CHAPTER-VI

Optical Properties
Of
Mn - Oxide Films.

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6.1 Introduction :

The study of optical absorption is essential in order to understand the type of transitions and to determine the bandgap energies of the semiconducting material. Ellipsometric measurements are important to determine the optical constants of the sdurface such as the refractive index and extinction index . In semiconductor industry ellipsometry is used to measure thickness and monitor the quality of composition of thin dielectric films deposited on semiconductor surfaces. Refractive index changes have been investigated in ion implanted silicon to provide insight in the doping process of semiconductors /1/. Measurements of optical properties of thin organic films under vacuum have been applied to contamination of optical surfaces for satellite applications and calibration of contamination monitors for skylab /1/. Ellipsometry has been used for analysis of surface roughness and surface layer defects also to measure specimen temperatures in ultra-high vacuum environments /2-7/. In electrochemistry, ellipsometry is used to analyze deposition and conversion films, boundary layer conditions, oxidation and corrosion of metals. Ellipsometry has been applied to immunological studies by measuring film thickness variations due to antigen -antibody reactions in biology and medicine. In this chapter the effects of concentration, substrate temperature and spray rate on optical properties mainly on optical absorption, transmission and refractive index of Mn-oxide films are reported.

6.2 Experimental :

Experimental setups for optical absorption and refractive index are described in this section.

6.2.1 Experimental setup for Optical Properties

a] Optical Absorption Measurements :

The optical absorption, transmission or extinction of Mn-oxide films deposited on glass substrate were studied with the help of spekol (Carl Zeiss Jena). The spekol is a photoelectric spectrophotometer for the visual spectral range. It is operated on the single-beam deflection principle. The main component of this instrument is a grating monochromator which has a relative aperture of 1:3:4 and is equipped with fixed slits for a spectral bandwidth of 11 nm. The function of monochromator is similar to a colour filter having a spectral half width of 11 nm. The other parts of it are the heat-insulated lamp (T-M 6 v 30 w projector type filament lamp), measuring attachments and standards, measurement arrangement, the spekol multi-purpose unit (a single-beam spectrophotometer with a constant spectral band width of 11 nm), the spekol zv booster amplifier. Before using this instrument for actual measurements setting up of the basic unit and adjustment of the incandescent lamp are done. After this adjustment set light shutter to "0" and switch on amplifier to "100". Mount the reference sample and open shutter "1", set "100" point. Remove the reference sample and inserting the specimen read out the optical density (αt) and transmission (T).

b] Ellipsometric Measurements :

The Gaertner Ellipsometer, Model L_{119} as shown in fig 6.1 was used to measure refractive index of Mn-oxide films. It consists of a modified standard spectrometer (L_{113}) fitted with the polarizing and analyzing components and can be used for all applications of a high quality spectrometer in addition to polarimetric measurements. The basic components are as follows:

An iris diaphragm or pinhole entrance aperture is mounted on a 250 mm e.f.i. collimator, 28.4 mm aperture, having rack and pinion focusing. The objective mount of the collimator supports a 6¼ in. diameter divided circle assembly with a 14 mm Glan-Thompson prism centered and aligned to the rotational bearing. The angular position of the prism is read with two opposing verniers to an accuracy of 0.01°. Each vernier is equipped with a right angle mirror and an adjustable magnifier. The divided circle assembly rotates through 360° and a fine motion tangent screw assembly is provided for precise fined adjustment. A similar divided circle assembly, complete with opposing verniers, mirrors, magnifiers and fine motion tangent adjustment supports a rotating dove-

