

## The Birefringence Modulator Method

An isotropic (fused silica) glass slab of thickness  $d$  (1cm) is set into longitudinal oscillation at its resonance frequency  $\omega_0$  where the wavelength of vibration is  $2L$ , with  $L$  the length of the slab. The periodic uniaxial strain  $s(\omega_0)$  which is produced in the center of the slab gives a periodic change in the refractive index for light polarised parallel to the oscillation direction, and this leads to a periodic variation  $\Delta n(\omega)$  in the refractive index difference for light polarised parallel and perpendicular to the oscillation direction given by

$$\Delta n(\delta, \omega_0) = \alpha s(\omega_0) \quad 1$$

with  $\alpha$  the piezo-optic constant. This strain-induced birefringence gives a phase shift between the light polarised in the two directions of

$$\delta(\omega_0) = 2\pi \Delta n d / \lambda = \delta_0 \sin(\omega_0 t) \quad 2$$

where  $\lambda$  is the wavelength of light.

### Optical Arrangement

Jaspersen and Schnatterley first used the birefringence modulator ellipsometer in association with their studies of optical properties of solids. Subsequently Beaglehole found this ellipsometer ideally suited to the study of small effects observed on liquid surfaces, and in that form the Picometer Ellipsometer is now finding extensive use, due to its high sensitivity, stability and ease of use. The Picometer has three components, Polariser P, Birefringence modulator BM placed before the sample, and Analyser.

The incident Polariser is usually oriented at  $45^\circ$  to provide equal  $s$  and  $p$  amplitudes, but in general at an angle  $P$ . The BM is oriented with the oscillation axis in the  $p$  direction, and introduces the phase shift  $\delta$  between the  $p$  and the  $s$  directions. The sample follows with complex amplitude reflectivities  $r_s$  and  $r_p$  and ratio  $r = r_s / r_p = \rho e^{i\Delta}$ .

The Analyser follows, usually oriented  $\pm 45^\circ$  but in general at angle  $A$ .

The intensity varies as

$$I = I_o \rho_s^2 \cos^2 A \cos^2 P \{1 + \rho'^2 + 2\rho' \cos(\Delta + \delta)\} \quad 3$$

where

$$\rho' = \tan A \tan P \rho \quad 4$$

Introducing the modulator time varying phase shift  $\delta$  and expanding the  $\cos(\Delta + \delta)$  sum we obtain three terms, a dc term (no time variation), a term with frequency  $\omega_o$ , and a term with frequency  $2\omega_o$ . These two signals are measured by the 50kHz and 100kHz lockins, and when the signals are normalised by the zero frequency (dc) signal then (assuming  $A = P = 45^\circ$ )

$$Y = \frac{\omega_o}{dc} = - \frac{4J_1(\delta_o) \text{Im}(r)}{1 + \rho^2 + 2J_o(\delta_o) \text{Re}(r)} \quad 5$$

$$X = \frac{2\omega_o}{dc} = \frac{4J_2(\delta_o) \text{Re}(r)}{1 + \rho^2 + 2J_o(\delta_o) \text{Re}(r)}$$

Other orientations of the Analyser and Polariser are given by the same equations if the substitution of equation 4 is made.

These expressions look complicated, but simplify in practice. The Bessel Functions  $J_o(\delta_o)$ ,  $J_1(\delta_o)$  and  $J_2(\delta_o)$  are shown in Figure 2.1. If  $\delta_o$  is adjusted to about 2.4 radians where  $J_o$  is zero,  $J_1$  and  $J_2$  are not far from their maximal values, and the denominator in the equations 5 simplify.

Near the Brewster angle for transparent substrates  $\rho$  is small; for metal substrates  $\rho \sim 1$ , but near the Brewster angle  $\text{Re}(r) = 0$ .

