and 1-2 interfaces are denoted by r_{01}, t_{01} (r_{10}, t_{10}) and r_{12}, t_{12} respectively the complex amplitudes of successive partial plane waves that make up the 'resultant reflected wave' in the medium-0 are given by r_{01}, $t_{01}r_{12}t_{10}e^{-i2\beta}$, $t_{01}r_{10}r_{12}^2t_{10}e^{-i4\beta}$, $t_{01}r_{10}^2r_{12}^3t_{10}e^{-i6\beta}$....where β is the phase change that the multiply reflected wave inside the film experiences as it traverses the film once from one boundary to the

other. The expression for β can be obtained in terms of the free space wave length of the light wave λ, film thickness d, the complex index of refraction of the film material N_1 and the (complex) angle of refraction ϕ_1 (ie., the angle between the direction of propagation of the wave in the film and the normal to the film boundaries) as,

$$\beta = 2\pi N_1 d \cos \phi_1 / \lambda \qquad (1.10)$$

Similarly one can write the expressions for the complex amplitudes of successive partial plane waves that make up the resultant transmitted wave in medium-2 as,

$$t_{01}t_{12}e^{-i\beta}, \; t_{01}r_{12}r_{10}t_{12}e^{-i3\beta}, \; t_{01}r_{12}^2r_{10}^2t_{12}e^{-i5\beta}\ldots\ldots$$

Addition of partial reflected waves leads to an infinite geometric series for the total reflected amplitude, (R)

$$R = r_{01} + t_{01}r_{12}t_{10}e^{-i2\beta} + t_{01}r_{12}^2r_{10}t_{10}r^{-i4\beta}$$

$$+ t_{01}r_{12}^3r_{10}^2t_{10}e^{-i6\beta} + \ldots\ldots$$

$$= r_{01} + \frac{t_{01}t_{10}r_{12}e^{-i2\beta}}{1-r_{10}r_{12}e^{-i2\beta}} \qquad (1.11)$$

The expression for R in eqn(1.11) can be further simplified using two relations

$$r_{10} = -r_{01} \quad \text{and} \qquad\qquad (1.12a)$$

$$t_{01}t_{10} = 1-r_{01}^2 \qquad\qquad (1.12b)$$

which can be proved very easily using the expressions for Fresnel coefficients given in eqns (1.2)-(1.9). After simplification the expression for R becomes,

$$R = \frac{r_{01} + r_{12}e^{-i2\beta}}{1 + r_{01}r_{12}e^{-i2\beta}} \qquad\qquad (1.13)$$

If one requires the reflected amplitude of p- or s-component alone it can be obtained as

$$R_p = \frac{r_{01p} + r_{12p}e^{-i2\beta}}{1 + r_{01p}r_{12p}e^{-i2\beta}} \qquad\qquad (1.13a)$$

and

$$R_s = \frac{r_{01s} + r_{12s}e^{-i2\beta}}{1 + r_{01s}r_{12s}e^{-i2\beta}} \qquad\qquad (1.13b)$$

Similarly total transmitted amplitude (T) is given by another infinite geometric series,

$$T = t_{01}t_{12}e^{-i\beta} + t_{01}r_{12}r_{10}t_{12}e^{-i3\beta} + t_{01}r_{12}^2r_{10}^2t_{12}e^{-i5\beta}$$

$$= \frac{t_{01}t_{12}e^{-i\beta}}{1 + r_{01}r_{12}e^{-i2\beta}} \qquad (1.14)$$

which is obtained after simplification using eqn (1.12a). Here also the transmitted amplitude for the two components can be obtained as

$$T_p = \frac{t_{01p}t_{12p}e^{-i\beta}}{1 + r_{01p}r_{12p}e^{-i2\beta}} \qquad (1.14a)$$

$$T_s = \frac{t_{01s}t_{12s}e^{-i\beta}}{1 + r_{01s}+r_{12s}e^{-i2\beta}} \qquad (1.14b)$$

The reflectivity (I_R) is the ratio of intensity of reflected light to that of the incident light. From

eqn (1.13) one can obtain the expression for the reflectivity as,

$$I_R = \frac{r_{01}^2 + r_{12}^2 + 2r_{01}r_{12} \cos(2\beta)}{1 + r_{01}^2 r_{12}^2 + 2r_{01}r_{12} \cos(2\beta)} \qquad (1.15)$$

Similarly the expression for the transmissivity (I_T), which is the ratio of intensity of transmitted light to that of the incident light can be written as,

$$I_T = \frac{N_o}{N_2} \frac{t_{01}^2 t_{12}^2}{1 + 2r_{01}r_{12} \cos(2\beta) + r_{01}^2 r_{12}^2} \qquad (1.16)$$

It should be noted that eqns (1.15) and (1.16) are common for both p- and s-polarisations. The general expressions can be obtained by substituting the values of Fresnel coefficients in eqns (1.15) and (1.16) and the expressions are too long to write. A much simplified version is obtained for the case of normal incidence and then the expressions for reflectivity and trans-missivity become,

$$I_R = \frac{(N_o^2 + N_1^2)(N_1^2 + N_2^2) - 4N_o N_1^2 N_2 + (N_o^2 - N_1^2)(N_1^2 - N_2^2)\cos(2\beta)}{(N_o^2 + N_1^2)(N_1^2 + N_2^2) + 4N_o N_1^2 N_2 + (N_o^2 - N_1^2)(N_1^2 - N_2^2)\cos(2\beta)}$$

$$(1.17)$$

$$I_T = \frac{8N_o N_1^2 N_2}{(N_o^2 + N_1^2)(N_1^2 + N_2^2) + 4N_o N_1^2 N_2 + (N_o^2 - N_1^2)(N_1^2 - N_2^2)\cos(2\beta)}$$

$$(1.18)$$

The normal reflectance exhibits oscillatory variations as shown in fig.1.2 which gives the variations of R with film thickness normalised by the wavelength of light[3]. The reflectivity at the positions of maxima and minima are as follows.

For $N_o \lesseqgtr N_1 \lesseqgtr N_2$,

$$I_R(max) = \left(\frac{N_2 - N_o}{N_2 + N_o}\right)^2 \text{ at } \lambda_{max} = \frac{2N_1 d}{m} \quad (1.19)$$

and

$$I_R(min) = \left(\frac{N_1^2 - N_o N_2}{N_1^2 + N_o N_2}\right)^2 \text{ at } \lambda_{min} = \frac{4N_1 d}{2m+1} \quad (1.20)$$

For $N_o \lessgtr N_1 \gtrless N_2$,

$$I_R(\max) = \left(\frac{N_1^2 - N_o N_2}{N_1^2 + N_o N_2}\right)^2 \text{ at } \lambda_{\max} = \frac{4N_1 d}{2m+1} \quad (1.21)$$

$$I_R(\min) = \left(\frac{N_2 - N_o}{N_2 + N_o}\right)^2 \text{ at } \lambda_{\min} = \frac{2N_1 d}{m} \quad (1.22)$$

where m is an integer.

In order to study the change of amplitude and phase separately, as the plane wave is obliquely reflected from or transmitted by a film covered substrate, the overall complex amplitude reflection (R_p, R_s) and transmission (T_p, T_s) coefficients are written in terms of their absolute values and angles.

$$R_p = |R_p| e^{i \Delta rp} \quad (1.23a)$$

$$R_s = |R_s| e^{i \Delta rs} \quad (1.23b)$$

$$T_p = |T_p| e^{i \Delta tp} \quad (1.24a)$$

$$T_s = |T_s| e^{i \Delta ts} \quad (1.24b)$$

From eqns (1.13a &b) and (1.14a &b) it is clear that, because the interface Fresnel reflection and trans- mission coefficients for the p- and s-polarisations are different, the overall reflection and transmission coefficients of an ambient-film-substrate system for these two polarisations are also different. This is the basis of reflection and transmission ellipsometry measurements on the ambient-film-substrate system where a change of polarisation takes place due to reflection and transmission as a result of the differ- ence in amplitude attenuation and phase shift exper- ienced by p- and s-components. From the above expressions one can calculate the ratio

$$\varrho = R_p/R_s = \frac{|R_p|}{|R_s|} e^{i(\Delta_{rp}-\Delta_{rs})} \qquad (1.25)$$

of overall complex amplitude reflection coefficients of ambient-film-substrate system for p- and s-polari- sations. In terms of ellipsometric parameters[4] ψ and Δ this can be expressed as

$$\varrho = \tan\psi\, e^{i\Delta} \qquad (1.26)$$

$$\tan\psi = |R_p|/|R_s| \qquad (1.27a)$$

$$\Delta = \Delta_{rp} - \Delta_{rs} \qquad (1.27b)$$

This is the case of 'reflection ellipsometry'. If the ratio for the transmission amplitudes is calculated it becomes 'transmission ellipsometry'.

Heavens[5] pointed out that for the application of the above theory to the practical film-substrate system, one must have (i) the lateral dimensions of the film to be many times its thickness so that the multiply reflected and transmitted partial waves can be summed to infinity (ii) the source band width, beam diameter, degree of collimation and film thickness to be such that the multiply reflected and transmitted waves combine coherently and (iii) the film material to be not amplifying. These conditions are readily met in most of the practical applications.

With the help of the above theory almost all the optical experiments performed on thin films can be explained. In the case of reflectometry one measures the reflectivity of the film at different wavelengths. This can be theoretically calculated using eqn (1.15). From the deviation of the experimental value, due to the absorption of the film, the electronic structure of the material of the film and such other important factors can be obtained. If the material of the film is

dielectric or semiconductor the band gap can be determined in this way.

Eqn (1.17) shows that the reflectivity exhibits an oscillatory variation. This is illustrated in fig.1.2 also. Hence it is clear from eqns (1.19)-(1.22) that one can either enhance or diminish the reflectivity of a substrate at a specified wavelength (most probably in a range of wavelength) by a suitable choice of the film index. This is the principle of reflection and antireflection coatings. The functioning of such selective mirrors is improved by using multilayer coatings. Another practical application of this principle is that this can be used as a spectrophotometric method for monitoring the thickness of single or multilayer films. The film thickness can be determined from maxima or minima of reflectivity using the expression[6]

$$2m\lambda/4 = n_f t \qquad (1.28)$$

where n_f is the refractive index of the film t is the film thickness, λ is the wavelength of light and m is the order of maximum or minimum. For example if $\lambda = 1\mu$ and SiO film ($n_f=2$) is deposited, a thickness of 1μ is obtained after four maxima or minima.
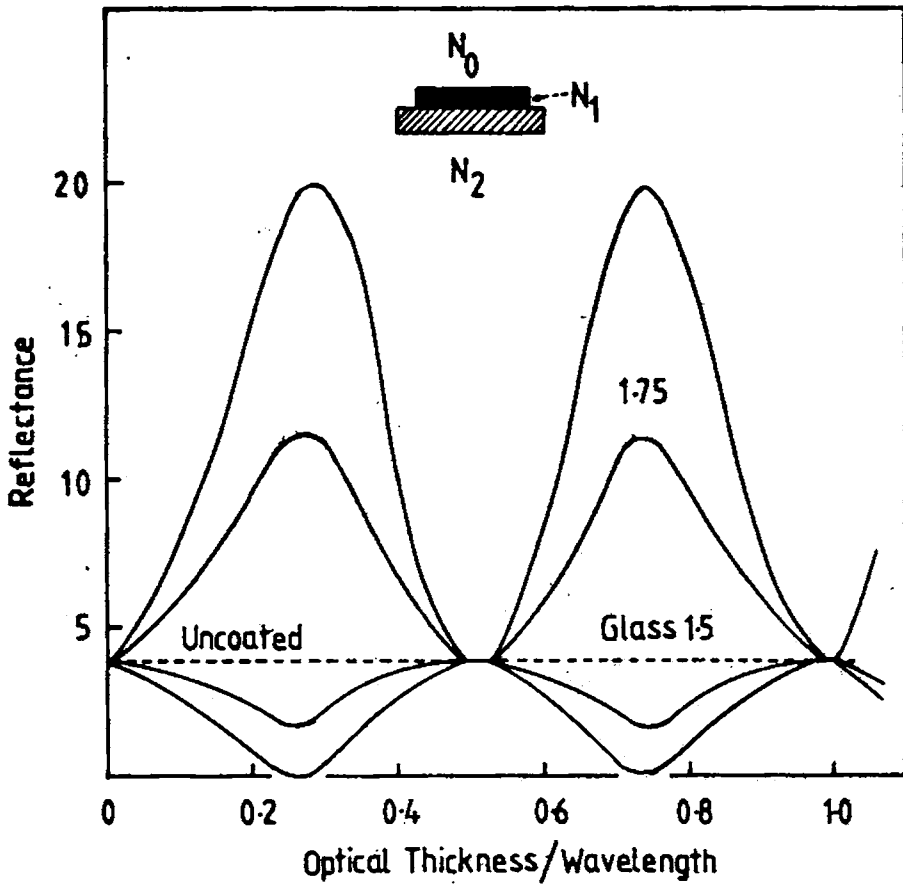
Fig.1.2   Theoretical variation of reflectivity
          (at air side) with normalised thickness
          for films of various refractive indices
          on glass substrates.

Now considering the ellipsometric measurements, one has to calculate ϱ from ψ and Δ values. But ϱ is defined as the ratio of R_p to R_s (eqn 1.25). Substituting the value of R_p and R_s in terms of refractive indices and angles from eqns (1.13a & b) the expression

$$= \tan\psi\, e^{i\Delta} = \frac{r_{01p} + r_{12p}e^{-i2\beta}}{1 + r_{01p}r_{12p}e^{-i2\beta}} \times \frac{1 + r_{01s}r_{12s}e^{-i2\beta}}{r_{01s} + r_{12s}e^{-i2\beta}}$$

$$(1.29)$$

Now it can be easily seen that eqn (1.29) relates the measured values of ψ and Δ to the optical properties of the three phase system namely the (complex) refractive indices of the ambient (N_o), film (N_1) substrate (N_2) and film thickness (d) for given values of the vacuum wavelength (λ) of the ellipsometer light beam and its angle of incidence ($\emptyset_o$) in the ambient. This dependence of ψ and Δ on the parameters can be written as

$$\tan\psi\, e^{i\Delta} = \varrho\ (N_o N_1 N_2 d \emptyset_o \lambda) \qquad (1.30)$$

Here anyone of the parameters can be determined if the values of others are known. If the film thickness (d) is the unknown quantity, β in eqn (1.29) is to be evaluated since it is the only factor involving d. The

function ℓ in eqn (1.30) is quite complicated and can
be handled satisfactorily only by a computer. But this
is a very sensitive technique and can give information
about layers formed on the surface having thickness as
little as $0.1\overset{o}{A}$ to as much as $5000\overset{o}{A}$ and this has been
proved to be superior to other surface analysis
techniques like photoelectron emission, water contact
angle measurement, surface potential difference etc[4].
The detailed theory of this method and its measuring
techniques are given in chapter VI.

1.2b Multilayer films

The case of multilayer films is also to be
considered here since it is more important when compared
to the case of single layer films. This is more compli-
cated in comparison with the earlier case and hence the
method of addition of multiple reflection is not
possible here. A more elegant approach employing
2x2 matrices is applied, which is based on the fact
that the equations that govern the propagation of light
are linear and that the continuity of the tangential
fields accross an interface between two isotropic media
can be regarded as a 2x2 linear matrix transformation[7,8].

Let the stratified structure consists of a
stack of $1,2,3,...j...m$ parallel layers sandwiched
between two semi-infinite ambient (O) and substrate
(m+1) media as in fig.1.3. Here also the media are
considered to be linear homogeneous isotropic and
having their interfaces to be parallel and ideally
flat. OLet the complex index of refraction of the
j^{th} layer be N_j and its thickness be 'd_j'. N_o and
N_{m+1} are the complex indices of the ambient and the
substrate media respectively. When a plane mono-
chromatic wave is incident on the first layer at
an angle of incidence ϕ_o, it generates a resultant
reflected wave in the medium-O and a resultant
transmitted wave in medium (m+1). The total field
in the jth layer, which is excited by the incident
plane wave, consists of two plane waves: a forward
travelling plane wave denoted by (+) and a backward
travelling wave denoted by (-). The wave vectors
of all plane waves lie in the same plane (ie., in the
plane of incidence) and the wave vectors of the two
plane waves in the jth layer make equal angles with
the z-axis (The z-axis is perpendicular to the plane
boundaries directed towards the substrate). When
the incident wave in the ambient is linearly polarised

Fig.1.3
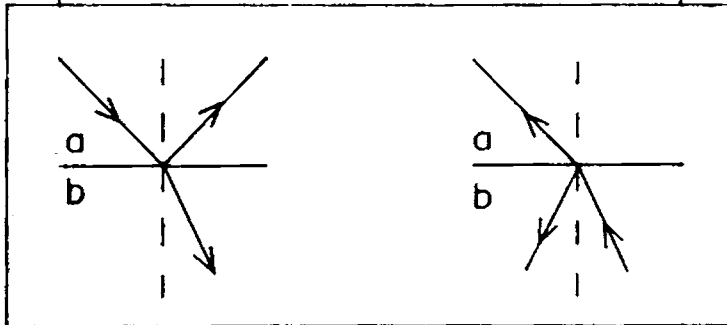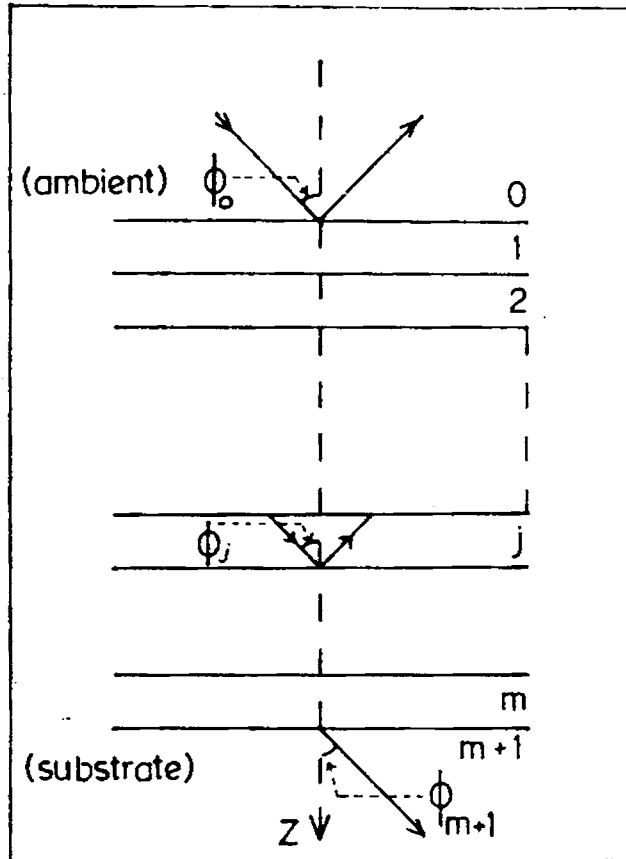
Fig.1.4A   Fig.1.4B

Fig.1.3 Reflection and transmission of a plane wave
         by a multi-film structure (films 1,2....m)
         sandwiched between the semi-infinite ambient (0)
         and substrate (m+1) media.

Fig.1.4A Reflection and transmission of a plane wave at
         a two-media (ab) interface.

Fig.1.4B The direction of propagation of the transmitted
         wave is assumed to be reversed.

with its electric vector vibrating parallel (p) or perpendicular (s) to the plane of incidence all plane waves excited by that incident wave in various layers of the stratified structure will be similarly polarised. In the following discussion it is assumed that all waves are either p- or s-polarised.

Let $E^+_{(z)}$ and $E^-_{(z)}$ represent the complex amplitudes of forward and backward travelling plane waves at an arbitrary plane z. The total field at z can be described by a 2x1 column vector,

$$E_{(z)} = \begin{bmatrix} E^+_{(z)} \\ \\ E^-_{(z)} \end{bmatrix} \qquad (1.31)$$

If one considers z' and z'' as two planes parallel to the layer boundaries then due to the linearity of the system $E_{(z'')}$ and $E_{(z')}$ are related as

$$\begin{bmatrix} E^+_{(z')} \\ \\ E^-_{(z')} \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} \\ \\ S_{21} & S_{22} \end{bmatrix} \begin{bmatrix} E^+_{(z'')} \\ \\ E^-_{(z')} \end{bmatrix} \qquad (1.32)$$

Or $\quad E_{(z')} = S \, E_{(z'')}$ $\qquad\qquad$ (1.33)

where $\quad S = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix}$ $\qquad\qquad$ (1.34)

Here S characterises that part of the stratified

structure confined between the two parallel planes

at z' and z''. Only the reflected wave in the ambient

medium and the transmitted wave in the substrate are

accessible for measurement and hence it is necessary

to relate their fields to those of the incident wave.

By considering the planes z' and z'' to be lying in the

ambient and substrate media, immediately adjacent to

the O-1 and m-(m+1) interfaces respectively eqn (1.33)

becomes,

$$E_{(z_1)} = S \, E_{(z_{m+1})} \qquad\qquad (1.35)$$

S is a scattering matrix which can be written as a

product of the interface and layer matrices I and L'

which describe the effect of individual interfaces

and layers of the entire stratified structure taken

in order and can be expressed as,

$$S = I_{01}L_1I_{12}L_2\cdots I_{(j-1)j}L_j\cdots L_mI_{m(m+1)}$$

(1.36)

Now one has to calculate the individual interface
and layer matrices I and L. The matrix I of an inter-
face between two media 'a' and 'b' relates the fields
on both sides as

$$\begin{bmatrix} E_a^+ \\ E_a^- \end{bmatrix} = \begin{bmatrix} I_{11} & I_{12} \\ I_{21} & I_{22} \end{bmatrix} \begin{bmatrix} E_b^+ \\ E_b^- \end{bmatrix}$$

(1.37)

Consider fig.1.4A in which a plane wave is incident
on the ab interface. The complex amplitude of the
transmitted wave in medium b and that of the reflected
wave in medium a can be expressed in terms of the
complex amplitude of the incident wave in the medium a
as,

$$E_b^+ = t_{ab} E_a^+$$

(1.38a)

$$E_a^- = r_{ab} E_a^+$$

(1.38b)

It is quite evident that $E_b^- = 0$ and r_{ab} and t_{ab} are

Fresnel reflection and transmission coefficients of the ab interface. But using the matrix notation in this case eqn (1.37) can be rewritten as

$$\begin{bmatrix} E_a^+ \\ E_a^- \end{bmatrix} = \begin{bmatrix} I_{11} & I_{12} \\ I_{21} & I_{22} \end{bmatrix} \begin{bmatrix} E_b^+ \\ 0 \end{bmatrix} \tag{1.39}$$

which can be expanded as

$$E_a^+ = I_{11} E_b^+ \tag{1.40a}$$

$$E_a^- = I_{21} E_b^+ \tag{1.40b}$$

Comparing eqns (1.40a &b) with eqns (1.38a &b),

$$I_{11} = 1/t_{ab} \tag{1.41}$$

$$I_{21} = r_{ab}/t_{ab} \tag{1.42}$$

Considering the fig.1.4B in which a plane wave is incident on the ba interface from the medium b at an angle of incidence equal to the angle of refraction in the medium b in the case represented in fig.1.4A,

one can write the expressions for the fields immediately adjacent to the ba interface as,

$$E_b^+ = r_{ba} E_b^- \qquad (1.43a)$$

$$E_a^- = t_{ba} E_b^- \qquad (1.43b)$$

Here $E_a^+ = 0$ and r_{ba} and t_{ba} are Fresnel reflection and transmission coefficients of ba interface respectively. Using the matrix notation from eqn (1.37)

$$\begin{bmatrix} 0 \\ E_a^- \end{bmatrix} = \begin{bmatrix} I_{11} & I_{12} \\ I_{21} & I_{22} \end{bmatrix} \begin{bmatrix} E_b^+ \\ E_b^- \end{bmatrix} \qquad (1.44)$$

Or

$$0 = I_{11} E_b^+ + I_{12} E_b^- \qquad (1.45a)$$

$$E_a^- = I_{21} E_b^+ + I_{22} E_b^- \qquad (1.45b)$$

Substituting for I_{11} and I_{21},

$$E_b^+ = t_{ab} I_{12} E_b^- \qquad (1.46a)$$

$$E_a^- = \left[\frac{r_{ab} r_{ba}}{t_{ab}} + I_{22} \right] E_b^- \qquad (1.46b)$$

Comparing eqns (1.46a&b) with eqns (1.43a&b) one gets,

$$I_{12} = -r_{ba}/t_{ab} \qquad (1.47)$$

$$I_{22} = (t_{ab} t_{ba} - r_{ab} r_{ba})/t_{ab} \qquad (1.48)$$

Using the relations in eqns (1.12a & b) these expressions of I_{12} and I_{22} can be further simplified and then the interface matrix becomes,

$$I_{ab} = \begin{bmatrix} 1/t_{ab} & r_{ab}/t_{ab} \\ r_{ab}/t_{ab} & 1/t_{ab} \end{bmatrix}$$

$$= 1/t_{ab} \begin{bmatrix} 1 & r_{ab} \\ r_{ab} & 1 \end{bmatrix} \qquad (1.49)$$

These Fresnel reflection and transmission coefficients occurring in eqn (1.49) must be evaluated using the complex indices of refraction of the two media that define the interface and the local angle of incidence. The latter can be obtained by the repeated application of Snell's law

$$N_o \, Sin \, \emptyset_o = N_1 \, Sin \, \emptyset_1 \, .. = N_j \, Sin \, \emptyset_j . = N_{m+1} Sin \, \emptyset_{m+1}$$

$$(1.50)$$

The effect of propagation through a homogeneous layer of index of refraction N and thickness d can be found out by getting the relationship between the fields inside

the layer at both ends. This can be written as

$$\begin{bmatrix} E_o^+ \\ E_o^- \end{bmatrix} = \begin{bmatrix} e^{i\beta} & 0 \\ 0 & e^{-i\beta} \end{bmatrix} \begin{bmatrix} E_d^+ \\ E_d^- \end{bmatrix} \qquad (1.51)$$

where the subscripts 'O' and 'd' denote the beginning and end of the layer (along the direction of the forward travelling wave) and the phase shift (layer phase thickness) β is given by,

$$\beta = \frac{2\pi dN}{\lambda}\cos \phi \qquad (1.52)$$

Here ϕ is the angle between the direction of propagation in the layer and the perpendicular to its boundaries (the z-axis). Therefore the layer matrix L can be written as,

$$L = \begin{bmatrix} e^{i\beta} & 0 \\ 0 & e^{-i\beta} \end{bmatrix} \qquad (1.53)$$

Thus from the interface and layer matrices I and L ie, from eqns (1.49) and (1.53), one can get the overall scattering matrix S of the stratified structure. It is

determined by direct matrix multiplication. Hence eqn (1.35) can be written as,

$$\begin{bmatrix} E_a^+ \\ E_a^- \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix} \begin{bmatrix} E_s^+ \\ 0 \end{bmatrix} \qquad (1.54)$$

where the subscripts a and s denote the ambient and the substrate and is quite clear that $E_s^- = 0$. From eqn (1.54) the overall reflection and transmission coefficients of the stratified structure is obtained as

$$R = \frac{E_a^-}{E_a^+} = \frac{S_{21}}{S_{11}} \qquad (1.55)$$

$$T = \frac{E_s^+}{E_a^+} = \frac{1}{S_{11}} \qquad (1.56)$$

Here also, for ellipsometry the stratified structure scattering matrix S has to be calculated for both linear polarisations, parallel (p-) and perpendicular (s-) to the plane of incidence. If S_p and S_s represent the scattering matrices for p- and s-polarisations, then,

$$R_p = \frac{S_{21p}}{S_{11p}} \qquad (1.57a)$$

$$R_s = \frac{S_{21s}}{S_{11s}} \tag{1.57b}$$

$$T_p = \frac{1}{S_{11p}} \tag{1.58a}$$

$$T_s = \frac{1}{S_{11s}} \tag{1.58b}$$

Considering the case of reflection ellipsometer one can write

$$\varrho = R_p/R_s = \frac{S_{21p}}{S_{11p}} \times \frac{S_{11s}}{S_{21s}} \tag{1.59}$$

For determining the optical constants alone, one can use either reflectivity measurements or ellipsometry using a monochromatic source of light. By these methods the surface nature of the film can also be studied. But for the study of the interior of the multilayer films one has to use reflectometry (spectrophotometry) or spectroscopic ellipsometry. Employing spectroscopic ellipsometry one can study the variation of index of refraction[9] or the complex dielectric constant[10,11] and these experimental values can furnish a lot more information[12,13]. For example, Meyer[14] has calculated

the surface state densities on clean semiconductor surfaces from ellipsometric measurements.

1.3 Recent developments in optical studies of thin films

The reflectivity measurements, which is just the ratio of reflected intensity of light to that of the incident light, gives information about the surface and optical constants of the film. But the variation of reflectivity with wavelength (reflectometry or spectrophotometry) can furnish information regarding the electronic structure of the material, absorption, variation of optical constants etc. This method has been used by several workers to study thin films and their optical properties[15-18]. In this itself, the method of differential reflectometry is gaining much importance recently[19-22]. This technique involves alternate scanning of two samples with a monochromatic light beam and this is achieved by means of an oscillating mirror. Another recent technique evolved in this field is the time-resolved optical reflectivity. This has been used to study the properties of amorphous

and crystalline silicon prepared by using the chemical
vapour deposition technique[23]. Attenuated total
reflection (ATR) is another branch which is gaining
more importance recently. This has been used by
Lopez-Rios et al[24] for the study of the silver film
surface. The theoretical aspects of ATR and its recent
trend in experimental side are described in detail
by Otto[25]. As the latest developments in thin film
optics, one can see the use of Photo acoustic spectro-
scopy (PAS-which involves the conversion of light waves
into sound or pressure waves) and Photo thermal deflection
spectroscopy (PDS) for the surface study,[26,27] thickness
measurement,[28]and optical constants measurement[29].