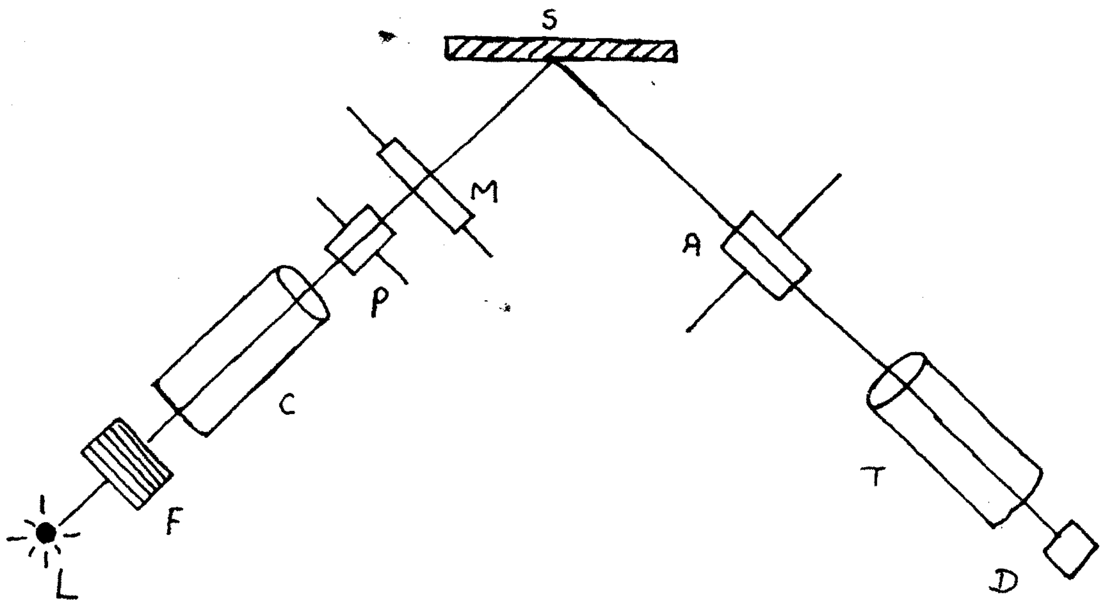


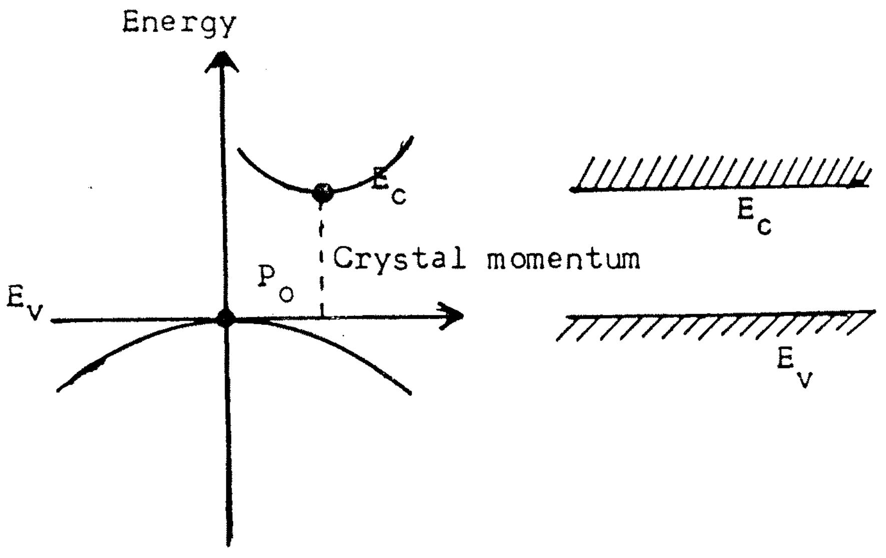
Fig. 6.1 Schematic representation of Gaertner ellipsometer.
L - light source, F - filter, C - collimeter
P - polarizer, M - compensator, S - substrate,
A - analyzer, T - telescope, D - detector (eye or microphoto meter)

tail mount, designed to accommodate either a suitably mounted mica wave plate or a Babinet-Seleil compensator. In standard form, the ellipsometer includes a mica quarter wave plate for 5461 A° ± 5% cemented between nonreflection coated cover glasses and mounted in a matching dovetail slide. A round horizontal support table, supplied with a vertically mounted polished stainless steel substrate mirror, 15 mm x 60 mm x 3 mm, is supported by three leveling screws and is rotatable concentric with the bearing of the telescope. The final component is a telescope and rotating Glan-Thompson prism assembly identical to the collimator but supported by a bearing which permits it to rotate around a central axis to change the angle of incidence and reflection to and from the substrate surface. This angle is measured with a horizontal divided circle, diameter $6\frac{5}{8}$ in., divided into increments of 20 minutes and read by opposing verniers to an accuracy of 20 seconds. Each vernier is equipped with an adjustable magnifier, filtered to minimize parallax. The entire assembly is supported by a single stable base designed to maintain the original alignment of components.

6.3 Results and Discussion

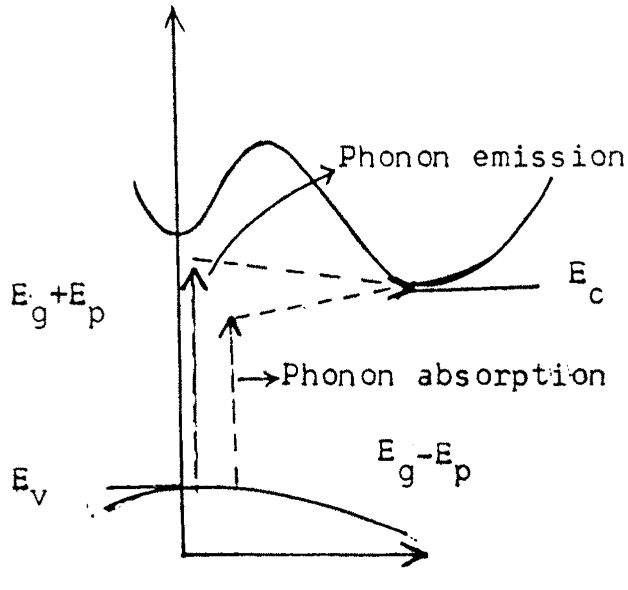
6.3.1 Optical absorption

Mn-oxide films are optically characterized by measuring their optical density (αt) in the wavelength range between



(a) (b)

Fig. 6·2.a & b : Energy crystal momentum relationships near the band edges for an indirect bandgap semiconductor.



(c) Crystal momentum, p

Fig. 6·2 c : Energy crystal momentum diagram of an indirect bandgap semiconductor showing the absorption of photons by two step processes involving phonon emission or absorption.

400 nm to 750 nm. Absorption coefficient is evaluated from αt by dividing the thickness of respective Mn-oxide film. The values of α are found to be of the order of 10^{+3} to 10^{+4} cm^{-1}. Relatively low values of absorption coefficients obtained, indicate indirect bandgap material. Since in indirect bandgap material basorption process involves an extra particle known as phonon which makes possibility of light absorption less than that of direct bandgap material as illustrated in fig. 6.2. Hence, the absorption coefficient is low and light can pass a reasonable distance into the semiconductor prior to the absorption /8/.

