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SECOND SEMIANNUAL REPORT

ON

Research on The Mechanism and Kinetics of

Oxidation of Silicon in Air

For the Period

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SUMMARY

This second semiannual report describes the progress of the work on the ellipsometer studies on the growth of thin oxide films on silicon. The experimental work involved the detailed calibration of the various components of the ellipsometer and the fabrication of a device for cleaving silicon in ultra high vacuum or liquids. Theoretically the interesting case of light being incident from a denser liquid on to the film has been considered when the angle of incidence is (i) less than the critical angle and (ii) greater than the critical angle. In the first case detailed calculations indicate that an increased sensitivity of up to about 10 times that reported so far can be achieved by working near the critical angle and there is a possibility of determining experimentally the refractive index <u>and</u> the thickness of the film individually. The theory for the case (ii) has been worked out and computations are currently being made to evaluate numerically Δ and Ψ.

I. INTRODUCTION

During the period December 1, 1965 to May 31, 1966, studies on the kinetics of oxidation of silicon, has proceeded along the following lines: (a) Experimental: - considerable effort was devoted to the precise calibration of the various components of the ellipsometer, the design and fabrication of the device for cleaving crystals in ultra high vacuum and perliminary studies on the oxidation kinetics has been started. (b) Theoretical: - the case where the light is incident on the film from a denser medium like Carbon Tetrachloride has been considered and this has led to some very interesting results. Since most of these studies are continuing, only an outline of the current status and recent progress will be given here.

II. EXPERIMENTAL

Since the ellipsometer is to be used in precision measurements of very small changes in the settings of the various components of the ellipsometer, it is necessary to check and calibrate the instrument as well as test the limitations of the method to be employed. This was carried out along the lines described below:

1. Aluminum Mirror Check

The first check of the ellipsometer performance was carried out by investigating the ellipticity of light reflected from an aluminum mirror, prepared by evaporation in vacuum. The most simple arrangement of the optical elements, namely $P_{45°}S\ A_{0-360°}$ (Polarizer oriented 45° to the plane of incidence - sample - analyser combination) was used with angle of incidence $\phi_o = 70°$, which is close to the quasi-polarizing angle. The rest of the optical train is the same as described in the last report. The

record of intensity vs analyser angle is shown on Fig. 1. From the curve it is easily possible to calculate all the necessary parameters for the ellipticity values. However it is evident, that the curve shows high asymmetry and large fluctuations in intensity values. The asymmetry was due to improper alignment of ellipsometer components as received from the manufacturer and hence the instrument was properly aligned till there was no asymmetry. The fluctuations in the readings of the amplified signals were considerably decreased by stabilizing the source and chopper power supply.

2. Silicon Oxide Layer Check

For cleaving silicon single crystals the techniques described by Gobeli and Allen(1) was employed. The useful area obtained was about 2 mm^2 and therefore an extremely narrow beam of light had to be used. The sample was suitably mounted on a goniometric head to secure fine alignment.

The same experimental procedure as described in the case of aluminum mirror was used for the first check. Fig. 2 shows the results obtained. It indicates a highly improved accuracy. Further the angle ω between the major axis of the ellipse and the plane of incidence can be measured in this way within an error of ±0.02° by taking several readings near the minimum position. The accuracy indeed depends on the ellipticity values, for small ellipticities the error becomes slightly higher. With approximately the same accuracy the ellipticity angle γ can be determined, where $\tan \gamma = a/b$, 2a and 2b being the minor and the major axis of the ellipse respectively. From the measured values ω and γ, the angles Δ and Ψ which define the ratio of the Fresnel coefficients for the s and p components, can be calculated. With the above mentioned $P_{45°}$ S A arrangement the

