Spectrophotometric studies of ultra low loss optical glasses III: ellipsometric determination of surface reflectances

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Abstract The method of measurement of low loss glasses by the comparison of the transmission through two samples of different length requires that the difference in reflection losses between samples be known. It has been shown that polished glass develops a surface layer with optical properties different to the bulk. Ellipsometry is used to assess the surface properties. This paper describes the development of an ellipsometer which has the refinements necessary for such measurements where small absolute ellipticities from low reflectance surfaces are observed. Discussion of the experimental procedure and precautions are included.

1 Introduction

The interest in glass fibre optical communication systems has given rise to the need for glasses with absorption coefficients of the order of 0·0001 cm^{-1}. To identify these glasses in bulk form special measuring instruments have been developed (Kao and Davies 1968, Jones and Kao 1969). The method of measurement involves the comparison of the transmission through two samples of different lengths. It is therefore necessary that the difference in reflection losses between the samples be known.

It has been shown (Vasicek 1936, Yokoto *et al.* 1964) that polished glass develops a surface layer with optical properties different from those of the bulk. Knowledge of the refractive index and thickness of this 'polish layer' allows direct calculation of the reflectance of the surface. It is to be expected that unless considerable care is exercised in preparing polished surfaces significant differences may occur. Investigations (Kinosita 1965, Vasicek 1947) undertaken to measure the optical properties of the polished layer with regard to polishing procedure and surface deterioration tend to confirm this.

Ellipsometry has been used to assess the surface properties of the samples in order to deduce the reflection losses. This paper describes the development of an ellipsometer which has the refinements necessary for such measurements where small absolute ellipticities from low reflectance surfaces are observed. Discussion of the experimental procedure and precautions are included.

2 Ellipsometry theory

Ellipsometry (Zaininger and Revesz 1964) is essentially the measurement of the state of polarization of polarized light after reflection. The instrument used, an ellipsometer, is shown schematically in figure 1.

Reflection from a film-covered surface may be conveniently expressed in terms of the Fresnel coefficients for the two plane-wave components having their electric field vectors vibrating parallel (r_p) and perpendicular (r_s) to the plane of incidence. For isotropic media the ratio of the reflectances for the two components (Heavens 1955) is given by:

$$\frac{R_p}{R_s}=\frac{r_{12p}+r_{23p}\,e^{-2i\delta}}{1+r_{12p}\,r_{23p}\,e^{-2i\delta}}\;\frac{1+r_{12s}\,r_{23s}\,e^{-2i\delta}}{r_{12s}+r_{23s}\,e^{-2i\delta}}$$

where subscripts 1, 2 and 3 refer to the surrounding medium, surface film and bulk material respectively (figure 2), r_{abp} and r_{abs} are the Fresnel coefficients with $a=1$ or 2, $b=2$ or 3.

For absorbing media the refractive indices n are complex, as are the angles of propagation ϕ within the media. Absorption in the materials studied here is considered insignificant.