For a semiconductor the dependence of absorption coefficient on absorption edge is usually given by /9/

$$\alpha h\nu = A\ (h\nu - E_g)^{n/2} \qquad \ldots (6.1)$$

where α is the absorption coefficient per cm., h is Plank's constant, ν is energy of photon, A is constant, E_g is bandgap energy and n is the order equal to one for direct bandgap semiconductor and equal to four for indirect bandgap semi conductor. With the help of above relation one can test again the type of the material by calculating value of n. In fig. 6.3 graph of $\alpha h\nu$ versus $(h\nu - E_g)$ is shown for a typical sample. The value of n is found to be equal to 4, confirming further that Mn-oxide is the indirect bandgap semiconductor.

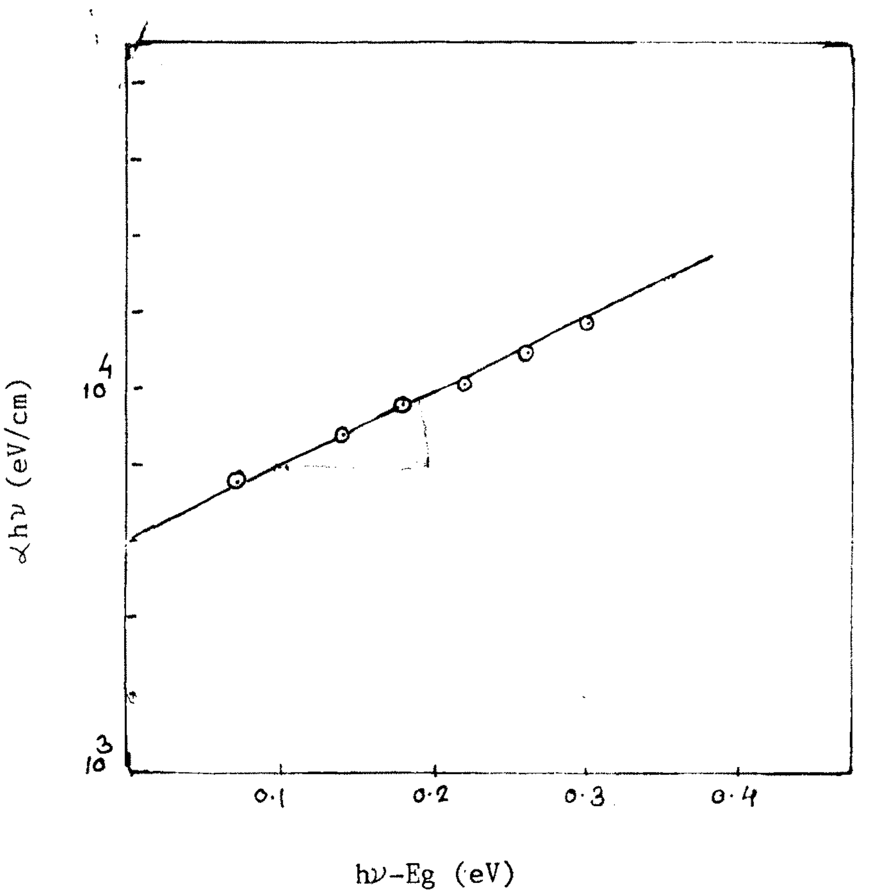


Fig. 6.3 Plot of $\alpha h\nu$ against ($h\nu$-Eg) for the film S_{400}.

In the case of indirect bandgap semiconductor the variation of α with ($h\nu$ $-E_g$) is given as below /10,11/,

$(\alpha) \propto (h\nu - E_g)^2$ ... for allowed direct transition.

$(\alpha) \propto (h\nu - E_g)^3$ ... for forbidden direct transition.

Thus from the values of α and the manner in which they depend on the energy of incident radiation it is possible to determine directly the nature of transitions whether direct or indirect, allowed or forbidden.

Fig. 6.4 shows the variation of α with $(h\nu - E_g)^2$. The straight line nature of the graph gives the type of Mn-oxide as allowed direct transition semiconductor. The plot of $(\alpha)^{\frac{1}{2}}$ versus ($h\nu$) for a typical sample is as shown in fig. 6.5. The bandgap energy for this sample is found to be of the order of 1.9 eV. Fig. 6.6 shows the graph of $(\alpha)^{\frac{1}{2}}$ against ($h\nu$) for the films which are deposited at different substrate temperatures. The bandgap energy is affected by substrate temperature. Here the bandgap energy increases with the substrate temperature. From fig. 6.5 and 6.6 it is clear that the bandgap energy is affected by the concentration of the solution. The variation of $(\alpha)^{\frac{1}{2}}$ with ($h\nu$) is not given here but it is found that the bandgap energy is unaffected by the spray rate.