In ellipsometry the main developments are in
the instrumentation and in the different types of uses.
Regarding the latter part description is given in
chapter VI. Considering the case of developments in
the field of instrumentation, the automatic ellipsometers
have been of great help in the study of some fast
surface reactions whose analysis require a large set
of data. In null as well as photometric ellipsometers
automation has taken place. In the case of null

ellipsometers the work of Takasaki[30], Ord et al[31] and

Roberts et al[32] are to be mentioned. There are two types

of automatic photometric ellipsometers; one is rotating

analyser ellipsometer (RAE) and the other is polarisation

modulated ellipsometer (PME). The RAE systems employ

both analog[33] and digital[34,35] signal detection. The

importance of this development (ie., automation) in the

field of ellipsometry lies in the fact that this made

the technique suitable for modern investigations. For

example, due to the work of Hauge et al[35] the ellipso-

metric set up could be used for measuring the thickness

of dielectric films on silicon wafers in a manufacturing

environment. The speciality of the set up is that it

requires just five seconds for sample alignment, data

acquisition, analysis and recording of film thickness

with an accuracy of about $1\overset{o}{A}$. Another new branch in the

field of ellipsometry is the spectroscopic ellipsometry.

Its theory experimental aspects and uses are described

by Aspnes[36]. The Muller Matrix Ellipsometer (MME)[37,38]

is a recently evolved set up, in this field. The

speciality of this set up is that it can determine the

Muller matrix[39] of the measured optical system completely.

Pulsed ellipsometry is a new technique used for high

temporal resolution studies and uses pulsed lasers as

the light source. In this, the multichannel technique[40,41] is to be noted here due to its speciality that the portions of the measured beam are individually routed to separate detectors having different polarisation sensitivities. This is achieved by using four separate beam splitters which provide four incident beams (nearly parallel) linearly polarised at $45°$. These rays after reflection (or transmission) at the optical system are detected by four separate detectors from which the four Stokes parameters[39] are obtained. A fifth detector is also provided to monitor the incident intensity and to measure absolute reflectance.

1.4 Factors affecting the optical properties of thin films

The theory discussed above (in section 1.2) for a single layer film and stratified structure touches almost all the aspects of their optical properties. But there are several factors affecting the film (especially its surface) and thereby causing variations in its optical properties. This can be represented in a simple way[42] as in fig.1.5. In that a single crystal film at OK, having no dislocations and vacancies and
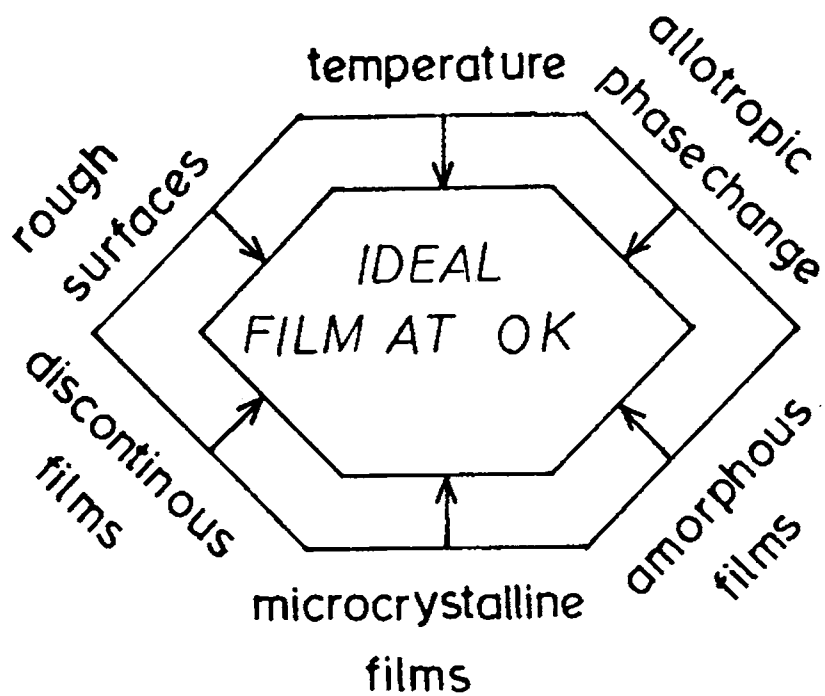
Fig.1.5 Factors affecting the optical
         properties of 'ideal film'.

having perfectly smooth and flat surfaces, is

considered to be an 'ideal film'. Any deviation from

this state represents a change in its structure and

hence influences the optical property. The variation

in temperature is an important factor affecting the

optical property considerably. Due to the increase

in temperature, the number of phonons increase and

this will affect both interband and intraband parts

of the absorption. The variation in intraband

part of the absorption has been reported by Fäldt

et al[42] by measuring the optical conductivity in

caesium. The effect on interband absorption has

been elucidated through the optical conductivity

measurements in aluminium[43]. The same effect has

been verified in the case of gold and copper by

Pells et al[44] and studies in the same direction

was carried out on gold and silver by Winsemius[45].

Phase transitions in materials is another

factor affecting their optical properties.

The difference between graphite and diamond

is a good practical example. Gallium is

another example for this. The conventional α-phase

of gallium which is stable at room temperature is

orthorhombic. But at temperatures below 70K one can

get monoclinic β-phase by quench condensation. These

two phases have entirely different optical absorption.

The α-phase has a group of parallel bands in the

region 1.3-2.3eV while the β-phase has a broad peak at

1.5eV[46,47]. The transition from amorphous to crystal-

line state can affect the optical properties of films

very much. For example amorphous films of germanium

has a broad absorption band centred at 3eV while the

optical absorption of its crystalline film has two

prominent peaks, one at 2.5eV and the other at

4.5eV[48]. Similarly in the case of gallium also, the

strong parallel band absorption peaks in the visible

and IR are completely absent in the amorphous state[46,47].

The 'amorphous spectrum' is quite similar to the spectrum

of liquid gallium. The same phenomenon is taking place

in the case of amorphous and crystalline bismuth also[49].

Another factor to be considered here is the micro-

crystalline character of thin films. Evaporated films

consist of small crystallites whose radius is (approxi-

mately) of the order of 1μm and these crystallites

are separated by a region of highly disordered material

along the grain boundaries. There is little or no

periodicity along the grain boundary whose thickness
is of the order of 10–15$\overset{o}{A}$ and this is independent of
the grain size. As the deposition temperature is
lowered there is considerable decrease in grain
size[50] and at liquid helium temperatures the grain
diameter of a large number of materials is of the
order of 50–100$\overset{o}{A}$. About 30% of the material is in a
highly disordered state in this type of (micro-
crystalline) samples and hence this can produce
drastic effects on their optical properties. This
effect has been observed by Welkowsky et al[51] in the
wavelength modulation spectrum of silver. Similarly
Hunderi et al[52] have obtained two peaks at 140K,
one at 2.4eV and the other at 3.2eV. These peaks
are attributed to modes excited by light polarised
perpendicular and parallel to the grain boundary.
Also these are absent when the films are annealed
at 300 K. The film formation starts with the form-
ation of islands and if the mass thickness is below
a critical value the film is discontinuous. These
islands cause anomalous absorption due to the excit-
ation of a charge density oscillation in them. A
theoretical model was set up by Maxwell-Garnett[53,54]
(the detailed discussion of which is given in chapter VIII)

in which the discontinuous film was treated as a
collection of small metallic spheres. This has been
verified experimentally and qualitative agreement
has been obtained[55]. Theoretical investigations
with an aim to extend and modify the idea of
Maxwell-Garnett are also carried out[56]. Another
important factor affecting the optical properties
of thin films is the surface roughness and this has
been an area of interest and several works have been
published (both theoretical and experimental) regarding
its effect on the optical properties of thin films[57-62].
In the theories of optical properties of thin films
the main assumption is that the surface (or interface
between two media) of the medium is ideally smooth
and flat. Also the variation in refractive index
(as light enters into one medium from another) is
considered to be sharp which will be true only if
there is no 'mixing' between the media at the inter-
face. These assumptions are hard to achieve in
practical case, the main difficulty being in the nature
of the surface itself. When the film surface comes
into contact with the atmosphere several factors
contribute to roughness. For example, the variation

in temperature is an important factor as far as

metallic films are considered. The interaction with

different impurities in the atmosphere (corrosion)

is another cause of surface roughness. Again, layer

formation (mainly oxide) over the film surface is

a factor affecting the smoothness of the same. These

factors causing surface roughness affect the optical

properties in a three fold way[42]. First of all a

part of the incident light is diffusely scattered

into various directions. Secondly, on a rough metal

surface, the incident wave may excite surface plasmons

and this may alter the reflection and transmission

coefficients very much. Finally a rough surface is

having a larger effective surface area and this can

increase, to some extent, the interband and intraband

absorptions.

Thus it can be easily seen that the type

of ideal film conceived in the theory is practically

very difficult to obtain and the experimental results

will be affected by many of the factors described

earlier. But some of them can be avoided. For example,

the variations due to thermal effects can be minimised

by using low temperature ambient for the film. However the factors like surface roughness or defects cannot be avoided and hence they must be taken into account while analysing the results.

1.5   Investigations in the present work

In the present work, the surface roughness due to thermal variation has been investigated optically. For this, reflectivity studies are done on silver and copper films. In the case of copper films electron micrographs are also taken. The variation of surface nature due to interdiffusion in Al-Ag films have been investigated by using reflectivity. Ellipsometric studies are performed to study the surface variation of silver films due to annealing (in low temperature range) and these results are again verified by using light scattering measurements. The apparatus and devices for these optical measurements were fabricated. The details of experimentation are provided at appropriate places in the following chapters.

A theoretical study, though on a different topic, carried out during the time of the investigation

is included in the appendix. It is a calculation
of the eigenvector magnitudes in ZnS crystal by
using the method of isotopic substitution.

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CHAPTER II

DESCRIPTION OF THE EXPERIMENTAL SET UP FOR THE DIFFERENT INVESTIGATIONS

2.1 Introduction

This chapter deals with the description of the experimental set up for the different experiments and also the method of preparation of the films in brief. This is divided into three parts. First part deals with the film preparation and its thickness measurement while the second one describes the method of annealing. The third part includes the optical measurements under three sub divisions dealing with reflectivity, ellipsometry and light scattering measurements.

2.2 Film preparation and thickness measurement

All the films were prepared on glass substrates of size 7.5cms x 2.5cm x .14cm. This was first cleaned by using a detergent like Teepole and then using Acetone. After rinsing in distilled water these substrates were then subjected to ultrasonic vibrations to remove all traces of dust particles.

These were used for the film preparation after dry-
ing in an enclosed chamber.

The vacuum evaporation technique had been
used for the preparation of films for all the experi-
ments. During the time of coating, the pressure was
always maintained at 10^{-5} torr. As usual in the
vacuum evaporation technique, this low pressure was
achieved in two stages. The pressure was lowered to
10^{-2} torr by using a Rotary pump and later for still
lower pressure, the Diffusion pump was used. The
block diagram of a typical vacuum evaporation unit is
shown in fig.2.1. When the pressure was brought down
($< 10^{-5}$ torr) the required material was evaporated
by heating it suitably. For aluminium, the heater
was a coil made of tungston wire while for silver and
copper it was molybdenum boats. When two materials
were evaporated one after the other (as in the case
of Al-Ag bilayer films) two heating sources were used
which were well separated using mica sheets. Always
the distance between the heating source and the
substrate was 15cms, their relative positions also
being kept constant.
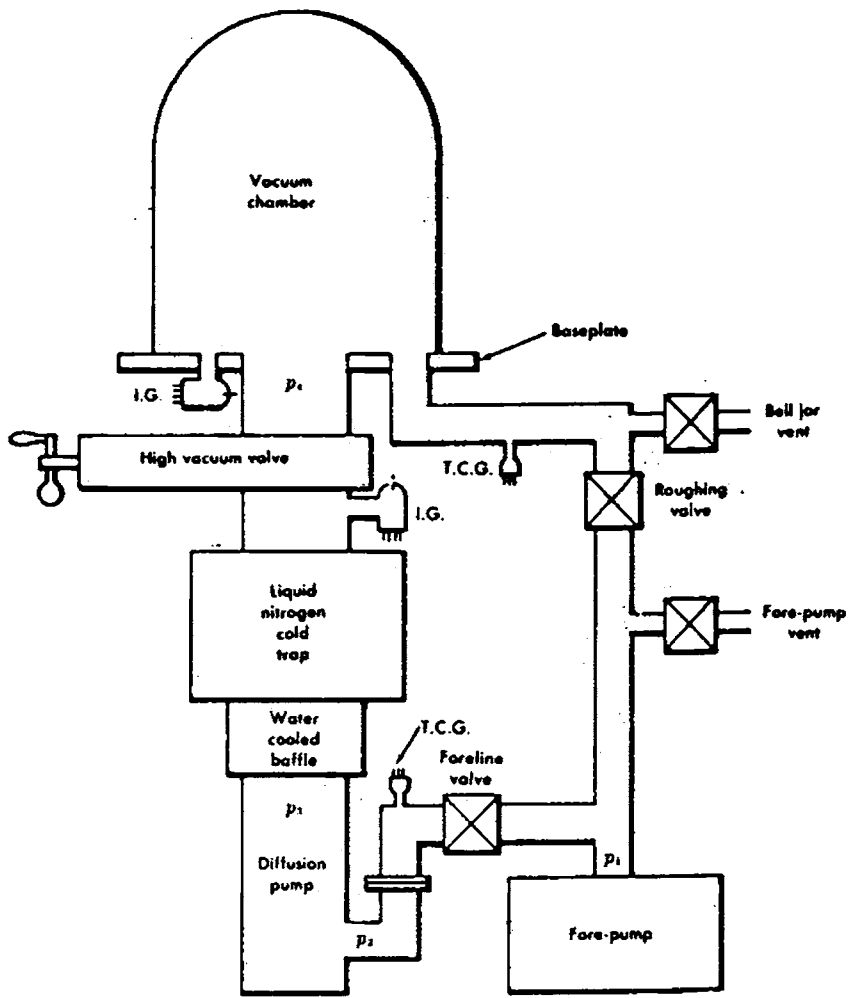
The required thickness for the films was

Fig.2.1 Typical vacuum coating unit.

obtained by evaporating the calculated quantity of
the material and for this the expression used was

$$m = 4\pi\rho\, d^2 t \quad \text{(for point source)} \qquad (2.1)$$

and

$$m = \pi\rho\, d^2 t \quad \text{(for small plane source)} \qquad (2.2)$$

where m is the mass, ρ is the density of the material,
d is the distance between source and substrate and
t is the required thickness. Among the films prepared,
one would be made with a sharp edge (obtained by keep-
ing the edge of a blade on the substrate). Later this
film was overcoated with silver or aluminium and the
thickness of the step thus formed was measured by
the method of multiple beam interferometry[2]. This is
illustrated in fig.2.2. the details of which is given
in a large number of text books dealing with thin
films and other related properties. Here it was
found that the thickness variation from the calculated
value was always within $\pm$ 50Å.

2.3 Annealing

Annealing of the thin films was done in
vacuum and also air. The pressure was maintained at
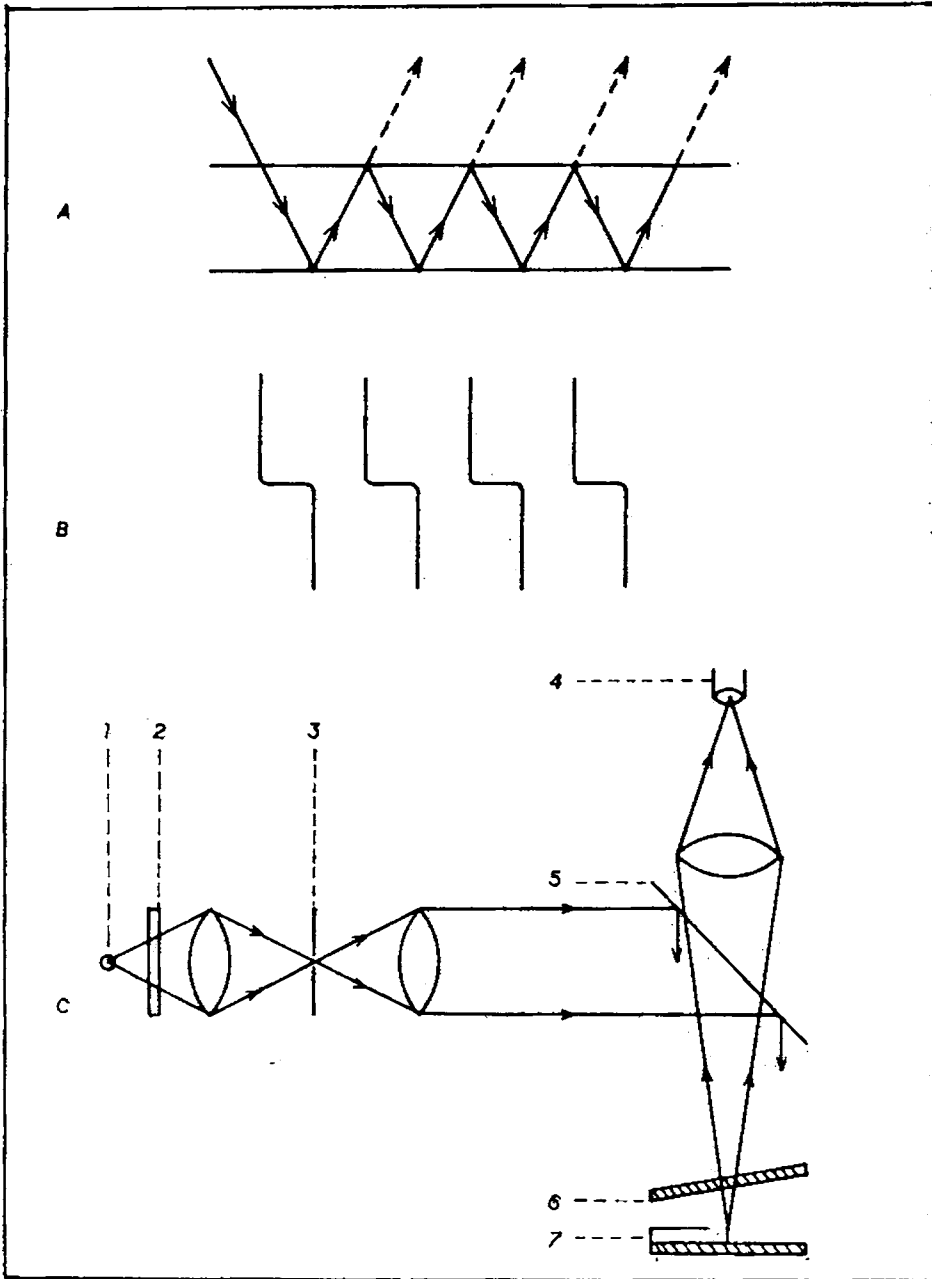
Fig.2.2   Optical method (multiple beam interferometry)
          for the film thickness measurement.
          A. Path of the light beam B. Shape of the
          fringes C. Experimental arrangement.
          1. Light source, 2. Filter, 3. Pin hole,
          4. Microscope, 5. Beam splitter .6. Reference
          plate, 7. Film.

10^{-2}torr for the annealing in vacuum. This was

achieved by using a rotary pump. Depending upon

the type of the optical measurement, the annealing

was performed in two different types of glass cells.

When the optical measurement was done

after the annealing of the film at a particular

temperature, it was done in an ordinary glass cell.

It had a length of 30cms and diameter 10cms. The

film to be annealed was kept at the centre of the

cell. The junction of an Iron-Constantan thermo-

couple was kept in contact with the surface of the

film. If the annealing was to be done in vacuum,

the pressure was first reduced to 10^{-2} torr before

heating started. The heating was applied radially

by using a heating tape which was wound round the

glass cell. The heating rate was controlled by

regulating the voltage applied to the tape using a

variac. Generally, the films were kept at the

annealing temperature for 20 minutes and during

this time the temperature was kept constant by

adjusting the voltage (If the annealing time is

different from this in any of the experiment that

is noted in the concerned chapter). The heating

rate for the films with larger thickness value (ie., those having thickness $>2000\mathring{A}$) was usually 1°C/minute and for the films with low thickness value (ie., thickness $<2000\mathring{A}$) it was 0.5^{o}C/minute. The temperature was measured by noting the voltage developed accross the thermocouple junction. This was done by using a microvoltmeter.

For in situ optical measurements during heating a special type of glass cell was designed (fig.2.3). This also had arrangements for evacuation. Its front side was made flat and it served as a glass window and hence the optical measurements could be done during heating itself. Here the heater coil was kept inside an aluminium block (electrically isolated from it by using mica sheets) and the film was kept in contact with the aluminium block. Generally, the films had their glass-side (back side) touching the aluminium block. The gradient drop of temperature across the thin substrate is negligible. In some cases, (especially for the Al-Ag bilayer films) heating was performed by keeping the front side of the film touching the aluminium block (see chapter IV). The temperature was measured by

using Iron-Constantan thermocouple. Its junction was kept in contact with the front side of the film without obstructing the light beam (see fig.2.3). Here also the heating rate was controlled with the help of a variac. The values of the heating rate were the same as before. But the optical measurement (most probably, the intensity of the reflected light) at a particular temperature was taken only after keeping the film at that temperature for five minutes.

The whole set up was fixed on a stand so that the film was always at a fixed position at the centre of the spectrometer (fig.2.4). The light from the collimator was made to fall on the film and the reflected light was collected by the telescope and subsequently by the PMT. When this cell was used, the angle of incidence was not varied, which was always 45°. This cell was very much useful for the diffusion studies of the Al-Ag bilayer films described in chapter V.

2.4 Optical measurements

This section deals with the description of the experimental set up for different optical
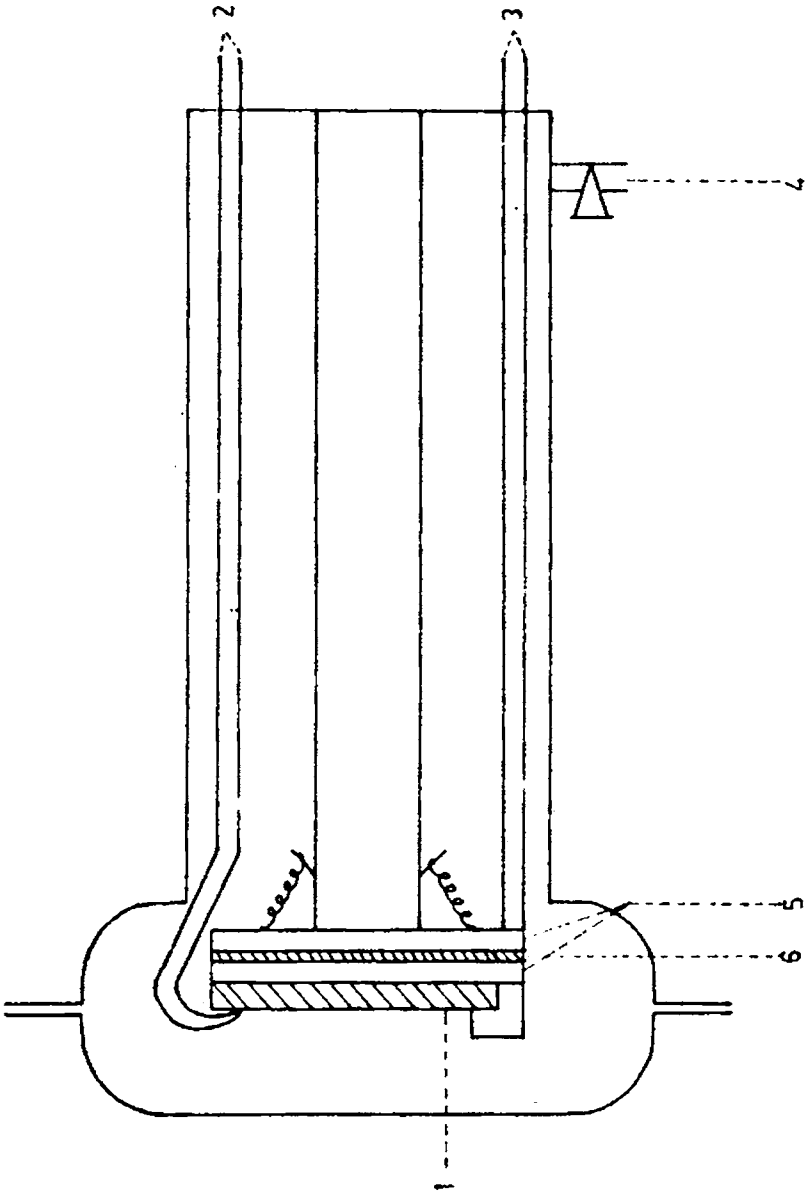
Fig.2.3   Glass cell for reflectivity measurements along with
         heating.
         1. Film,   2. Thermocouple,   3. Current leads (for heater),
         4. Connection to pump,   5. Aluminium blocks,   6. Heater.
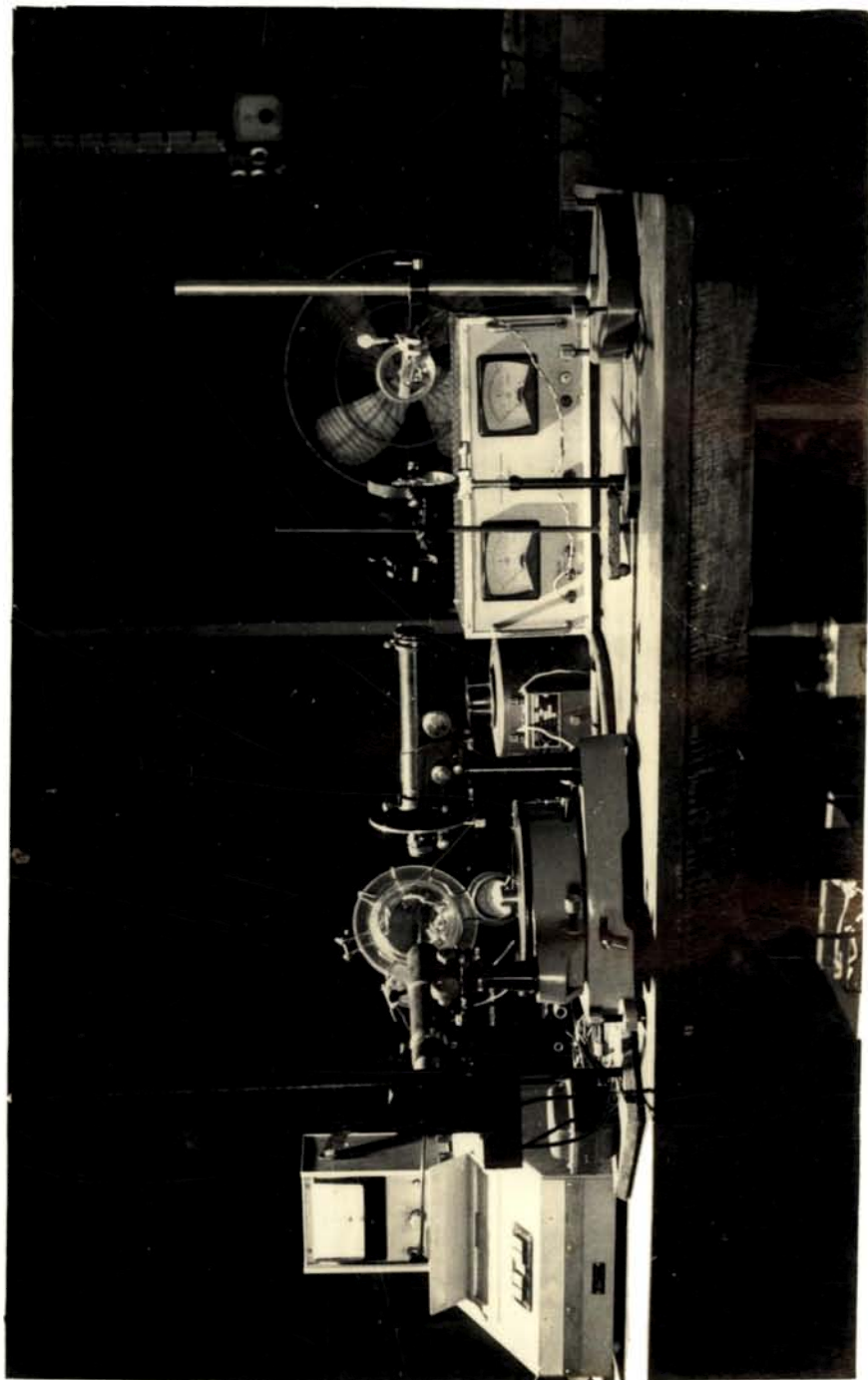
Fig. 2.4   Exptl. set up for reflectivity measurement

experiments divided into three sub-headings. First one is the reflectivity measurements used for the study of silver films (chapter III), copper films (chapter V) and the interdiffusion in Al-Ag bilayer films (chapter IV). The second part describes the ellipsometric set up with which the hillock growth on silver films is studied (chapter VII) and the third part deals with the light scattering measurements on silver films (chapter VIII).

In all these experiments the light signal reflected from the surface is detected by a photomultiplier tube (PMT) 931-A RCA. Its maximum sensitivity is in the region 4000$\overset{o}{A}$-4500$\overset{o}{A}$. Hence in all the experiments (unless specified otherwise) the wavelength of light used was 4400$\overset{o}{A}$ and for this a filter was used. The output of the PMT was given to a Multiflex galvanometer and the deflection was noted. The D.C.voltage required for the PMT was in the range 750-1000V. The power supply for this was fabricated in the Laboratory and always 750V was given to the PMT.

The light source for the experiments was a tungsten filament lamp (36W). The power supplied to it was stabilised using a stabilised D.C.power supply.

The collimeter of a spectrometer was adjusted to give a parallel beam of light, which was used as the incident beam. The size of the beam was 1mm diameter. The reflected light was collected by the telescope. At the place of its eye-piece, the PMT was fixed and thus the intensity of the reflected light was measured. The film was fixed on the circular prism table using a clamp. But when the special type of heating cell (described in section 2.3) was in use, the prism table was removed and the cell was placed there (see fig.2.4).

2.4a Reflectivity measurements

When the reflectivity is measured along with heating the angle of incidence was kept constant and the film was kept inside the cell described in section 2.3. The well collimated light beam was adjusted to be incident on the film. The intensity of the reflected beam was measured using the PMT Galvanometer arrangement described earlier. After taking the initial reading the heating could be started and reflectivity was measured at different values of temperature. This arrangement is shown in fig.2.4.

