Ellipsometry of surface films on a uniform layer

John Lekner

Department of Physics, Victoria University of Wellington, Wellington, New Zealand

Received November 19, 1987; accepted March 3, 1988

A perturbation theory is used to construct general expressions for the s and p reflection amplitudes off a uniform layer with adsorbed thin films on one or both sides. In a special case (identical media on both sides of the sample, and at the Brewster angle for the uniform layer), calculations indicate a stable ellipsometric signal, provided that the thickness of the uniform layer is within a broadly defined range. (Uniform here means homogeneous and of constant thickness.)

1. INTRODUCTION

In a recent paper, Beaglehole[1] posed the problem of the ellipsometry of thin nonuniform (stratified) films on an otherwise uniform layer. (The film may be either on the illuminated side or on the back of the uniform layer, or there may be films on both sides, if we generalize the Beaglehole formulation somewhat.) When the uniform layer is transparent and thin relative to the beam width (e.g., 10 μm), as, for example, with thin sheets of mica dipped into a solution, "the reflection from the back surface could not be separated from that of the front, or removed by roughening of the back surface. Since the resulting interference effects cause dramatic changes in the locus of r_p/r_s in the complex plane, it was not evident that there remained any sensitivity to the properties of the front surface." This quotation is from the paper by Beaglehole,[1] who showed by numerical calculations for uniform films that in the neighborhood of the Brewster angle the locus is displaced along the imaginary axis by an amount of the order of that which would be measured if the substrate were semi-infinite.

We examine this problem theoretically here, treating the inhomogeneous thin films or adsorbates as a perturbation. The configuration under discussion is shown in Fig. 1. In Section 2 we derive formulas for the changes δr_s and δr_p in the reflection amplitudes that are due to the presence of the thin films, and thus the change in the ellipsometric ratio $\rho = r_p/r_s$. The general formulas are simplified considerably in the special case discussed in Section 3, namely, $\epsilon_a = \epsilon_b$ and ρ measured at the Brewster angle for the uniform film. We use an example to illustrate this case in Section 4.

2. CHANGES IN r_s and r_p CAUSED BY THE THIN FILMS

A plane electromagnetic wave, propagating in the zx plane, is incident from medium a, at an angle of incidence θ_a, upon the system shown in Fig. 1. The exact s-wave reflection amplitude r_s is related to the reflection amplitude r_{s0} of the uniform layer (designated by the dashed lines in Fig. 1) by the comparison identity[2,3]

$$r_s = r_{s0} - \frac{\omega^2/c^2}{2iq_a}\int dz(\epsilon - \epsilon_0)EE_0, \tag{1}$$

where ω is the angular frequency of the wave, c is the speed of light in vacuum, and q_a is the component of the wave vector normal to the interface in medium a, given by $cq_a/\omega = \epsilon_a^{1/2}\cos\theta_a$. The dielectric functions $\epsilon(z)$ and $\epsilon_0(z)$ are the permittivities of the actual and the bare layers divided by the permittivity of free space; they are represented by the solid and dashed lines in Fig. 1. The electric fields in the two cases are $E(z)$ and $E_0(z)$ times the amplitude of the incident electric field, times $\exp[i(Kx - \omega t)]$, where K is the (invariant) wave-vector component along the interface. If the adsorbed films are thin compared with the wavelength of the incident light, then the actual electric field E is approximated well by E_0, and we have

$$\delta r_s \equiv r_s - r_{s0} \approx \frac{-\omega^2/c^2}{2iq_a}\int dz(\epsilon - \epsilon_0)E_0^{\,2}. \tag{2}$$