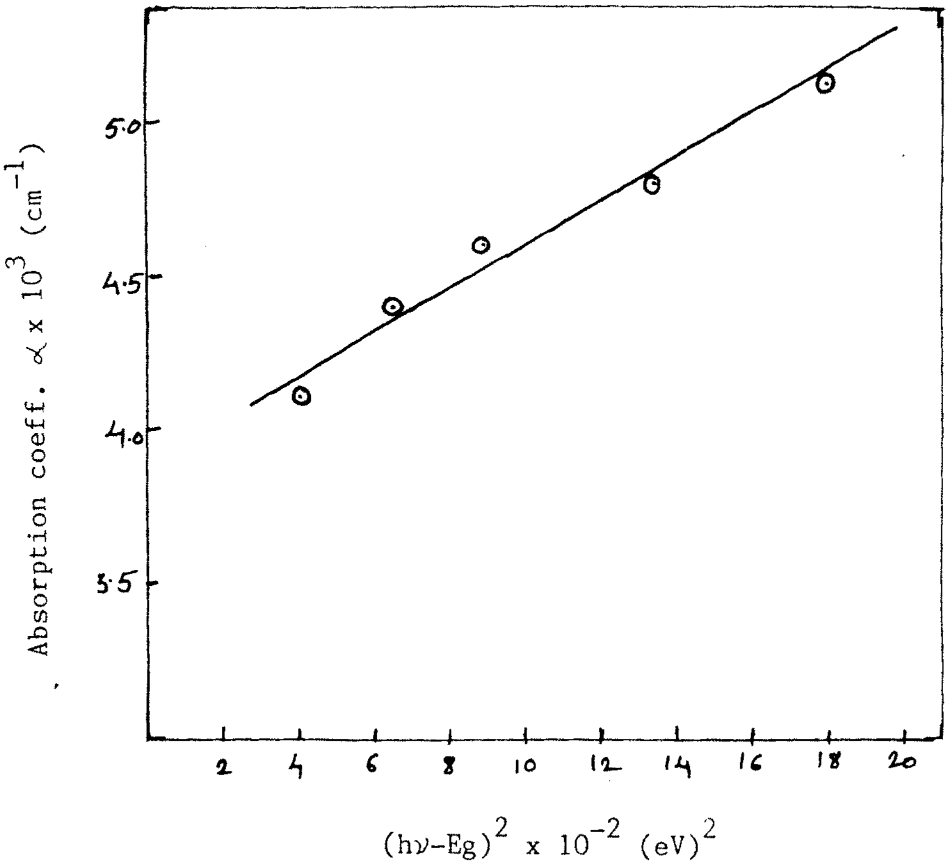


Fig. 6.4 Variation of α with $(h\nu-Eg)^2$.

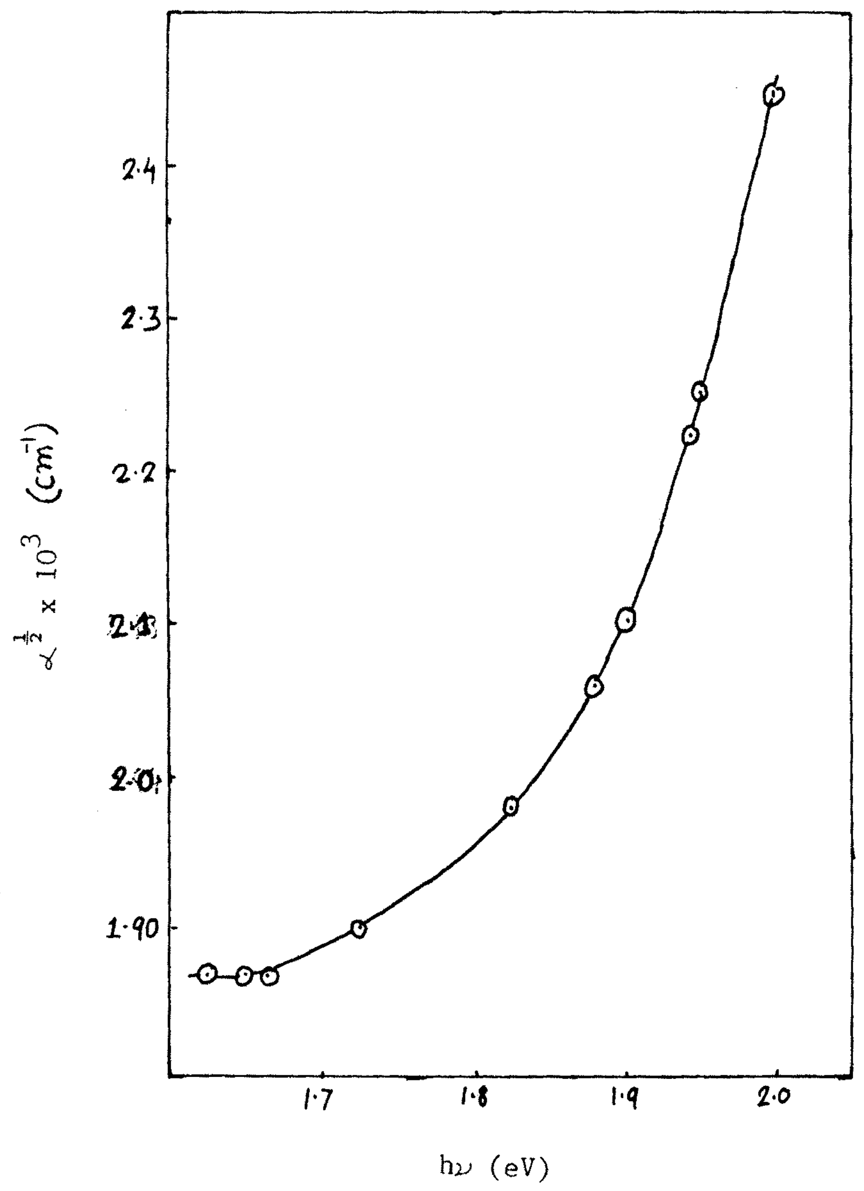


Fig. 6.5 Variation of $\alpha^{\frac{1}{2}}$ with hν for a typical film $S_{0.5}$.