But when the reflectivity is measured
after annealing, the experiment is performed in a
different way. Here the film was annealed in a
simple cell described in section 2.3. After this,
it was cooled to room temperature (at the same
rate as the heating was done) and was fixed on to
the prism table using the clamp. The intensity of
the reflected beam was measured as explained earlier,
at different angles of incidence. The whole
procedure was repeated after annealing the film at
a different temperature. In the reflectivity
measurements care was taken to have the incident
beam falling on the same portion of the film always.
In all the cases the experiments were repeated a
number of times.

2.4b Ellipsometric set up

The experimental set up consisted of
polariser-system-analyser (PSA) arrangement. Its
detailed theory and the method of measurement are
given in chapter VI while the experimental results
obtained using this is included in chapter VII.
The polariser was introduced after the collimator
and the analyser was fixed on the telescope (see
fig.2.5). Both polariser and analyser could be

Fig. 2.5   Ellipsometric set up

used to measure a change in the polarisation as low as 1′. The plane of incidence was fixed on the polariser by keeping a plane glass plate in the position of the film at an angle of incidence, equal to the polarising angle. Keeping the polariser at a fixed azimuth with respect to the plane of incidence (at $+45^{\circ}$, 0 and -45°). This was repeated for different angles of incidence (The range of angle of incidence was between 50° and 80°). During these measurements the film was kept fixed on the prism table by means of a clamp. The whole process was performed after each annealing.

2.4c   Light scattering measurements

The experimental arrangement for this was almost similar to that of the ellipsometric set up with the only difference that here no analyser was used (see fig.2.6). The polariser was having its azimuth such that the plane of polarisation was always parallel to the plane of incidence (ie., the incident light beam is p-polarised). This was merely to make the theoretical calculation of the reflected intensity of light from the ideally smooth
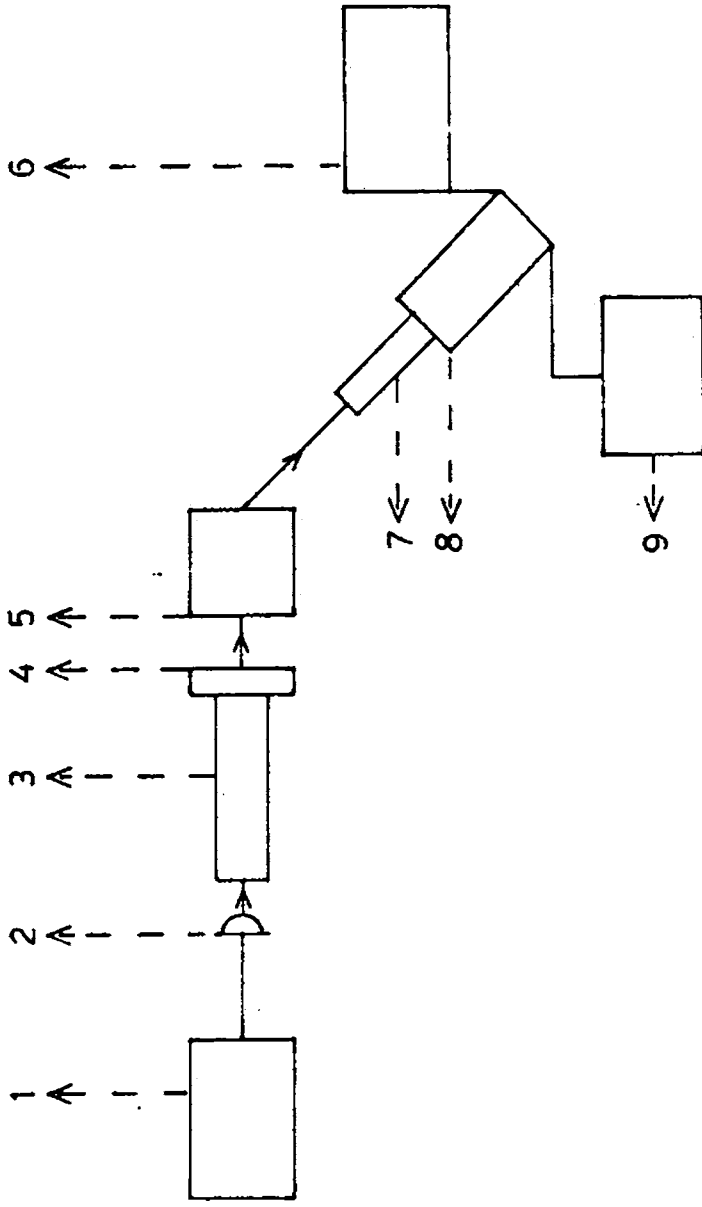
Fig.2.6   Block diagram of the experimental set up for the light
          scattering measurements.
          1. Stabilised low voltage power supply 2. light source
          3. Collimator   4. Polariser   5. Optical system (film)
          6. PMT Power supply   7. Telescope   8. PMT
          9. Galvanometer.

surface (I_{so}) much easier. Theoretical aspects regarding the scattering of light waves from a rough surface and the calculation of the rms value of roughness are given in chapter VIII. It also contains the results of the measurements done on silver films.

Here also, the film was kept fixed on the prism table and the intensity of reflected light was measured at different angles of incidence (θ). The graph was plotted with $\cos^2 \theta$ on X-axis and $\ln R_s$ on Y-axis (R_s is the ratio of the intensity of reflected light from the rough surface (I_s) to that from an ideally smooth surface (I_{so})). The size of the roughness is obtained from the slope of the curve.

2.5 The scanning electron micrographs

The pictures of the surface of copper films (before and after heating) given in chapter IV were obtained by using the scanning electron microscope at the Regional Research Laboratory, Trivandrum. The magnification was 5000X. The analysis using the electron microscope showed that the smoothing of the surface

due to annealing is taking place on all the films
and the micrograph given in chapter V is that of
the film with lowest thickness (ie., 500$\overset{\text{o}}{\text{A}}$).

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CHAPTER III

OPTICAL STUDY OF THE EFFECTS OF ANNEALING
ON SILVER FILMS

3.1 Introduction

Silver films have been extensively studied by many workers mainly due to two reasons. One is that it has got very high reflectivity in the visible region[1,2]. The second reason is that it is highly inert under different ambient conditions. It is not oxidised even in the presence of oxygen at a pressure of 90.7 kP and in the temperature range $-78^{o}C$ to $400^{o}C$[3] . Hence these films find extensive use in solar reflectors and also in other branches of physics, like lasers, holography etc., where very high reflectivity is essential.

However even for the inert films there can be considerable variations in their optical properties, due to heating[4] . This happens as a result of the changes occurring in their structure and in the nature of their surface. This is much pronounced in the case of silver thin films. Hence several investigations

have been carried out to study the thermal effects on
these films and most of them are centred around their
optical properties. Of these Richard Zito[5], has
studied the variations in reflectivity and resistance
due to heating and he explained these on the basis of
hillock growth. A.E.B.Presland et al[6,7] has given a
theoretical approach for the changes produced by
heating. Sharma and Spitz, through a series of publi-
cations, have gone much deeper into the problem and
their study was mainly by using electron microscope[8-12].
A lot of other workers have also studied different
aspects of heating on silver and other thin films[13-19].
In almost all the publications, it is shown that heating
results in hillock growth on the surface of films.
This has a strong dependence of factors like ambient
conditions in which films are heated, thickness of the
film, its structure etc. In order to understand these
factors, the theory behind hillock growth may be
considered in detail.

3.2 Theory of hillock growth

When thin metal films are bonded to rigid
substrates, thermal stress arises upon heating it above
the deposition temperature. This is due to the difference

in coefficients of thermal expansion between the substrate and the film. If the coefficient of thermal expansion of the substrate is smaller than that of the film (which is the case when film is metallic and substrate is a material like glass) the thermal stress in the film plane is compressive upon heating and tensile on cooling. Sufficiently large thermal stress can cause slip in epitaxial films and both slip and hillock formation in polycrystalline films[20-23].

Through a rigorous mathematical analysis, Presland[6,7] has shown that the hillock growth occurs due to surface diffusion and this is closely linked with surface energy and the stress in the film. He has given the equation for the diffusion flux, as

$$j = \frac{D_s}{kTr_c} (\sigma - \frac{2\gamma}{r})$$
(3.1)

where D_s is the surface diffusion coefficient, k is Boltzmann's Constant, T is the absolute temperature σ is the stress in the film, γ is the surface energy, r_c is half the interhillock distance and r is the

radius of the circle from which the diffusion takes
place for the hillock growth. From the above equation
it is easily seen that if hillock growth is to occur,

$$\gamma \leq \frac{\sigma r_o}{2} \tag{3.2}$$

where r_o, is the (average) size of initial surface
irregularities. Thus in hillock growth as in the case
of void growth (where the applied stress must be
sufficient to overcome the increase in surface energy
caused by creating a void) the applied stress is only
sufficient to create hillocks if it outbalances the
surface energy.

But the surface energy (γ) strongly depends
upon the partial pressure of oxygen (P_{O_2}) and is inde-
pendent of temperature. Its relation with pressure
of oxygen is governed by the equation[24]

$$\gamma = 228 - 188 \log_{10}P_{O_2} \tag{3.3}$$

The second factor to be considered (in eqn.3.1) is r.
It is variations can be studied by noting the variations
in 'catchment area' (ie., the area from where the

material for the hillock growth comes by diffusion).
This also is not affected by the variations in
temperature. But a strong relationship with oxygen
pressure has been noted[25] similar to that in the case
of surface energy as

$$A_c = 0.67 - 0.16 \log P_{O_2} \qquad (3.4)$$

This relation between P_{O_2} and A_c is illustrated in
fig.3.1. The diffusion coefficient (D_s) is also
found to be free from temperature effects. But here
also, the presence of oxygen can produce a slight
increase in the value of D_s which is not a significant
change[6]. From eqns.3.3 and 3.4 it is· clear that the
diffusion flux (j) has a much higher value when heating
is done in presence of oxygen (ie., in air). Or in
other words heating in air results in larger hillocks.

The only factor in eqn.3.1 to be considered
is the stress in the film (σ). It is found that
heating directly affects its value. Hence to under-
stand the thermal effects deeply, one has to consider
the stress in the film in a more detailed manner.
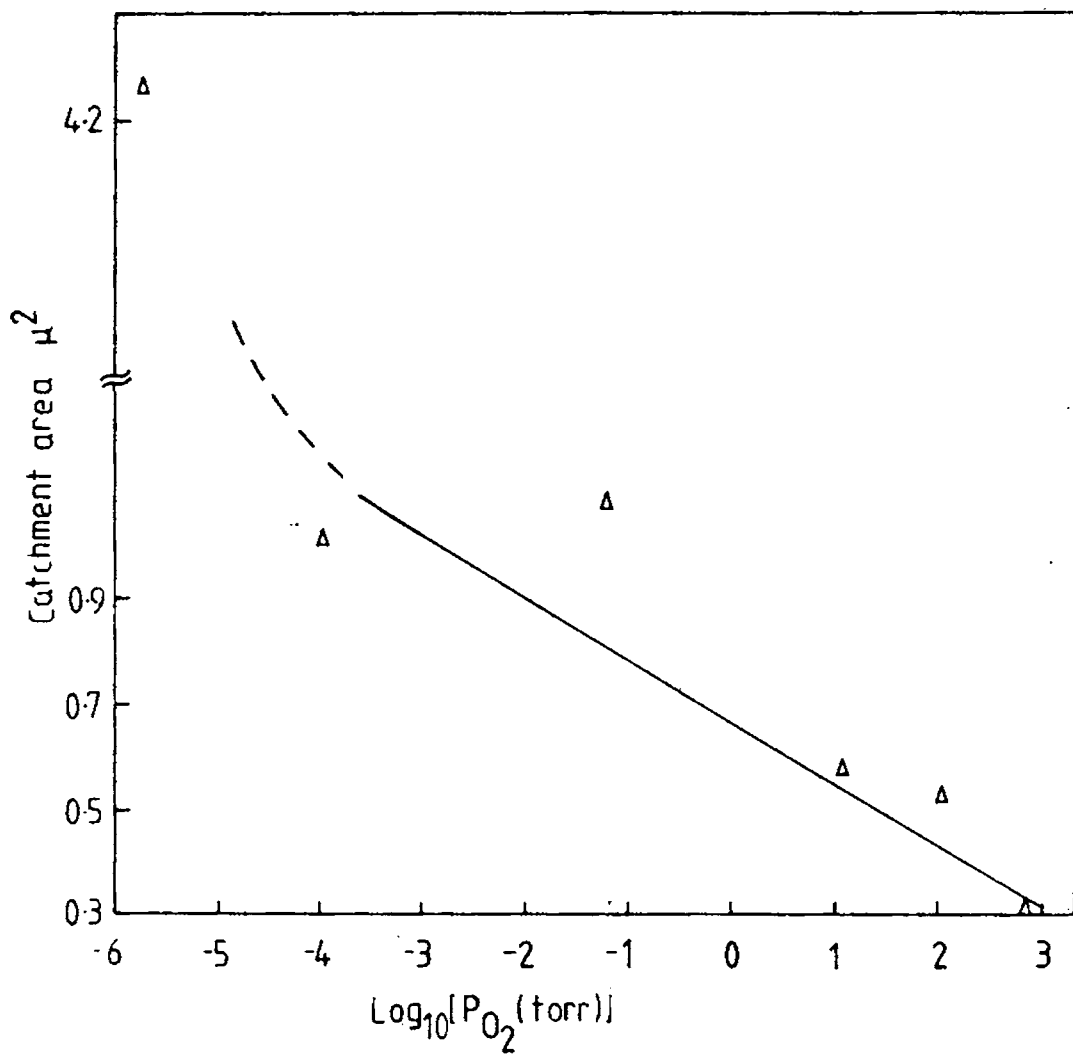
Fig.3.1 Variation of catchment area (A_c) with pressure of oxygen (P_{O_2}) for silver films.

3.2a Stress in thin films (metallic)

Nearly all films irrespective of their method of preparation, have internal stress. This may be compressive (in which case the film would 'like'to expand parallel to the surface) or tensile (in which case the film would 'like' to contract) as explained in section 3.2. This internal stress will be normally of the order of 10^8 to 10^{10} dynes cm^{-2} for metallic films when the deposition temperature is between $50^{\circ}C$ and a few hundred $^{\circ}C$.

In general, the stress in a film can be written as a sum of three components as

$$\sigma = \sigma_{intrinsic} + \sigma_{thermal} + \sigma_{external} \qquad (3.5)$$

In this eqn. the first term on RHS $(\sigma_{intrinsic})$ arises from different factors. One is that there can be a temperature gradient across the substrate due to the radiant heat from the source and the latent heat of evaporant[26]. The second factor causing the intrinsic stress is the difference in thermal expansion of the film and substrate and the third factor behind

this is the nonuniformity in the expansion of the substrate itself[27]. This stress is found to be tensile in nature[23,27] for metallic films.

The second term on RHS of eqn.3.5 arises only when the film is heated such that its temperature increases above its deposition temperature. The nature of this stress is compressive for metallic films deposited on glass substrates (as explained in the section 3.2). The third term (ie., $\sigma_{external}$) represents any stress applied externally on the film.

Thus it becomes clear that the intrinsic stress and thermal stress are mutually opposite. Or in other words, if one is taken to be positive the other is to be taken as negative. Also, if the film is heated to a temperature above its deposition-temperature the component $\sigma_{thermal}$ alone increases. Hence the resultant stress in the film (σ) which is the algebraic sum of these, is reduced and becomes a minimum at a particular temperature whose value depends on the value of $\sigma_{intrinsic}$. As the value of stress in the film is reduced, the condition for

hillock growth given in eqn.3.2 is not satisfied
whereby the hillock growth is stopped. To get a film
of minimum stress, is of great importance since it
has applications in different applied fields. The
present work on silver films was done to investigate
this aspect in detail and also to study variations
of the surface energy of silver films in different
ambient conditions.

3.3 Experimental details

The films were prepared by vacuum evapo-
ration technique which is described in detail in
chapter II. The pressure during the deposition was
10^{-5} torr and the substrates were maintained at room
temperature itself. To ensure uniform coating,
substrates were kept at a large distance (ie., 15cm)
from the heating source. The thickness of the films
was approximately 1000Å. For this the mass of the
evaporant was calculated using the expression[28],

$$m = \pi \rho d^2 t \qquad\qquad (3.6)$$

where ρ is the density of the material, d is the

distance between heating source and the substrate and
t is the thickness of the film. Later the thickness
was verified by using the multiple beam interferometry[29].

Annealing was done both in air and vacuum,
maintaining a pressure of 10^{-2} torr in the latter
case. The details of the cell used for this purpose
are given in chapter 2. The heating rate was always
kept fixed at $1^{o}C$/minute since fast heating was found
damage the film surface appreciably. The annealing
time, ie., time for which the film is kept at the
annealing temperature, was 30 minutes in all the
cases. Cooling was also done at a slow rate ie.,
$1^{o}C$/minute to avoid damage due to sudden cooling.
All the films were heated on the glass-side (ie., sub-
strate side).

The reflectivity measurement was performed
by using a PMT and galvanometer arrangement (as described
in the earlier chapter). The wavelength of the light
used for the investigation was 4400Å since the PMT has
a maximum sensibility in this region.

3.4 Results

Results can be considered separately for films annealed in air and vacuum. Fig.3.2 gives the variations in reflectivity with angle of incidence due to annealing in vacuum while fig.3.3 gives those for films annealed in air. One thing to be noted in common for both cases is that before annealing they are having similar reflectivities for all angles of incidence.

3.4a Annealing in vacuum

Due to vacuum annealing the reflectivity is found to be increasing upto a temperature of $\sim200^{\circ}C$. Beyond that the increase is almost stopped, which is clear from the fig.3.2. A steep increase is occurring as a result of annealing at $105^{\circ}C$. But afterwards the increase is reduced and finally it is almost stopped at $286^{\circ}C$. About 20 percent increase in reflectivity is obtained when films are annealed at $105^{\circ}C$.

3.4b Annealing in air

From the fig.3.3 it can be seen that annealing at $104^{\circ}C$ does not produce much effect. Only
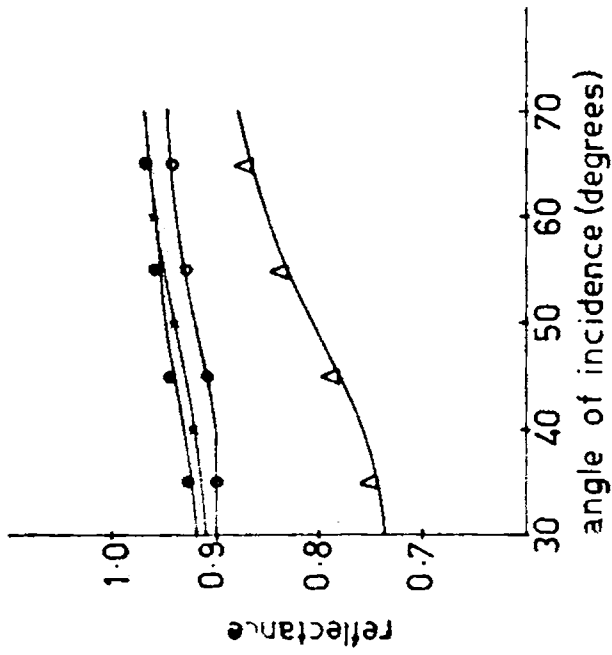
Fig.3.2   Reflectivity of silver films annealed in vacuum (wavelength – 4400A):
Δ—Δ before annealing;
o—o after annealing at 105°C
x—x after annealing at 210°C
●—● after annealing at 286°C
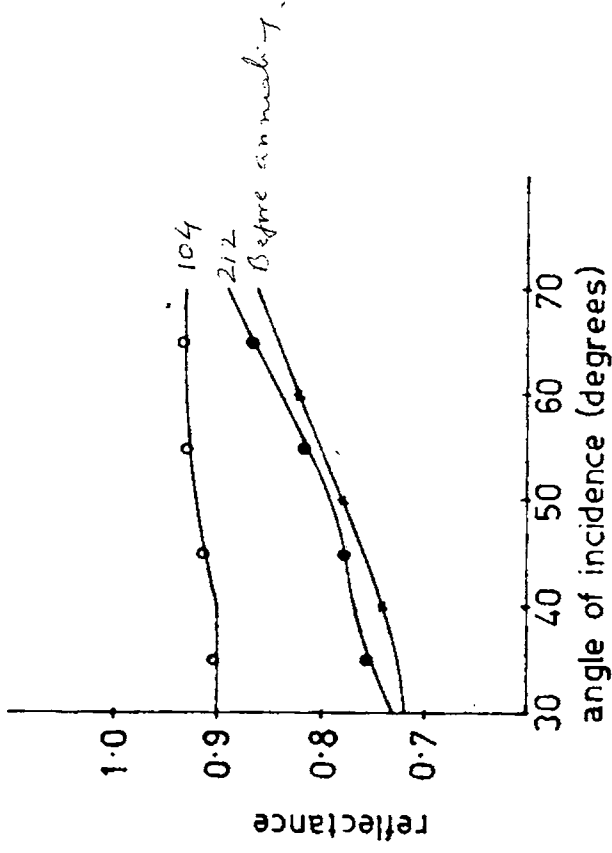
Fig.3.3   Reflectivity of silver films annealed in air (wavelength – 4400A):x—x before annealing; o—o after annealing at 104°C;212°C ●—● after annealing at 212°C 104°C

by annealing the films at 212°C an appreciable increase

in reflectivity ($\sim$ 20%) is obtained. Hence the

results of vacuum annealing that take place at 105°C

occur only at 212°C.[30]

3.5 Discussion

In the case of vacuum annealing it is quite

clear that due to annealing at 105°C the film surface

is smoothened as a result of which the reflectivity

increases. But on increasing the annealing tempera-

ture, this phenomenon is almost stopped indicating the

film surface becoming rough. The only thing which can

take place on the surface of silver thin films due to

heating is hillock growth and hence these results can

be explained on that basis.

One knows that the film surface becomes

irregular due to hillock growth and this occurs only

when the condition in eqn.3.2 is satisfied. On heating

the film to a temperature above deposition temperature,

the thermal stress ($\sigma_{thermal}$) starts increasing and

since this stress is opposite to the intrinsic

stress ($\sigma_{intrinsic}$), this results in reduction of

resultant stress (σ) in the film. When the value of σ is reduced to such an extent that $\gamma > \dfrac{\sigma r_0}{2}$, no hillock growth occurs and film surface is smooth. This results in the increase of reflectivity. Hence there is sharp increase in reflectivity for the films annealed in vacuum, upto $105^{\circ}C$.

But further increase in temperature results in the increase of thermal stress considerably so that it becomes the major component of the stress in the film (σ). Or in other words, the value of thermal stress goes much above that of the intrinsic stress and hence the stress in the film is steadily increasing along with the thermal stress. Therefore the condition for the hillock growth (eqn.3.2) is reestablished ie., the film surface starts to become irregular thereby causing reduction in the increase of reflectivity.

In the case of films annealed in air these results occur only at a high temperature. The sharp increase in reflectivity occurs at $212^{\circ}C$. This can be explained by considering eqn.3.3 which gives the relation between surface energy γ and the pressure of oxygen. It is clear from the eqn. that γ is considerably

decreased in presence of oxygen. Hence for the films
annealed in air, the value of γ will be much small.
But to have the film surface smoothened, one should
have,

$$\gamma > \frac{\sigma r_o}{2} \qquad (3.7)$$

Since γ is having a very low value in this case to
satisfy the condition in eqn.3.7, the value of σ should
also be lowered very much. For this, the value of
thermal stress $(\sigma_{thermal})$ should be increased much.
This can take place only at a higher temperature,
compared to the case of vacuum annealing. Hence in
this case the surface smoothening occurs only at a
temperature of about $212^{\circ}C$.

3.G Conclusion

In this work, mainly two things are studied
optically. First one is the relation between surface
roughness and the stress in the film while the second
aspect is the variation of surface energy in the
presence of oxygen.

In the former case, it has been found that,
the stress in the film can be reduced to a minimum by

annealing it and the temperature at which the stress is
minimised depends upon the value of intrinsic stress
in the film, which in turn, depends on different
parameters. Regarding the second aspect, it is found
that the surface energy (of silver) is considerably
reduced when the film surface is in contact with
oxygen and hence the minimum value of stress can be
achieved only at a very high temperature, when compared
with vacuum annealing.

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CHAPTER IV

STUDY OF THE SURFACE CHANGES ON COPPER FILMS
DUE TO THERMAL TREATMENT

4.1 Introduction

Copper, like silver, is well-known for its
high conductivity and good reflectivity. Hence this
is used in different electronic devices as the conduct-
ing lead. Also copper thin films are used as mirrors
in some lasers and solar reflectors. But in all these
instances temperature variations cause drastic effects
which are even detrimental in some cases. For example,
an increase in temperature can cause interdiffusion
between different layers (in the case of multilayer
films), the formation of an oxide layer on the surface
of the film, changes in the grain size of the film,
or variations on the surface smoothness of the film
depending upon the conditions and nature of heating.
Hence active research is going on in the case of
copper (both in thin film and bulk form) in order to
understand the nature of changes due to heating and
to find out the ways to minimise them. Some of the
recent works in the most important aspects of copper
are briefly reviewed below.

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One of the active areas of research in the case of this material is the variations of particle (grain) size due to heating[1-7]. Of these, Sen[5] had reported that there can be a change of 800Å in the grain size due to annealing the copper films at 120°C for 2 hours. But Gangulee[3] observed a two stage process in the phenomenon of grain growth as a result of heating. First stage is upto 200°C for which the activation energy is 0.3 - 0.4eV and in this stage only minor changes are taking place in grain size. The second stage occurs above 200°C and is having an activation energy of 0.65eV. In this stage major changes are taking place. Hofer et al[1,2] also have some observations supporting the above results.

Studies on thermoelectric power[8-13] can reveal a lot about transport mechanism and also distortions in Fermi surface. Research work in this direction is also very active in the case of copper. However, there is wide divergence among the experimentally obtained values by different workers[13].

Another important area of research is perhaps the optical properties and the variations of the same under different conditions[14-26] (especially due to

heating). This broad topic includes the surface damages due to laser irradiation[14-17], the variations in optical properties due to surface roughness[25,26] and the studies on the film surface so as to know in detail about its use as a solar reflector[21-24]. Of these, Harding et al[22] have reported that copper surface will be stable upto 400°C in vacuum. In another reported work, Turley et al[23] have shown that the structure of copper surface, which is mechanically polished, is crystalline. Wu et al[26] reported that electrodeposited copper foils have two types of irregularities on their surfaces—one is cone shaped and the other, small nodules-like. Also Thomas et al[14] have studied the variations in performance of the coppor mirrors finished by different methods.

There has been not much published work on the study of variation of reflectivity with continuous variation of temperature. This may be of importance regarding the use of copper films as mirrors in different ambient conditions where temperature increase is expected to take place. Hence in this chapter the results of such a work is described in which the temperature is varied upto 200°C. This particular

temperature range has been selected because the stress

minimisation is taking place in this range as described

in chapter III.

4.2 Experimental set up

All the films used in this study were prepared

by the vacuum evaporation technique as described else-

where[27]. The pressure during deposition was lower

than 10^{-5} torr and the films were prepared both at

room temperature and at higher temperature. The

distance between the source and substrate was 15cm

to ensure uniform coating. All the samples were prepared

under identical conditions.

Films of thickness ranging from 500Å to

3000Å were prepared. The mass of the evaporant required

for each thickness was calculated using the expression[28]

given in the chapter III. After evaporation the thick-

ness was again measured by using the method of multiple

beam interferometry[29]. In each case the film thickness

was found to be accurate within the limit of $\pm$ 50Å.

Heating of the films was done in a special

type of glass cell described in chapter II, in which

both heating and reflectivity measurements could be
done simultaneously. Films were always heated on the
glass-side and temperature was measured by using
an Iron-Constantan thermocouple. Heating rate was
very low (1°C/minute) for all the films to avoid any
damage due to high heating rate. Also for all films,
the pressure was below 10^{-2} torr during heating which
helped to have identical ambient conditions in each
case.

The measurement of reflectivity was done
in the same way as described in chapter III and the
set up is described in detail in chapter II. Here the
only difference was that reflectivity was measured
during heating at different temperature values.
Before taking the reading the film was kept at the
particular temperature for five minutes.