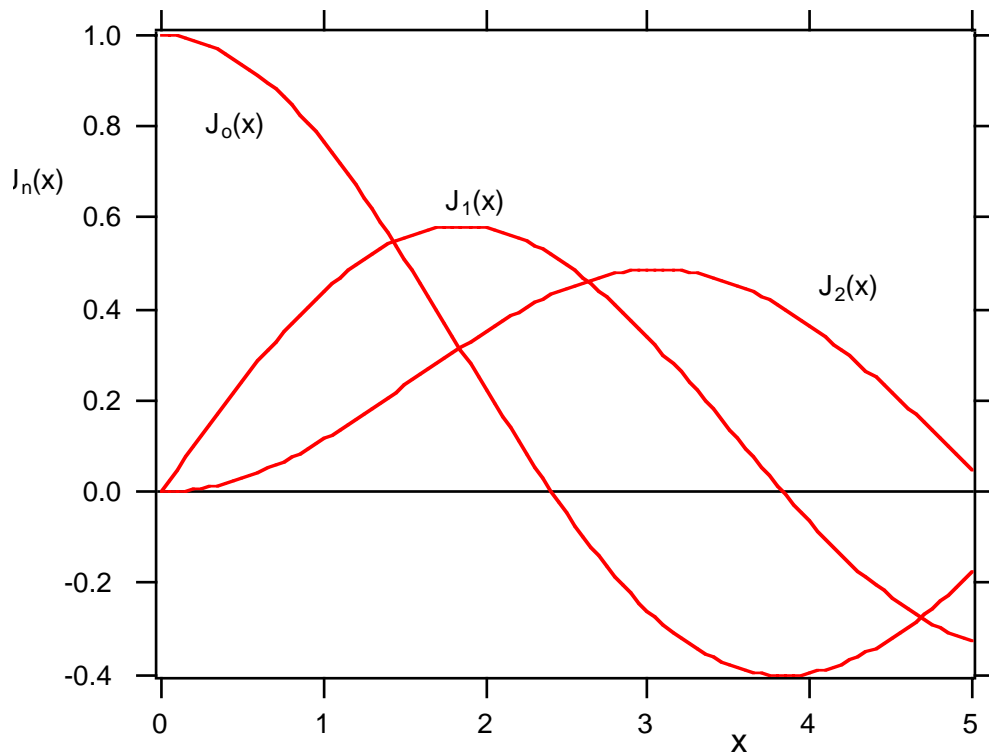


Figure 2.1 The integer Bessel functions  $J_n(x)$  for  $n = 0, 1$  and  $2$  versus  $x$ . Note zero in  $J_0(x)$  at approximately  $x = 2.4$ .

### Optical Calibration

In direct transmission with  $\tan A = \tan P = 45^\circ$ ,  $J_0 = 0$ , we have  $\rho = 1$  and  $\Delta = 180^\circ$ . Then  $\text{Im}(r) = 0$ , and  $\text{Re}(r) = -1$ . The Y signal is zero in principle, but stray instrumental phase shifts can be present, see below. The measured X signal is  $X_{\text{cal}} = \pm 2J_2(\delta_0)$ .

With a quarter wave plate inserted in the optical beam with its fast axis in the p direction,  $\tan A = \tan P = 1$ ,  $J_0 = 0$ , then  $\rho = 1$  and  $\Delta = 90^\circ$ , and the  $\omega/\text{dc}$  signal ratio =  $Y_{\text{cal}} = \pm 2J_1(\delta_0)$ .

In measurements near the Brewster angle  $\rho \sim 0$ , and  $Y = \pm 4J_1(\delta_0) \text{Im}(r)$ , and  $X = \pm 4J_2(\delta_0) \text{Re}(r)$ . Thus approximately

$$\text{Im}(r) = Y/2Y_{\text{cal}}, \text{ and } \text{Re}(r) = X/2X_{\text{cal}}. \quad 6$$