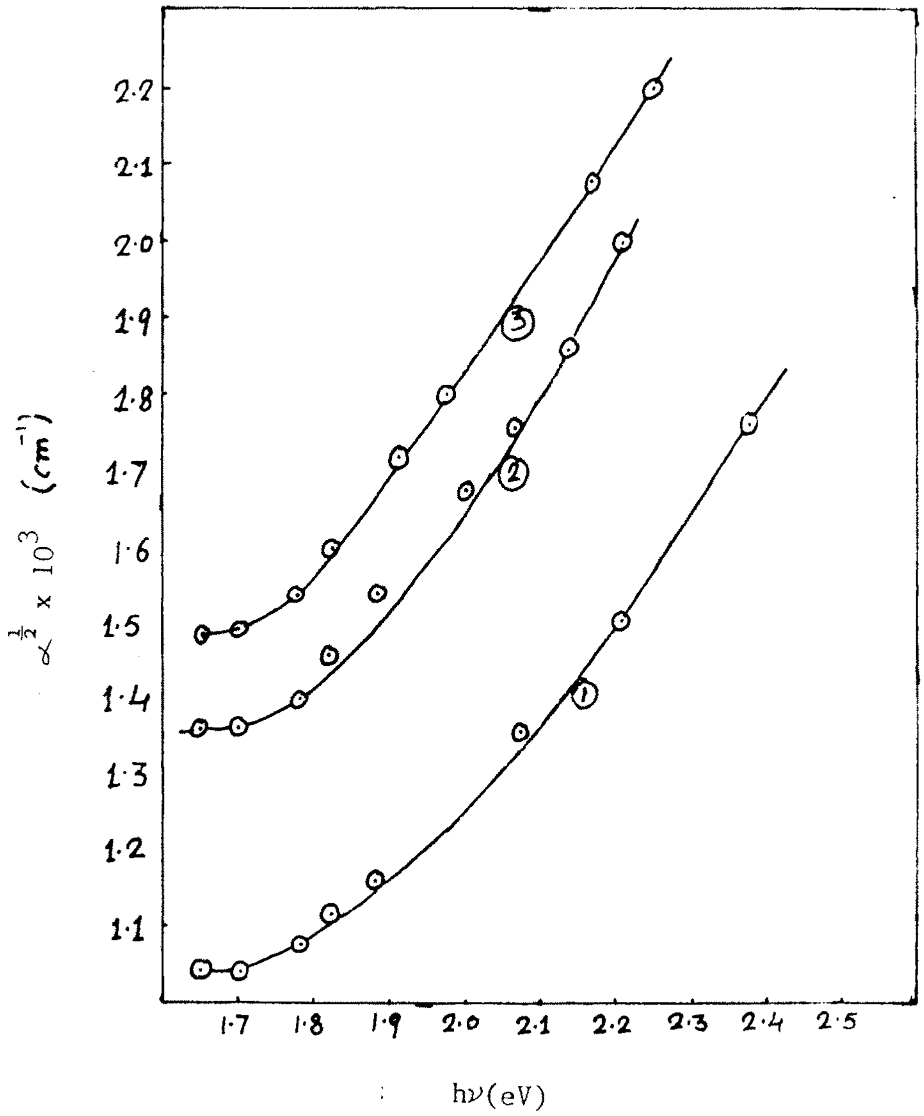


Fig. 6.6 Variation of $\alpha^{\frac{1}{2}}$ with hν for films prepared at different substrate temperature (1) 400°C (2) 425°C (3) 450°C.

6.3.2 Transmission

Transmission (T) for Mn-oxide films is measured in the wavelength range between 400 nm to 750 nm. The variation of transmission with wavelength is shown in fig. 6.7, 6.8 and 6.9 to understand the effect of concentration, substrate temperature and spray rate on transmission. In all plots the transmission increases with the wavelength but beyond 6500 A° the increase in the transmission with the wavelength is less.

Fig. 6.7 is the plot of transmission versus wavelength for two different concentrations. The transmission is found to be decreasing with increase in concentration. The graph of transmission against wavelength for different substrate temperatures is as shown in fig. 6.8. The transmission decreases with decrease in substrate temperature. Fig. 6.9 gives the variation of transmission with wavelength for different spray rates. The variatioin shows that the transmission decreases with decrease in spray rate.

6.3.3 Refractive Index

The refractive index of Mn-oxide films is measured with the help of ellipsometer by taking readings of the angle Δ, defined as the change in phase and given as

$$\Delta = (\beta_p - \beta_s)_{\text{reflected}} - (\beta_p - \beta_s)_{\text{incident}} \qquad \ldots(6.2)$$

and the angle ψ, the arctangent of the factor by which the amplitude ratio changes. ψ is given as