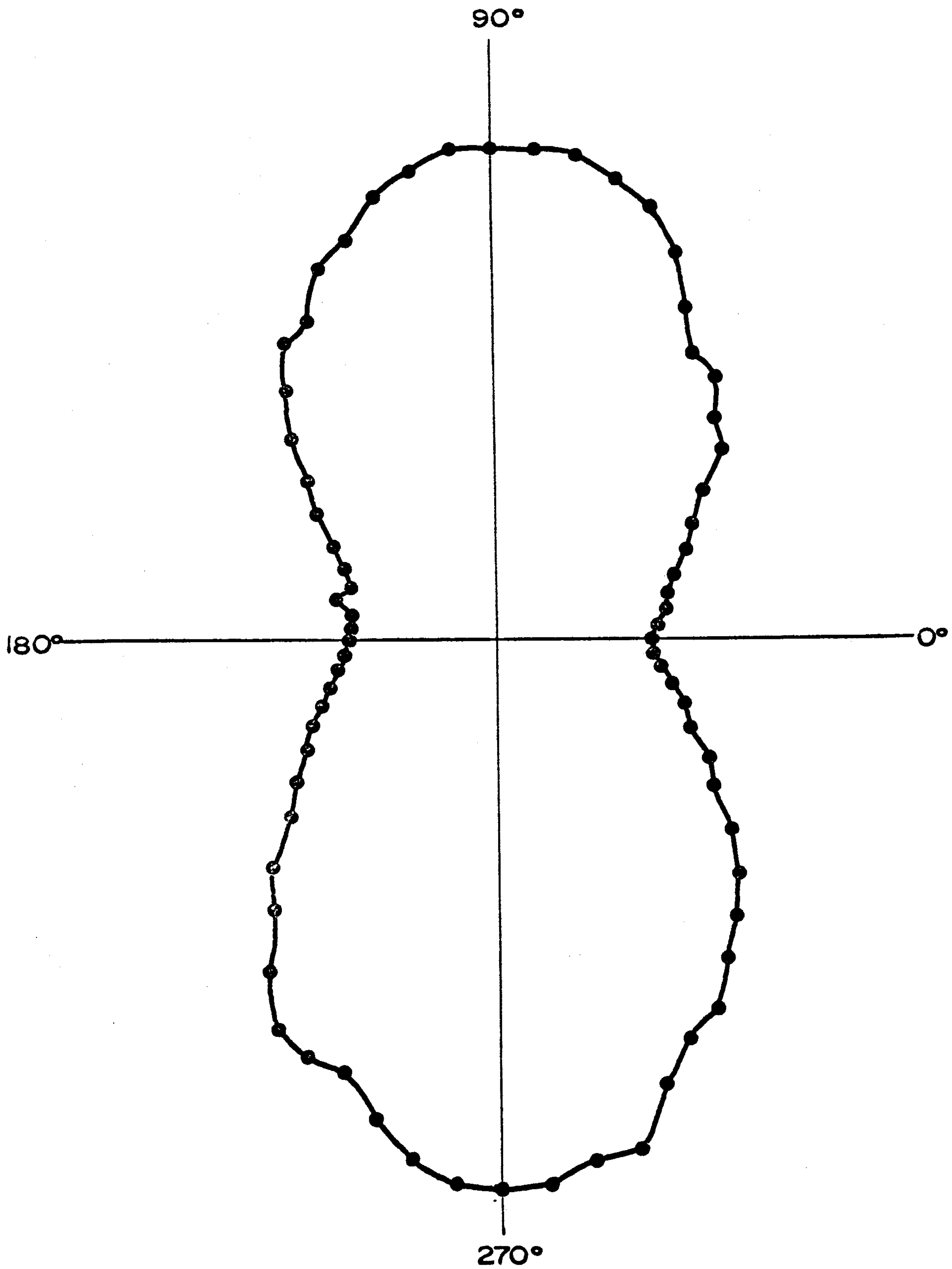


Fig. 1

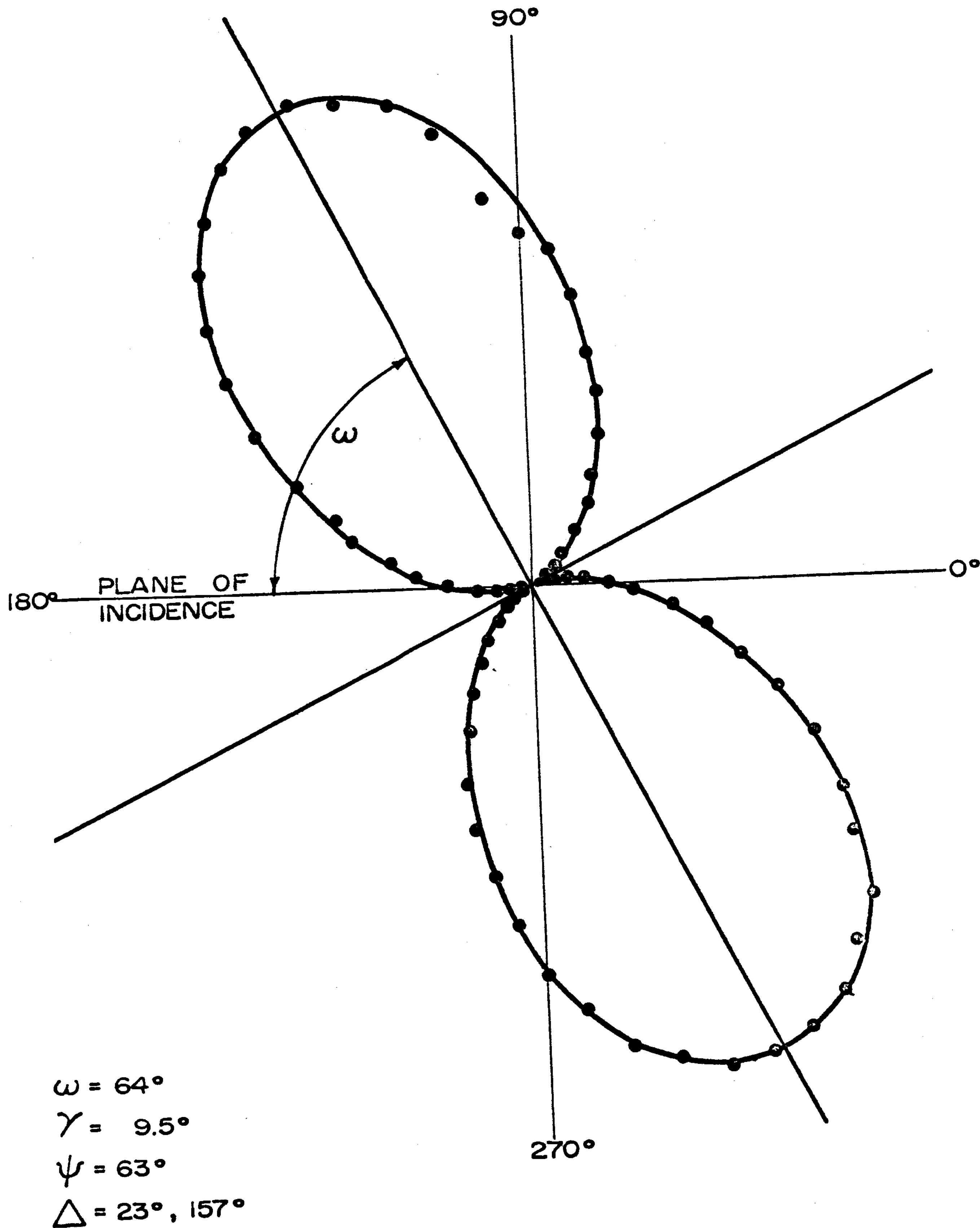


Fig. 2

necessary relations are given by

$$\tan 2\omega = \tan 2\Psi \cos \Delta \qquad \text{(i)}$$

$$\cos 2\Psi = \cos 2\gamma \cos 2\omega \qquad \text{(ii)}$$

where

$$-90^\circ < \omega < 90^\circ$$
$$\gamma < 90^\circ$$
$$\Psi < 90^\circ$$
$$-\pi < \Delta \leq \pi ,$$

or by similar equations, which can be derived from equations (i) and (ii). Graphically these relations are self evident from Fig. 3. From Fig. 2 we can calculate the approximate values

$$\omega = 64^\circ \qquad \gamma = 9.5^\circ \Rightarrow \Psi = 63^\circ, \ \Delta = 157^\circ$$