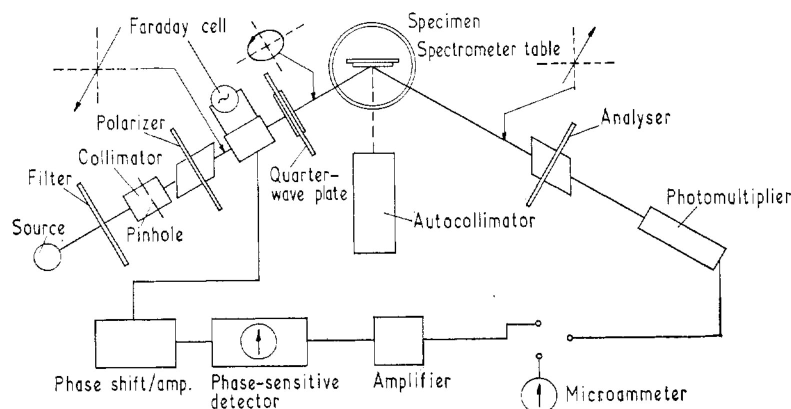

Figure 1 Diagram of the ellipsometer

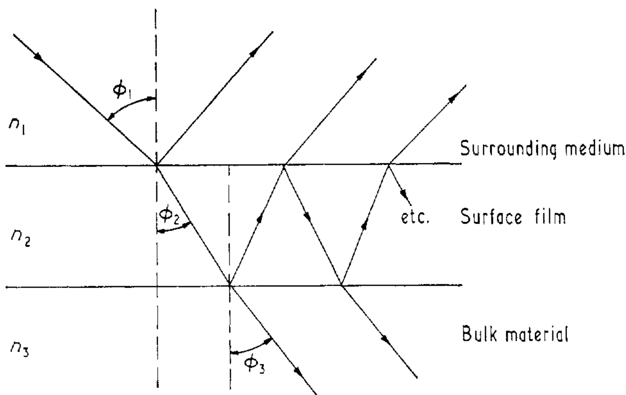

Figure 2 Reflection and refraction of light at a planar surface film on a bulk material

The change in phase δ of the beam traversing the layer is given by:

$$\delta = \frac{2\pi d}{\lambda} n_2 \cos \phi_2 = \frac{2\pi d}{\lambda} (n_2{}^2 - \sin^2 \phi_1)^{1/2}$$

where d is the layer thickness in the same units as the wavelength λ.

Since $r_{12s} \neq r_{12p}$ and $r_{23s} \neq r_{23p}$, the components of the incident beam that are perpendicular and parallel to the plane of incidence suffer unequal amplitude and phase changes upon reflection. The state of polarization, after reflection, is elliptical. The ratio R_p/R_s is a complex quantity and may be written in the form

$$\frac{R_p}{R_s} = \tan \psi \, e^{i\Delta}. \quad (1)$$

$\tan \psi$ represents the change in the amplitude ratio of the two plane-wave components on reflection and Δ their relative phase change. Equation (1) can be considered as the fundamental equation of ellipsometry. The quantities Δ and ψ are deduced from ellipsometer measurements.

It may be emphasized that the ellipticity introduced by a film-covered surface is a function of the refractive index of the surrounding medium (n_1) and the substrate (n_3), the vacuum wavelength λ, the angle of incidence ϕ_1 and the refractive index n_2 and thickness d_2 of the film.

3 Ellipsometer

The components of the ellipsometer are shown schematically in figure 1. The source is imaged at the pinhole, followed by a lens to produce a collineated beam. Iris diaphragms are situated through the system to define the beam size and facilitate alignment. Wavelength selection is by interference filters situated before the polarizing prism. The polarizer and the analyser are identical; both consist of a Glan–Thomson prism in a divided circle. The collineated polarized beam passes through a Faraday cell and a quarter-wave plate compensator. The Faraday cell has a strain-free dense flint glass core and anti-reflection coatings on each face. A magnetic field, produced within the solenoid, along the axis of the core rotates the plane of polarization of an incident linearly polarized beam. Modulation of the beam by a 50 Hz a.c. input to the cell is used to improve the measurement sensitivity. The quarter-wave plate is mounted, normal to the beam, before reflection. This compensator may be rotated, the fast axis normally being set at 45° to the plane of incidence. The reflecting surface under investigation is mounted at the centre of the divided circle of a spectrometer table. Adjustments are provided to set the surface normal to the incident beam, after which the angle of incidence is selected by rotating the sample table. The spectrometer arm carrying the analyser and detector travels about the centre of the spectrometer table to collect the reflected beam. The photomultiplier detector has a suitable gain and response at the required wavelengths. The detector output is monitored directly by a microammeter and by using a phase-sensitive detector. Measurements of the orientations of polarizer and analyser at extinction are used to calculate the ellipticity.

This instrument has been modified from the one described by Claussen and Flower (1963) to achieve a specification for determining small absolute ellipticities on low-reflectance surfaces. The specification adopted is adequate for obtaining results which are required for the loss measurements.