4.3 Results

Fig.4.1 gives the reflectivity variations
with temperature for the films prepared at room
temperature. Fig.4.2 shows the same for films prepared
at higher temperature. In both the figures, readings
from $\sim100^{\circ}$C is only shown since there is almost
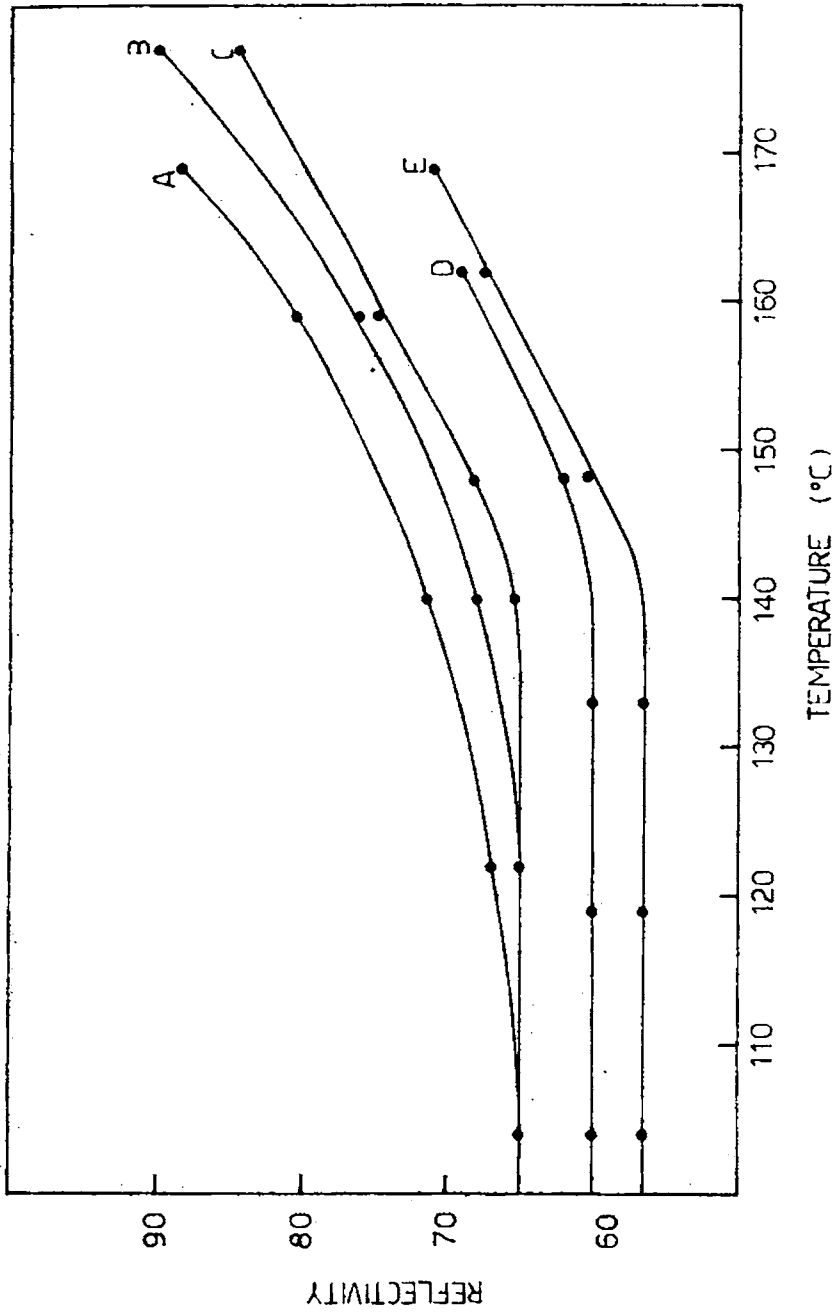
Fig.4.1 Variation in reflectivity with temperature for copper films of various thicknesses deposited at room temperature (wavelength - 4400A). A - 3000A, B - 2000A, C - 1500A, D - 1000A, E - 500A.
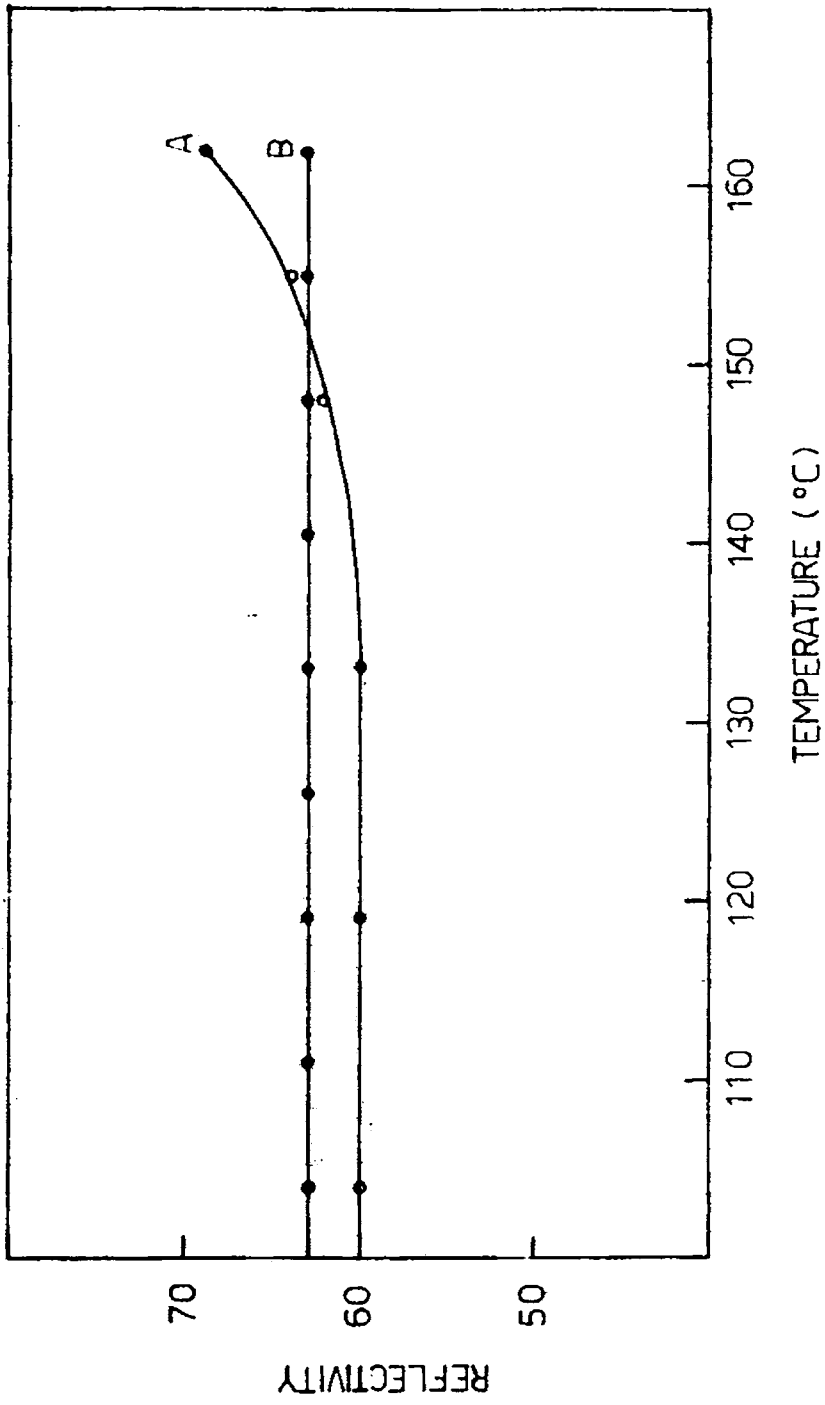
Fig.4.2 Variation in reflectivity of copper films with temperature
(film thickness – 1000A, wavelength – 4400A).
A – for film deposited at room temperature
B – for film deposited at 200°C.

no variation in reflectivity before that temperature.

One can easily understand from the fig.4.1
that for all the films reflectivity increases after
a particular temperature and the temperature at which
this occurs is different for different thickness.
In the case of films with thickness 500$\overset{o}{A}$ and 1000$\overset{o}{A}$
the increase starts at almost the same temperature
ie., ~150°C (see curves D and E). As the thickness
increases the temperature value decreases. For 1500$\overset{o}{A}$
the increase takes place at ~140°C while for 2000$\overset{o}{A}$
and 3000$\overset{o}{A}$ thick films the temperature values are
130°C and 120°C respectively.

In fig.4.2 curve A shows the variations in
the reflectivity of a film of thickness 1000$\overset{o}{A}$ deposited
at room temperature (This is same as the curve D in
fig.4.1). But the curve B in fig.4.2 is for a similar
film of same thickness with the only difference that
its deposition temperature was different (ie.,200°C).
Here the curve B does not show any increase in reflecti-
vity.

Figures 4.3 and 4.4 are electron micrographs
showing the structure of the surface of a film before

Fig. 4·3   SEM   before   annealing

Fig. 4.4   SEM after annealing

and after heating. The thickness of the film was 500Å
and was deposited at room temperature. It is quite
clear from fig. 4.3 that the surface of the film is
rough before heating and becomes much smooth after
the heat treatment (fig.4.4). Since this is the case
for all the other films (of different thicknesses)
only one case is shown here as an example.

4.4 Discussion

As the reflectivity is also a measure of
the surface smoothness and since it is found to be
increasing, one can take it for granted that there is
surface smoothening due to heating. Heating directly
affects the stress in the film and hence the variation
in the stress in the film may be the reason for the
surface smoothening which in turn causes the reflectivity
increase.

In order to understand clearly the reason
for this phenomenon, one has to see fig.4.2 also. In
this case the reflectivity curve of the film deposited
at a higher temperature (200°C) does not show any
increase upto 170°C while the reflectivity of a similar
film deposited at room temperature shows the usual

increase (curve A). If any variation in the thermal
stress of a film is to occur, it has to be heated
above its deposition temperature[30,31]. Since in the
case of curve B the film is heated only upto $170^{\circ}C$,
which is well below its deposition temperature, there
may not be any change in its thermal stress value
and hence there is no smoothening process taking place.
But in the case of the film deposited at room tempera-
ture, the thermal stress will be increasing due to
heating. This results in the reduction of resultant
stress in the film since the intrinsic stress is
opposite to the thermal stress as explained in
chapter III. When the resultant stress (σ) is reduced
to such an extent that

$$\gamma \; > \; \frac{\sigma r_o}{2} \qquad\qquad (4.1)$$

(where γ is surface energy of the film and r_o is the
radius of initial irregularities) the smoothening
process starts.

It is also found that the temperature at
which this happens varies with film thickness. This
will be clear only after seeing fig.4.5 in which
curve A gives the variations of intrinsic stress with

the film thickness[32,33] (for copper films). It is obvious from the figure that for films upto a thickness of 1000Å the intrinsic stress is very high ($\sim$1.5x10^9 dyne/cm^2) and as the thickness increases further, the stress decreases. Hence for 'thinner films'(ie., with thickness upto $\sim$1000Å) the thermal stress has to go to a very high value in order to satisfy the condition in eqn 4.1 for the surface to become smooth. In the case of 'thicker films' (ie., with thickness greater than 1000Å) this can take place at a lower temperature since the intrinsic stress value is much smaller.

4.4a Calculation of the intrinsic stress

One can calculate the thermal stress in a film using the expression[34],

$$\sigma_{thermal} = \frac{\alpha_f - \alpha_s}{1 - \nu} E(\Delta T) \qquad (4.2)$$

where α_f and α_s are linear thermal expansion coefficients of the film and substrate, E is the Young's modulus of the film material, ν is Poisson's ratio of the film and ΔT is temperature difference. If an approximation is made that the thermal stress is almost equal to

the intrinsic stress in the film at the temperature
when reflectivity just starts increasing one can get
the approximate value of intrinsic stress. Since
these values for different thickness are calculated[9,10]
by other methods, they can be compared. This comparison
with earlier intrinsic stress values is done in fig.4.5.

It is found that, except for very low
thickness both values are in good agreement which is a
strong support for the theory in the present work.

4.5 Conclusion

The variation in reflectivity of copper
films due to heating is studied. It is found that the
reflectivity increases after a particular temperature
whose value depends on the film thickness. From the
scanning electron micrographs it becomes clear that
there is surface smoothening due to heating. Since
there is a thickness dependence for this process, this
can be related to the stress minimisation phenomenon
due to heating. This is again verified by doing the
same experiment on similar films prepared at higher
temperature. There the increase in reflectivity does
not occur indicating that the stress variation should
be the reason for surface smoothening.
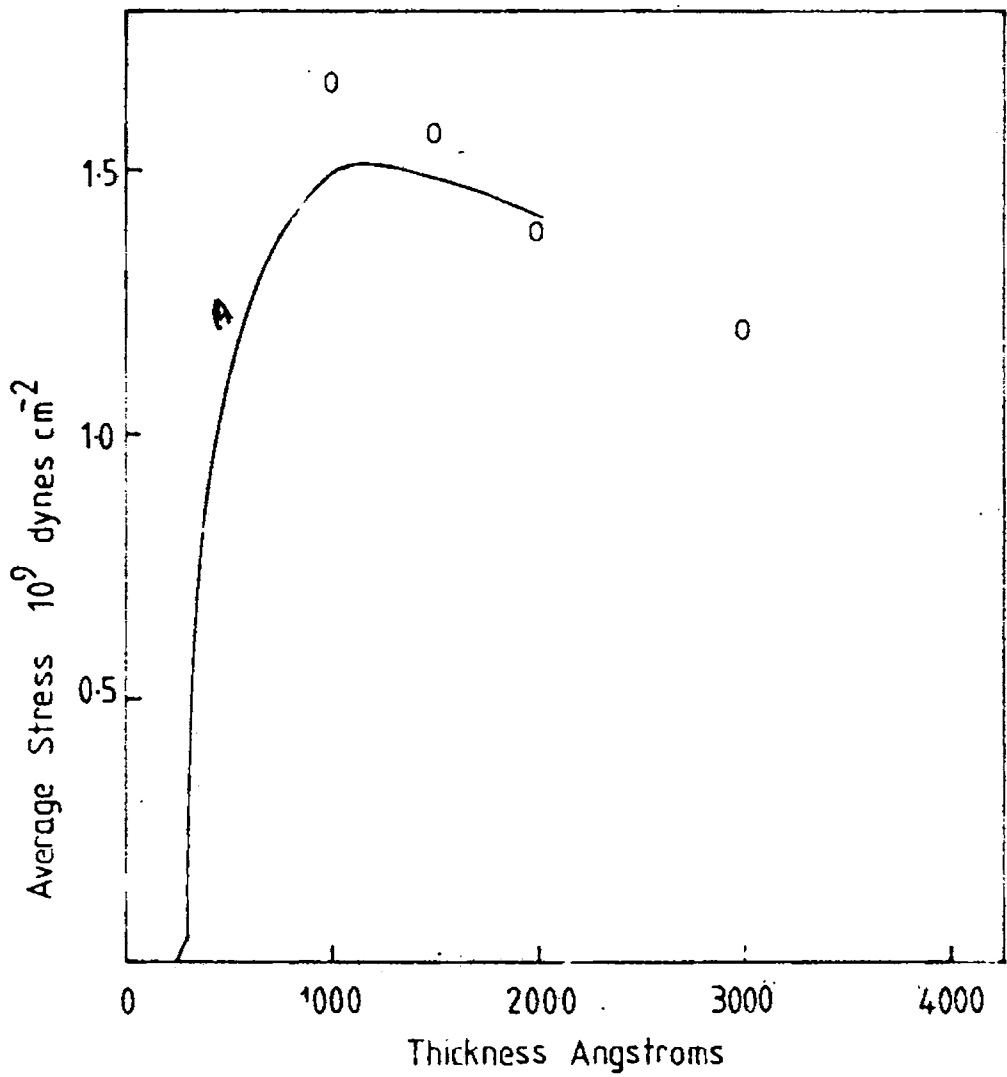
Fig.4.5 Variation of intrinsic stress in copper
films with thickness.
——— obtained by earlier workers.,
o, obtained in the present work.

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CHAPTER V

OPTICAL STUDY OF INTERDIFFUSION IN Al/Ag BILAYER FILMS

5.1 Introduction

Metal films of uniform thickness can easily
be produced by vacuum deposition and when two such films
of different metals are deposited one on top of the other
and the resultant bimetallic film is annealed, diffusion
generally takes place (unless the metals are completely
immiscible). This leads to the formation of solid
solutions or intermetallic compounds or both. As the
films are having a columnar growth they have a fine
meshed network of grain boundaries perpendicular to the
film plane. The lattice periodicity is completely broken
down in the grain boundaries resulting in looser atomic
packing. As a result of this change the grain boundaries
act as a highly diffusive channel system in which con-
centration gradients are rapidly smoothed out. Since the
grain boundary area may much exceed the area of the
interface, diffusion into and out of the lattice is to be
expected preferably via grain boundaries. In fact, the
grain boundaries are very effective short circuit path
for diffusion at temperatures well below the melting
point.

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The study of interdiffusion in multilayer films is important since it can give information about the intermetallic compounds, the coefficient of diffusion of the materials etc. But it is still more important and relevant as far as technological aspects are concerned. Almost all the electronic devices now-a-days contain thin film integrated circuits and diffusion may take place between the layers of different materials of these devices due to their functioning at elevated temperatures or in an ambient which promotes diffusion. Hence, in the case of materials used in electronic devices, it becomes necessary to study in detail the problem due to interdiffusion, the compounds formed by that phenomenon and ways to minimise it. Thus metals like silver, platinum, copper, gold, aluminium, nickel and semi-conductors like silicon, germanium, gallium arsenide etc. become very important in this context.

A large number of workers have studied the interdiffusion of these materials using different experimental techniques. The main among them are X-ray interference, electron spectroscopy for chemical analysis (ESCA), and electron scanning microscopy. Optical methods like 'attenuated total reflection (ATR)

and spectroscopic ellipsometry are also used in this area of research. Since the interdiffusion in thin films is the basis of all the surface changes[1], surface analysis by optical methods can give a lot of information regarding the interdiffusion. For example, measurement of refractive indices or ellipsometric parameters[2] ψ and Δ or simple reflectivity measurement furnishes the required information. Another important aspect supporting the optical method is that it is nondestructive unless the materials are photosensitive (which will be the case most generally).

Considering the importance of the topic a brief review of the earlier works is also included in this chapter. These are selected on the basis of importance of materials studied or application of the result obtained in technological side or due to the speciality of experimental technique.

5.1a   Brief review of earlier works

The number of review articles and books published in this area itself gives the idea of the amount of work done on this aspect. Of these only

very important reviews[3-7] are considered here.
Weaver[3] gives review of interdiffusion in different
bilayer metallic films with a stress on the optical
study while Gupta[7] gives an elaborate study of the
matter considering experimental and theoretical
aspects. There has been a large number of publi-
cations on interdiffusion taking place in different
materials studied by using different experimental
techniques from which very important and recent works
are considered here[8-25]. Saha et al[18] have given a
theoretical study on diffusion while Loisel et al[19]
report the diffusion in Al/Au system in the tempera-
ture range $64^{\circ}C$-$80^{\circ}C$ using ATR method. Another
important work is that of Ilkka Suni et al[21] in which
the study of the interdiffusion in Cu/Ni system is
presented. These materials are important due to
their use in solar cells. Hwang et al[14], using Auger
sputter profile, studied the diffusion of aluminium
into silicon in the temperature range $350^{\circ}C$-$425^{\circ}C$.
This is another important work since these two
materials are much used in thin film integrated
circuits. Also Wagendristel et al[16] have reported
the formation of Au_2Al in Au/Al system and they used
X-ray diffraction technique for this study.

In order to understand the effect of
different ambients on the interdiffusion of both
bimetal and metal-semiconductor films one need go
through the series of publications by Chin-An
Chang[26-34]. Since his study includes materials like
gallium arsenide, germanium, silicon, platinum,
nickel, copper etc. this is very important from the
point of view of applied science also. In one of
his publications Chang has reported that, in presence
of oxygen, diffusion of chromium and platinum in
silicon is considerably reduced[26]. Also in another
work he showed that the interdiffusion in Au/Cr
in presence of air can be completely suppressed by
the presence of CO[31]. The presence of oxygen has
been found to be capable of reducing the mixing
between copper and chromium and platinum and copper
in Cu/Cr and Pt/Cu/Cr film systems[34].

Coming to the case of Al/Ag thin film
system there have been various studies on different
aspects of interdiffusion by using different experi-
mental methods[35-42]. Of these, some[35-37] provide
the analysis of the properties of this bilayer system
to find out the possibility of using it as a solar
reflector. This is because, silver has good reflecti-
vity and is inert to the ambient conditions[43] while

aluminium is having good adhesion also[44]. If these two are combined, one can get a good solar reflector. Weaver et al[38] have studied this thin film system using optical techniques (ie., by reflectivity measurements) and to supplement these observations they used electron microscope also. Khan et al[41] have obtained the activation energy from diffusion measurements. Wagendristel et al[42] also calculated the activation energy from diffusion coefficient measurements. Here they used the X-ray interference method for the study and annealing temperature was within the range $80^{\circ}C$ to $110^{\circ}C$.

In the present work also, Al/Ag system is selected because of two reasons. First one is that availability of experimental data both in thin film and bulk form. Second is that this system has larger application in electronic as well as energy conversion devices. Here the temperature of the film is continuously increased and reflectivity variations are recorded, which provide the data for the study of interdiffusion.

5.2 Experimental

The multilayer films for the experiment were prepared by the method of vacuum deposition as in other

cases (see chapter II). However in this case a double source evaporation technique was used since both silver and aluminium were to be evaporated one after the other. Silver was taken in a molybdenum boat while aluminium was in a coil made up of tungsten wire. Both sources were well separated using a mica sheet. For all the samples, silver formed outer layer and aluminium was the inner one. This was to avoid the oxidation of aluminium layer due to exposure to the atmosphere. Pressure during the evaporation of both the materials was well below 10^{-5} torr. The distance between heating sources and substrate was always 15 cms.

Two types of films were prepared which differed in the ratio of their thickness. The layer thickness is a very important factor for these materials. Since both these materials are having same atomic size and same structure their thickness ratio corresponds to the ratio of number of atoms of the materials[38,42]. Here in the first type, the ratio of thickness between aluminium and silver was 1:2 and in the second type it was 1:1 (In both, aluminium was having a thickness of 500A). The required thickness was obtained by taking the calculated mass of the evaporant using the expression[45] given in earlier chapters. Later the thickness was

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measured by using the multiple beam interferometry[46].
It was found that the thickness was having variation
of the order of $\pm$ 50Å from the calculated value which
did not however affect the thickness ratio.

Heating of the films was done in the glass
cell described in chapter II and IV. The pressure
during heating was always 10^{-2} torr. The heating
rate was 1°C/minute when films were heated on the
glass side (back side). But the rate was 0.5°C/minute
when heating was done on the film side (silver side).
This was to avoid damages due to heating since it was
directly applied on the film.

Here the reflectivity measurements were
taken during heating. This was done using the set up
described in chapter II ie., a PMT galvanometer
arrangement. The wavelength of the light used was
4400Å. Always the reflectivity was measured at an
angle of incidence equal to 45°.

5.3 Results

The reflectivity measurements were also done
on both surfaces of the film ie., on silver side (front
side of the film) and on glass side (back side of the
film). All the observations are shown in figs.5.1,
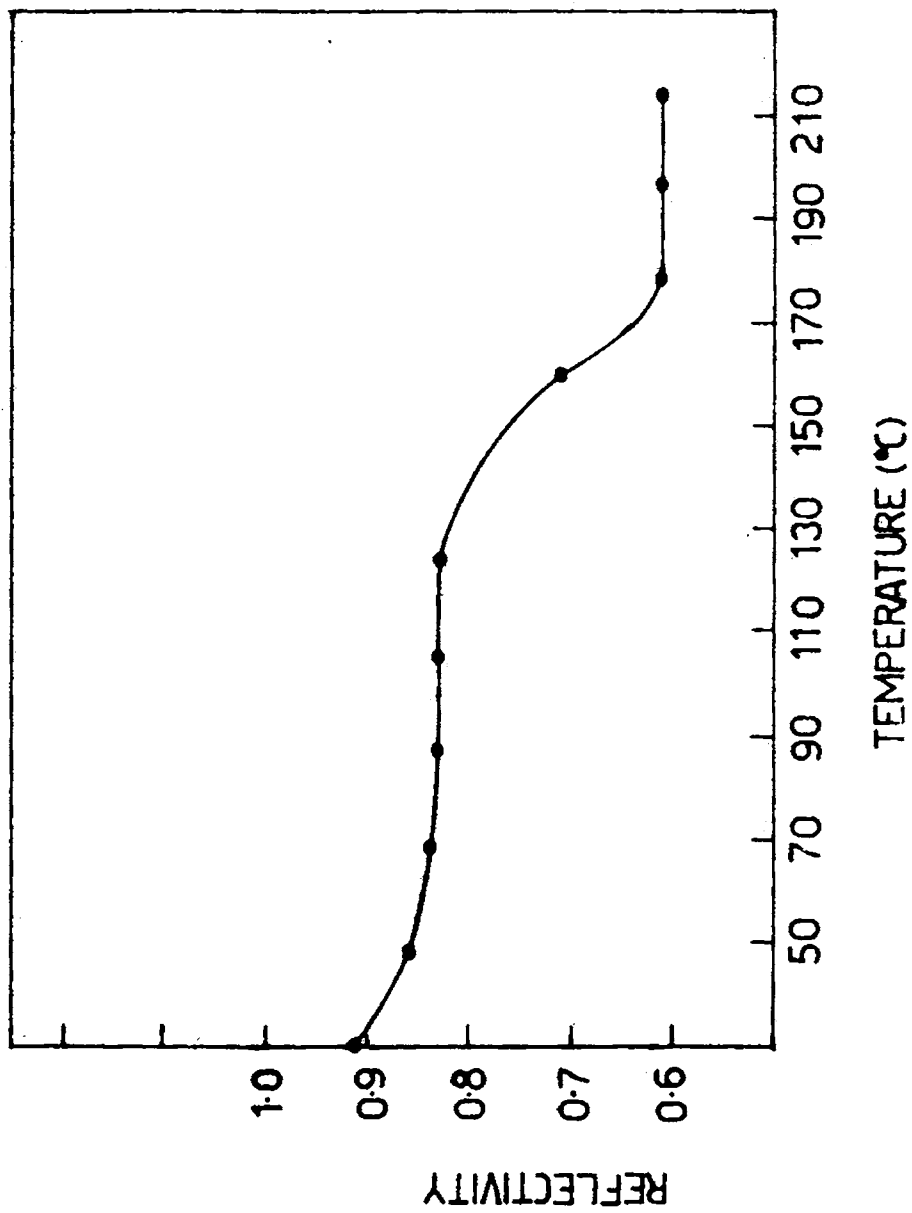
Fig.5.1 Variation in reflectivity with temperature of the Al-Ag bilayer film with thickness ratio 1:2 (wavelength 4400A).
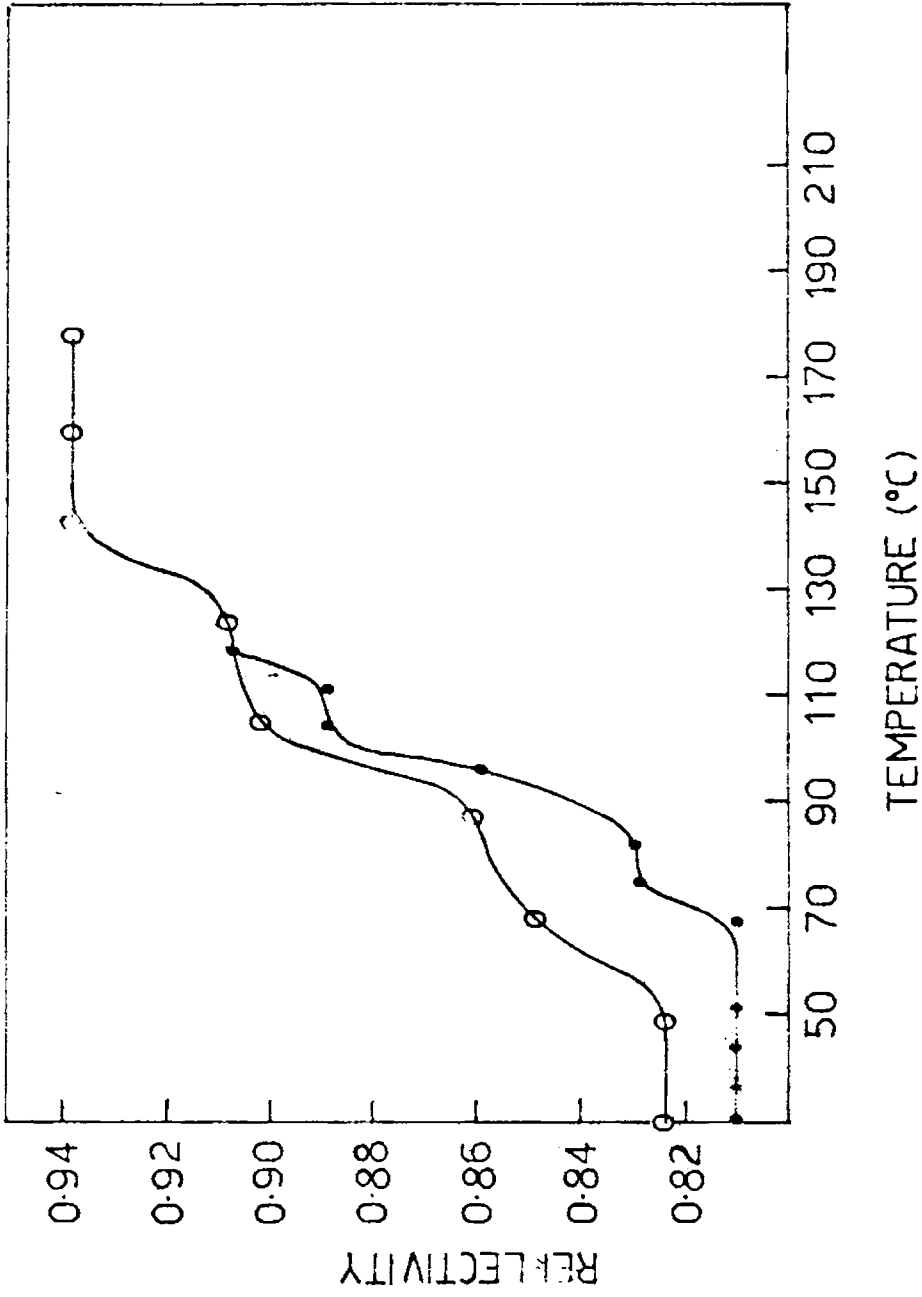
Fig.5.2   (O—O) Variation in reflectivity of the Al-Ag bilayer
film with thickness ratio 1:1 (measurement on the
front surface of the film).
The second curve for a similar film (●—●) gives the
temperature value (at which the step formation takes
place) more precisely.
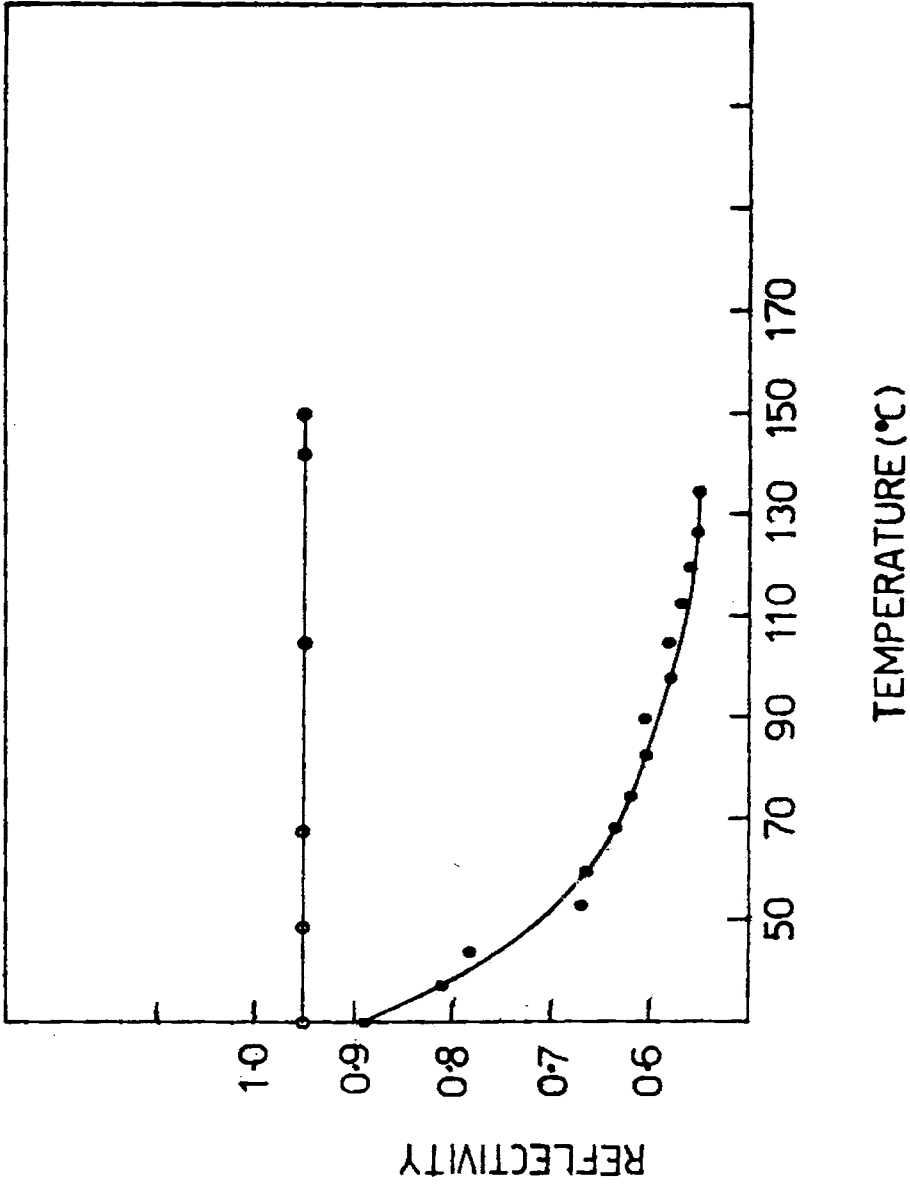
Fig.5.3   Variation in reflectivity (at glass side) of the Al-Ag
          layer film with temperature

o—o   for the thickness ratio 1:1
●—●   for the thickness ratio 1:2

5.2 and 5.3. In this, the first one gives the reflectivity variations on the silver side of the films with thickness ratio 1:2 (first type) and the second one gives the same for the films of thickness ratio 1:1 (second type). The third figure shows the variations of reflectivity on the glass side for both types of films.