This method is quite accurate, the accuracy limit being given mainly by the accuracy of setting P and A. On the other hand, the determination of the angle ω requires several readings near the minimum position and γ has to be obtained by direct intensity measurements both at the minimum and maximum positions of the analyser. This means that for one pair of values of Δ and Ψ several minutes of measurements are needed, which makes this method inconvenient for oxidation kinetics measurements, where Δ and Ψ change rapidly with increasing thickness of the SiO_2 layer. Therefore the conventional method employing the quarter wave plate was used for further studies.

3. Measurement of SiO_2 layer using $\lambda/4$ Plate

(a) Arrangement P_{45° S Q_{0-360} A_{0-360}

A mica quarter wave plate Q was set between the sample and the polarizer to convert the elliptically polarized light into plane polarized light whose

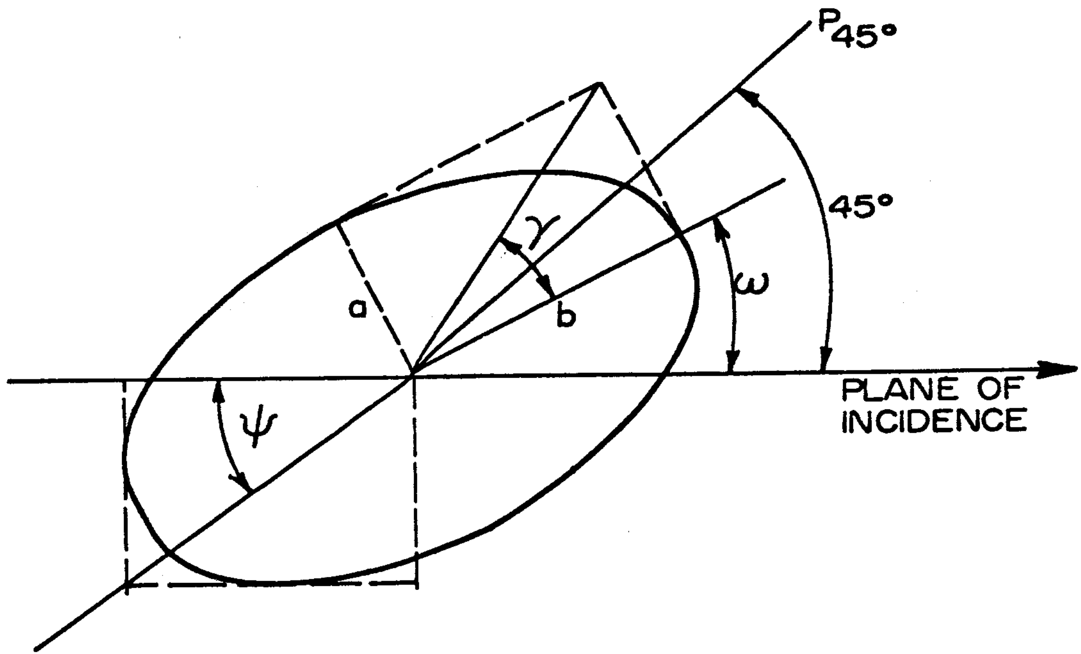


Fig. 3

plane of polarization was then determined by the analyser. By rotating Q and A simultaneously, the position of absolute minimum of intensity can be found. Then the settings of Q and A give directly the angles ω and γ respectively. This method enables quick measurement of the values of ω and γ, but the accuracy is much lower, being several tenths of 1° in the best case. This is mainly due to the imperfection of the mica $\lambda/4$ plate usually employed. From Fig. 4 we can see the very strong dependence of the position of A on the position of Q. In the ideal case, when Q is rotated by 90°, the analyser position should be exactly symmetrical with respect to the Q position. But in practice with a mica $\lambda/4$ plate as Q, an asymmetry is usually noticed. This asymmetry is caused by the pleochroic property of the mica i.e. by the different absorption of light polarized in the two fundamental directions of the $\lambda/4$ plate. As seen in Fig. 5 the amplitude in the principal direction v_2 is k-times smaller than that in the principal direction v_1, k being the ratio of the absorption coefficients along the two principal directions. On rotating the $\lambda/4$ plate by 90° the amplitude of the linearly polarized light changes accordingly. In view of this differential absorption, in practice the observed ellipticity is γ' and γ'' respectively in the two cases, instead of the true ellipticity γ. However from γ' and γ'' the true γ can easily be determined. In the case of Fig. 4 it is seen that $\gamma' = 9°$, $\gamma'' = 3°$. From these values k and γ were evaluated to be 0.575 and 5° respectively. Since $\omega = 18°$, it can be shown from equations (1) and (2) that $\psi = 19°$, $\Delta = 163°$. The film thickness d is given by

$$d = (m\pi + \delta)C,$$

where δ is the additional phase difference introduced by the SiO_2 film, m is an integer number, and