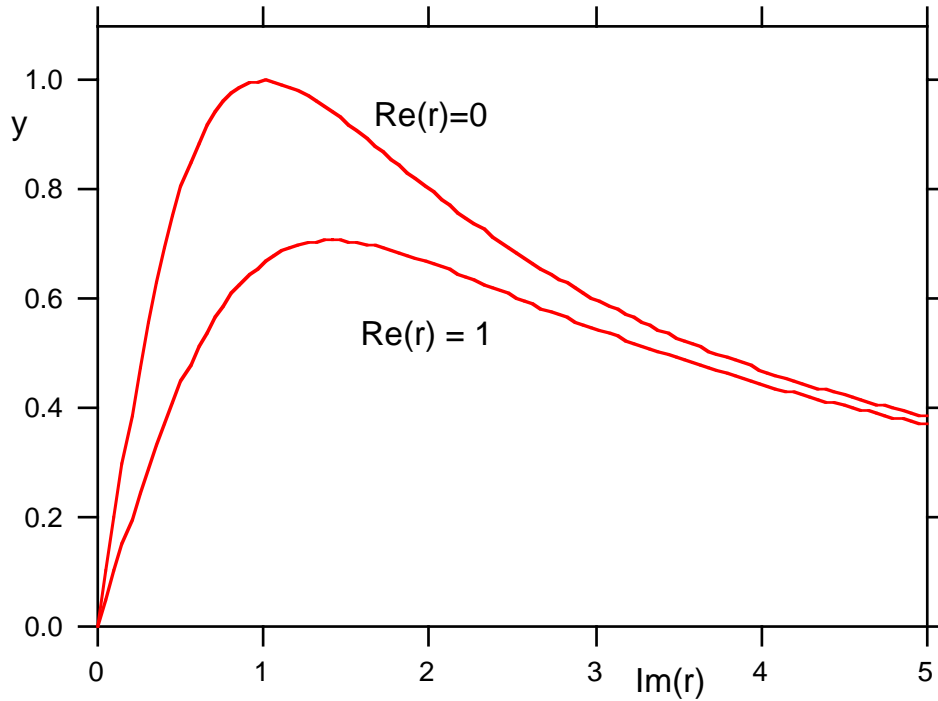


Figure 2.2 Variation of  $y$  with  $\text{Im}(r)$ . Note the linear relation at small  $\text{Im}$ , with a second root for a given value of  $y$  at large  $\text{Im}$ .

When  $\rho$  is not small the full expressions must be used:

$$y = Y/Y_{\text{cal}} = 2 \text{Im}(r) / (1+\rho^2),$$

$$x = X/X_{\text{cal}} = 2 \text{Re}(r) / (1+\rho^2), \quad 7$$

with  $\rho^2 = \text{Re}^2(r) + \text{Im}^2(r)$ . The signals become less sensitive to  $\rho$  as  $\rho$  increases, so it is preferable to choose a configuration where one or other of these is small. The equations can be inverted to give  $\text{Re}(r)$  and  $\text{Im}(r)$ .

$$i = \text{Im}(r) = \frac{y (1 \pm \sqrt{1 - (x^2 + y^2)})}{(x^2 + y^2)}$$

$$r = \text{Re}(r) = \frac{x (1 \pm \sqrt{1 - (x^2 + y^2)})}{(x^2 + y^2)}$$

The variation of  $x$  and  $y$  with  $\text{Re}$  and  $\text{Im}$  are shown in Figure 2.2. For small  $x$  and  $y$  we use the negative root. On the occasions that  $x$  and / or  $y$  are large there is a possibility of moving to the positive root. If uncertainty is present, then the  $\tan A \tan P$  product can be reduced to bring the signal into the small range.

## Reflection of light and ellipsometry theory

In this section we describe ellipsometry, and the operating principles of the Picometer ellipsometer

Light reflected from uniform surfaces is characterised by two reflection amplitudes  $r_p$  and  $r_s$ , the first for light polarised in the p direction, which is in the plane of incidence, and the second for light polarised in the s direction which is perpendicular to the plane of incidence (and parallel to the surface) see Figure 1.1. It is necessary to decide upon a convention for the positive directions of the incident and reflected electric fields, and various authors use different conventions. The conventions are shown in the figure. Which is the most sensible? At normal incidence  $\theta = 0$  there is no way to distinguish between the s and p directions, since with both the electric fields lie in the surface. It is natural to choose  $r_p = r_s$  for this angle of incidence; taking the reflected s field parallel to the incident s field also seems natural. Thus we use the convention 2 shown in Figure 1.1b.