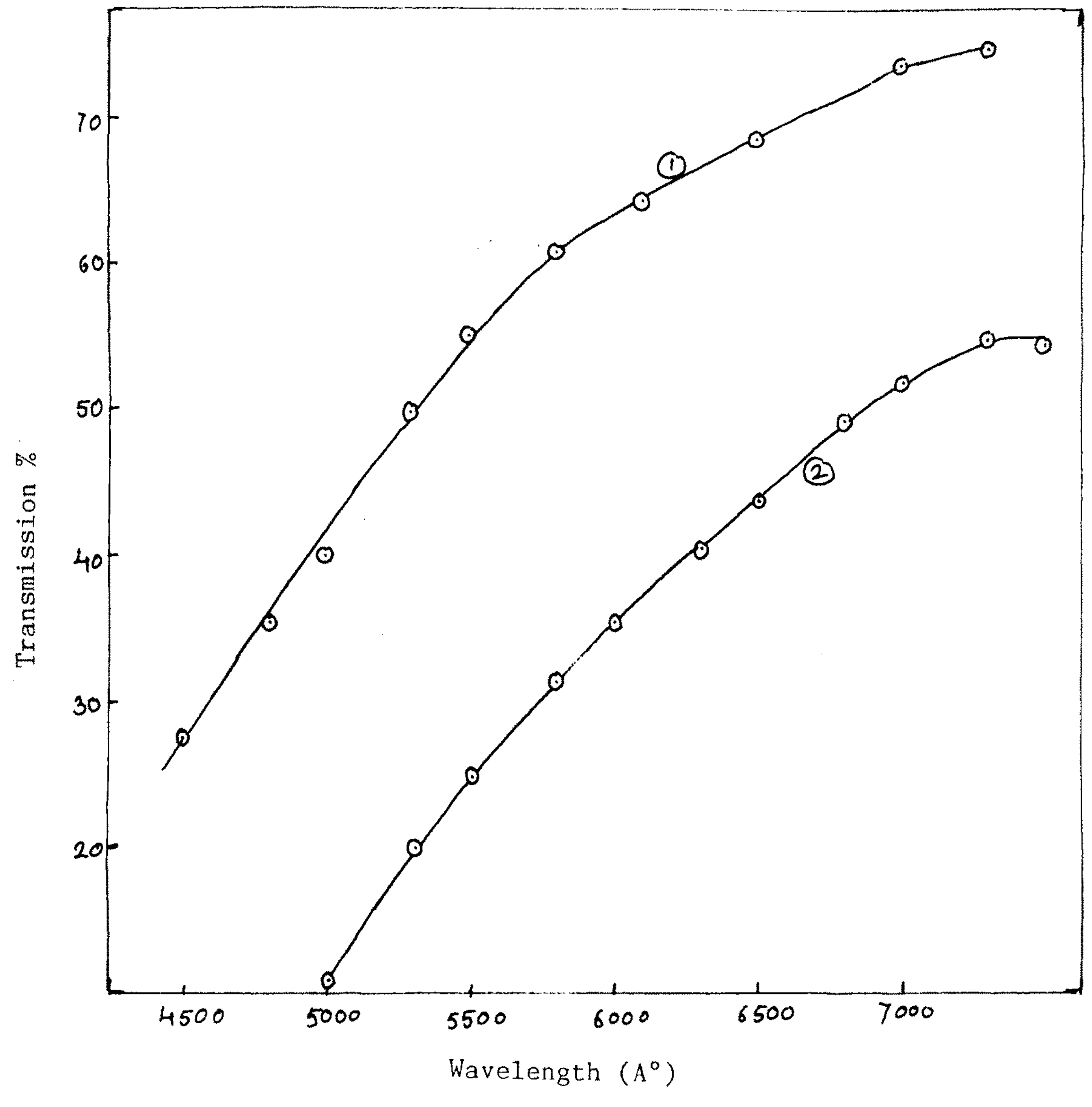


Fig. 6.7 Plot of transmission versus wavelength for films prepared with different concentrations of spraying solution.
(1) 0.1 M (2) 0.25 M

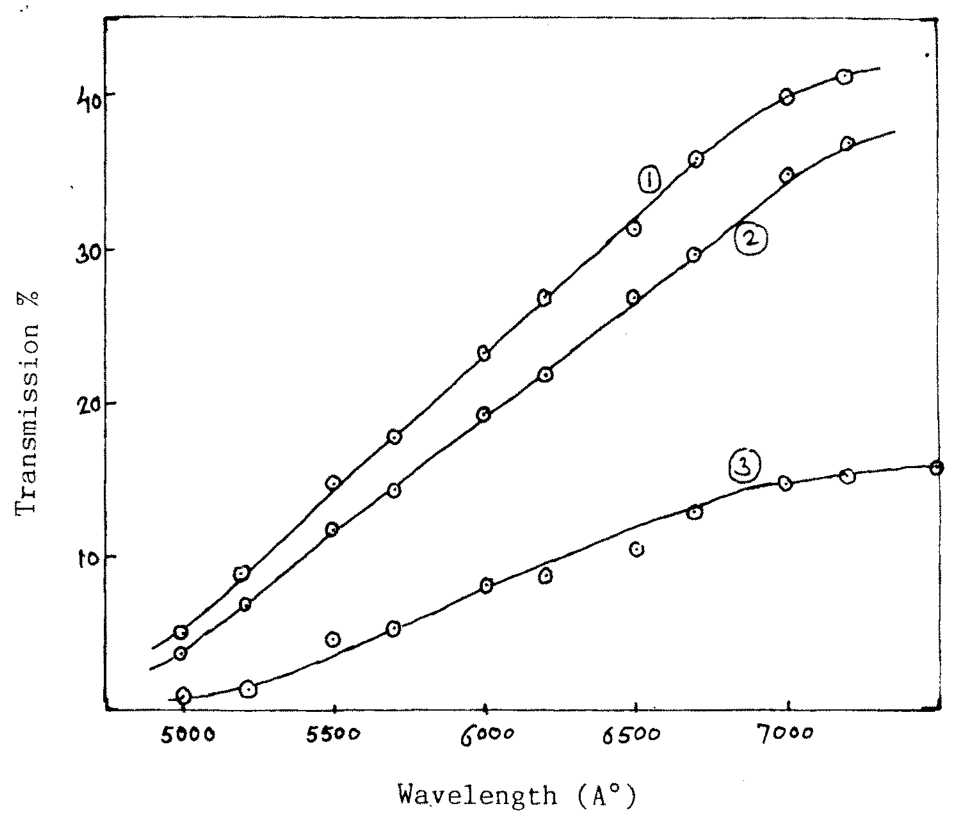


Fig. 6.8 Plot of transmission versus wavelength for films prepared at different substrate temperatures.
(1) 450°C (2) 400°C (3) 350°C.