$$C = \frac{\lambda}{2\pi}\left(n_1^2 - n_0^2 \sin^2 \varphi_0\right)^{-1/2}$$

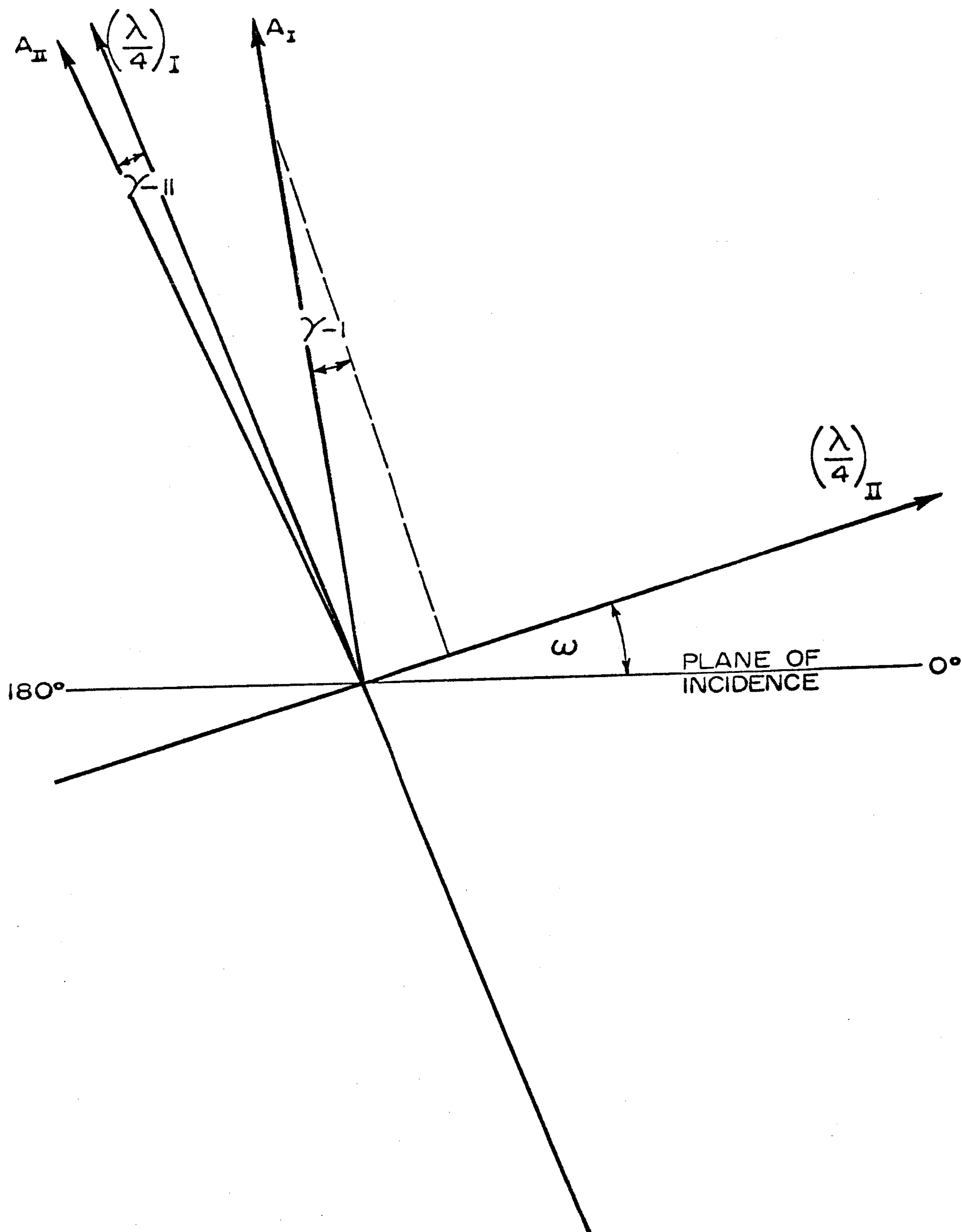
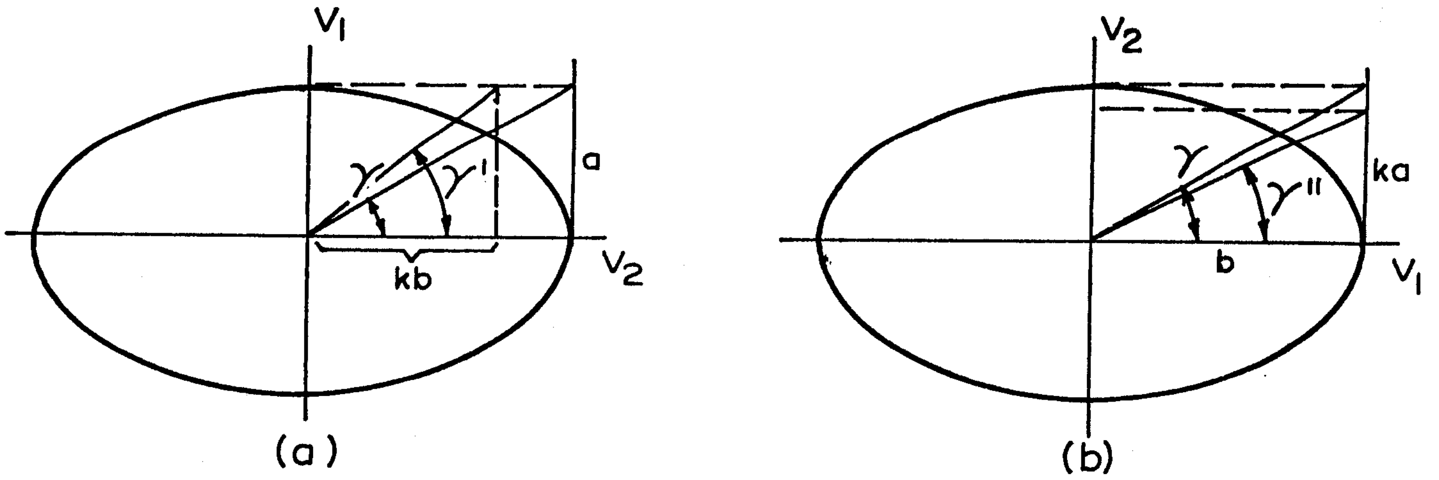