From fig.5.1 it can be seen that the reflectivity decreases to 0.83 at about 80°C. On increasing the temperature further decrease occurs in this value and it reaches 0.62 at about 175°C. It remains constant thereafter. But in fig.5.2, the reflectivity increases from 0.81 to 0.94. This curve also shows two steps--one between 70°C and 80°C the other between 110°C and 120°C. The fig.5.3 shows considerable difference from the other two. Here the reflectivity of first type of films steadily decreases to a value 0.55 as the temperature increases to 130°C. But for the second type of films, there is no change in reflectivity.

5.4 Discussion

5.4a The silver side

In the case of films having thickness ratio

1:2 the reflectivity, which was well above 0.9, is reduced to 0.83 (fig.5.1) and remains constant for a comparatively long range of temperature (ie., from 80°C to 125°C). But this value of reflectivity has been shown to be that of the compound Ag_3Al by different workers[38,45,46]. This can happen as a result of diffusion of aluminium into silver due to heating. It can easily occur since silver film is aggregate in structure[38,44] thus allowing grain boundary diffusion to take place. Due to this diffusion a small quantity of aluminium is coming into contact with large quantity of silver and Ag_3Al is the most probable compound to be formed[49]. This compound seems to be unstable at high temperature and probably this may be the reason for the decrease in reflectivity from 125°C. As the temperature reaches 180°C the reflectivity value comes down to 0.63 and further increase in temperature makes no change in this value. This reflectivity value has been shown to be that of the compound Ag_2Al[38,47,48] in air. Hence it can be taken for granted that Ag_2Al is the final intermetallic compound, which is stable at higher temperature.

As the thickness ratio is changed to 1:1, the results are very much altered. From fig.5.2 it can be seen that the reflectivity is increasing with the temperature (ie., from 0.81 to 0.94). This clearly indicates that, in this case, no intermetallic compound like Ag_3Al or Ag_2Al is formed on the surface. The increase in reflectivity can be explained by considering certain other factors. Here, even if the whole silver present in the film is utilised for the formation of the stable compound Ag_2Al almost half of the aluminium present in the film will be left unreacted since the ratio of thickness in this case is 1:1. It has been pointed out earlier that the thickness ratio for these materials corresponds to the ratio of the number of atoms in them. Hence aluminium will be diffusing out through the grain boundaries to form a surface layer and then the reflectivity increases. A very similar result has been reported by Wood et al[50]. This was a study of interdiffusion in Au/Ag thin film system and they found gold on the surface of silver film due to diffusion through grain boundaries. The analysis was done by using ESCA.

The steps found in the reflectivity curve in fig.5.2 also supports the above argument. The
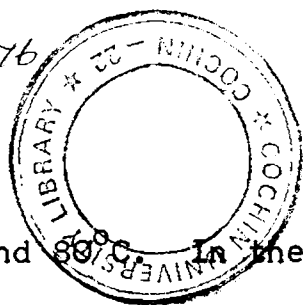
first step occurs between 70°C and 80°C. In the fig.5.1, the formation of Ag_3Al also starts in this region. Hence due to this reaction, the quantity of pure aluminium available on the surface of the film is reduced, which results in the reduction of reflectivity and hence in the step formation. But this reduction in the quantity of aluminium on the surface does not last long due to two reasons. One is that the quantity of silver present in the film is small (since the thickness ratio is 1:1) and hence the reaction may not last long. A second reason is that the quantity of aluminium diffusing out increases as temperature is increased. These factors lead to the formation of a layer of aluminium over the phase layer and as a result the reflectivity again increases. The second step occurs in between 110°C and 120°C. This also exactly coincides with the temperature at which Ag_2Al formation starts. At about 140°C the curve reaches a constant value (ie., 0.94) indicating the formation of a comparatively thick layer of aluminium over the film surface.

5.4b Aluminium side

In the case of first type of films, the reflectivity is found to be decreasing steadily

until it reaches a value of 0.55 at about 125°C
(fig.5.3). It has been shown by earlier workers
that this is the reflectivity of the compound
Ag_2Al through glass[38,47,48]. Also at this tempera-
ture (ie., 125°C) the formation of Ag_2Al starts on
the silver side of the film (in fig.5.1). Since
the thickness ratio is 1:2, the whole material in
the film will be utilised for the formation of
Ag_2Al and hence the final compound observed on both
surfaces of the film is Ag_2Al. No other phase
formation is indicated on this side of the film.

When the thickness ratio is changed to
1:1 there is a marked variation in reflectivity
on this face also. It can be seen that (fig.5.3)
the reflectivity, in this case, is more or less
constant. This happens because, the whole aluminium
is not required for converting the whole quantity
of silver present in the film into Ag_2Al when
thickness ratio is 1:1. Only half of the total
quantity of aluminium is required for this ie.,
half the thickness of the aluminium layer (ie., 250Å)
is left unreacted. But aluminium films of thickness
(approximately) 300Å are found to be opaque for
ordinary light[38]. Hence even if a layer of Ag_2Al

is formed at a distance of 300Å from the surface of the aluminium film, that cannot make any change in the reflectivity of the film. Due to this, the reflectivity of this film on aluminium side remains constant and it can be concluded that for the second type of films (on the aluminium side) there is a layer of unreacted aluminium.

5.5 Conclusion

The heat treatment of Al/Ag bilayer films produces very interesting results, which is found to be strongly dependent on the thickness ratio of the two layers. For films with ratio 1:2, it is found that the phase Ag_3Al is formed within the temperature range $80^{\circ}C$ to $125^{\circ}C$, after which it decomposes. At about $180^{\circ}C$, the formation of Ag_2Al is complete and is found to be stable at high temperature ($> 200^{\circ}C$). For the same type of film, on the aluminium side, the only phase detected is Ag_2Al.

When the second type of films are heated, the reflectivity is found to be increasing on the silver side and this is considered to be due to the formation of a layer of aluminium which is left unreacted. On the aluminium side of the same type

of film, it is found that a layer of aluminium of
thickness 250$\overset{o}{A}$ is remaining unreacted even after
the whole silver is converted into Ag_2Al. It may be
this aluminium, which is diffusing out onto the
silver side causing an increase in reflectivity.

Analysing these results, it is found that
the diffusion of aluminium through silver is mainly
through the grain boundaries of silver film and hence
comparatively larger quantity of aluminium is diffusing
out (note the formation of an aluminium layer on the
surface of second type of films). On the other hand,
the diffusion of silver through aluminium is mainly
aided by the lattice diffusion and hence only small
quantity of silver is diffusing into the aluminium
layer (note that Ag_3Al is not formed on the aluminium
side of first type of films).

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CHAPTER VI

ELLIPSOMETRY

6.1 Introduction

Ellipsometry is a non-destructive, sensitive and highly accurate optical method which is used for different purposes like, measurement of optical constants, testing of surface accuracy, study of corrosion etc. This technique though well known even a century ago[1] was not widely used mainly because the equations used to interpret the measured parameters involved tedious computations. In recent years these difficulties have been resolved by the introduction of automatic ellipsometers, high speed and rather cheap computers and development of better computer programmes for reducing the data. All these things resulted in the quick development of ellipsometry in the 1970's and now the technique is widely used in different areas including industries where the applications include the study of molecular contaminants on the performance of space born optical systems and the monitoring of dielectric layers deposited over silicon chips in semiconductor industry.

The basis of ellipsometry is the characterisation of changes in the state of polarisation of light reflected (transmitted) by an optical surface

(transparent material). The changes in polarisation is described by two angles Δ and ψ which correspond to the phase difference and amplitude attenuation of the electric field vectors perpendicular and parallel to the plane of incidence. Using these two parameters and the value of angle of incidence one can calculate the optical constants 'n' and 'k' of the material (ie., the real and imaginary parts of the refractive index). If the surface of the material is covered by a film its thickness can also be calculated, provided the refractive indices of both film and substrate (surface over which the film is formed) are known. An advantage of this method is that Δ and ψ are not dependent on the absolute light intensities but only on the ratio of intensities. Another important study using ellipsometry is on the nature of surfaces; the variation of ellipsometric parameters can characterise surface features. It is found that ψ is very sensitive to the surface roughness which is relatively insensitive to the thickness of dielectric (eg. oxide) films on the surface. But Δ is extremely sensitive to the film thickness and relatively insensitive to the surface roughness[2]. The phase shift Δ can be used to detect as little as 0.1Å to as much as 5000Å of oxide or a film of contamination on the top of an oxide.

Another point supporting the ellipsometric technique is its capability to be used as a set up for in situ studies of different reactions which many other experimental techniques used in this direction (like electron microscopy) do not have. For example, ellipsometry can be used for the study of reaction taking place at a solid-liquid interface, which cannot be analysed by using an electron microscope since the surface to be analysed using it should be kept in high vacuum. The fact that the area of the surface to be studied can be very small, is another advantage over other methods of analysis. Along with these specialities it is also to be taken into account that this is a nondestructive technique.

6.1a Brief review of earlier works

The studies conducted by various investigators testify to the extent of applicability of this method. Meyer[3] employed ellipsometry for the calculation of surface state densities of semiconductors for which he estimated the dielectric constants from the values of refractive indices. This technique was also adopted by different groups[4,5] for studying the effect of doping

in different materials. For example, Tyagai et al[4] studied the morphology of silicon surfaces after doping it with silver while Briska et al[5] have analysed the effect of doping arsenic. They studied variations due to different arsenic concentrations at different temperatures in different ambient conditions. Hare et al[6] have investigated the properties of F centres in KCl crystals using ellipsometry. These centres were formed as a result of bombardment by electrons with energy in the range 2-10KeV. It has been shown that, unlike earlier methods, this technique can give reproducible and consistent results. The study of oxide layer formation on different materials under different conditions is an important area in which this optical technique finds maximum application[7-13]. Among these, Allen[7] developed an IR ellipsometer for studying the oxide layer formation by anodisation of aluminium and the instrument operated at 10.6μm. Boggio[8] investigated ellipsometrically the oxidation of (111) face of copper single crystals at 21°C for oxygen pressure from 0.03 to 760 torr and found that a mono-layer of CuO forms on the top of Cu_2O film at high oxygen pressure. Habraken et al[9] have also analysed

the oxidation of (111) face of copper for which they used Auger electron spectroscopy and LEED along with ellipsometry. The oxygen pressure in this investigation was very low (10^{-6}- 10^{-4} torr) while the temperature range was quite wide (23°-400°C). Idaezak et al[10] have published an algorithm to determine the refractive index and thickness of oxide layers on absorbing substrate. The growth of very thin oxide layers (15-80$\overset{o}{A}$) on polycrystalline silicon has been studied by Horiuchi[12] in low oxygen pressure (10^{-8} atm.) and high temperature range (850-1050°C). Another important study is performed by Belyaev[14] in which this technique is used for noting the changes in ellipticity of light after passage through thin homogeneously oriented layers of liquid crystals. The use of this technique in the field of amorphous silicon is recently gaining prominence[15-17]. Theeten[15] has given a good review regarding the use of ellipsometry in connection with vapour phase epitaxy or plasma processing of semiconductors. In this paper it is shown that this surface sensitive, nondestructive real time method can be used to monitor the kinetics of thin film deposition and also to analyse the interface regions between successive layers. Drevillon et al[16] used fast real time ellipsometry

for studying the growth of amorphous hydrogenated
silicon deposited in low pressure D.C. discharge of
silane. Flamme[17] developed a new method for measuring
refractive index absorption index and thickness of
thin films using ellipsometry and applied it on
amorphous silicon films (with thickness less than
1050$\overset{o}{A}$) prepared by low pressure chemical vapour
deposition technique.

The use of ellipsometry in the area of
corrosion is reviewed by Petit et al[18]. They show
that this method is very much useful in the case
of localised corrosion. Another good review in
this direction is given by Kruger et al[19] in which
the necessary theory and experimental set up are
described in an elaborate manner with due stress on
materials like copper, aluminium, titanium iron and
steel etc.

Analysis of surface roughness (of thin films and
and bulk materials) is a field where ellipsometry
has a unique place. Works in this field, using this
technique are reviewed in detail in chapter VII.

In order to get a clear idea about different
types of ellisometers and their specified uses one

has to go through the concerned reviews. Aspenes[20],
in his review, touches all aspects of spectroscopic
ellipsometers. Muller[21] gives the operating principles
and capabilities of automatic ellipsometers. Also he
hints about the possible developments. Kinosita et al[22]
describe quick methods to evaluate the refractive index
and thickness from the ellipsometric parameters using
modern ellipsometers. They also consider the analysis
of submonolayers. Hauge[23] in his recent review gives
a good description of modern ellipsometers along with
necessary theory. He describes the developments in
different branches of ellipsometry.

6.2 Theory

For interpreting ellipsometric data, when
polarised light is reflected from or transmitted through
bare or filmed substrates, one should use the electro-
magnetic theory to derive expressions of complex ampli-
tude reflection and transmission coefficients from
macroscopic optical properties. A large amount of
theoretical work has been done on this topic and detailed
discussions can be found in a number of books[24-26] and
review articles[27-30]. Here a simple structure consisting

of a planar interface separating two homogeneous optically

isotropic media (medium-0 and medium-1) is considered.

On to this interface a plane polarised light beam is

incident at an angle of incidence ϕ_0. This is

illustrated in fig.6.1. This model just enables one

to get an idea about the relation between the ellip-

sometric parameters (ψ and Δ), Fresnel's reflection

(transmission) coefficients and the refractive index.

In the following treatment, the complex refractive

index of an absorbing medium is always taken as

$$N = n - ik \qquad (6.1)$$

where n is called index of refraction (or real part

of N) and k the extinction coefficient (or imaginary

part of N). Also the expression for the electric

vector of an optical plane wave travelling in the

positive direction of Z axis in an isotropic absorbing

medium, with planes of constant phase and constant

amplitude parallel, is given by

$$E = E_0\, e^{i(\omega t + \delta)}\, e^{-i\omega Nz/c}$$

$$= E_0\, e^{i(\omega t + \delta)} e^{-i\omega nz/c} e^{-\omega kz/c} \qquad (6.2)$$

where δ is a constant phase angle, c is free space
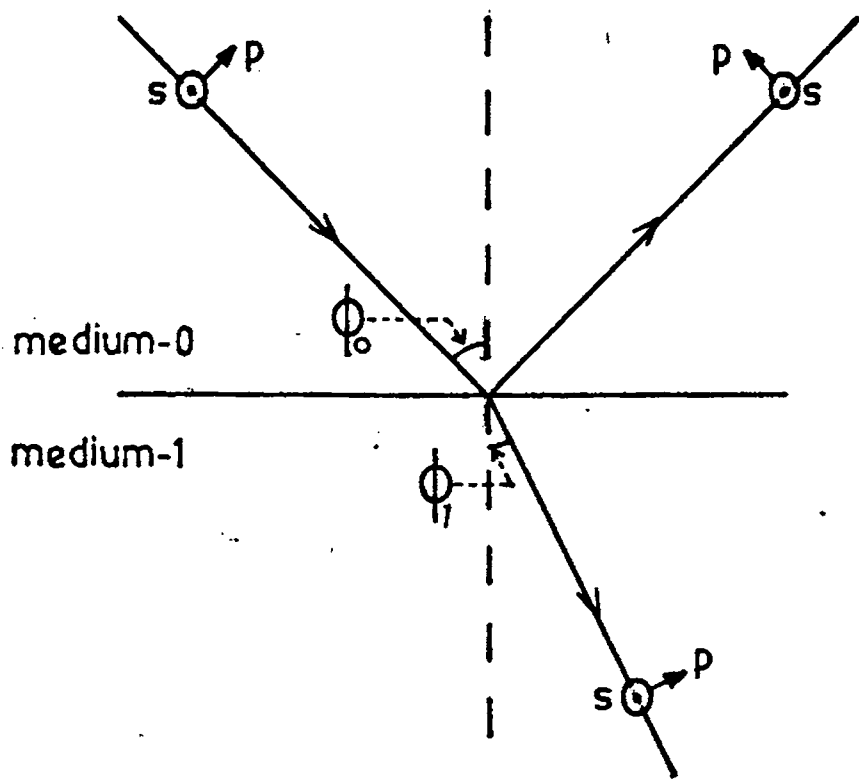
Fig.6.1 Oblique reflection and transmission
of plane wave at planar interface
between two semi-infinite media 0 and 1.

velocity and E_o (which is in general complex) defines both amplitude and the polarisation of the wave. From eqn.(6.2) it is clear that the wave amplitude decays exponentially along the direction of propagation at the rate of $\omega k/c$.

From fig.6.1 it is quite clear that $\emptyset_1$ is the angle of refraction in medium-1 and the plane of incidence is the plane of the paper. It is assumed that N_o and N_1 are the complex refractive indices of medium-0 and medium-1 and the change of refractive index across the interface is abrupt. Now according to Snell's law we have,

$$N_o \sin \emptyset_o = N_1 \sin \emptyset_1 \qquad (6.3)$$

If both media are transparent, N_o and N_1 are real numbers, the angles $\emptyset_o$ and $\emptyset_1$ are also real and the case is very simple. However, when either one or both media is absorbing, the angles and refractive indices, in general, become complex and the physical picture becomes much complicated.

It is well-known that when incident wave is linearly polarised, with its electric vector vibrating

parallel (p) to the plane of incidence both reflected and transmitted waves will also be similarly polarised with their electric vectors vibrating parallel to the plane of incidence. Similarly, when the incident wave is linearly polarised perpendicular (s) to the plane of incidence, the reflected and transmitted waves are found to be linearly polarised perpendicular to the same plane. Hence the linear vibrations parallel (p) and perpendicular (s) to the plane of incidence are called the 'Eigenpolarisations' of reflection and refraction.

Now one can consider the amplitudes of reflected and transmitted waves in terms of those of the incident wave. For this, an arbitrarily polarised incident wave is considered and its electric vector is resolved into p and s components. Each component is treated separately and the results are combined later. Let E_{ip} and E_{is} represent the p and s components of the complex amplitudes of the electric vectors of the incident wave. Similarly (E_{rp}, E_{rs}) and (E_{tp}, E_{ts}) be the corresponding components of the electric vectors of the reflected and transmitted waves respectively.

Matching the tangential E and H fields across the interface one gets

$$\frac{E_{rp}}{E_{ip}} = r_p = \frac{N_1 \cos \phi_0 - N_0 \cos \phi_1}{N_1 \cos \phi_0 + N_0 \cos \phi_1} \qquad (6.4)$$

$$\frac{E_{rs}}{E_{is}} = r_s = \frac{N_0 \cos \phi_0 - N_1 \cos \phi_1}{N_0 \cos \phi_0 + N_1 \cos \phi_1} \qquad (6.5)$$

$$\frac{E_{tp}}{E_{ip}} = t_p = \frac{2N_0 \cos \phi_0}{N_1 \cos \phi_0 + N_0 \cos \phi_1} \qquad (6.6)$$

$$\frac{E_{ts}}{E_{is}} = t_s = \frac{2N_0 \cos \phi_0}{N_0 \cos \phi_0 + N_1 \cos \phi_1} \qquad (6.7)$$

These are called Fresnel's complex amplitude reflection (r) and transmission (t) coefficients for p and s polarisations. Snell's law (eqn (6.3)) can be used to change eqns.(6.4)-(6.7) such that these coefficients are dependent on ϕ_0 and ϕ_1 only.

In order to study the effect of reflection and transmission (refraction) on the amplitude and phase of

the waves separately one can write the complex

Fresnel coefficients as

$$r_p = |r_p| \, e^{i \delta rp} \qquad\qquad (6.8)$$

$$r_s = |r_s| \, e^{i \delta rs} \qquad\qquad (6.9)$$

$$t_p = |t_p| \, e^{i \delta tp} \qquad\qquad (6.10)$$

$$t_s = |t_s| \, e^{i \delta ts} \qquad\qquad (6.11)$$

Here $|r_p|$ gives the ratio of amplitude of the

vibrations of electric vectors of reflected wave

to that of the incident wave when the latter is

polarised parallel to the plane of incidence with

similar meanings for $|r_s|$ $|t_p|$ and $|t_s|$. δ_{rp} represents

the phase shift due to reflection experienced by the

electric vector parallel to the plane of incidence with

similar meanings for δ_{rs} δ_{tp} and δ_{ts}.

It is obvious from eqns.(6.4)-(6.7) that

the Fresnel complex amplitude reflection (r) and

transmission coefficients have different values for

p- and s-polarisations. Hence due to reflection (or
transmission) the relative amplitude and phase relation-
ship between these two components will be changed.
It is also clear that if the incident light wave is
polarised in an arbitrary state (other than p or
s states) the polarisation of the reflected and
transmitted waves will be changed due to the difference
in absolute values or the angles (or both) of the
Fresnel coefficients of reflection and transmission.

In reflection ellipsometry one measures the
states of polarisation of incident and reflected
waves and determines the ratio (ϱ) of complex
Fresnel reflection coefficients for p and s polarisations
as

$$\varrho = \frac{r_p}{r_s} \qquad (6.12)$$

Using eqns.(6.8) and (6.9) one can rewrite the above
eqn. as

$$\varrho = \frac{|r_p|}{|r_s|} \, e^{i(\delta rp - \delta rs)}$$

$$= \tan \psi \, e^{i\Delta} \qquad (6.13)$$

Hence, ψ and Δ represent the differential changes in amplitude and phase respectively due to reflection by the component vibrations of the electric vector parallel and perpendicular to the plane of incidence.

Substituting values of r_p and r_s from eqns.(6.4) and (6.5) in eqn (6.12) one gets,

$$= \frac{N_1\cos\phi_0 - N_0\cos\phi_1}{N_1\cos\phi_0 + N_1\cos\phi_1} \times \frac{N_0\cos\phi_0 + N_1\cos\phi_1}{N_0\cos\phi_0 - N_1\cos\phi_1}$$

$$(6.14)$$

This on simplification using Snell's law (eqn.(6.3)) gives the following expression

$$\frac{N_1}{N_0} = \sin\phi_0[1 + (\frac{1-\ell}{1+\ell})^2 \tan\phi_0] \qquad (6.15)$$

Hence N_1 the refractive index of medium-1 can be computed provided one has ℓ and ϕ_0.

6.2a   Ellipsometric evaluation of ℓ

In this section, the theoretical aspects of the measurement of ellipsometric parameters ψ and Δ and the computation of ℓ and the refractive index from

them are considered. For this, the most general ellip-
sometric set up consisting of Polariser, Compensator,
System and Analyser (the PCSA arrangement) is taken
into account and is shown in fig.6.2. The light waves
(which is well collimated, unpolarised and monochro-
matic) from the source L is rendered plane polarised
by the polariser P after which it passes through the
compensator C. The emergent beam from C is reflected
by the optical system, S which is under investigation
and the reflected beam then comes to the detector D,
after passing through the analyser A. Here the optical
system S is assumed to be having its eigenpolarisations
along the orthogonal coordinates X and Y (ie., in the
case of a reflecting film, the p and s polarisations
will be coinciding with X and Y coordinates). Also
the orientations of polariser, compensator and analyser
around the beam axis are specified by the azimuth
angles P, C and A respectively in fig.6.2. For the
polariser and analyser, azimuths P and A define the
orientation of their transmission axes (ie., the
directions of transmitted linear eigenpolarisations)
while for the compensator the azimuth C defines
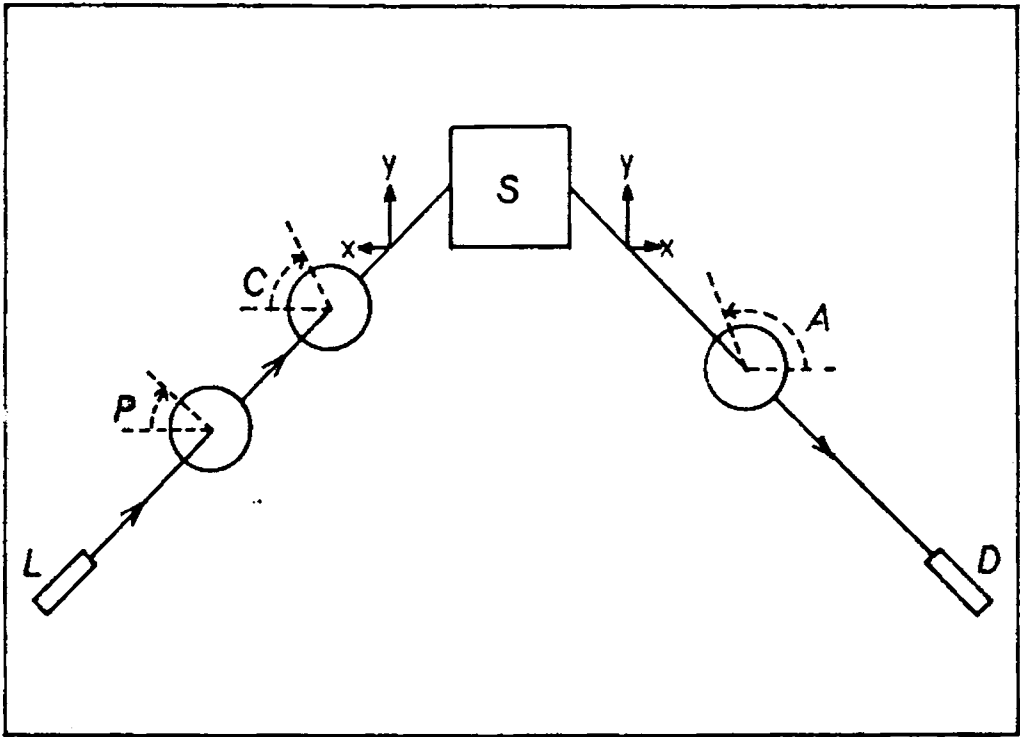orientation of its fast axis (ie., the direction of the

Fig.6.2 The Polariser-Compensator-System-Analyser
         (PCSA) arrangement.
         L - Light source;   D - Detector.

fast linear eigenpolarisation). All these azimuths
P, C and A are measured from the direction of the X
linear eigenpolarisation of the optical system, S and
the angles are taken to be positive in anticlockwise
direction when looking against the direction of
propagation of the beam. Here the light beam is
described by its Jones vector and the optical elements
by their Jones matrices[31] since, by this method, one
can easily follow the state of polarisation of the
light beam as it progresses through the components
of the ellipsometer.

The notation used in the following treatment
can be explained in a simple way as follows. The
superscripts denote the coordinate system with respect
to which the Jones vector or matrix is referenced.
In the subscript the first letter denotes the optical
component while the second shows whether the beam is
its input or output. For example E_{CO}^{fs} is the Jones
vector (representing the electric field) of the light
beam at the output of the compensator, in its fast
slow principal frame of reference (The frame of reference
is the coordinate system in which the Jones matrix of
an optical component is diagonal). Another important

matter to be considered is the change of coordinate system, which becomes a necessary matter when the light beam after emerging from a system enters into a new one. This is accomplished by using the rotation matrix $R(\alpha)$ and the counter rotation matrix $R(-\alpha)$ and is written as

$$R(\alpha) = \begin{bmatrix} \text{Cos } \alpha & \text{Sin } \alpha \\ -\text{Sin } \alpha & \text{Cos } \alpha \end{bmatrix} \qquad (6.16)$$

The effect of the polariser is to be considered first. The output of this system will be plane polarised light which can be denoted as,

$$E_{PO}^{te} = A_c \begin{bmatrix} 1 \\ 0 \end{bmatrix} \qquad (6.17)$$

Here, A_c contains information regarding the intensity and absolute phase of the wave emergent from the polariser. The superscript 'te' denotes the 'transmission-extinction' principal frame of reference.