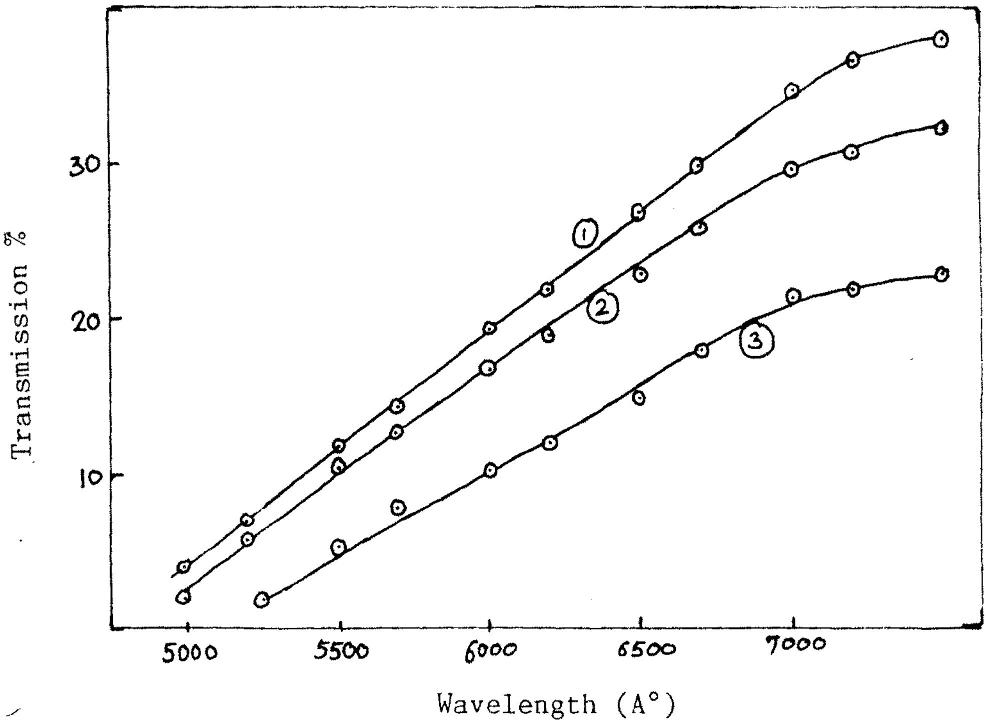


Fig. 6.9 Plot of transmission versus wavelength for films prepared with different spray rates (1) 12 cc/min (2) 10 cc/min (3) 8 cc/min.

$$\psi = \arctan\left(\frac{R_p}{R_s}\ \frac{E_s}{E_p}\right) \qquad \ldots (6.3)$$

where β_p and β_s are the phase angles of the wave which is in the plane of incidence (p) and normal to the plane of incidence (s) respectively, R_p, E_p and R_s, E_s are the amplitudes of the reflected and incident beams of p and S respectively.

Before taking readings of Δ and ψ to calculate refractive index the alignment of the spectrometer, calibration of the polarizer, calibration of the analyzer, calibration of the wave plate circle should be done. After calibration of ellipsometer extinction settings are determined by direct visual method.

Certain azimuth settings of the polarizer cause the light reflected from the specimen to become completely linearly polarized. When the polarizer is at one of these azimuth settings, the analyzer can be rotated to a position where almost no light reaches the photodetector, giving the extinction meter its lowest reading. From the angular settings of the polarizer and analyzer at this condition, the ellipsometric parameters Δ and ψ are derived respectively. When the compensator is set at +45° to the plane of incidence, the relation between Δ and the polarizer setting P is

$$\tan\Delta = \sin\delta \ \tan\,(90 - 2P_2)$$

and $$\tan\Delta = \sin\delta \ \tan\,(270 - 2P_1)$$

where $P_2 = P_1 \pm 90$.
The relation between ψ and the analyzer setting A is

$$\tan^2\psi = \tan(180 - A_2)\tan A_1$$

For a perfect compensator, a quarter wave plate with $\delta = 90°$, the relatiion between polarizer P and analyzer A settings and also Δ and ψ becomes rather simple, namely,

$$\Delta = 90° - 2P_2 = 270° - 2P_1 \qquad \ldots (6.4)$$

and $$\psi = 180° - A_2 = A_1 \qquad \ldots (6.5)$$

It should be noted that the polarizer settings P_1 and P_2 are related to analyzer setting A_1 and A_2 respectively. ψ varies from 0° to 90° and Δ can assume values from 0° to 360°. Fig. 6.10 illustrates the range of Δ depending on the P_1 settings corresponding to the A_1 settings in the range of 0° to 90°.