Fig. 4



v_1, v_2	Principal directions of $\lambda/4$ plate
a, b	Semi minor and major are of the ellipse
k	ratio of the absorption coefficients along the principal direction of Q.
γ	the true ellipticity
γ', γ''	the observed ellipticity at Q_α and $Q_{90} + \alpha$

From the values Δ and ψ , δ can be determined using the calculations described in the previous report. Introducing $n_1 = 1.460$, $n_0 = 1.00$, $\phi_o = 70°$ we get the value for the thickness d

$$d = 2100Å \quad (+ m \times 2448Å)$$

In this way, the applicability and the limitations of the method using $\lambda/4$ plate in the sequence $P_{45}\ S\ Q_{0-360}\ A_{0-360}$ was checked.

The observed variations in the intensity with the position of the analyser, at various settings of the quarter wave plate are shown in Fig. 6. It is seen the observed accuracy is only about ±0.5°.

(b) Arrangement $P_{0-360}\ Q_{45}\ S\ A_{0-360}$

In this arrangement the $\lambda/4$ plate cancels the ellipticity due to the reflection from the sample and the light after reflection is plane polarized. P and A are simultaneously rotated till the absolute minimum of intensity has been found.

Then $$\Delta = 90° - 2P \qquad (3)$$

$$\psi = -A \qquad (4)$$

where P and A are the angles of polarizer and analyser settings respectively.

In this case the method is more accurate since the $\lambda/4$ plate remains at a fixed position and hence the pleochroism of the $\lambda/4$ plate will not affect the results, particularly when we are considering the relative variations in Δ and ψ. Fig. 7 shows a representative observed variation of the intensity with the position of the polarizer, for various settings of the analyser. For