Before examining the effect of the compensator one has to change the reference coordinate system, from the transmission-extinction principal frame of the

polariser to the 'fast-slow' principal frame of the compensator. This is achieved by using the rotational matrix R(P-C) as,

$$E_{CI}^{fs} = R(P-C) \ E_{PO}^{te}$$

$$= A_C \begin{bmatrix} Cos(P-C) & -Sin(P-C) \\ Sin(P-C) & Cos(P-C) \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

$$= A_C \begin{bmatrix} Cos(P-C) \\ Sin(P-C) \end{bmatrix} \qquad (6.18)$$

The compensator is having a slow-to-fast complex amplitude transmittance given by,

$$\varrho_c = T_C \ e^{i\delta c} \qquad (6.19)$$

This equation shows that the component of the electric vector incident on the compensator parallel to its slow axis is retarded by - c and is attenuated in amplitude by T_C relative to the component parallel to its fast axis. Its Jones matrix can be written as

$$T_C^{fs} = K_C \begin{bmatrix} 1 & 0 \\ 0 & \varrho_c \end{bmatrix} \qquad (6.20)$$

system, S it can be taken that,

$$E_{CO}^{XY} = E_{SI}^{XY} \qquad (6.23)$$

Hence the Jones vector of the beam at the output of S is given by the equation,

$$E_{SO}^{XY} = T_{S}^{XY} E_{SI}^{XY} \qquad (6.24)$$

In the above equation the Jones matrix of the system, T_{S}^{XY}, is diagonal since it is assumed to have orthogonal linear eigenpolarisations, parallel to X-Y coordinate axes and the matrix can be written as

$$T_{S}^{XY} = \begin{bmatrix} V_{ex} & 0 \\ 0 & V_{ey} \end{bmatrix} \qquad (6.25)$$

where V_{ex} and V_{ey} represent the eigenvalues of the X and Y linear eigenpolarisations. Substituting the values of E_{SI}^{XY} and T_{S}^{XY} in eqn.(6.24) we get,

$$E_{SO}^{XY} = K_{C}A_{C} \begin{bmatrix} V_{ex} \left[CosC \ Cos(P-C) - \ell_{c} \ SinC \ Sin(P-C) \right] \\ V_{ey} \left[SinC \ Cos(P-C) + \ell_{c} \ CosC \ Sin(P-C) \right] \end{bmatrix}$$

$$(6.26)$$

This beam, coming from S has to pass through the analyser A which can be rotated around the beam axis. To study the effect of the analyser on the polarisation of the beam, one has to make a co-ordinate rotation from the optical system's X-Y principal frame to the analyser's t-e principal frame as

$$E_{AI}^{te} = R(A) \ E_{AI}^{xy} \tag{6.27}$$

Taking that $E_{AI}^{xy} = E_{SO}^{xy}$ and substituting for $R(A)$ the above equation becomes,

$$\begin{bmatrix} E_{AI,t} \\ E_{AI,e} \end{bmatrix} = \begin{bmatrix} (CosA \ E_{AI,x} + SinA \ E_{AI,y}) \\ (-SinA \ E_{AI,x} + CosA \ E_{AI,y}) \end{bmatrix} \tag{6.28}$$

(In eqn.(6.28) the third term in the subscripts denote the corresponding coordinate axis). The Jones matrix of the analyser is given by the expression

$$T_A = K_A \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \tag{6.29}$$

where K_A represents the amplitude and phase changes experienced by the transmitted linear eigenpolarisation.

Then the electric vector at the output of the analyser
is obtained as,

$$E_{AO}^{te} = T_A^{te} E_{AI}^{te} \qquad (6.30)$$

Substituting for the value of T_A from eqn.(6.29),

$$E_{AO}^{te} = K_A \begin{bmatrix} E_{AI,t} \\ 0 \end{bmatrix} \qquad (6.31)$$

Now the intensity of the detected signal I_D is given
by the expression,

$$I_D = K_D (E_{AO}^{\dagger} E_{AO})$$

$$= K_D K_A K_A^* (E_{AI,t} E_{AI,t}^*)$$

$$= K_D |K_A|^2 |E_{AI,t}|^2 \qquad (6.32)$$

where K_D is a real factor which depends on the
intensity profile of the light beam and nature of the
photodetector. From eqn.(6.28) it can be easily be

written as,

$$E_{AI,t} = CosA \ E_{AI,x} + SinA \ E_{AI,y} \qquad (6.33)$$

But the values of $E_{AI,x}$ and $E_{AI,y}$ are given by eqn.6.26. Substituting these values in eqn.(6.33) one gets

$$E_{AI,t} = K_C A_C \Big\{ V_{ex} CosA[CosC \ Cos(P-C) - \ell_c \ SinC \ Sin(P-C)]$$

$$+ V_{ey} SinA[SinC \ Cos(P-C) + \ell_c \ CosC \ Sin(P-C)] \Big\}$$

$$(6.34)$$

Now eqn.(6.32) can be written in a more convenient form as

$$I_D = G \ L \ L^* = G \ \big|L\big|^2 \qquad (6.35)$$

where $G = \big|A\big|^2 \big|K\big|^2 \big|K_A\big|^2 \ K_D \qquad (6.36)$

and $L = V_{ex} CosA[CosC \ Cos(P-C) - \ell_c \ SinC \ Sin(P-C)]$

$$+ V_{ey} SinA[Sin \ C \ Cos(P-C) + \ell_c \ CosC \ Sin(P-C)]$$

$$(6.37)$$

The above result has been obtained by analysing the state of polarisation at different points along the

path of the beam. The same result can be achieved
by using the fact that the effect of a large number
of devices placed in the path of the light beam is
given by the resultant Jones matrix which is obtained
by multiplying the Jones matrices of different
devices taking into account of their arrangement and
coordinate transformation. Applying this, the Jones
vector of the output of the analyser is given by
the expression

$$E_{AO} = T_A^{te} R(A) T_S^{xy} R(-C) T_C^{fs} R(P-C) E_{PO}^t \qquad (6.38)$$

The eqns.(6.35) and (6.37) show that

$$I_D = f(P,C,A,\ell_c,V_{ex},V_{ey}) \qquad (6.39)$$

which means that the detected signal intensity is a
function of (i) the azimuth angles of polarizer
compensator and analyser (ii) the slow-to-fast relative
complex amplitude transmittance of the compensator
and (iii) the complex eigenvalues V_{ex} and V_{ey} of the
optical system to be analysed. In both photometric
and null ellipsometric systems, one tries to gather
information about V_{ex} and V_{ey} by proper use of eqn.(6.39).

6.3a Null ellipsometry

This is based on finding a set of azimuth angles for the polariser, compensator and analyser (P,C,A) to make the intensity of light falling on the detector to be zero. This condition can be represented as

$$I_D = 0 \qquad (6.40)$$

for which the necessary condition is

$$L = 0 \qquad (6.41)$$

Substituting this condition in eqn.(6.37) one gets

$$0 = V_{ex}CosA[CosC\ Cos(P-C)-\ell_c\ SinC\ Sin(P-C)]$$

$$+ V_{ey}SinA[SinC\ Cos(P-C)+\ell_c\ CosC\ Sin(P-C)]$$

Or

$$\frac{V_{ex}}{V_{ey}} = -\frac{SinA[SinC\ Cos(P-C)+\ell_c\ CosC\ Sin(P-C)]}{CosA[CosC\ Cos(P-C)-\ell_c\ SinC\ Sin(P-C)]}$$

$$(6.42)$$

Or

$$\ell = -\frac{tanA[\ tanC + \ell_c\ tan(P-C)]}{1-\ell_c tanC\ tan(P-C)} \qquad (6.43)$$

where $\ell = \dfrac{V_{ex}}{V_{ey}}$ $\qquad (6.44)$

which is the same constant defined in eqns.(6.12) and (6.13). If one gets the values of one set of 'nulling angles' P,C and A and also the value of slow-to-fast relative complex amplitude transmittance ℓ_c, the value of ℓ can be easily calculated. Using ℓ and the angle of incidence ϕ_0, the refractive index of the material (which forms the optical system S) can be computed for which the expression in eqn.(6.15) may be used.

6.3b Photometric ellipsometers

In this type of ellipsometers, as the name indicates, the detected intensity is never zero. Actually here the variation of the detected light flux as a function of the azimuth angles, phase retardation or angle of incidence is noted. For different intensity values, different equations (of the type given in eqn.(6.45)) can be formed and by solving them the value of ℓ and hence the refractive index can be calculated.

$$I_D = G \left| V_{ey} \right|^2 \left| \ell CosA[CosC\ Cos(P-C) - \ell_c\ SinC\ Sin(P-C)] \right.$$

$$\left. + SinA[SinC\ Cos(P-C) + \ell_c\ CosC\ Sin(P-C)] \right|^2$$

$$(6.45)$$

Eqn.(6.45) is directly obtained from eqn.(6.35)
when $V_{ex} = \ell \, V_{ey}$ is substituted.

There are two types of photometric ellipso-
meters; one is dynamic and the other is static.
Both differ in the way by which the parameters
P,C,A and ℓ_c are varied. In dynamic photometric
ellipsometers, some of these parameters are periodi-
cally varied with time and the detected signal
intensity is analysed using Fourier analysis. But
in the static photometric ellipsometers the intensity
of the signal is measured at predetermined fixed
values of P C A and ℓ_c .

6.3b.1 Dynamic photometric ellipsometers

A very brief note on this type of ellipso-
meters is included here merely to complete the
description of methods of evaluation of ℓ and hence
the refractive index. In this type, as stated earlier,
one or more optical parameters is modulated and the
detected signal is Fourier analysed. Depending upon
the parameter or combination of parameters selected
for modulation there are large number of possibilities
and here the most important and recent systems are
considered.

The first one is the Rotating Analyser
Ellipsometer (RAE). This has either polariser-
compensator-system-analyser or polariser-system-
compensator-analyser arrangement. Keeping other
elements (P,C) set at fixed azimuths, the analyser
is rotated at a constant angular velocity ω and the
intensity of the detected signal is Fourier analysed.
The detailed description regarding its working,
theory, method of computation and accuracy are given
in several recent publications[32-37].

The next one is the Polarisation Modulated
Ellipsometer (PME). In this, the state of polarisation
of the light beam at a suitable point in its path is
modulated in a prescribed fashion so that information
on the optical system under investigation is retrie-
vable from harmonic analysis of the resulting time-
varying detected intensity. Here also, there are
several possibilities, depending upon the position
and method of modulation. A convenient arrangement is
the one proposed by Jasperson[38,39] in which the
sequence of the optical components is polariser (P),
modulator (M), the optical system under investigation (S)
and analyser (A). This PMSA arrangement can be con-
sidered to be the same as the conventional PCSA

arrangement in which the compensator's relative retardation $\mathcal{S}c$ is periodically modulated as a function of time. The main advantages of this ellipsometer are that all optical components remain stationary and it allows very high speed of measurement.

6.3b.2 Static photometric ellipsometers

The theory of this type of ellipsometers will be dealt in detail here since it is this type which is constructed and used for the present work. Since no compensator is required one can consider the polariser-system-analyser (PSA) arrangement. The detected signal is a function of azimuth angles P and A only and this is directly obtained by setting C = O and ℓ_c = 1 in eqn.(6.45) and it becomes,

$$I_D = G \left| V_{ey} \right|^2 \left| \mathcal{C} \cos A \cos P + \sin A \sin P \right|^2$$

$$= G \left| V_{ey} \right|^2 \left| \tan \psi e^{i\Delta} \cos A \cos P + \sin A \sin P \right|^2$$

$$(6.46)$$

On further simplification eqn.(6.46) becomes,

$$I_D = F'[1-\cos 2\psi(\cos 2A + \cos 2P) + \cos 2A \cos 2P$$
$$+ \sin 2\psi \cos \Delta \sin 2A \sin 2P] \quad (6.47)$$

(where F' is a constant).

If I_{D1}, I_{D2} and I_{D3} represent the detected intensities for three different settings $(P_1 A_1)$ $(P_2 A_2)$ and $(P_3 A_3)$ of the polariser and the analyser, three equations of the type in eqn.(6.47) can be formed. F' can be avoided by dividing any two of the equations by the third one. Using the remaining two equations the two unknown quantities ψ and Δ can be obtained.

In the above method, nothing is stated regarding the choice of the settings of the polariser and analyser and is left arbitrary. However, to make the computations still easier, one can select $\pi/4$ as the azimuth of the polariser and $+\pi/4, 0$ and $-\pi/4$ to be the three analyser settings for which the corresponding intensity values are I_{D1}, I_{D2} and I_{D3}. From eqn.(6.47) one gets,

$$I_{D1} = I_D(\pi/4, -\pi/4) = F'(1 - \sin 2\psi \cos \Delta) \quad (6.48a)$$

$$I_{D2} = I_D(\pi/4, 0) = F'(1 - \cos 2\psi) \quad (6.48b)$$

$$I_{D3} = I_D(\pi/4 -\pi/4) = F'(1 + \sin 2\psi \cos \Delta) \quad (6.48c)$$

From these three equations two simpler equations

can be formed as

$$I_{D1} + I_{D3} = 2F' \qquad (6.49a)$$

$$I_{D3} - I_{D1} = 2F' \, \text{Sin} \, 2\psi \, \text{Cos} \Delta \qquad (6.49b)$$

Using eqns.(6.48b), (6.49a) and (6.49b) one gets

$$\psi = \tfrac{1}{2} \, \text{Cos}^{-1}[(I_{D1} - 2I_{D2} + I_{D3})/(I_{D1} + I_{D3})]$$
$$(6.50)$$

$$\Delta = \text{Cos}^{-1}[(\tfrac{1}{2}\text{Sin} \, 2\psi)(I_{D3} - I_{D1})/(I_{D1} + I_{D3})]$$
$$(6.51)$$

Knowing ψ and Δ , the value of ℓ and hence the value of the refractive index can be computed.

An ellipsometer working on this principle has been constructed and its details are given in chapter II. Using this set up the nature of the surface changes due to heating on silver films has been studied. The experimental details along with the relevant theory are given in chapter VII.

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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 experi-
mental 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, ellipso-
metry finds a unique place in this field. Of the two
parameters ψ and Δ 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 $<100\overset{\text{o}}{\text{A}}$ 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.

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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[2-4] and the other on Kirchhoff's theory of diffraction. The work by Fenstermaker et al[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 ($\sim 50\overset{o}{A}$). Smith also used the same theory for the study of the surface of aluminium in different conditions[1,6,7]. In the study of aluminium surface during fatigue cycling[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[1]
itself he analysed 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 al[8-12] through a series of publi-
cations developed a theory to deal with the variations
of Ψ and Δ due to surface roughness and is based on
the Kirchhoff's theory of diffraction. In their
earlier works[8,9] they developed the theory by which
they analysed the variations in Ψ and Δ caused by
rough surfaces of isotropic materials. Later in
another publication[10] 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[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[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[15] studied the surface of gold film on glass substrate and showed that Ψ and Δ depend not only on surface roughness, but also on the root mean slope of the irregular height. Chan[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[2-4] and the study was performed on platinum, molybdenum and vacuum annealed molybdenum. Scanning electron microscopy was also used along with ellipso-metry. Marten[17] also elucidated the capability of Maxwell Garnett theory for the study of roughness ·of silicon surfaces. Svilashov et al[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[19] also noted the effect of roughness on ellipsometric parameters. They found that, due to roughness, the values of ψ and Δ 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 (ie., upto $\sim 250^{\circ}C$) produces very interest-
ing result of minimisation of hillock growth at a
particular temperature.[20] 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) ellipso-
metric 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 genefal, there
is a relative phase change Δ and a relative amplitude
reduction Ψ 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[5]. 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

7.1a
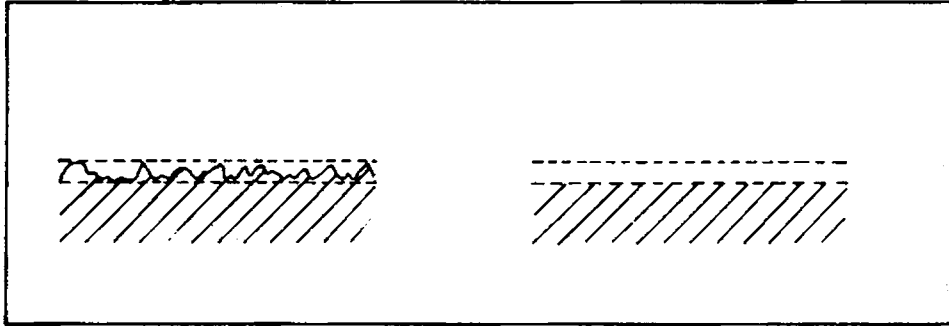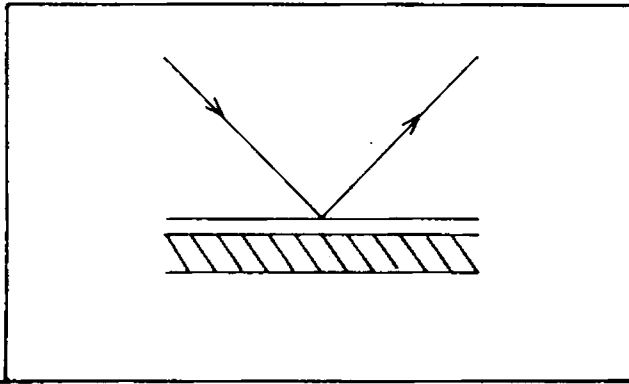
7.1b(i)   7.1b(ii)

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])

$$\frac{N_e^2 - N_a^2}{N_e^2 + 2N_a^2} = Q \frac{N_f^2 - N_a^2}{N_f^2 + 2N_a^2} \qquad (7.1)$$

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[21] given in chapter III. Later the thickness was verified by using the multiple beam interferometric technique[22] 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 ψ and Δ 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° 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 thick-
ness 1500Å and 3000Å respectively. Figs.7,4a and
7.4b give the Δ values at different temperatures
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
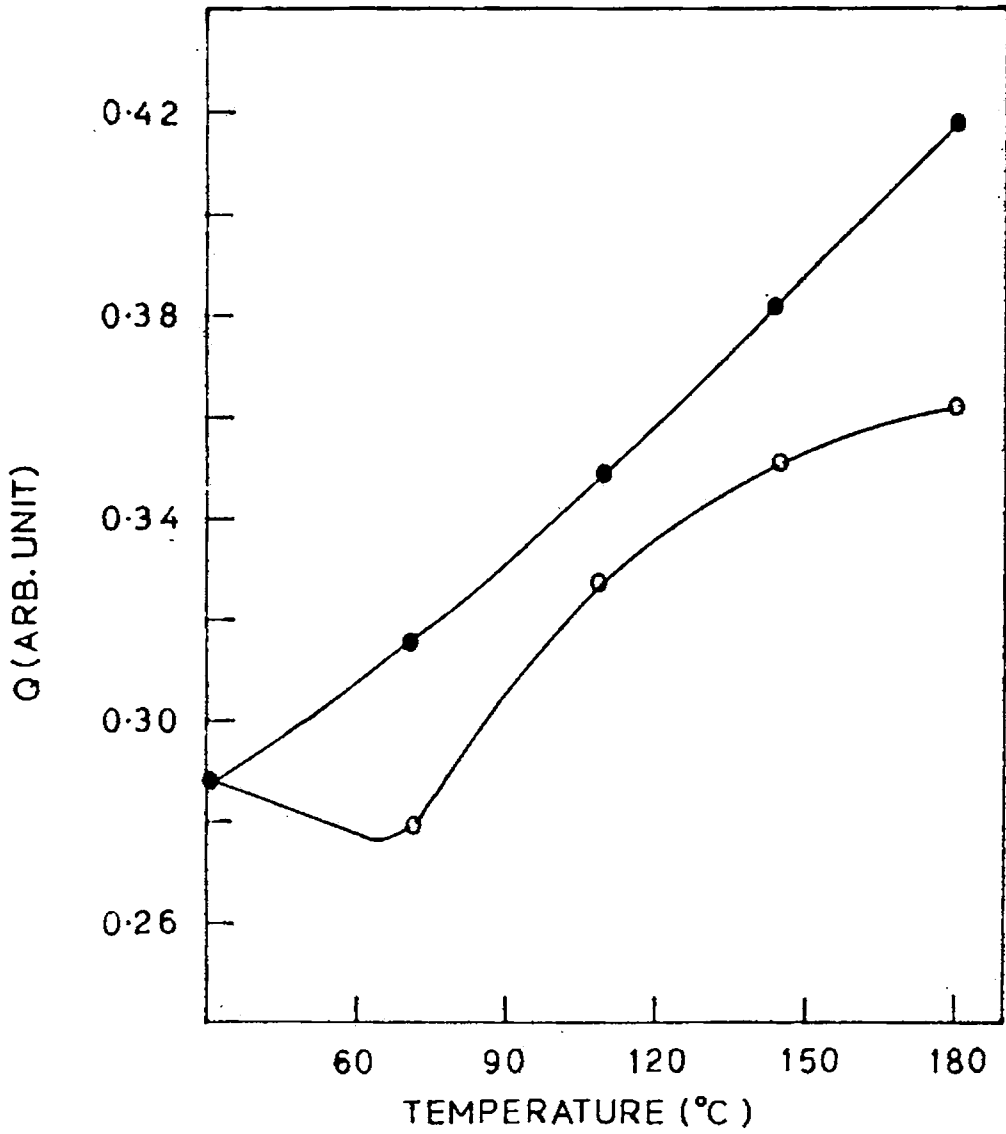Q-factor value at first shows a very slight decrease

Fig.7.2 Variation in Q-factor with annealing
temperature for silver films of thick-
ness 1500A.
o—o when annealed in vacuum;
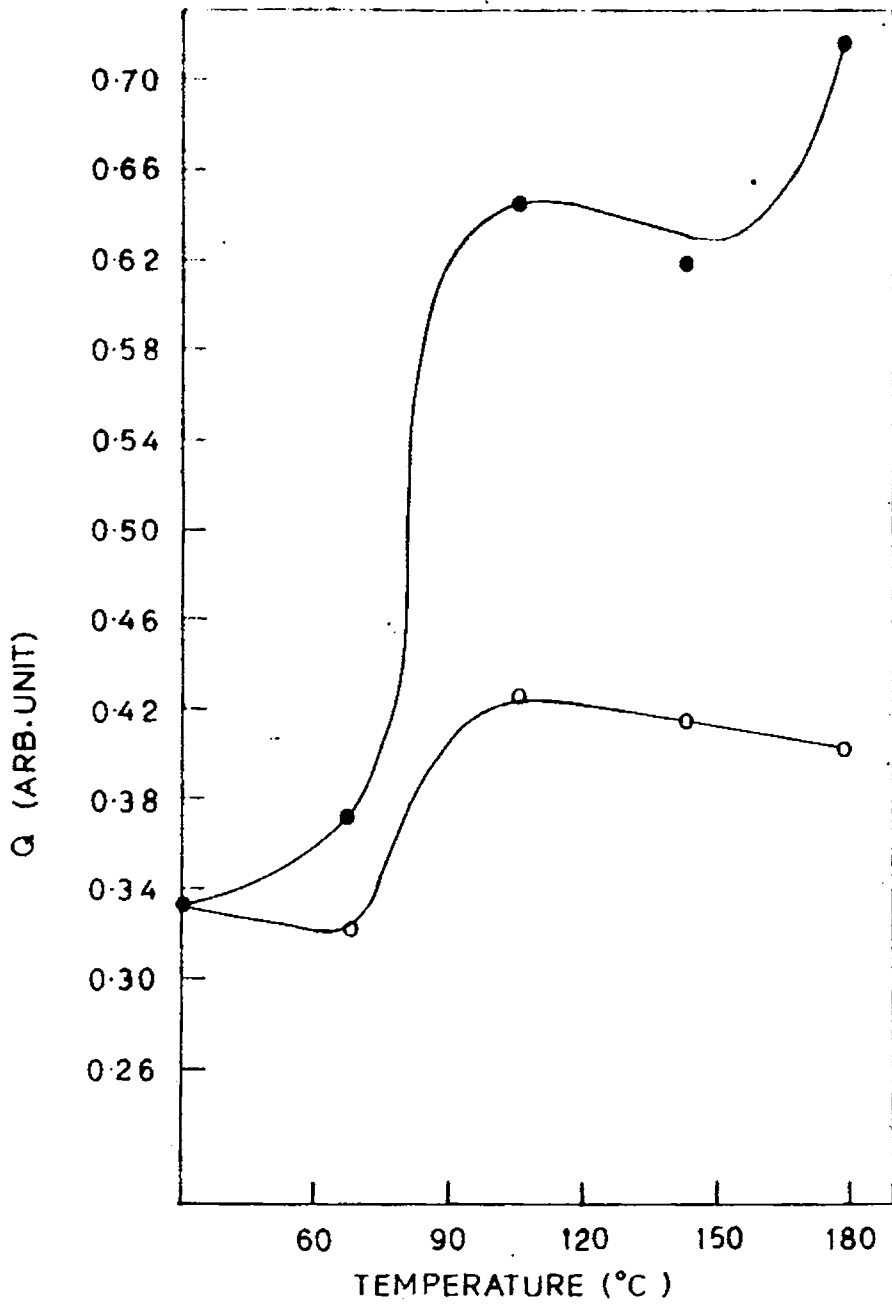●—● when annealed in air.

Fig.7.3 Variation in Q-factor with annealing
temperature for silver films of thick-
ness 3000A.
o—o when annealed in vacuum,
●—● when annealed in air.

upto ∿ 70°C and then increases. As the temperature
value reaches ∿ 160°C the increase in Q-value is almost
stopped and it tends to remain a constant.

The variations in Δ values are also of the
same nature (Figs.7.4a and 7.4b). Due to annealing in
air, Δ 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 Δ value upto 109°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 Δ values
with annealing temperature lead to the same conclusion.
When these are annealed in vacuum, upto ∿ 70°C there
is no hillock growth and thereafter the growth takes
place upto ∿ 160°C. As the temperature increases
above 160°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 3000Å

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.7.4b

Fig.7.4a

ANGLE OF INCIDENCE (DEGREES)

Δ (DEGREES)

Fig.7.4a   Variation in Δ values with angle of incidence for silver films (of thickness 1500A) at different annealing temperatures (annealing in vacuum): ▲—▲ , before annealing; O—O after annealing at 109°C, ●—● , after annealing at 180°C.