4 Measurement procedure

Of the number of possible experimental methods for characterizing elliptically polarized light, a compensator in fixed azimuth before reflection has been used here.

The polarizer and analyser orientations at the extinction position are noted (P_1, A_1) and the polarizer rotated through $\pm 90°$ to determine a second extinction position (P_2, A_2) as above. The two measurements are made where the compensator is other than an exact quarter-wave plate. Subject to the quarter-wave plate not exhibiting dichroism, $P_1 = P_2 \pm 90°$.

The angles P_1, P_2, A_1 and A_2 are measured with respect to the plane of incidence. They are considered positive if an anti-clockwise rotation would be seen by an observer looking at the source along the direction of propagation. Δ and ψ are calculated from the following equation:

$$\tan \Delta = \sin \delta \cot 2P$$
$$\cos 2L = -\cos \delta \cos 2P$$
$$\tan \psi = -\cot L \tan A_1 = -\tan L \tan A_2$$
$$\tan^2 \psi = \tan A_1 \tan A_2$$

where δ is the actual retardation of the compensator the value of which provides a check on the consistency of measurements. A computer program is available to process experimental data where Δ, ψ, δ and the real imaginary parts of R_p/R_s, are calculated and printed out.

The plane of incidence is the reference plane of measurements and is determined by the method due to McCrakin *et al.* (1963) to $\pm 0{\cdot}002°$.

5 Calculation procedure

The ellipsometry equation (1) for the ratio R_p/R_s derived earlier for a film-covered surface, is transcendental in Δ and ψ. It cannot be solved explicitly for the refractive index and thickness of a surface layer. Since no justifiable assumption can be made for either parameter of the polish layer on glass, to simplify the equations, a numerical or graphical solution must be sought. The availability of electronic computers readily allows this to be carried out to any specified accuracy. A numerical method has been described (McCracken *et al.* 1963) and a computer program based upon this is available (McCracken and Colson 1964). This program has been modified to provide a suitable output. The computed results are analysed further by a graphical method, and that adopted here is to plot the real and imaginary parts of the ratio R_p/R_s, on an Argand diagram. Both the film refractive index and thickness may then be deduced by comparison with a theoretical net calculated as a function of thickness, for a range of likely film refractive indices. The program modification mentioned above provides the theoretical real and imaginary points. Theoretical curves originate from the point of zero film thickness, which corresponds to the state of polarization that would be observed from the substrate or bulk material alone. For a glass substrate exhibiting no absorption the

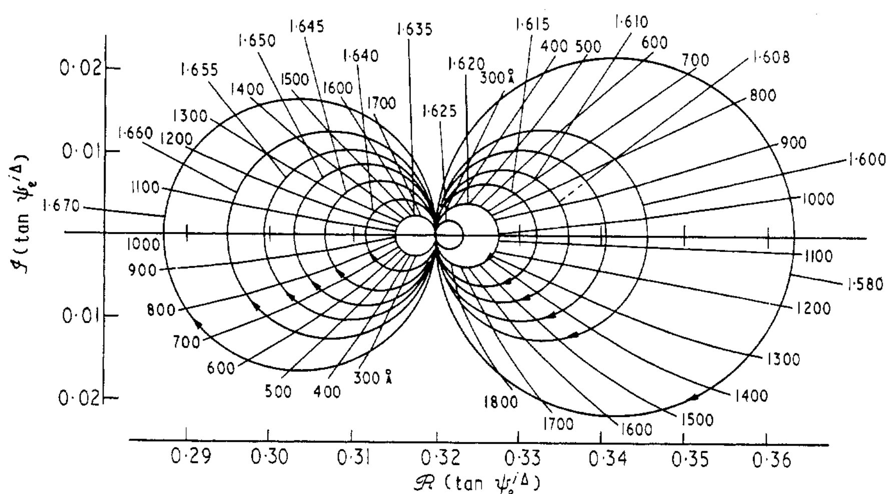

Figure 3 Theoretical net for surface layer on glass

curves originate on the real axis, i.e. $\Delta = 0$. For a non-absorbing layer the curves form closed figures, one complete cycle corresponding to one wavelength transit in the surface layer. Absorption in the layer causes the curves to spiral to a point corresponding to the state of polarization of an infinitely thick film. The polish layer on optical glass is a case of non-absorbing film on non-absorbing substrate. A theoretical net is as shown in figure 3, the arrows indicating the direction of increasing thickness.