Fig 1.1a

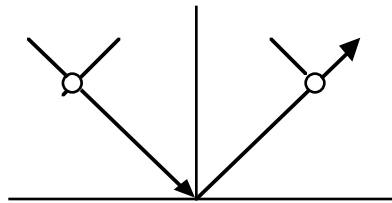
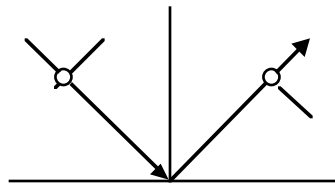


Fig 1.1b



There are further differences between authors in the convention used for the description of the

propagating electric field. Some use  $e^{i(k.z-\omega t)}$ , some use  $e^{i(\omega t-kz)}$ . This produces a sign difference in the complex part of the refractive index. We use  $n_c = n + ik$ , while some others use  $n_c = n - ik$ . A similar sign difference occurs for the complex dielectric constant.

The ellipsometry method compares the p reflected field with the s reflected field, thus eliminating the necessity of measuring separately the incident intensity and the reflected intensity, which is done in reflectivity measurements. In ellipsometry the comparison is made by polarising the incident beam so that it has two coherent s and p waves, whose amplitude and phase are then altered by reflection. The reflected light becomes elliptically polarised. Formally, we measure the complex ratio of amplitude reflectivities for p and s polarised electromagnetic waves

$$r = \frac{r_p}{r_s} = \text{Re}(r) + i \text{Im}(r) \quad 1$$

Good discussions of ellipsometry theory are given by Azzam and Bashara, *Ellipsometry and Polarised Light* (North Holland 1977) and by Lekner, *Theory of Reflection* (Nordhoff 1989). A review on liquid application is given in *Interfacial Fluid Phenomena*, ed C.A.Croxton, Chapter 11, (D.Beaglehole, Experimental Studies of Liquid Interfaces).

## Reflection at the surface of a homogeneous isotropic medium

Fresnel's equations, usually seen written in terms of the angles of incidence and propagation, can be written

$$r_s = \frac{(q_1 - q_2)}{(q_1 + q_2)} \quad r_p = -\frac{(Q_1 - Q_2)}{(Q_1 + Q_2)} \quad 2$$

Here  $q_1$  and  $q_2$  are the normal components of the wavevector in the incident medium labeled 1 and the reflecting medium labeled 2. We have

$$q_1 = \frac{\omega}{c} \sqrt{\epsilon_1} \cos \theta_1 \quad Q_1 = q_1 / \epsilon_1 \quad \text{etc} \quad 3$$

$\epsilon$  is the relative dielectric constant of the medium, given in terms of the refractive index by  $\epsilon = n^2$ .

The locus of  $r$  can be calculated as a function of the angle of incidence. Light which enters a transparent dielectric passes through with no attenuation, and the electric field wave vector in medium 2 is real. With reflecting or absorbing materials the electric field is attenuated in the passage into the material, and the wavevector becomes complex, the complex part being a measure of the attenuation. Thus the refractive index  $n$  and dielectric constant  $\epsilon$  are both real for transparent materials, while they both become complex for attenuating materials; equations 2 and 3 likewise become complex. The locus of  $r$  as a function of the angle of incidence are shown in Figure 1.2 for the cases of silicon and gold. Note for both cases  $r$  starts from  $r = 1$  at normal incidence, and proceeds to  $r = -1$  at grazing incidence  $\theta = 90^\circ$ , passing through  $\text{Re}(r) = 0$  at an angle of incidence we call the Brewster angle.