In general there are two contributions to the integral in relation (2), from the two thin regions near $z = z_a$ and $z = z_b$ where $\epsilon(z)$ deviates from $\epsilon_0(z)$. To lowest order in the film thickness, the function $E_0(z)$ in these two regions is approximated by E_a and E_b, these being equal to the values of E_0 calculated at z_a and z_b. From Ref. 3, Sec. 2-4, or Ref. 4, Sec. 4.3, we find that

$$E_a \equiv E_0(z_a) = \exp(iq_a z_a)\,\frac{(1 + s_a)(1 + s_b Z)}{1 + s_a s_b Z}, \tag{3}$$

where $Z = \exp(2iq\Delta z)$ and where

$$s_a = \frac{q_a - q}{q_a + q}, \qquad s_b = \frac{q - q_b}{q + q_b} \tag{4}$$

are the s-wave Fresnel reflection amplitudes appropriate to reflection at the discontinuities in the dielectric function at z_a and z_b; q_a, q, and q_b are the z components of the wave vector in medium a, the uniform layer, and medium b, respectively. The unperturbed electric field at z_b is given by a similar formula:

$$E_b \equiv E_0(z_b) = \exp(iq_a z_a)\,\frac{(1 + s_a)(1 + s_b)Z^{1/2}}{1 + s_a s_b Z}. \tag{5}$$

To lowest order in the thickness of the films adsorbed or deposited at z_a and z_b,

0740-3232/88/071044-04$02.00

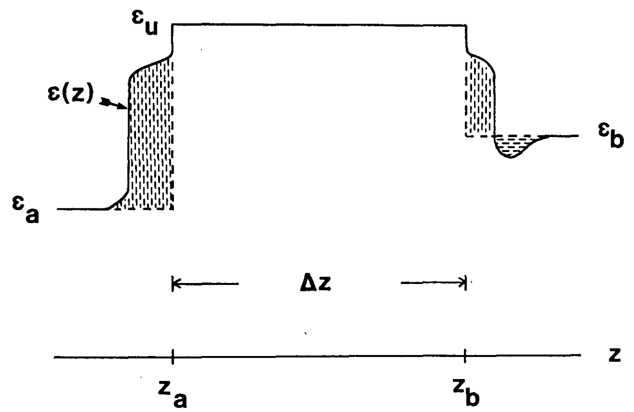

Fig. 1. Uniform layer with a dielectric constant ϵ_u and thickness Δz, with adsorbed or otherwise attached nonuniformities at its boundaries z_a and z_b. The attached thin films are treated here as a perturbation on the uniform layer.

$$\delta r_s = \frac{-\omega^2/c^2}{2iq_a}\{E_a{}^2 l_a + E_b{}^2 l_b\}, \tag{6}$$

where l_a and l_b are integrals over the difference between the actual dielectric function $\epsilon(z)$ (with the adsorbed films) and the dielectric function $\epsilon_0(z)$ representing the bare system (medium a–uniform layer–medium b):

$$l_a = \int_{(a)} \mathrm{d}z(\epsilon - \epsilon_0), \qquad l_b = \int_{(b)} \mathrm{d}z(\epsilon - \epsilon_0). \tag{7}$$

[In Eqs. (7) the integrations extend from $z_a - \delta z_a$ to z_a and from z_b to $z_b + \delta z_b$, respectively, where δz_a and δz_b are the film thicknesses at the a and b boundaries of the uniform layer.]

A similar set of results can be found for the p polarization, starting from the comparison identity [Ref. 5, Eq. (46), or Ref. 3, Eq. (3.42)]

$$r_p = r_{p0} + \frac{1}{2iQ_a}\int \mathrm{d}z\left\{\left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon}\right)K^2 BB_0 + (\epsilon - \epsilon_0)CC_0\right\}, \tag{8}$$

where $Q_a = q_a/\epsilon_a$, the magnetic field is $[0, B(z)\exp i(Kx - \omega t), 0]$, and $C = \mathrm{d}B/\epsilon\mathrm{d}z$. The subscript zero again denotes a quantity relating to the bare system. The change in r_p that is due to the adsorbed films is

$$\delta r_p \equiv r_p - r_{p0} \approx \frac{1}{2iQ_a}\int \mathrm{d}z\left\{\left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon}\right)K^2 B_0{}^2 + (\epsilon - \epsilon_0)C_0{}^2\right\}, \tag{9}$$