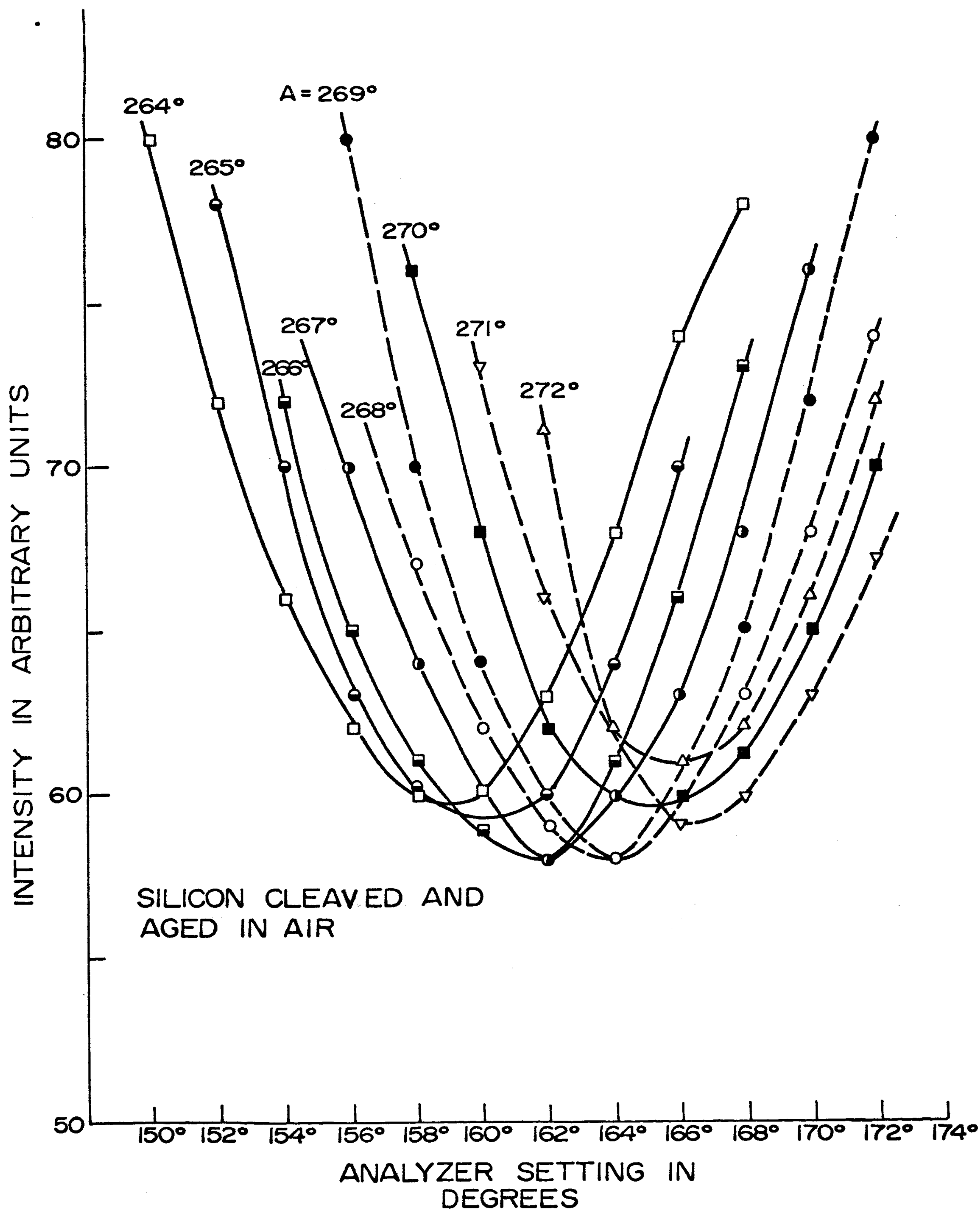


Fig. 6

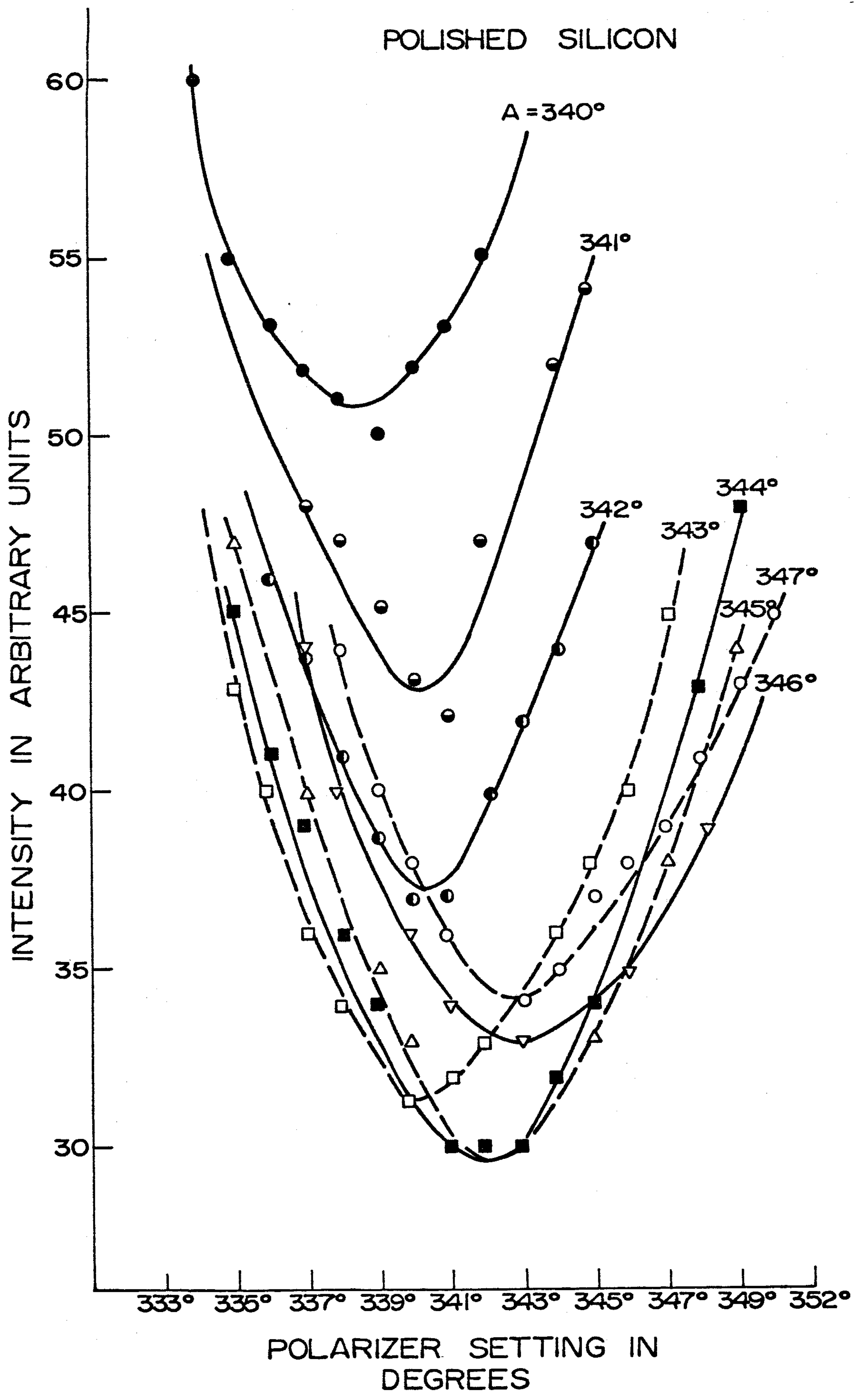


Fig. 7

large thicknesses of the film, the observed accuracy of $\pm 0.1°$ is quite sufficient and for very small thicknesses of the film the accuracy is mainly limited by the instrument i.e. $\pm 0.01\%$, particularly when one employs the symmetrical position method.