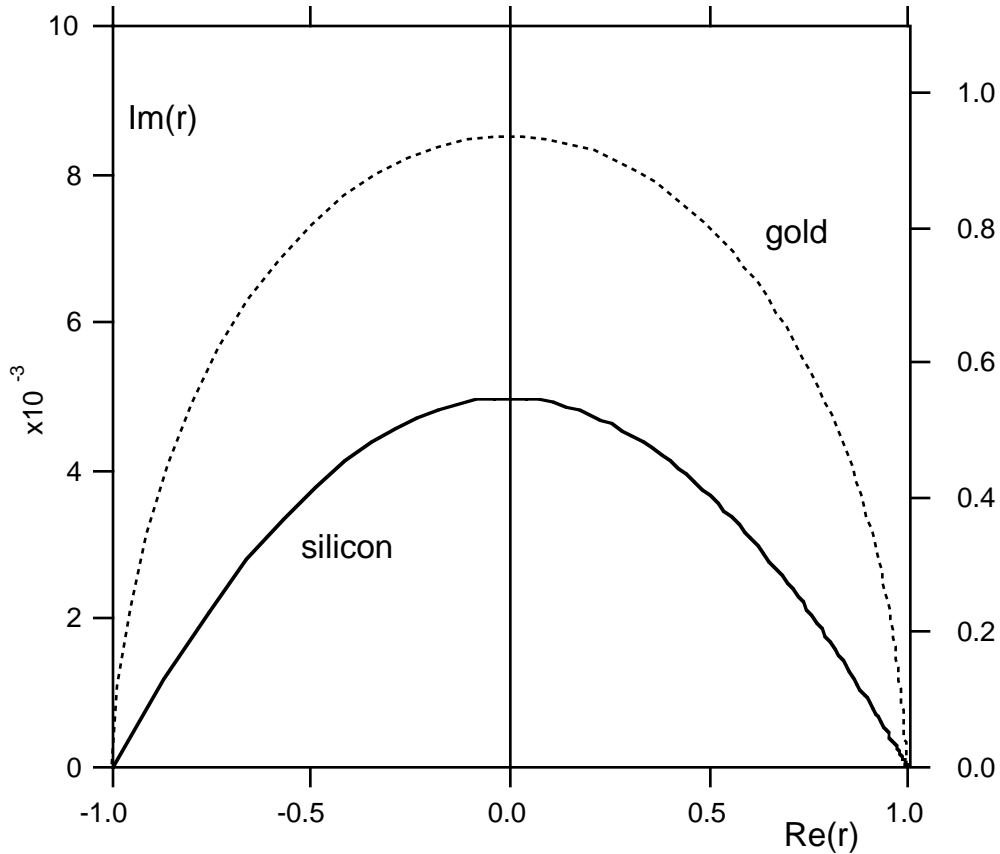


Figure 1.2 Locus of  $\text{Im}(r)$  versus  $\text{Re}(r)$  as the angle of incidence varies from  $0^\circ$  ( $\text{Re}(r) = 1$ ) to  $90^\circ$  ( $\text{Re}(r) = -1$ ), for gold (right axis) and silicon (left axis).

The locus changes with the other conventions, for instance

$$\Delta(\text{Azzam}) = 180^\circ - \Delta \quad n-ik,$$

$$\Delta(\text{Aspnes}) = -\Delta \quad n+ik.$$

Note that for non-transparent materials there is usually a large  $\text{Im}(r)$  at the Brewster angle, positive for reflecting metals (in our convention). (Silicon in the red is only weakly absorbing, and  $\text{Im}(r)$  is  $\sim 0.001$  at the Brewster angle.)

An alternative notation is often used

$$r = \rho e^{i\Delta} = \tan\psi e^{i\Delta} \quad 4$$

$\rho$  is the length of the vector joining the origin and the point  $r$  in the complex plane, and  $\Delta$  is the phase angle, measured from the positive real axis. Traditionalists use  $\psi$  and  $\Delta$  to represent  $r$ .

Inversion takes the experimental parameters  $\text{Re}(r)$ ,  $\text{Im}(r)$  and  $\theta$  and from these derives the optical

$$\frac{\epsilon_2}{\epsilon_1} = s^2 + s^2 t^2 \left( \frac{1+r}{1-r} \right)^2 \quad 5$$

where  $s = \sin\theta_1$  and  $t = \tan\theta_1$ . In terms of the real and imaginary parts of  $\epsilon_2$  using the notation  $r_r = \text{Re}(r)$ ,  $r_i = \text{Im}(r)$ ,

$$\frac{\epsilon_r}{\epsilon_1} = s^2 + s^2 t^2 \frac{(1-r_r^2 - r_i^2)^2 - 4r_i^2}{((1-r_r)^2 + r_i^2)^2} \quad 6$$

$$\frac{\epsilon_i}{\epsilon_1} = s^2 t^2 \frac{4(1-r_r^2 - r_i^2)r_i}{((1-r_r)^2 + r_i^2)^2}$$