Having obtained Δ and ψ values, the film thickness and the refractive index of the film are then determined. Using the theoretical background as follows:

The relationship between Δ and ψ and the properties of a reflecting system is expressed by the Fresnel reflection coefficients. The Fresnel reflection coefficient, r, of an interface is the ratio of the electric field vector, R', of the reflected wave to that, E', of the incident wave, in terms of the amplitudes of the incident and reflected waves E and R respectively and the phase change, β ,accompanying

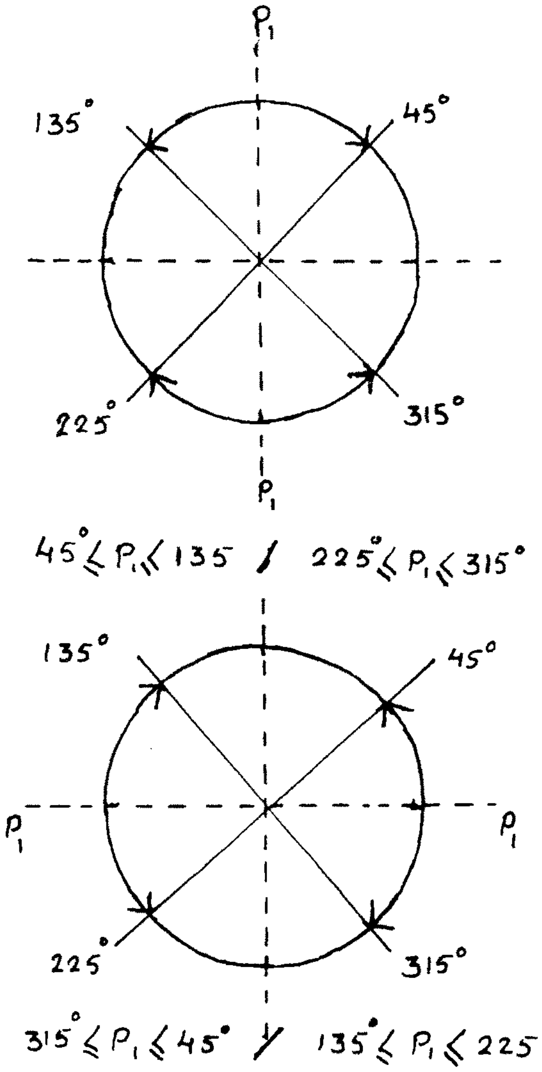


Fig. 6.10 Relationship of amplitude ratio (Δ) to Polarizer settings
(1) $0° \leqslant \Delta \leqslant 180°$ (2) $180° \leqslant \Delta \leqslant 360°$

reflection,

$$r = R'/E' = (R/E)\, e^{+i\beta} \qquad \ldots (6.6)$$

The coefficient depends upon the orientation of the wave relative to the plane of incidence and the reflection of a wave of any polarizatioin is described by the two coefficients, r_s and r_p, for the component waves. The ratio of these reflection coefficient is

$$\frac{r_p}{r_s} = \frac{R_p}{R_s} \; \frac{E_s}{E_p} \; e^{i(\beta_p - \beta_s)} \qquad \ldots (6.7)$$

From equations (6.2) and (6.3) it follows that /12/

$$\frac{r_p}{r_s} = \tan\psi \; e^{i\Delta} \qquad \ldots (6.8)$$

For an optically isotropic substrate with a clean surface the Fresnel reflection coefficients are

$$r_{12}^{p} = \frac{n_1 \cos\phi_2 - n_2 \cos\phi_1}{n_1 \cos\phi_2 + n_2 \cos\phi_1} \qquad \ldots (6.9)$$

$$r_{12}^{s} = \frac{n_1 \cos\phi_1 - n_2 \cos\phi_2}{n_1 \cos\phi_1 + n_2 \cos\phi_2} \qquad \ldots (6.10)$$

The subscrips 1 and 2 refer to the media bounding the reflecting interface, ϕ_1 is the angle of incidence and ϕ_2 the angle of refraction. The Fresnel transmission coefficients express the ratio of the refracted wave to the incidence wave

$$t_{12}^{p} = \frac{2n_1 \cos\phi_1}{n_1 \cos\phi_2 + n_2 \cos\phi_1} \qquad \ldots (6.11)$$

$$t^{s}_{12} = \frac{2n_1 \cos\phi_1}{n_1 \cos\phi_1 + n_2 \cos\phi_2} \qquad \ldots (6.12)$$

For an optically absorbing medium the complex index of refraction of the substrate,

$$\bar{n} = n - ik \qquad \ldots (6.13)$$

is substituted for n_2 in equation (6.9) through (6.13). k is the extinction coefficient is related to the absorption coefficient α (in units of cm^{-1}) by

$$k = \frac{\alpha \lambda}{2\pi} \qquad \ldots (6.14)$$

λ is the vacuum wavelength. The formulae for deriving the optical constants from values of Δ and ψ are derived from equations 6.8, 6.9, 6.10 and 6.14. The resdults are

$$n^2 - k^2 = t^2 \frac{(\cos^2 2\psi - \sin^2 2\psi \sin^2\Delta)}{(1 + \sin 2\psi \cos\Delta)^2} + \sin^2\phi \ldots (6.15)$$

$$2nk = t^2 \frac{\sin 4\psi \sin\Delta}{(1 + \sin 2\psi \cos\Delta)^2} \qquad \ldots (6.16)$$

$$t = \sin\phi \tan\phi$$

where ϕ is the angle of incidence.

The results obtained from the measurements and calculations are tabulated in tables 6.1 and 6.2. The table 6.1 gives the refractive index for the Mn-oxide films which are prepared at different substrate temperature. The refractive index is found to be nearly constant for different substrate

Table No. 6.1

Substrate temperature in °C	Refractive index
350	1.92
375	1.92
400	1.94
425	1.92
450	2.10

Table No. 6.2

Spray rate in in cc/min	Refractive index
6	1.86
8	1.91
10	1.95
12	1.95

temperature but for 450°C substrate temperature it is different. The table 6.2 gives the refractive index for the Mn-oxide films which are deposited with different spray rate. The refractive index increases with spray rate but remains constant for spray rates 10 cc/min and 12 cc/min.

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