III. THEORETICAL

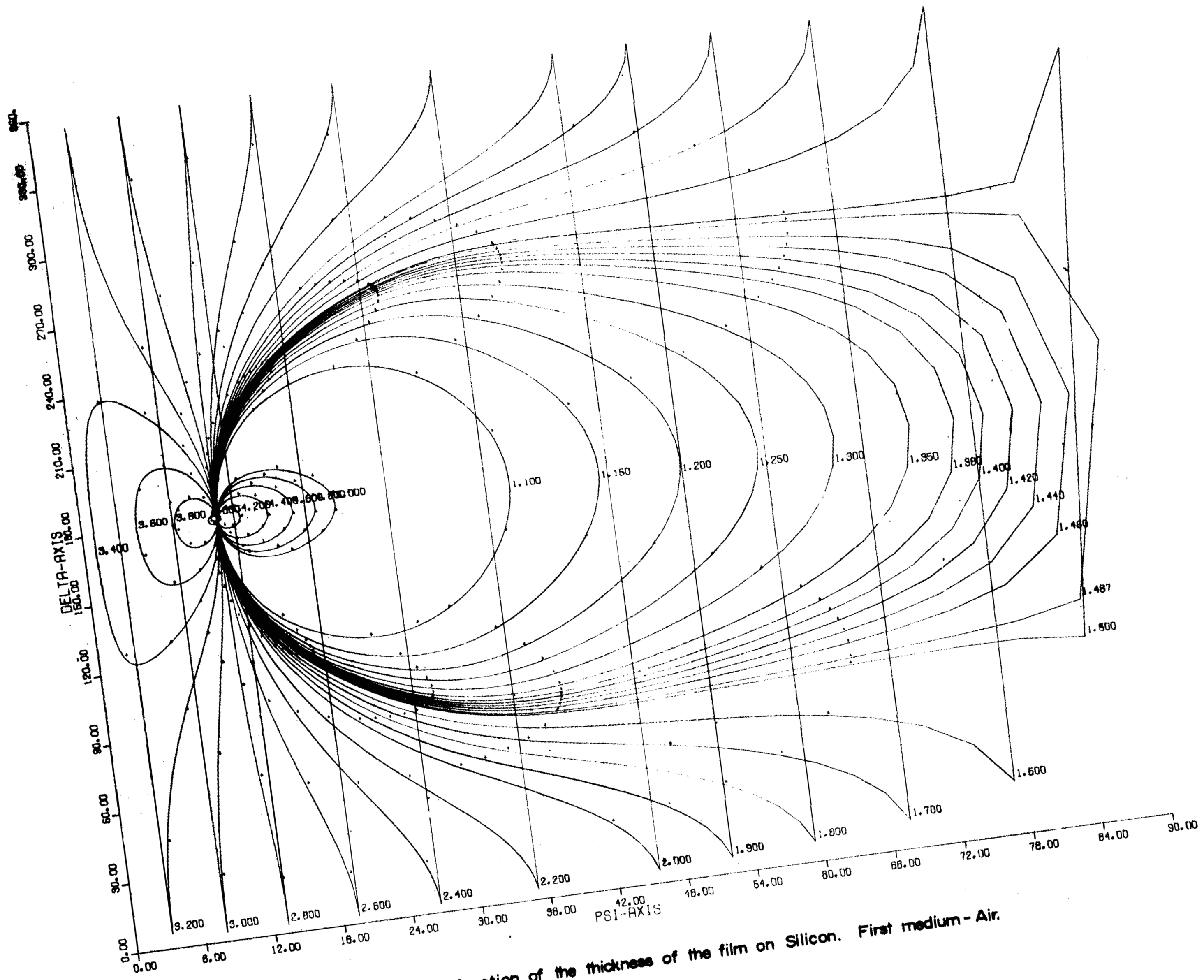
Ultraclean surfaces of silicon can be prepared by cleaving silicon in an inert liquid like carbon tetrachloride and the studies on the oxidation kinetics can be carried out by bubbling oxygen through the liquid and following the changes in Δ and Ψ. In such a case light is incident from the liquid on to the surface of the film. The refractive index of the liquid can often be greater than the refractive index of the film, as indeed is the case of CCl_4 and SiO_2 film combination.

Thus far all the theoretical and experimental investigations have been carried out only for the case when the light is incident from air on to the film i.e. from a rarer on to a denser medium. When the first medium is denser than the film we have to consider two possibilities (i) when the angle of incidence ϕ_o is less than the critical angle ϕ_c and (ii) when the angle of incidence ϕ_o is greater than the critical angle ϕ_c.

Case (i): In this case Drude's exact equations can be used with the help of the computer program described in the last report, after suitably substituting the refractive index of the liquid for the refractive index of air. Such calculations have been made for different values of the refractive index of the liquid in the range 1.38 to 1.60, to yield values of Δ and Ψ for different values of δ and for different values of the refractive index of the film in each case. Fig. 8 is a representative graph for the case of carbon tetrachloride as the first medium. For an angle of incidence of 70°, the minimum value of the refractive index of the film satisfying the condition of case (i) is 1.380. The corresponding graph for the case when the first medium is air is also given in Fig. 9.

Δ and ψ as a function of the thickness of the film on Silicon. First medium - CCl_4.

Fig. 8



Δ and ψ as a function of the thickness of the film on Silicon. First medium - Air.

Fig. 9

It is seen from Fig. 8 that Δ and Ψ are very sensitive to small changes in δ for vanishing film thickness, near the critical angle. For example when the refractive index of the film n_1 is 1.380, a change in δ from 0 to 2° causes a change in Δ of 70° and a change in Ψ of 7.6°. In comparison if the first medium were air for the same change in δ the change in Δ is only about 8.4° and the change in Ψ is only about 0.1°. This indicates that one can attain a sensitivity 10 times that obtained so far by other workers, by a proper choice of a liquid for the first medium.

So far in all the investigations it has not been <u>strictly</u> possible to determine the refractive index <u>and</u> the thickness of the film individually. The use of a liquid as the first medium opens up a possibility of such individual determinations. By varying the refractive index of the liquid slightly and working near the critical angle one can determine the refractive index <u>and</u> δ (and thus the thickness of the film) individually. This would lead to a critical testing of the validity of the assumptions that the refractive index of a surface layer is the same as that of the bulk material.

<u>Case (ii)</u>: When the angle of incidence ϕ_o is greater than the critical angle ϕ_c, total reflection takes place at the liquid-film interface. However a disturbance is propagated inside the film and this decays exponentially. For very small film thicknesses one would expect this disturbance to be reflected from the interface between the film and the substrate and affect the values of Δ and Ψ.

Vasicek[2] has considered this problem for the case when the substrate is a nonabsorbing dielectric medium like glass. But for an absorbing substrate like silicon, the results will be different. Suitable expressions for Δ and Ψ have been derived for such a case as shown below:

Let us consider light incident from a medium of refractive index n_o on a film of refractive index n_1 and let this film lie on a substrate of complex refractive index $\overline{n_2}$. If $n_o > n_1$, and the angle of incidence ϕ_o greater than the critical angle ϕ_c, then the reflection coefficients at the first boundary are

$$r_p' = e^{i\delta_p'} \qquad (1)$$

$$r_s' = e^{i\delta_s'} \qquad (2)$$

where δ_p' and δ_s' are given by

$$\tan\tfrac{1}{2}\delta_s' = (n_o^2\sin^2\Phi_o - n_1^2)^{1/2}/n_o\cos\Phi_o \qquad (3)$$

and

$$\tan\tfrac{1}{2}\delta_p' = \frac{n_o^2}{n_1^2}\tan\tfrac{1}{2}\delta_s' \qquad (4)$$

We have to use the Fresnel's formulae

$$r_p e^{i\delta_p} = \frac{r_p' + r_p'' e^{-iX}}{1 + r_p' r_p'' e^{-iX}} \qquad (5)$$

$$r_s e^{i\delta_s} = \frac{r_s' + r_s'' e^{-iX}}{1 + r_s' r_s'' e^{-iX}} \qquad (6)$$

where

$$X = -i\frac{2\pi}{\lambda}\cdot 2d\,(n_o^2\sin^2\Phi_o - n_1^2)^{1/2} = -2iX' \qquad (7)$$

and d is the thickness of the film.