Fig.7.4b   Variation in Δ values with angle of incidence for silver films of same thickness at different annealing temperatures (annealing in air): ▲—▲ , before annealing; O—O , after annealing at 109°C, ●—● , after annealing at 180°C.
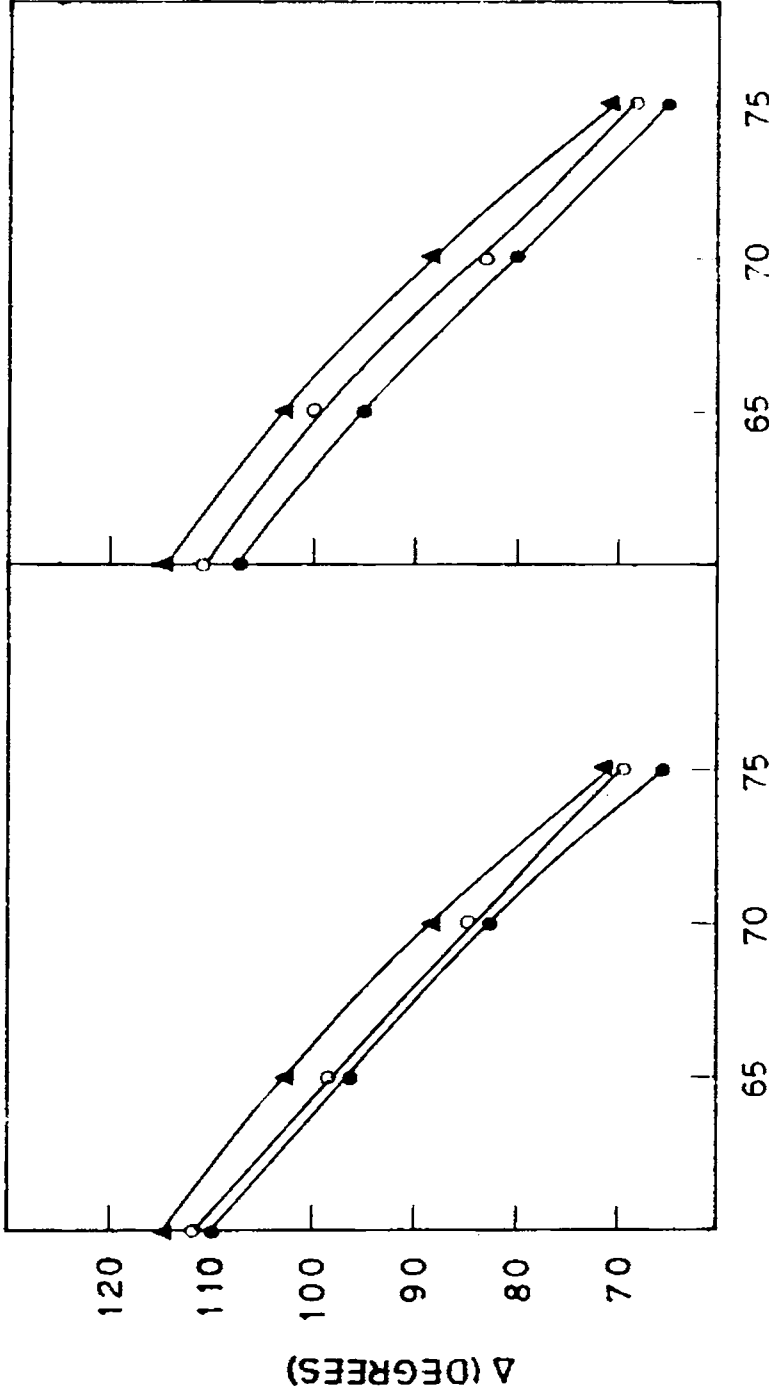
ANGLE OF INCIDENCE (DEGREES)

Fig.7.5a Variation in Δ values with angle of incidence for silver films
(thickness - 3000Å) at different temperatures (annealing in vacuum)
▲—▲, before annealing; Δ—Δ, after annealing at 105°C, a
o—o, after annealing at 143°C; ●—●, after annealing at 180°C.
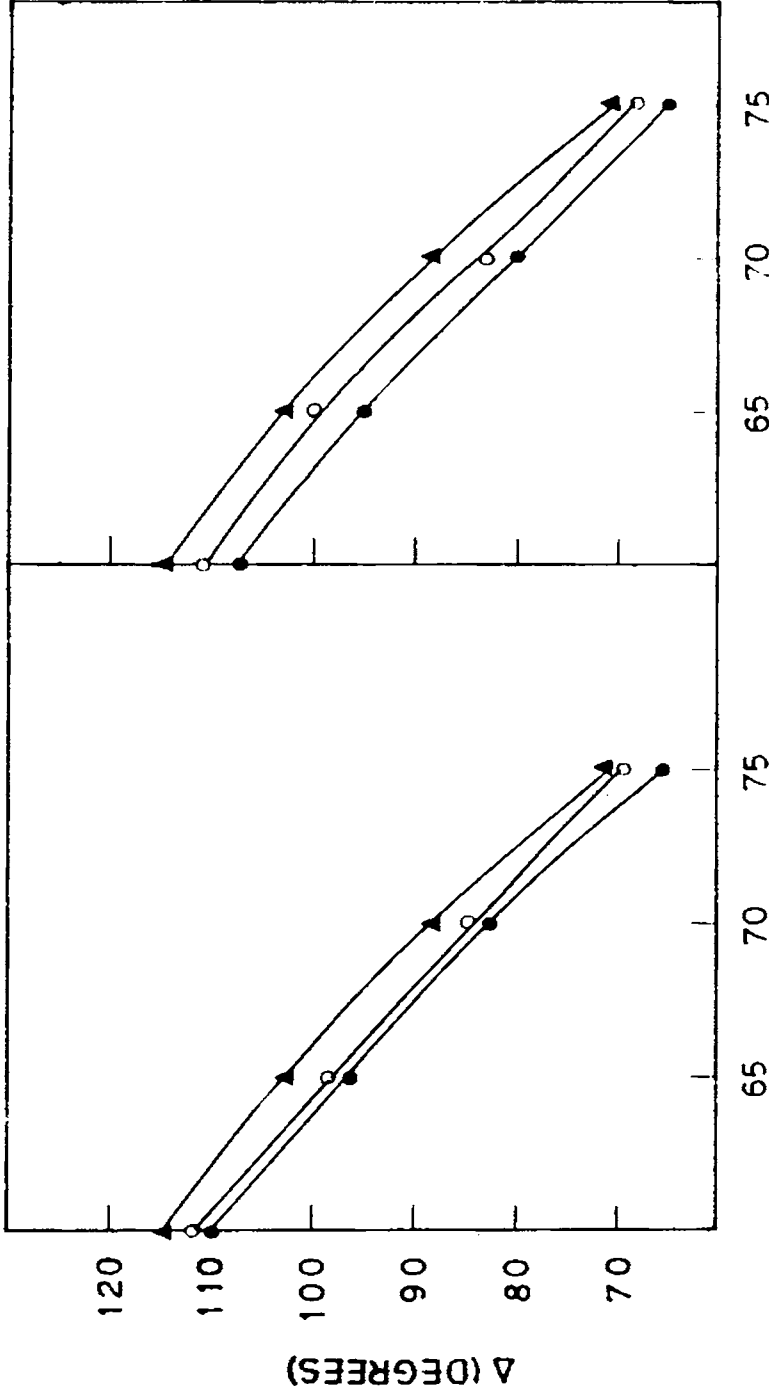
Fig.7.5b Variation in Δ values with angle of incidence for silver films of
same thickness at different temperatures (annealing in air)
▲—▲, before annealing; Δ—Δ, after annealing at 67°C; o—o, after
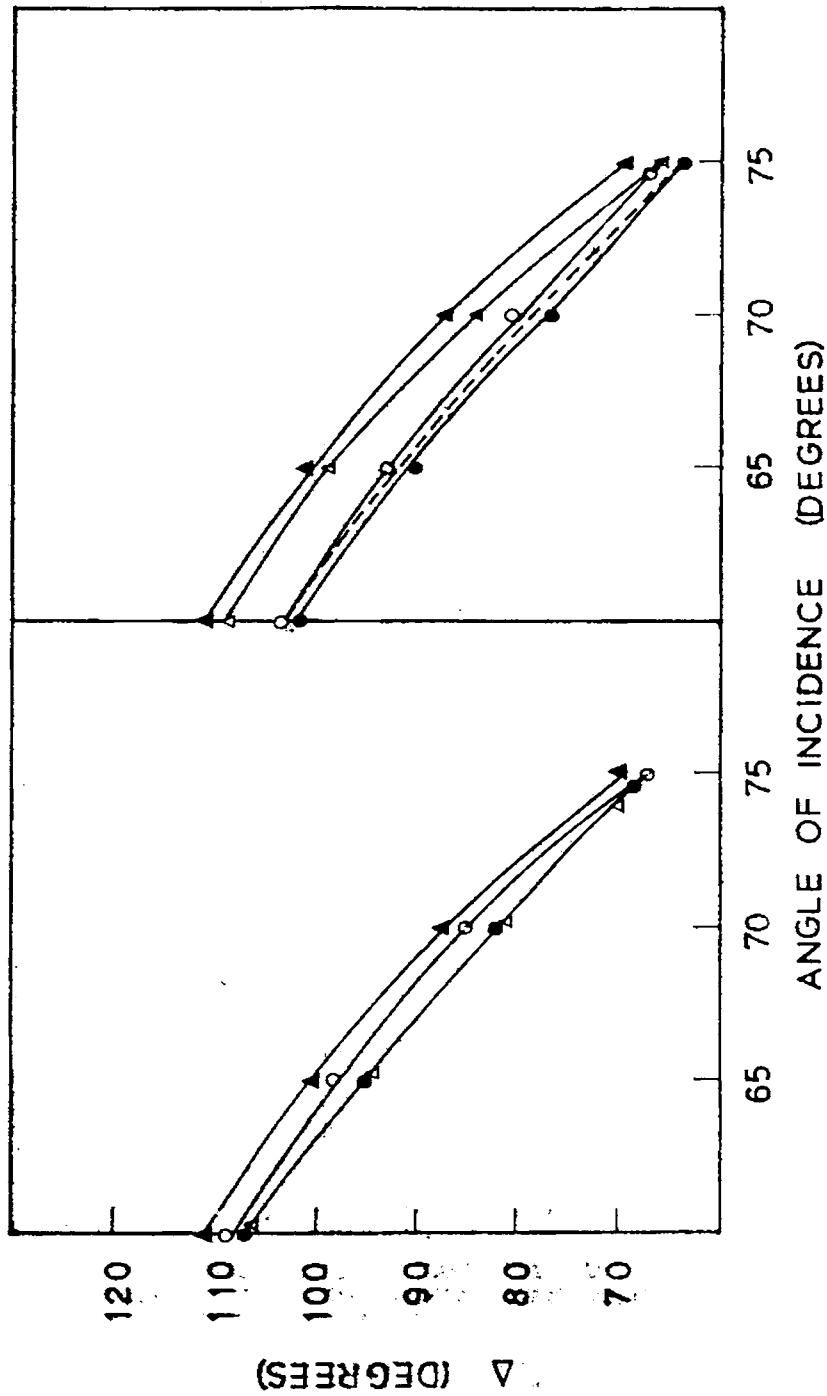annealing at 105°C; -----, after annealing at 143°C; ●—●, after
annealing at 180°C.

in Q-factor value. But this happens upto $\sim 120^\circ$C
only. Beyond that temperature the Q-factor is constant
upto $\sim 150^\circ$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 Δ 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 Δ 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 Δ value variations support the
Q-value variations. Here, the Δ values show a slight
decrease at 67°C while at 105°C the decrease is consi-
derably 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°, there is no change in its value for 105°C and 143°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, Δ 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°C and 150°C which is not observed in the case of films with thickness 1500Å.

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[23], is the condition for hillock growth to take place and that can be written as

$$\gamma \leqslant \frac{\sigma \, r_o}{2} \qquad (7.2)$$

where γ, σ and r_o 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 1500A this happens at $\sim 160^{\circ}C$
(fig.7.2) and for the other type of films (3000Å thick)
it occurs at $\sim 100^{\circ}C$ (fig.7.3). These observations are
again supported by Λ 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 $\sim 1500\text{\AA}$, have maximum intrinsic stress and as the thickness increases further, the intrinsic stress decreases. Hence for the films with thickness $1500\text{\AA}$, 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 upto $\sim 70^{\circ}\text{C}$. This may be due to the 'induction time effect' observed by
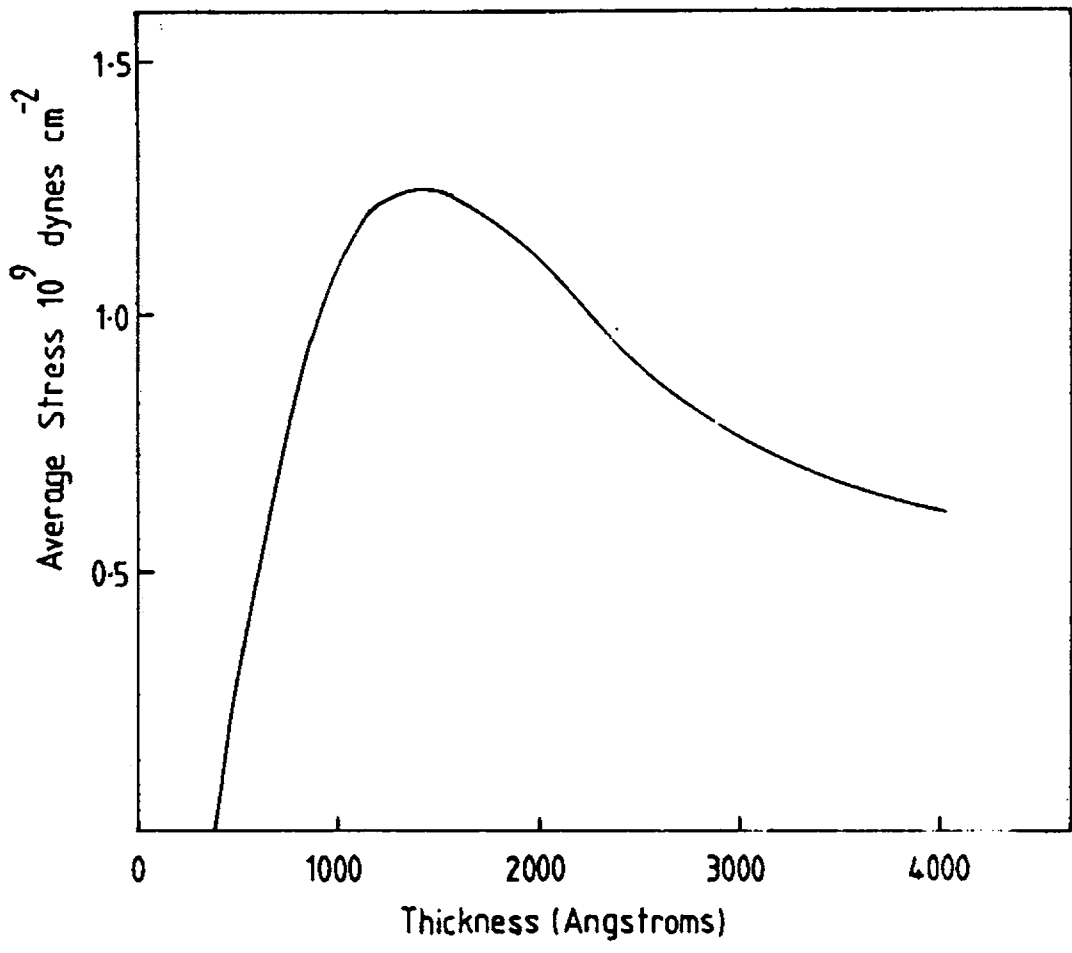
Fig.7.6   Variation of intrinsic stress in silver
films with thickness.

Presland et al[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_j). They also found that t_i
is very much reduced in presence of oxygen and the
variation is governed by the relation

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

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[26],

$$\sigma_{thermal} = \frac{\alpha_t - \alpha_s}{1 - \nu} E(\Delta T) \qquad (7.4)$$

where α_f and α_s are linear thermal expansion coefficients of film and substrate, E is the Young's modulus of the film material, ν is Poisson's ratio of the film and ΔT 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

The intrinsic stress ($\sigma_{intrinsic}$) values for silver films

Thickness $\overset{\circ}{A}$	$\sigma_{intrinsic}$ (from earlier works) x 10^9 dynes cm^{-2}	$\sigma_{intrinsic}$ (present work) x 10^9 dynes cm^{-2}
1500	1.25	1.5
3000	0.75	0.82

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 (γ). It will be considerably reduced in presence of oxygen in air and the variation is given by the relation (ref.24 of chapter III)

$$\gamma = 228 - 188 \log_{10} P_{O_2} \qquad (7.5)$$

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

$$\gamma > \frac{\sigma\, r_o}{2} \qquad (7.6)$$

When annealing is in air, to satisfy the above condition σ (the resultant stress in the film) must be reduced to a very low value for which the thermal stress must be increased very much (ie., the temperature at which the difference between the thermal stress and intrinsic stress becomes less than γ, 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 upto 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 Δ . It has been found that due to
annealing in low temperature range (ie., < 200°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.

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CHAPTER VIII

LIGHT SCATTERING MEASUREMENTS ON SILVER
FILM SURFACE

8.1 Introduction

This is another optical method by which
the material surface nature can be analysed. Compar-
ing with other techniques this is much simple. Here,
the variation of intensity of the reflected light
with the angle of incidence (most generally) is noted.
Another important factor, supporting this method is
that this is also a non-distructive technique. The
general theory which describes the scattering of the
electromagnetic radiation by rough surfaces is based
on Kirchhoff method in diffraction theory. This
theory can be used for different purposes depending
upon the wavelength of the radiation used. For
example, in the smaller wavelength region, this can
be used to explain the characteristics of reflection
of elementary particles from metal surfaces as scatter-
ing of De Broglie waves from rough metal surfaces[1],
while in the longer wavelength side, the scattering
of radio waves by terrain, sea or atmospheric layers
can be studied.

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Usually, in the visible range, this is used as a supplementary method along with some other major experimental technique. Here also this technique has been used to analyse the film surfaces which are already studied by using the ellipsometric technique (in chapter VII) to serve as an additional verification of the results obtained there. It should also be noted here that the analysis by using the light scattering measurements is performed after the final annealing described in the last chapter (ie., after annealing at 180°C). Thus in the present work the surface roughness of silver films due to annealing is studied by using this method. The variation of the roughness with film thickness and due to the annealing in vacuum and air are also studied. The detailed theory of the technique is given in the next section.

8.2 Theory

The theory of light scattering by rough surfaces has been developed by several workers[2-12] over the last 30 years for the application to both periodic and random rough surfaces. Probably the most comprehensive development of the theory has been given by Beckmann[9,10]. Houchens and Hering[13],

in their review of Kirchhoff theory, have concluded
that Beckmann model is applicable over a wide range
of roughness parameters. The Kirchhoff theory has
been applied to the study of rough metal surfaces
by several authors[14-18]. Almost all of them describe
the theory in some detail and compare the results
obtained from measurement of intensity of the
specular component with determinations of the
roughness using a mechanical stylus. In this work
also the Beckmann model is used and hence that is
described in this section.

Let the surface irregularity be denoted
by a function $Z(x,y)$ where Z is the deviation from
the mean x-y plane. When the surface is statistically
rough the function is a random process depending on
the space coordinates x and y only (Here the roughness
having some periodic nature, like that of a grating,
is not considered. As the most general case one can
consider the surface irregularities fluctuating in
time as the surface of the sea. In that case, the
function will depend on time also as $Z(x,y,t)$. But
that is also avoided in the present discussion).

Let a plane electromagnetic wave be incident on this surface and the coordinates be so considered that the wave vector $\bar{k}_1$ of the incident wave be in the x-z plane and the angle of incidence, θ_1 be between $\bar{k}_1$ and the z-axis (See fig.8.1). One can represent the electric vector of the wave as,

$$E_1 = E_o e^{i(k_1 \cdot r - \omega t)} \qquad (8.1)$$

where ω is the angular velocity and $\bar{r}$ is the position vector,

$$\bar{r} = x\bar{x}_o + y\bar{y}_o + z\bar{z}_o \qquad (8.2)$$

with $\bar{x}_o$, $\bar{y}_o$ and $\bar{z}_o$ as the unit vectors of the co-ordinate system. In this work, the aim is to find out the field scattered into the arbitrary direction defined by θ_2, θ_3 (from fig.8.1). If it is assumed that the radius of curvature of the surface is much larger than the wave length of the light incident on it and the surface to be locally perfectly reflecting, one can apply the Kirchhoff method. If $\bar{k}_2$ is the wave vector along the direction of scattering (defined by θ_2, θ_3) the scattered field E_2 at a point P is
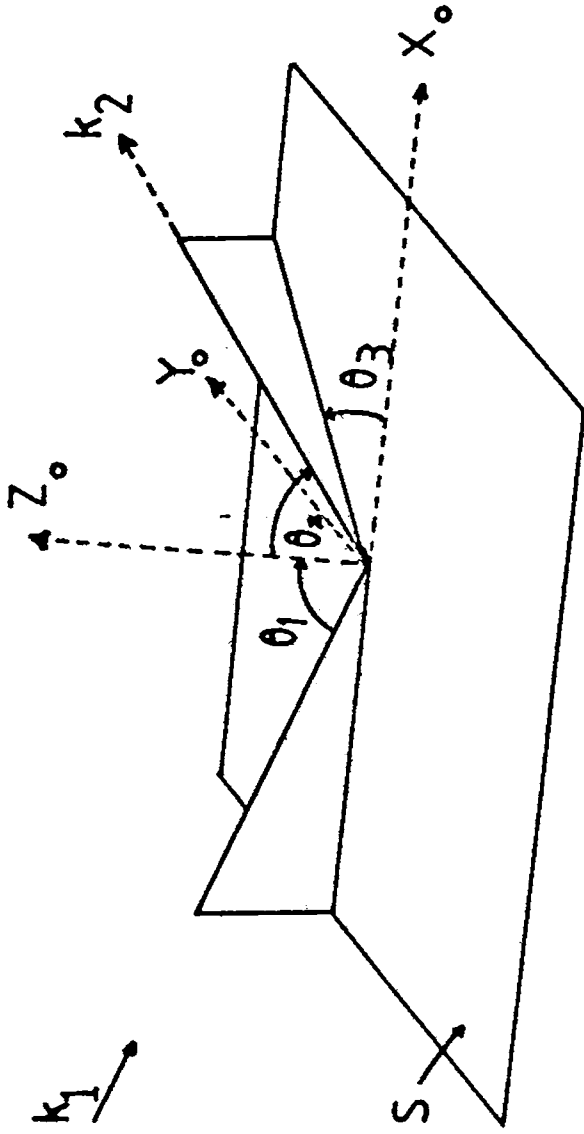
Fig.8.1 Orientation of coordinate system and scattering geometry θ_1, θ_2, θ_3. The incident wave propagates in the direction of the propagation vector K_1 and the scattered wave in the direction K_2.

given by the Helmholtz integral,

$$E_2(P) = \frac{1}{4\pi} \iint (E \frac{\partial \psi}{\partial n} - \frac{\partial E}{\partial n}) ds \qquad (8.3)$$

where $\psi = \frac{e^{i\bar{k}_2 \cdot \bar{R}_2}}{R_2}$ $\qquad (8.4)$

where $\bar{R}_2$ is the distance of P from a variable point on the rough surface S, E is the field on the surface and $\frac{\partial}{\partial n}$ is the derivative along the normal to the surface. Since it is assumed that the radii of curvature of the surface are much larger than the wavelength, one can consider each point on the surface S to make the same contribution to the scattered field as if it were a part of the tangent plane to the rough surface S at that point ie., one can consider the surface S as 'locally flat'. Using these conditions, the field and its normal derivative on the surface S can be obtained, with the help of the boundary conditions, as

$$(E)_S = (1+R)E_1 \qquad (8.5)$$

$$\left(\frac{\partial E}{\partial n}\right)_S = (1-R)E_1 \; \bar{k} \cdot \bar{n} \qquad (8.6)$$

where $\bar{n}$ is the normal to the surface and R is the local reflection coefficient.

The dimensionless 'scattering coefficient' is defined as

$$\rho = E_2/E_{20} \qquad\qquad (8.7)$$

where E_2 is the scattered field and E_{20} the field that would be reflected in the specular reflection (ie., when $\theta_2 = \theta_1$ and $\theta_3 = 0$) by a smooth reflecting plane of same dimensions under same angle of incidence at the same distance. Adopting the method of Beckmann[9] it can be obtained from the eqns.(8.2)-(8.7) as,

$$\rho = \frac{F(\theta_1, \theta_2, \theta_3)}{A} \iint\limits_A e^{i\bar{v}\cdot\bar{r}}\, dx\, dy \qquad (8.8)$$

where

$$F(\theta_1, \theta_2, \theta_3) = \frac{1 + \cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos\theta_3}{\cos\theta_1(\cos\theta_1 + \cos\theta_2)}$$

$$(8.9)$$

A is the area subtending the surface in x-y plane

$$\bar{v} = \bar{k}_1 - \bar{k}_2$$

$$= k[(\sin\theta_1 - \sin\theta_2 \cos\theta_3)\bar{x}_0 - \sin\theta_2 \sin\theta_3 \bar{y}_0$$

$$- (\cos\theta_1 + \cos\theta_2)\bar{z}_0] \qquad (8.10)$$

and $\overline{r} = x\overline{x}_o + y\overline{y}_o + Z(x,y)\overline{z}_o$ (8.11)

is the position vector describing the rough surface.
The factor k in eqn.(8.10) represents the magnitude
of the wave vector and is equal to $2\pi/\lambda$.

The integral in eqn.(8.8) is the general
Kirchhoff solution of the problem and one can apply
it to either periodic or random rough surfaces.

8.2a   Random rough surfaces

In most of the applications the scattering
surface is statistically rough ie., $Z(x,y)$ is a random
function of position and Z is a random variable assuming
values z with probability density $p(z)$. Now one should
know the joint probability density $p_2(z_1,z_2)$ where
z_1 and z_2 are the values of Z at points (x_1,y_1) and
(x_2,y_2) respectively. In almost all the cases, it can
be assumed that the two dimensional probability density
$p_2(z_1,z_2)$ depends only on the distance between the
points (x_1,y_1) and (x_2,y_2) and not on these points.
Hence, one can get the two dimensional characteristic

function (the Fourier transform) associated with the distribution $p_2(z_1\ z_2)$ as,

$$\chi(t_1,t_2) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} p_2(z_1 z_2)e^{it_1 z_1 + it_2 z_2}\,dz_1 dz_2$$

(8.12)

and the one dimensional characteristic function as

$$\chi(t) = \int_{-\infty}^{\infty} p(z)e^{itz}\,dz$$ (8.13)

Hence the mean scattered field in any direction may be obtained from eqns(8.8) and (8.13) as

$$\langle e \rangle = \frac{F\chi(v_z)}{A}\int_{-X}^{X}\int_{-Y}^{Y} e^{iv_x x + iv_y y}\,dxdy$$ (8.14)

which on integration gives,

$$\langle e \rangle = \frac{F}{A}\chi(v_z)e_0$$ (8.15)

where, $e_0 = \dfrac{\sin v_x X}{v_x X}\ \dfrac{\sin v_y Y}{v_y Y}$ (8.16)

is the scattering coefficient of a plane sheet of equal area $A = 4XY$.

The mean square of eqn.(8.8), which is proportional to the mean scattered power, is given by $\langle \ell \ell^* \rangle$ and it can be obtained from eqns.(8.8) and (8.12) as

$$\langle \ell \ell^* \rangle = \frac{2\pi F^2}{A} \int_0^\infty J_0(v_{xy}\tau) \, \chi_2(v_z - v_z\tau)\tau \, d\tau \qquad (8.17)$$

$$\text{where } v_{xy} = \sqrt{(v_x^2 + v_y^2)} \qquad (8.18)$$

$$\text{and,} \quad \tau = \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2} \qquad (8.19)$$

which is the distance between (x_1, y_1) and (x_2, y_2) and J_o is the Bessel function of first kind of order zero.

The integral in eqn.(8.17) is the basis for the calculation of the scattered field from the random rough surfaces and for computational purpose, one can assume particular type of the random process $Z(x,y)$. If $Z(x,y)$ is a normal process with mean, zero standard deviation σ and the autocovariance $C(\tau)$ to be Gaussian as

$$C(\tau) = e^{-\tau/T^2} \qquad (8.20)$$

(where T is the correlation distance) one gets the general solution to be[9]

$$\langle \ell \ell^* \rangle = e^{-g} \left(\ell_0^2 + \frac{\pi T^2 F}{A} \sum_{m=1}^{\infty} \frac{g^m e^{-v_{xy}^2 T^2/4m}}{m!\, m} \right)$$

$$(8.21)$$

where $\sqrt{g} = v_x \sigma = \frac{2\pi\sigma}{\lambda} (\cos \theta_1 + \cos \theta_2)$ $\quad(8.22)$

The first term, which forms eqn.(8.16) vanishes everywhere except in the neighbourhood of the specular direction and is the coherent (specular) component. The scattered field consists of both specular and diffusely scattered components. When $g \rightarrow 0$ the specular component will be dominant and for $g \gg 1$ the diffusely scattered field is the only important component. For the specular direction one has $v_x = v_y = 0$ and hence from eqn.(8.16) $\ell_0 = 1$ and the specular term in eqn.(8.21) becomes

$$\langle \ell \ell^* \rangle_{spe} = \exp\left[-\left(\frac{4\pi\sigma \cos \theta_1}{\lambda} \right)^2\right] \qquad (8.23)$$

If one has I_s to be the intensity of the specularly reflected light from the rough surface and I_{so} that from an ideally smooth surface (under the same conditions)

then,

$$R_s = I_s/I_{so} = \langle \ell \ell^* \rangle = \exp[-(\frac{4\pi\sigma \cos \theta_i}{\lambda})^2] \quad (8.24)$$

Here, if the incident beam is plane polarised with electric vector in the plane parallel to the plane of incidence (p-plane) the intensity of the reflected wave from the smooth surface (I_{so}) can be easily calculated using Fresnel's coefficients (chapter VI sec. 2). Hence if a graph is plotted with $\cos^2 \theta$ on the X-axis and $\ln R_s$ on the Y-axis, it will have a slope $m = -(4\pi\sigma/\lambda)^2$. From this, the value of σ, which is the rms value of the height of the irregularities, can be obtained.

8.3 Experimental

The silver films used for the ellipsometric study were used in this experiment also. Hence, the two types of films with thickness 1500Å and 3000Å were analysed by using the light scattering technique. But, here the experiment was performed after the final annealing (ie., after the annealing at 180°C). The film preparation method and the annealing techniques are the same as described in chapter VII. For this

study also annealing in vacuum and air were separately
done on two sets of films.

The optical system consisted of the light
source, filter, collimator, polariser, the film
PMT and galvanometer. It is same as that described
in chapter III (See fig.2.6) with the difference that
here polariser was also used. Its detailed description
is included in chapter II. The calculations were done
using a mini-computer (Micro-78).

8.4 Results

The graphs (ln R_s vs. $\cos^2 \theta$) for all the
films are shown in fig.8.2. Here the curves before
annealing for the two types of films are found to be
almost coinciding and hence only one curve is given
with average values of both films. From the slope of
the graphs, the value of σ for each film is calculated
and is given in table 8.1 along with the percentage
of increase, in σ value. It can be seen that the σ
value increases with thickness of the film. Also,
for the same thickness annealing in air results in
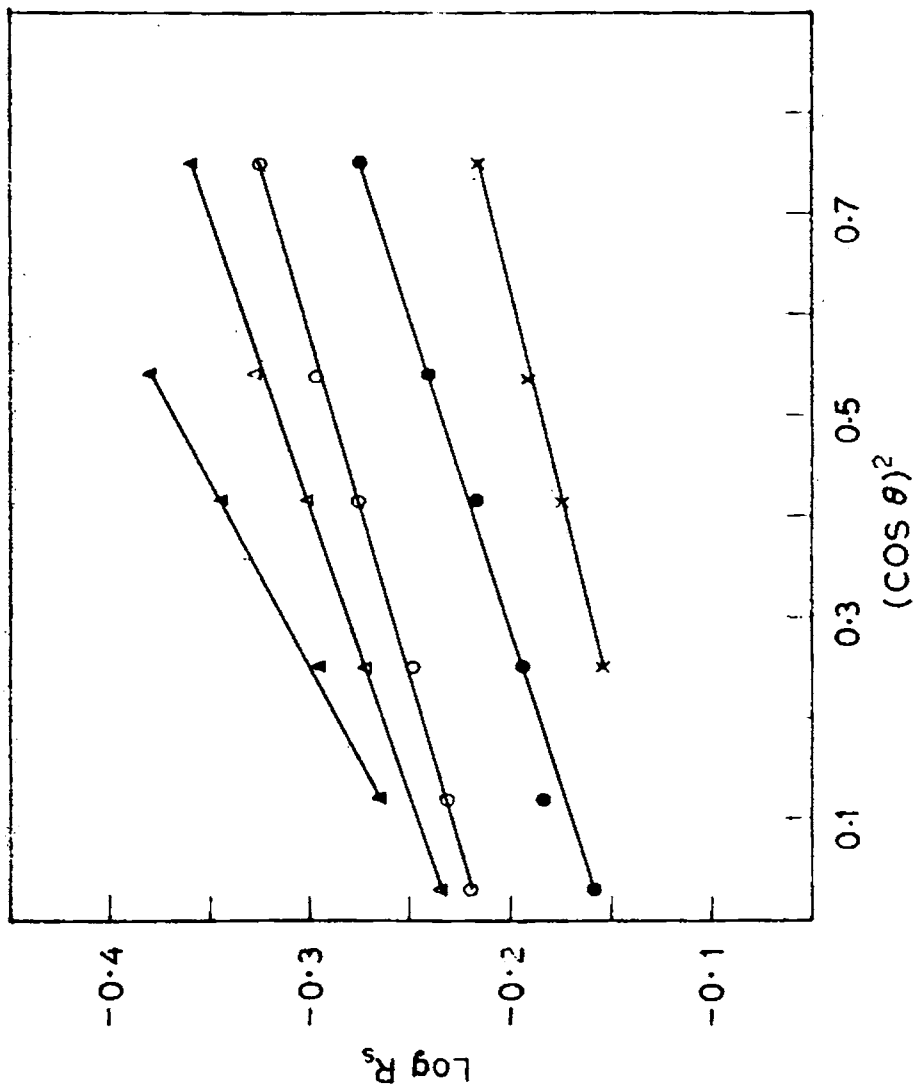larger σ value. The largest σ value is obtained for

Fig.8.2 Log R_s vs. Cos$^2\theta$ curves for films of thicknesses 3000A (▲—annealed in air; ● —annealed in vacuum) and 1500A (△— annealed in air; O — annealed in vacuum) x — unannealed film averaged for both types of films.