### Horizontally uniform medium with thin surface layers

Drude first considered this type of surface, which occurs for instance at a liquid - vapour interface. The density of molecules makes a smooth transition from the vapour to deep within the liquid;  $\epsilon(z)$  becomes a function of the normal coordinate  $z$ . The transition layer induces a phase shift between the s and p waves, which makes  $r$  complex even for transparent liquids. For thin transition layers or thin surface films of arbitrary profile the first order change  $O(t/\lambda)$  in the reflection properties is determined by the quantity  $\eta$  (in Drude's notation, or script I ( $= -\eta$ ) in Lekner's notation) which is given by

$$\eta = \int dz \frac{(\epsilon - \epsilon_1)(\epsilon - \epsilon_2)}{\epsilon} \quad 7$$

where the integral is taken through the interface. For instance the  $\text{Im}(r)$  at the Brewster angle is given by

$$\text{Im}(r) = \bar{\rho} = \frac{\pi \sqrt{(\epsilon_1 + \epsilon_2)}}{\lambda (\epsilon_1 - \epsilon_2)} \eta \quad 8$$

while the  $\text{Re}(r)$  is not affected (to first order). Just this one quantity determines all the first order changes at all angles of incidence.

For thin uniform layers one can take  $\epsilon$  as constant through the layer thickness  $d$ , and use the same expression for  $\eta$ .

It is often thought that ellipsometry can give both the thickness and refractive index of a layer. For thin transparent layers or transition regions on transparent surfaces this is not the case. One can only determine  $\eta$ . With absorbing media however  $\eta$  is complex and thin layers affect both the  $\text{Im}(r)$  and  $\text{Re}(r)$  providing additional information.

Quite often the dielectric constant of the surface layer  $\epsilon$  is close to that of the substrate. Then  $\eta$



$$\eta = \frac{(\epsilon_2 - \epsilon_1)}{\epsilon_2} \int dz (\epsilon - \epsilon_2) = \frac{(\epsilon_2 - \epsilon_1)}{\epsilon_2} \Gamma_\epsilon \quad 9$$

where  $\Gamma_\epsilon$  is the total surface excess dielectric constant. (The same form of approximation can be made when  $\epsilon$  is close to  $\epsilon_1$ .) So for transparent media it is possible to obtain  $\Gamma_\epsilon$  accurately, even though the thickness and dielectric constant cannot be separately determined.  $\Gamma_\epsilon$  is directly to the total Gibbs Adsorption.

In the case of uniaxial surface anisotropy the expression for  $\eta$  becomes

$$\eta = \int dz (\epsilon_x + \epsilon_1 \epsilon_2 / \epsilon_z - \{\epsilon_1 + \epsilon_2\}) \quad 10$$

with  $\epsilon_x$  and  $\epsilon_z$  being the dielectric constant components of the layer in the x (normal to the plane of incidence) and z (normal to the surface) directions, so that

$$\eta = \Gamma_a + \eta(\epsilon_z) \quad 11$$

where the function  $\Gamma_a$  is the "anisotropy excess"  $\Gamma_a = \int dz (\epsilon_x - \epsilon_z)$  and  $\eta(\epsilon_z)$  is the  $\epsilon_z$  excess.

The ellipsometry properties of anisotropic substrates involves other expressions for  $\eta$ , see Lekner, *Theory of Reflection*, and Lekner, *J.Phys.Cond Matter* **4** (1992) 6569.

In practice weakly absorbing materials such as silicon act effectively as transparent dielectrics, having only a small value of  $\text{Im}(r)$  at  $\theta_B$ . Thin oxide layers on the surface of silicon add to the background value for  $\text{Im}(r)$  at the Brewster angle. Changes in  $\text{Im}(r)$  due to a layer are still given by the function above.

When the substrate is highly reflecting (a metal) then  $\text{Im}(r) \sim 1$  at  $\theta_B$ . Thin layers cause a change in  $\text{Re}(r)$  which is linear in layer thickness up to  $100\text{\AA}$  or so. Again the complete layer equation can be used to take into account non-linearities.