To calculate r_p'' and r_s'' let us take the limiting case $x = 0$

In this case the medium of refractive index n_o is in direct contact with medium of complex refractive index $\bar{n}_2$ and the reflection coefficients $r_p^o e^{i\delta_p^o}$ and $r_s^o e^{i\delta_s^o}$ are given by

$$r_p^o e^{i\delta_p^o} = \frac{\bar{n}_2 \cos \Phi_o - n_o \cos \bar{\Phi}_1}{\bar{n}_2 \cos \Phi_o + n_o \cos \bar{\Phi}_1} \qquad (8)$$

$$r_s^o e^{i\delta_s^o} = \frac{n_o \cos \Phi_o - \bar{n}_2 \cos \bar{\Phi}_1}{n_o \cos \Phi_o + \bar{n}_2 \cos \bar{\Phi}_1} \qquad (9)$$

$$\bar{n}_2 \cos \bar{\Phi}_1 = \sqrt{\bar{n}_2^2 - n_o^2 \sin^2 \Phi_o} = \bar{n}_2 \cos \bar{\Phi}_1 - i n_2 k_2 \qquad (10)$$

Hence
$$r_p^o e^{i\delta_p^o} = \frac{e^{i\delta_p'} + r_p''}{1 + e^{i\delta_p'} r_p''} \qquad (11)$$

Hence
$$r_p'' \left[r_p^o e^{i(\delta_p^o + \delta_p')} - 1 \right] = e^{i\delta_p'} - r_p^o e^{i\delta_p^o} \qquad (12)$$

$$r_p'' = - e^{i\delta_p'} \frac{\left[1 - r_p^o e^{i(\delta_p^o - \delta_p')}\right]}{\left[1 - r_p^o e^{i(\delta_p^o + \delta_p')}\right]} \qquad (13)$$

Similarly for r_s''

$$r_s'' = - e^{i\delta_s'} \left[\frac{1 - r_s^o e^{i(\delta_s^o - \delta_s')}}{1 - r_s^o e^{i(\delta_s^o + \delta_s')}} \right] \qquad (14)$$

Now for an arbitrary thickness d of film,

$$r_p e^{i\delta_p} = \frac{e^{i\delta_p'} - e^{i\delta_p'} \dfrac{[1 - r_p^o e^{i(\delta_p^o - \delta_p')}]}{[1 - r_p^o e^{i(\delta_p^o + \delta_p')}]} e^{-iX}}{1 - e^{i\delta_p'} e^{i\delta_p'} \dfrac{[1 - r_p^o e^{i(\delta_p^o - \delta_p')}]}{[1 - r_p^o e^{i(\delta_p^o + \delta_p')}]} e^{-iX}} \tag{15}$$

or

$$r_p e^{i\delta_p} = \frac{e^{i\delta_p'}\left[(1 - r_p^o \exp i(\delta_p^o + \delta_p')) - e^{-X'}(1 - r_p^o \exp i(\delta_p^o - \delta_p')\right]}{[1 - r_p^o e^{i(\delta_p^o + \delta_p')}] - e^{-X'}[1 - r_p^o e^{i(\delta_p^o - \delta_p')}]e^{i2\delta_p'}} \tag{16}$$

$$r_s e^{i\delta_s} = \frac{e^{i\delta_s'}\left[(1 - r_s^o \exp i(\delta_s^o + \delta_s')) - e^{-X'}(1 - r_s^o \exp i(\delta_s^o - \delta_s'))\right]}{[1 - r_s^o e^{i(\delta_s^o + \delta_s')}] - e^{-X'}[1 - r_s^o e^{i(\delta_s^o - \delta_s')}]e^{i2\delta_s'}} \tag{17}$$

Since

$$\tan\Psi \, e^{i\Delta} = \frac{r_p}{r_s} e^{i(\delta_p - \delta_s)} \tag{18}$$

one can evaluate ψ and Δ from equations 16, 17 and 18.

Currently a computer program is being written to solve for Δ and ψ from these equations.

IV. REFERENCES

1. G. W. Gobeli and F. A. Allen. Jour. Phys. Chem. Solids 14, 23 (1960).

2. A. Vasicek. "Optics of Thin Films" North Holland Publishing Company, Amsterdam 1960, p. 365.

V. CONCLUSIONS AND RECOMMENDATIONS

It appears to be more advantageous to carry out ellipsometric measurements with a liquid as the first medium and working near the critical angle of incidence on the film. This technique would also possibly provide us unabmiguously with the values of the refractive index of the film which at present is assumed by all workers to be the same as that of bulk material.

It is recommended that the work be allowed to proceed along the lines outlined above.

VI. PERSONNEL

Besides the Principal Investigator* the following persons are working on this project:

Dr. V. Prosser, Senior Research Associate, 1/4 time.

Mr. R. Rai, Graduate Assistant, 1/2 time.

Dr. R. Srinivasan, Senior Research Associate, even though not supported by this agency, has been assisting this project in its theoretical aspects. The many hours of fruitful discussions as well as his unstinting help is hereby gratefully acknowledged.

*K. Vedam, Associate Professor of Solid State Science.