Table 8.1

The values of σ and its percentage of increase

Thickness °A	Nature of annealing	σ °A	Percentage of increase
1500 and 3000	Unannealed	171	—
1500	In vacuum	189	10.3
1500	In air	206	20.3
3000	In vacuum	198	15.4
3000	In air	259	51.1

the film with thickness 3000$\overset{o}{A}$ annealed in air (σ = 259$\overset{o}{A}$). The most important point to be noted here is that these results are in close agreement with those obtained using ellipsometry.

8.5 Discussion

It has been clearly stated earlier (in chapters III and VI) that the important variation occurring on the silver film surface while it is kept in air (in presence of oxygen) is that its surface energy is much decreased and hence there can be increased surface

diffusion on heating. This results in larger surface irregularities or hillock growth. This is exactly shown by the larger σ values (rms value of hillock height) for films annealed in air[19].

In chapter VII it is stated that for silver films, the intrinsic stress is maximum when thickness is $\sim 1500\overset{o}{A}$ and as the thickness increases the intrinsic stress is decreasing., Hence a minimisation of stress occurs, due to annealing and this happens at a temperature below $180^{o}C$ in the case of thicker films ($3000\overset{o}{A}$ thick) and above or near $180^{o}C$ in the case of thinner films ($1500\overset{o}{A}$ thick). This is reflected in the hillock growth also and due to this reason, σ value is smaller for the films with thickness $1500\overset{o}{A}$ and larger for the $3000\overset{o}{A}$ thick films.

8.6 Conclusion

The important conclusion is that these obser-vations lend support to ellipsometric results. It is also seen,(in agreement with results mentioned earlier) that, annealing in air results in larger hillocks. Also, with thickness of the film, the rms value of

hillock height increases which clearly shows the relationship between the stress in the film and the surface diffusion.

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CHAPTER IX

SUMMARY OF CONCLUSIONS

The studies presented in this thesis are centred around the variations of the nature of surface of some metallic thin films due to heating (annealing) and interdiffusion. The results and conclusions in the different chapters are summarised here.

In chapter III, the changes on the surface of silver thin films due to annealing are presented. The study is based on reflectivity measurements. From the results one can arrive at the conclusion that there is a minimisation of surface roughness created by heating (annealing). The value of temperature, at which it happens, strongly depends on the ambient condition in which the film is annealed. In this case, due to vacuum annealing, the surface smoothening takes place at $100^{\circ}C$ while the annealing in air results in this phenomenon at $212^{\circ}C$. This can be due to the difference in the surface energy of the film and hence, the relation between the surface roughness due to annealing (hillock growth) and the stress in the film is revealed. It has been shown that the surface smoothening takes place as a result of the stress minimisation in the film.

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Similar work on copper films (with thickness
varying from 500$\overset{o}{A}$ to 3000$\overset{o}{A}$) is presented in chapter IV,
with the difference that in this case the reflectivity
measurements were taken during heating keeping the
sample in vacuum. Here also surface smoothening is
taking place which is indicated by the sharp increase
in the reflectivity. The electron micrographs of the
films before and after heating also indicate this very
clearly. The temperature value at which the smoothening
takes place shows a strong dependence on thickness of
the films. This again points out the relationship
between stress in the film and surface smoothening.
It has been shown by earlier workers that copper films
with thickness in the range 500$\overset{o}{A}$ to 1000$\overset{o}{A}$ have maximum
intrinsic stress and as the thickness further increases,
the stress decreases. This is clearly indicated by
the temperature values also. The intrinsic stress
values calculated from optical results also agree well
with those obtained by earlier workers.

The relationship between the surface smoothen-
ing and thickness of film (and hence the stress in the
film) was studied in the case of silver films also.
For this a more sensitive and precise method viz.,
ellipsometry, has been employed. These results are

given in chapter VII. It is again found that, for silver films with a thickness of 1500Å, the surface smoothening occurs at a higher temperature while for the 3000Å thick films, it takes place at a lower temperature. Also it has been shown that the intrinsic stress is maximum when thickness is 1500Å and for further increase in thickness there is corresponding decrease in the stress. The relation between stress and surface smoothening is thus elucidated. The dependence of ambient condition (described in chapter III) is verified again in this chapter. Intrinsic stress in silver thin films (for thickness 1500Å and 3000Å) has been calculated and these values show good agreement with values obtained by earlier workers by different methods.

The films used for ellipsometric investigations are also analysed using light scattering technique. This is included in chapter VIII. Here, by measuring the actual size of the surface irregularities the thickness dependence and ambient dependence are once again verified.

The variations of the surface nature of a bi-layer film (Al-Ag) are also studied optically. These

results are given in chapter V. From the results obtained it can be concluded that

i) the diffusion of aluminium through silver is much easier due to the predominance of grain boundary diffusion and the reverse case is not so easy as aluminium film, which is more continuous in nature, does not promote the grain boundary diffusion,

ii) when the thickness ratio between aluminium and silver layers is 1:2, due to diffusion of aluminium into silver, the intermetallic compound Ag_3Al is formed first, which decomposes to give Ag_2Al at higher temperature,

iii) due to diffusion of silver into aluminium, only Ag_2Al is formed for the same thickness ratio, and

iv) a layer of aluminium is formed over the film surface when the thickness ratio is changed to 1:1.

APPENDIX - I

LATTICE DYNAMICS AND EIGENVECTOR MAGNITUDES
IN ZnS CRYSTAL

A.1 Introduction

In any solid the atoms are continuously oscillating about their equilibrium positions with an energy governed by the temperature of the solid. These oscillations are responsible for a large number of characteristic properties like specific heat, optical and dielectric properties and electrical resistance. In crystals these oscillations are called Lattice vibrations. At the limit of long wavelength the vibrations of the lattice are described by the classical theory of elasticity. In this, the solid is considered as a continuum having macroscopic elastic constants. As the wavelength becomes shorter and approaches the inter-atomic distance the micro-scopic crystal structure and the forces between individual pairs of atoms become the dominant features in determining the nature of modes of vibration. The theoretical and experimental studies on these vibrations yield information about the interatomic force and frequencies of the vibrations which in turn can be

directly used to predict the temperature dependence of some incoherent scattering properties of crystals.

In the present work, the phonon frequencies along [100], [111] and [110] directions of the wave-vector are determined for ZnS by employing the Rigid ion model (which will be described later). Also the eigenvector values are obtained by using the method of isotopic substitution ie., by replacing ^{32}S with ^{34}S in the ZnS crystal.

A.1a Brief review of earlier works

The lattice dynamics of ZnS crystal (and more generally crystals of Zinc blende structure) has been a topic of interest for the solid state physicists and a large number of works have been published regarding different aspects in this field and using different models. The work by Smith[1], using the central force model, can be considered to be the pioneering one on this type of crystals. Rajagopal et al[2] modified it using the rigid ion model in which the Coulomb interaction between ions is also taken into account. Vetelino et al[3] had also used the rigid ion model for their calculation of phonon frequencies of ZnS. Almost at

the same time, Feldkamp et al[4] obtained the dispersion

curves by neutron scattering along all the three

directions of the wave vector. Another notable

development in this direction was the calculation

of effective charges in crystals of zinc blende

structure by Mani et al[5,6]. In this work they performed

the calculation for crystals like GaAs, CdTe, AlSb,

InSb and ZnS. They also obtained the dispersion

curves using rigid ion model. The development of

the deformable bond model by Kunc et al[7] is another

important point to be noted here. They used this model

to determine the dispersion relation of fifteen crystals

(including ZnS) with zinc blende structure[8]. Later the

deformable ion model was employed by Jaswal[9] in the

case of ZnS and obtained good agreement with experi-

mental results. Soma[10] theoretically calculated the

thermal expansion against temperature for ZnS, ZnTe

and ZnSe. He also obtained dispersion relations of

the crystals at metallic transition pressure. Kushwaha[11]

employed the newly developed Bond bending force model

(BBFM) for phonon dispersion in ZnS, GaAs and GaSb.

Using the Deformation dipole model (DDM), Yadav[12]

obtained lattice specific heat and Debye-Waller factor

for ZnS. Very recently Soma et al[13] calculated the

the phonon dispersion relations in crystals with
zinc blende structure with the help of the pseudo-
potential method.

A.2 Theory

The pioneering work in this field ie.,
lattice dynamics was by Born and Von Kārmān[14,15].
From then onwards different lattice models have been
developed to describe the interatomic forces responsi-
ble for a stable structure of the crystal depending
on the empirical data available and the physical
nature of the problem. The model put forward by
Born and Von Kārmān, which is the basis for all the
later models, considers the atoms as point masses
arranged in some effective potential provided by
their mutual interaction which determines their motion.
The difficulty of this model is to reconcile this
simple picture with the crystal seen as an assemblage
of nucleii and electrons.

Here a brief summary of the theory leading to
the rigid ion model is included. Detailed description
and review of investigations are given in book by
Born and Huang[16] and in review articles by de Launay[17],

Blackman[18], Leibfried[19], Cochran[20] and Cochran and
Cowley[21]. Another book by Maradudin et al[22] contains
all the basic theories of lattice dynamics and also
the modern developments like neutron scattering,
effect of defects and disorder and surface effects on
lattice dynamics.

A.2a Approximations in the theory

It will be extremely difficult if one attempts
to solve the many particle Schrodinger equation for a
complicated system like a crystal and to obtain its
properties. Hence the easiest method is to approach
the problem with some approximations in the beginning
and at a later stage to remove the same to the possible
extent especially when they hinder in the prediction
and explanation of some of the properties of the solid.

The most important and basic ingredients in
the theory of lattice vibrations are crystal symmetry,
Adiabatic approximation and Harmonic approximation.
The crystal symmetry is the one simplifying the initial
many body problem. By invoking the symmetry arguments
one can calculate the properties of entire crystal from
a knowledge of the behaviour of a very small region.

However this is applicable only to perfect ideal
crystals without defects. In the adiabatic approxi-
mation or Born-Oppenheimer approximation[23] the essential
idea is that the atomic nuclei being much heavier,
moves much more slowly than the electrons. Therefore
at any instant the electrons 'see' the nuclei fixed
in some configuration. When the nuclei move the
electrons follow the nuclear motion adiabatically
in the sense that electronic state follows a smooth
variation merely keeping in step with no abrupt transi-
tions. Hence the electronic energy becomes a function
of nuclear coordinates and appears as potential energy
in the Shrodinger equation. Essentially this approxi-
mation neglects any interaction between the valence
electrons and lattice vibrations. Deviation from
this approximation gives rise to electron-phonon
interaction. In the harmonic approximation, it is
assumed that the force on an atom is proportional to
the first power of its displacement. Hence neglect-
ing the electronic excitations, the Hamiltonian of
the crystal consists of the kinetic energy (T) of
the nuclei and the potential energy ($\emptyset$) which is a

function of nuclear coordinates and which is a minimum for certain configuration. Thus the Hamiltonian (H) can be written as

$$H = T + \phi \qquad (A.1)$$

In this the potential energy ϕ can be expanded in Taylor series in powers of nuclear displacements from the equilibrium configuration as,

$$\phi = \phi_o + \sum_{lk\alpha} \phi_\alpha(lk)U_\alpha(lk)$$

$$+ \frac{1}{2} \sum_{\substack{lk\alpha \\ l'k'\beta}} \phi_{\alpha\beta}(lk;l'k')U_\alpha(lk)U_\beta(l'k') + \cdots$$

$$(A.2)$$

where ϕ_o is the potential energy of the non-vibrating crystal and

$$\phi_\alpha(lk) = \frac{\partial\phi}{\partial U_\alpha(lk)}\bigg|_o \qquad (A.3)$$

$$\phi_{\alpha\beta}(lk;l'k') = \frac{\partial^2\phi}{\partial U_\alpha(lk)\partial U_\beta(l'k')}\bigg|_o \qquad (A.4)$$

Here the subscript 'O' in the eqns.(A.3) and (A.4)

denote that the derivatives are evaluated in the equilibrium configuration. The subscript l denotes the unit cell and k distinguishes the different atoms in that cell. Also $U_\alpha(lk)$ is the α-Cartisian component of $U(lk)$ with $\alpha = x,y,z$. If the terms upto the second power in eqn.(A.2) are retained one is said to be within the harmonic approximation. Thus one can restrict oneself to two body forces under this approximation and deviation from this leads to phonon-phonon interaction.

From eqn.(A.3) one can easily see that $\phi_\alpha(lk)$ denotes the negative of the force acting in the α-direction on the atom at (lk) in the equilibrium configuration. However in the equilibrium configuration the force on any particle must vanish and hence one has

$$\phi_\alpha(lk) = 0 \qquad\qquad (A.5)$$

Now the kinetic energy can be written as,

$$T = \frac{1}{2} \sum_{lk\alpha} M_k \dot{U}_\alpha^2(lk) \qquad\qquad (A.6)$$

The expression for the Hamiltonian becomes (in harmonic approximation)

$$H = \frac{1}{2} \sum_{lk\alpha} M_k \dot{U}_\alpha^2(lk) + \emptyset_0 + \sum_{\substack{lk\alpha \\ l'k'\beta}} \emptyset_{\alpha\beta}(lk;l'k')U_\alpha(lk)U_\beta(l'k')$$

(A.7)

Hence the equations of motion of the lattice follow immediately.

$$M_k \ddot{U}_\alpha(lk) = -\frac{\partial \emptyset}{\partial U_\alpha(lk)} = -\sum_{l'k'\beta} \emptyset_{\alpha\beta}(lk;l'k')U_\beta(l'k')$$

(A.8)

Here the coefficients $\emptyset_{\alpha\beta}(lk;l'k')$ are called the atomic force constants. (They are the second derivatives of the potential energy with respect to atomic displacements). The coefficient represent the negative of the force exerted in the α-direction on the atom (lk) when the atom (l'k') is displaced a unit distance in the β-direction, all the other atoms being kept at their equilibrium positions. If one chooses as the solution to the eqn.(A.8) a function of the form,

$$U_\alpha(lk) = M_k^{-1/2} U_\alpha(k)\exp[-i\omega t + iK\,x(l)]$$

(A.9)

the eqn.(A.8) becomes

$$\omega^2 U_\alpha(k) = \sum_{k'\beta} D_{\alpha\beta}(kk'|K)U_\alpha(k') \qquad (A.10)$$

where the elements of the matrix $D(k)$ (called the Fourier transformed dynamical matrix) are given by

$$D_{\alpha\beta}(kk'|K) = (M_k M_{k'})^{-\frac{1}{2}}\sum_{l'} \phi_{\alpha\beta}(lk;l'k')\exp[-i\bar{K}\left\{x(l)-x(l')\right\}]$$

$$(A.11)$$

Here $x(l)$ and $x(l')$ denote the position vectors of l and l' unit cells respectively and the vector K is called the Wavevector. Also M_k and $M_{k'}$ are the masses of kth and k'^{th} atoms. The condition that the sets of eqns.(A.10) have a nontrivial solution is that the determinant of the coefficients vanish.

$$\left|D_{\alpha\beta}(kk'|\bar{K}) -\omega^2\delta_{\alpha\beta}\,\delta_{kk'}\right| = 0 \qquad (A.12)$$

The number of solutions of eqn.(A.12) is equal to thrice the number of atoms in a unit cell (ie., thrice the number of values of k). If there are 'r' atoms in the unit cell, the number of solutions is 3r. Thus for each value of $\bar{K}$ there can be 3r values of $\omega^2(\bar{K})$

and the 3r functions of $\omega_j^2(\overline{K})$ (where $j=1,2,\ldots 3r$) can be regarded as the branches of a multivalued function $\omega^2(\overline{K})$. This relation can be written as,

$$\omega = \omega_j(\overline{K})$$

which is called the 'dispersion relation'.

For each of the 3r values of $\omega_j^2(\overline{K})$ corresponding to a given value of $\overline{K}$, there exists a vector $e(k|\overline{K}j)$ whose components are the solutions to the set of eqns.(A.10) and this can be denoted as

$$\omega_j^2(\overline{K})e_\alpha(k|\overline{K}j) = \sum_{k'\beta} D_{\alpha\beta}(kk'|\overline{K})e_\beta(k'|\overline{K}j) \quad (A.14)$$

The squared frequencies $\omega_j^2(\overline{K})$ are called the eigenvalues and the vectors $e(k|\overline{K}j)$ are called the eigenvectors.

In rigid ion model the elements of the dynamical matrix $D_{\alpha\beta}(kk'|\overline{K})$ are considered to be constituted by two parts; one representing the Coulomb interaction and the other representing the non-Coulomb interaction part. Hence the force constants $\emptyset_{\alpha\beta}(1k;1'k')$ are taken as a sum of two terms $\emptyset^C_{\alpha\beta}(1k;1'k')$ and $\emptyset^N_{\alpha\beta}(1k;1'k')$ representing Coulomb and non-Coulomb parts respectively. Considering these things the

dynamical matrix can be written as,

$$D_{\alpha\beta}(kk';|\overline{K}) = T_{\alpha\beta}(kk'|K) + R_{\alpha\beta}(kk'|K) \qquad (A.15)$$

where

$$T_{\alpha\beta}(kk'|K) = (M_k M_{k'})^{-\frac{1}{2}}\sum_{l'}\phi^C_{\alpha\beta}(lk;l'k')\exp[-iK\cdot x(lk)$$

$$-x(l'k')] \qquad (A.16)$$

$$R_{\alpha\beta}(kk'|K) = (M_k M_{k'})^{-\frac{1}{2}}\sum_{l'}\phi^N_{\alpha\beta}(lk;l'k')\exp[-iK\{x(lk)$$

$$-x(l'k')\}] \qquad (A.17)$$

In order to get the dynamical matrix the two parts $T_{\alpha\beta}(kk'|K)$ and $R_{\alpha\beta}(kk'|K)$ are to be evaluated separately and added together from which one gets the eigenvalues.

It is quite well-known that the replacement of an atom in the crystal by its isotope gives rise to shifts in the normal mode frequencies of the crystal. Since the potential and hence the interatomic force depend only on the position coordinates of the substituted atom the frequency (or eigenvalue) is inversely proportional to the square root of the mass of the atom (see eqns.(A.10) and(A.11)) ie., there is no

change in the dynamical matrix of the crystal when one

of the atoms is substituted with its isotope except

for the term involving the mass. Margaret[24] has

shown that the frequency shift due to isotopic sub-

stitution can be used for the calculation of eigen-

vectors and the expression can be written as

$$\frac{\omega_j^{*2}(\overline{K}) - \omega_j^2(\overline{K})}{\omega_j^2(\overline{K})} = \sum_{k=1}^{r} \frac{M_k - M_k^*}{M_k^*} e^{\dagger}(k|\overline{K}j).e(k|\overline{K}j)$$

(A.18)

Here * denotes the quantity for substituted material

and † denotes the complex conjugate.

In the present work two crystals, $Zn^{32}S$ and

$Zn^{34}S$, are considered and the phonon frequencies of

both are calculated using the rigid ion model for

the [100], [111] and [110] wavevector directions.

Here the part of the dynamical matrix representing

Coulomb interaction (eqn.(A.16)) is calculated by

using the method of Kellerman[25] and the part for non-

Coulomb interaction (eqn.(A.17)) the expressions given

by Smith[1] and Rajagopal[2] are employed, Using the

expression given by Margaret[24] (in eqn.A.18) the

eigenvector magnitudes are also determined[26]. Fig.A.1

gives the dispersion curves of normal crystal $(Zn^{32}S)$
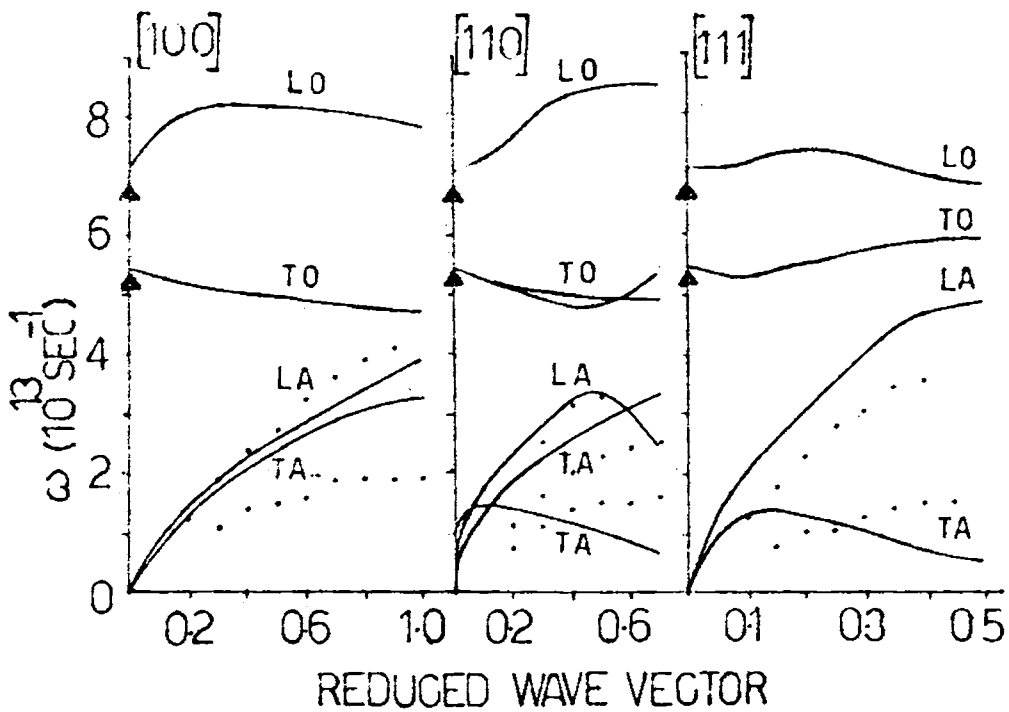
Fig.A.1   Phonon dispersion relations for Zn^{32}S in
          [100], [110] and [111] directions.
          ——, present theoretical study;
          ▲, experimental Raman frequency (Ref.27);
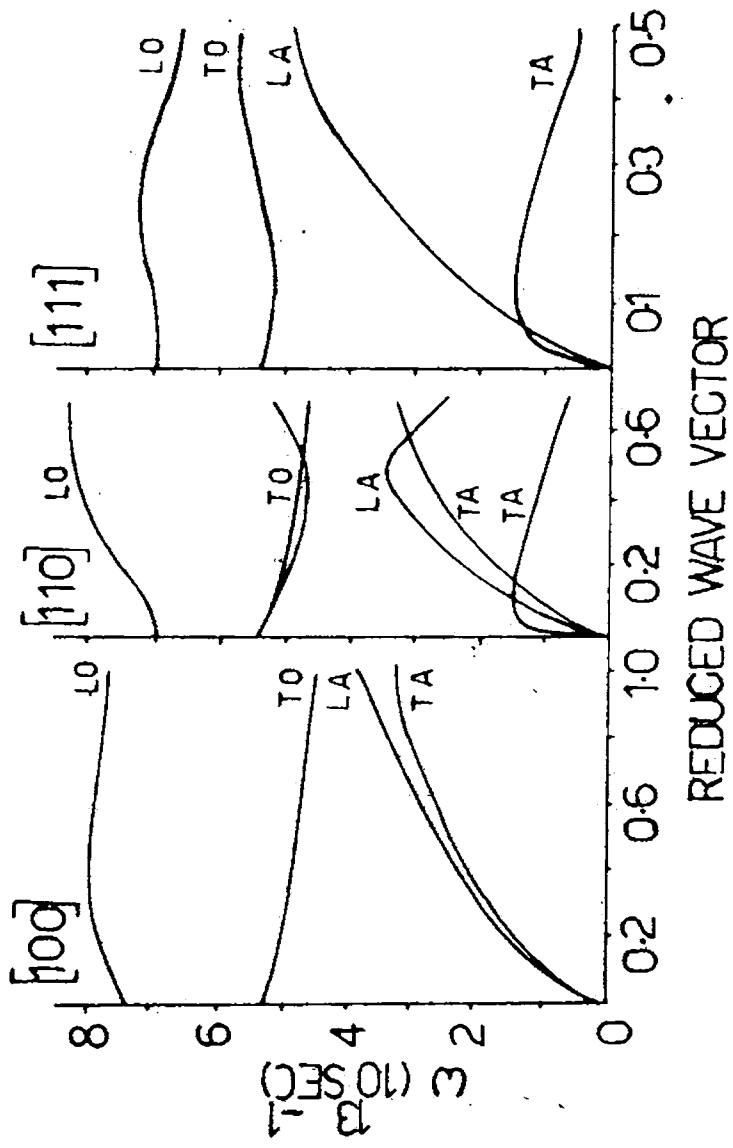   •• , inelastic neutron scattering data (Ref.4).

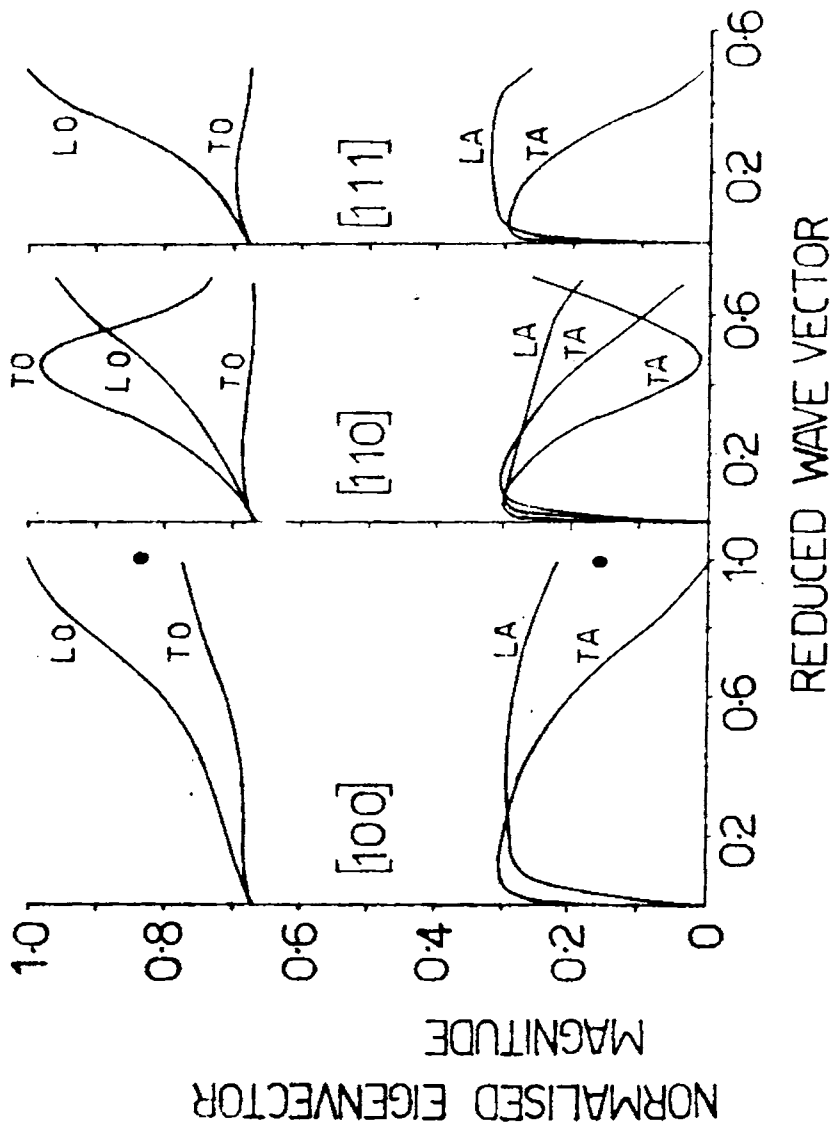Fig.A.2 Phonon dispersion relations for $Zn^{34}S$.

Fig.A.3 Normalised eigenvector along [100], [110] and [111] directions.———, present theoretical study; •, calculated values from literature (Ref.24).

and fig.A.2 shows that of the substituted crystal $(Zn^{34}S)$. Fig.A.3 shows the eigenvector magnitudes.

In fig.A.3 it can be seen that, as the wave-vector value approaches the Brillouin zone boundary, the eigenvector values corresponding to the transverse acoustic modes are decreasing while those corresponding to longitudinal optical modes are increasing. But in [110] direction, at the reduced wavevector value of 0.4 (approximately) the eigenvalues for transverse acoustic mode have a minimum and those for transverse optical mode have a maximum. At the Brillouin zone boundary, in [100] direction the eigenvector values agree very well with those given by Margaret[24].

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