Lekner has obtained explicit expressions for  $\epsilon$  and  $d$  in terms of  $\theta$ ,  $\text{Re}(r)$  and  $\text{Im}(r)$  for transparent layers on transparent substrates.

### **Thick layers: angle of incidence and spectroscopic studies**

When transparent layers are thick interference between light reflected from the front ( $r_1$ ) and back  $r_2$  surfaces of the layer interfere. The equation for the s and p reflectivities become

the ellipticity locus follows a circle, and shows a periodic interference pattern, for simple transparent dielectrics, of (approximately) circles in the complex plane, Figure 1.3 a and b. If the layer is absorbing the wavevector is complex and the locus decays with thickness, moving to the point in the complex plane characteristic of an infinitely thick layer.

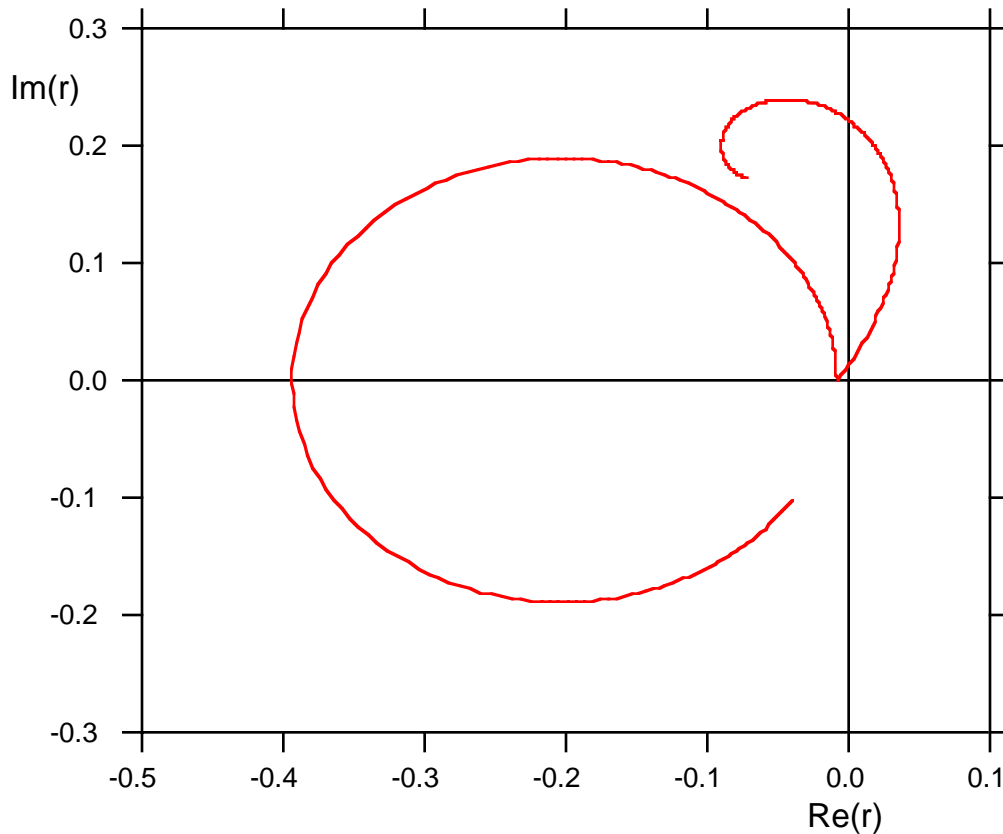


Figure 1.3 Variation of  $\text{Im}(r)$  versus  $\text{Re}(r)$  for a layer on glass, starting near the Brewster angle ( $\text{Re}(r) \sim 0$ ), of increasing thickness anticlockwise until  $d = 2.5$ , where  $d$  is the reduced thickness  $d = t \cdot 2\pi/\lambda$ . Ellipse dielectric constant = 1.8, spiral an absorbing medium with dielectric constant (1.8,1). Glass dielectric constant 2.5.

The wave-vector in the layer can also be changed at fixed layer thickness by altering the angle of incidence. Oscillations in the ellipticity are observed imposed on the general angle of incidence variation of the substrate. For a layer the period of rotation in the complex plane ( $2qd$  in equation 11) varies with angle of incidence, and this allows one to remove the uncertainty in the thickness modulus one period.