and, as before, we can replace B_0 and C_0 by their values at z_a and z_b, namely,

$$B_a \equiv \exp(iq_a z_a)\frac{(1 - p_a)(1 - p_b Z)}{1 + p_a p_b Z}, \tag{10}$$

$$B_b = \exp(iq_a z_a)\frac{(1 - p_a)(1 - p_b)Z^{1/2}}{1 + p_a p_b Z}, \tag{11}$$

$$C_a = iQ_a \exp(iq_a z_a)\frac{(1 + p_a)(1 + p_b Z)}{1 + p_a p_b Z}, \tag{12}$$

$$C_b = iQ_b \exp(iq_a z_a)\frac{(1 - p_a)(1 - p_b)Z^{1/2}}{1 + p_a p_b Z}. \tag{13}$$

Here p_a and p_b are the Fresnel reflection amplitudes at the (bare) interfaces,

$$p_a = \frac{Q - Q_a}{Q + Q_a}, \qquad p_b = \frac{Q_b - Q}{Q_b + Q}, \tag{14}$$

and $Q = q/\epsilon_u$ and $Q_b = q_b/\epsilon_b$. From relation (9), the change in r_p to the lowest order in the thickness of the adsorbed films is

$$\delta r_p = \frac{1}{2iQ_a}\{C_a{}^2 l_a + C_b{}^2 l_b + K^2[B_a{}^2 L_a + B_b{}^2 L_b]\}, \tag{15}$$

where l_a and l_b are as defined in Eqs. (7) and

$$L_a = \int_{(a)} \mathrm{d}z\left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon}\right), \qquad L_b = \int_{(b)} \mathrm{d}z\left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon}\right). \tag{16}$$

All terms in δr_s and δr_p carry the common phase factor $\exp(2iq_a z_a)$, as do the reflection amplitudes r_{s0} and r_{p0}. Thus the observables $R_s = |r_s|^2$, $R_p = |r_p|^2$, and $\rho = r_p/r_s$ are independent of the (arbitrary) value of z_a.

Equations (6) and (15), which give the corrections to the s and p reflection amplitudes to the first order in the thickness of the films, are simple enough in form but difficult for an experimenter to apply because of the dependence on the layer thickness as well as on the other parameters in the problem. In Section 3 we consider a special case that may be useful because of its simplicity.

3. THIN FILMS ON A UNIFORM LAYER BETWEEN LIKE MEDIA

When $\epsilon_b = \epsilon_a$ (the media a and b are optically identical at the experimental frequency), the Fresnel reflection amplitudes at either side of the uniform layer are equal in magnitude and opposite in sign ($s_a = s = -s_b$, $p_a = p = -p_b$), and the reflection amplitudes for the bare layer become

$$r_{s0} = \exp(2iq_a z_a)\frac{s(1 - Z)}{1 - s^2 Z}, \qquad r_{p0} = \exp(2iq_a z_a)\frac{p(1 - Z)}{1 - p^2 Z}. \tag{17}$$

Since p is zero at the Brewster angle $\theta_B = \arctan(\epsilon_u/\epsilon_a)^{1/2}$ (Ref. 6, Sec. 4), $r_{p0} = 0$ at this angle and the real and imaginary parts of $\rho_0 = r_{p0}/r_{s0}$ together pass through zero. At θ_B we have

$$s = \frac{\epsilon_a - \epsilon_u}{\epsilon_a + \epsilon_u}, \qquad \left(\frac{cK}{\omega}\right)^2 = \frac{\epsilon_a \epsilon_u}{\epsilon_a + \epsilon_u}, \qquad \left(\frac{cQ_a}{\omega}\right)^2 = \frac{1}{\epsilon_a + \epsilon_u}, \tag{18}$$

and $B_a = B_b/Z^{1/2} = C_a/iQ_a = C_b/iQ_a Z^{1/2} = \exp(iq_a z_a)$. Thus δr_p becomes