6 Experimental errors

Investigation of experimental errors led to final design of the instrument; both of these are discussed below.

6.1 *Alignment*

The angle of incidence is a parameter used for generating the theoretical nets and will affect the absolute accuracy. An uncertainty of 0·5 minute of arc corresponds to a change of the real part of R_p/R_s of 0·0002 for a typical case of F.7 glass with 70° angle of incidence. For other glasses and angles of incidence the exact value can be calculated using the computer program.

Divergence on the beam causes some difficulty in determining the angle of incidence. It affects the sensitivity of alignment and the signal amplitude. Otherwise the effect on the absolute accuracy is negligible if the divergence is symmetric. ± 3 minutes of arc giving a final beam size of 5 mm is a good compromise.

Since the extinction position of the analyser is determined by averaging the orientations, giving an equal intensity either side of the minimum transmission position, any variation in the source output reduces the accuracy of this measurement. The sensitivity of the determination is governed by the available signal at the detector. A light source of high brightness is necessary.

These criteria led to the use of a stable, high intensity source, careful collineation and a standard procedure for sample alignment. The use of an autocollimator rigidly mounted to view the sample face allows alignment to better than 1 minute of arc nominal but is not better than $\pm 5'$ absolute. This procedure allows for the inaccuracies of the spectrometer table and the source element movement for relative measurement. This is expedient in minimizing the cost of the equipment. The normalizing techniques adopted (described in §7) allow absolute measurement to be obtained.

To cover the wavelengths 775 nm and 900 nm, a continuous source is chosen. This is a tungsten ribbon filament lamp (108 w), which is run from a constant current/voltage supply giving 1 in 10^4 stability after a 30 minute warm-up period. The light from the source is collected by a F.2·8, 28 mm camera lens (the lens is achromatic over the wavelength spectrum concerned) and focused to a 200 μm pinhole. The pinhole is used as a secondary source. An F.3·5, 35 mm camera lens is used to produce the collineated beam.

6.2 *Detector*

For a suitable response and gain in the wavelength range 775–900 nm, a photomultiplier with an S1 photocathode was chosen. The tube is supplied by a stabilized e.h.t. unit. The anode current from the tube is monitored directly by a microammeter or switched through a load resistor from which the a.c. modulation introduced by the Faraday cell may be amplified and the null position determined using a phase-sensitive detector. The time constant of 1 second was chosen to give a high signal-to-noise ratio.

6.3 *Bandwidth*

Intensity considerations precluded the use of very narrow-band interference filters. The effect of bandwidth on accuracy was investigated. This is estimated by calculating the uncertainty for a particular case of film on F/7 at 775 ± 20 nm and 900 ± 20 nm. The result indicates that ± 20 nm wavelength spread gives an uncertainty of the order of 0·0002 at a thickness of less than 300 Å. The bandwidth varies with the angle of incidence to the plane of the filter. With the filter inserted into the system at $\pm 5°$ from normal, this error is again negligible.

The displacement of the beam through the filter is significant. It can produce an angle of incident uncertainty. However, with the normalizing technique this influence is compensated.

6.4 *Bulk refractive index*

The refractive index of the bulk material is a further parameter that must be known before any conclusions can be drawn about the surface layer. With the data from which experimental results may be interpreted the index must be known accurately to four places for the uncertainty to be within experimental error.

The refractive index of the material may be measured using appropriate techniques to a high degree of accuracy, say to five decimal places. The values used in this paper, however, are determined from published data and extrapolated to the wavelengths concerned by using an established formula.

6.5 *Polarizing prisms*

The setting of the polarizing prism can produce an error in the angle of incidence should the prism be set with the prism

face other than normal to the incident beam. By using the normalizing procedure this error is minimized as the polarizer setting for both fused silica and the sample on test is within a few degrees.