Alternatively the wavelength of light can be changed showing interference patterns for varying colours. This method is the basis of Spectroscopic Ellipsometry. If everything remained transparent throughout the wavelength range then there would be little advantage to this type of study. However if one can move into a region where the layer is absorbing, then there is a dramatic effect on the ellipticity which is very useful in eliminating the uncertainty associated with the periodicity in the transparent

region. It becomes possible to unravel the thicknesses of multilayers if one knows the optical properties of each layer.

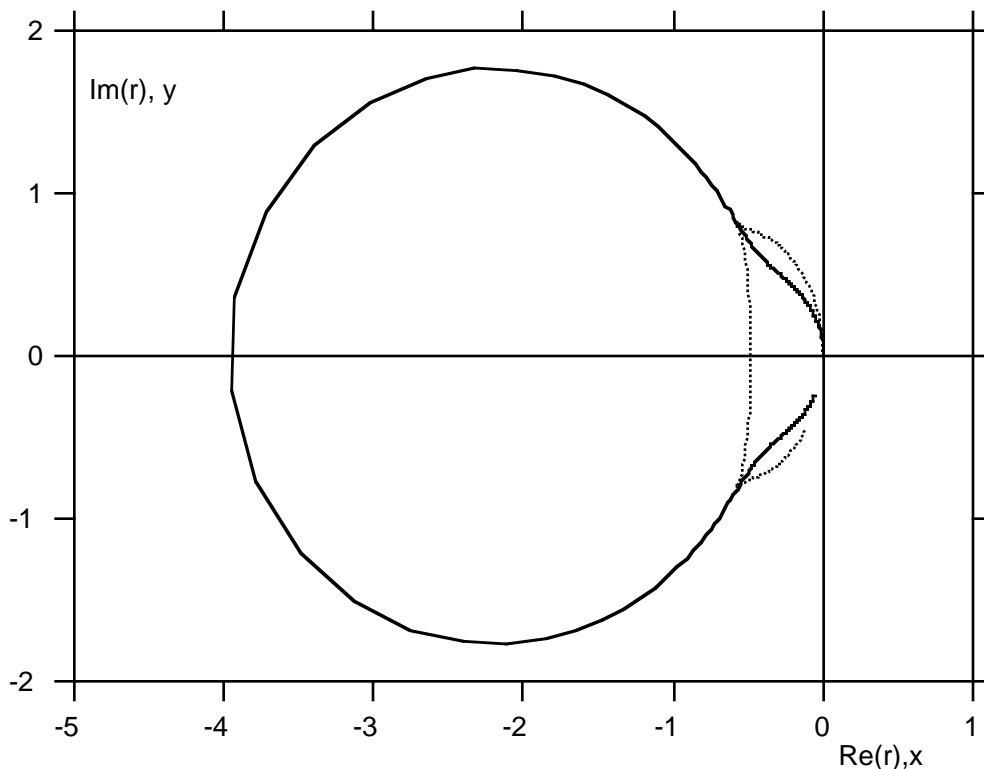


Figure 1.4  $\text{Im}(r)$  vs  $\text{Re}(r)$  for an oxide on silicon at the Brewster angle. Note the unusual feature of very large values for both  $\text{Re}(r)$  and  $\text{Im}(r)$ , which arise from small values of  $r_s$  in the ratio  $r_p / r_s$ .  $d$  varies between 0 to 2.5. The dotted line shows the variation of  $y$  versus  $x$ , see Chapter 2.

An interesting special case is for a thin layer between two like media. In this case it turns out that both  $\text{Re}(r)$  and  $\text{Im}(r)$  are always zero at the Brewster angle.

## Reflectivities

Intensity measurements near normal incidence give  $R = r r^*$ . Note when  $\theta = 0$  using a bare substrate

$$r_s = r_p = \frac{(n_1 - n_2)}{(n_1 + n_2)} \quad 12$$

Thin transition layers produce second order changes in the reflectivity, so reflectivity measurements are inherently less sensitive than ellipticity measurements. Interference effects are observed for the reflectivities of thick layers, just as for ellipticity of thick layers.