The Glan–Thomson prisms used for both polarizer and analyser are mounted in a divided circle which may be read directly to 0·01° with estimation to 0·002°. With a correctly aligned system the precision of extinction settings is ±0·002° for the polarizer. It is expected that if phase-sensitive detection is applied to the analyser, similar precisions to that of the polarizer may be possible. Polarizer and analyser scales track to ±0·002° over 360°.

6.6 *Faraday cell*

The modulation waveform applied to the Faraday cell must produce equal deviation of polarization for the positive- and negative-going half-cycle, otherwise an unbalanced signal would result at the true balance. This was checked by observing the null without a.c. modulation and noting that the modulating waveform is free from harmonic distortion and the d.c. polarization swing of the Faraday cell is symmetric.

A dense flint glass core with Verdet constant of 0·15 min^{-1} G^{-1} cm^{-1} and a low stress optical constant is used.

6.7 *Quarter-wave plate*

The characterization of elliptically polarized light is readily achieved by the use of a compensator, usually with 90° retardance, i.e. a quarter-wave plate. Well-known relationships exist between the orientations of the linearly polarized light vector and the principal axes of the compensator. It has been shown that compensators with retardance other than quarter-wave will produce or compensate any ellipticity by suitable orientation. It has been shown that differential absorption along the principal directions and multiple reflection within compensators can lead to errors, but these can be considered negligible for small ellipticities and not at a resonant frequency.

The compensator used here is a mica quarter-wave plate at 1000 nm mounted between glass plates. The assembly is rotatable about the direction of propagation to provide the setting of the orientation of the principal axis of the plate. The plate may be set to ±0·002°.

6.8 *Surface preparation*

In order to reduce errors due to surface contamination in the samples a standard cleaning routine is adopted. Considerable care is exercised with all samples, especially to avoid touching the polished surfaces. Before measurements are made the faces are lightly washed in Teepol and water and thoroughly rinsed in de-ionized water. Finally, the faces are vapour degreased in A.R. acetone for 1½–2 hours. Samples are stored between measurements in a low-humidity cabinet over silica gel.

7 Interpretation of results

The double-beam spectrophotometer (Jones and Kao 1969) is constructed to measure attenuations of the order of 5 dB km^{-1} in samples differing in length by 15–20 cm. The difference in loss by reflection between the samples for such measurements is not to be greater than 0·01%. Ellipsometer measurements are made at 775 nm and 900 nm within the range of the spectrophotometer.

Results are shown for measurements on both faces of a long and a short sample. The material is Schott F.7 glass. The interpretation of these graphical results is presented in table 1. Figure 4 shows the theoretical plots constructed for F.7 at 775 nm together with those for fused silica from which these results are deduced.

The results show that the surface film of silica is of higher refractive index than the bulk, i.e. the experimental point has a negative imaginary component. It is noted that the points lie off the theoretical curve. This can indicate that the theoretical curves are calculated for an angle of incidence different from that used during the actual measurement. Assuming that the optical thickness of the film is small ($nd < 20$ nm) (R J King, private communication), it is possible to estimate the shift in the angle of incidence required to bring the experimental point on to the calculated curve. Using this shift, theoretical curves can be constructed for the glass measurement corresponding to the correct experimental angle of incidence. For convenience, since the form of the curves depends only on the bulk refractive index and wavelengths, whereas the origin of thickness depends only upon the angle of incidence, it is permissible to shift the experimental point by the appropriate amount.

It can be seen that by this normalizing technique the measured points for F.7 glass do fall on the appropriate curves. This offers a justification for the assumption that the optical thickness of the film on silica is small. Since the imaginary part of the silica measurement is small, any error

Table 1 Polished layers on samples of f/7 glass and effect of reflectances

Wavelength (nm)	Sample and end	Polished layer n	Polished layer dA	Calculated normal reflectance R (%)	Total reflectance (%)	Difference (%)
775	Short 1	±0·01 1·50 −0·01	160 ±10	5·52±0·022	10·82±0·03	
Bulk n 1·61508	Short 2	+0·01 1·52 −0·02	190 ±10	5·40±0·028		0·10±0·03
	Long 1	+0·01 1·50 −0·02	140 ±10	5·45±0·02	10·92±0·025	
	Long 2	+0·01 1·50 −0·01	120 ±10	5·47±0.015		

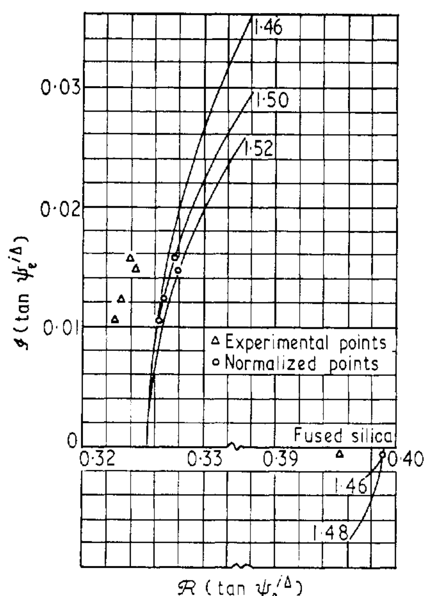

Figure 4 Section of theoretical nets for glass

introduced will also be small. Previous measurements on fused silica surfaces, which indicated the surface layer to be thin (~200 Å) and of refractive index higher by 0·005 than the bulk, tend to confirm this.

The precision of measurements on replacing silica samples is ±0·0002 for the real and imaginary parts. This leads to an accuracy for the reflectance difference for the F.7 samples of ±30%. It must be emphasized that the figure placed on the accuracy is specific to a sample with the given resolution of the instrument. It may be seen from the theoretical nets that this figure depends largely on the optical thickness (*nd*) of the surface layer.

The ratio R_p/R_s, converted to film thickness and refractive index by the graphical analysis, is then used to calculate the reflectance. It is to be noted that the theoretical curves for refractive index and film thickness are derived by assuming the existence of a discrete film of certain thickness and uniform refractive index. In the actual polished sample the film is likely to be a layer with varying refractive index. Thus it is assumed that the graded or varying refractive index layer can be replaced by an equivalent layer of constant refractive index and that the reflectance produced is identical.

8 Conclusions

An ellipsometer which has the refinements necessary for the measurements of small absolute ellipticities from low reflectance surfaces has been developed. The major design criterion distinguishing this instrument is the provision of a source detection combination which has the required sensitivity to enable the full accuracy of polarizer and analyser setting to be used. The relative accuracy is high, tending to a reflectance uncertainty of approximately 5×10^{-5} for a typical polished glass surface. The absolute accuracy depends on the absolute mechanical setting of the instrument and can only be achieved directly by improving the precision of the mechanical structure. An alternative way is adopted for this instrument using a normalizing technique. This involves the calibration of this instrument setting by using a fused silica standard, resulting in a high absolute accuracy to about 3×10^{-4} for a typical polished glass surface.

It is to be emphasized that the accuracy of the measurement is specific to a sample. It may be seen from the theoretical curves that this depends very much on the optical thickness of the surface film and the substrate refractive index. The smaller the optical thickness the less accurate the measured figure. However, since the reflectance is the important parameter for this application, this loss of accuracy is not too serious.

The measured results showed that a surface film existed on the glass samples concerned. The two samples were polished on different occasions and the measurements indicated that the surfaces were not identical. The two ends of the same sample appeared to have similar finish.

For spectrophotometric measurement of these two samples the difference of the reflectances was approximately 10% of the bulk loss difference. This amount of error is acceptable. For lower loss samples the surface preparation must be further controlled. The simultaneous polishing of each end of both samples could give the required consistency. The instrument resolution of 5×10^{-5} gives a systematic error of about 5% for a pair of samples of 20 cm length difference with a bulk loss of 20 dB km^{-1}.

Acknowledgments

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