$$[(\omega/c)\exp(2iq_a z_a)/2i(\epsilon_a + \epsilon_u)^{1/2}][\epsilon_a \epsilon_u(L_a + ZL_b) - (l_a + Zl_b)]$$
$$\equiv [(\omega/c)\exp(2iq_a z_a)/2i(\epsilon_a + \epsilon_u)^{1/2}][I_a + ZI_b], \tag{19}$$

where

$$I = \epsilon_a \epsilon_u \int \mathrm{d}z\left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon}\right) - \int \mathrm{d}z(\epsilon - \epsilon_0)$$
$$= \int \mathrm{d}z\,\frac{(\epsilon - \epsilon_a)(\epsilon_u - \epsilon)}{\epsilon} \tag{20}$$

and the subscripts a and b indicate the region of integration. Note that the last integral in Eq. (20) has an analytic form similar to that of the integral invariant I_1, which determines the ellipsometric signal for an inhomogeneous transition layer between two uniform media a and b [see, for example, Ref. 3, Eqs. (3.37) and (3.46)], namely,

$$I_1 = \int dz \frac{(\epsilon - \epsilon_a)(\epsilon_b - \epsilon)}{\epsilon}. \tag{21}$$

From Eqs. (3), (5), and (6) we find that

$$\delta r_s = -\frac{(\omega/c)(\epsilon_a + \epsilon_u)^{1/2} \exp(2iq_a z_a)}{2i\epsilon_a} \frac{(1+s)^2}{(1-s^2Z)^2} \times \{(1-sZ)^2 l_a + (1-s)^2 Z l_b\}. \tag{22}$$

From Eqs. (17), (19), and (22) we find the ellipsometric ratio

$$\rho(\theta_B) = \frac{r_p}{r_s} \approx \frac{\delta r_p}{r_{s0} + \delta r_s} = \frac{\dfrac{\omega/c}{2i(\epsilon_a + \epsilon_u)^{1/2}}(I_a + ZI_b)}{\dfrac{s(1-Z)}{1-s^2Z} - \dfrac{(1+s)^2}{(1-s^2Z)^2}\dfrac{(\epsilon_a + \epsilon_u)^{1/2}\omega/c}{2i\epsilon_a}\{(1-sZ)^2 l_a + (1-s)^2 Z l_b\}}. \tag{23}$$

Note that we have kept the δr_s term in the denominator; we must do so because r_{s0} can be zero. This occurs when $Z = 1$, that is, for $q\Delta z = n\pi$ ($n = 0, 1, 2, \ldots$), which at θ_B happens when

$$\frac{\epsilon_u}{(\epsilon_a + \epsilon_u)^{1/2}} \frac{\omega}{c} \Delta z = n\pi. \tag{24}$$

At such thicknesses, ρ is a ratio of two terms that are each first order in the film thickness; on using $s = (\epsilon_a - \epsilon_u)/(\epsilon_a - \epsilon_u)$, we find that

$$\rho(\theta_B, Z = 1) \approx -\frac{\epsilon_a}{\epsilon_a + \epsilon_u} \frac{I_a + I_b}{l_a + l_b}. \tag{25}$$

At this combination of angle of incidence and thickness of the uniform layer it is thus possible to get a large ellipsometric signal, even for thin films. Note that $\rho(\theta_B, Z = 1)$ is real if the films are nonabsorbing.

Another simple case occurs when $Z = -1$; at θ_B this happens when

$$\frac{\epsilon_u}{(\epsilon_a + \epsilon_u)^{1/2}} \frac{\omega}{c} \Delta z = (n + 1/2)\pi. \tag{26}$$

In this case we can omit the δr_s term and obtain

$$\rho(\theta_B, Z = -1) \approx \frac{\epsilon_a^2 + \epsilon_u^2}{\epsilon_a^2 - \epsilon_u^2} \frac{\omega/c}{2i(\epsilon_a + \epsilon_u)^{1/2}} (I_a - I_b). \tag{27}$$

If similar (or identical) films are adsorbed on either side of the uniform layer, the signal at $Z = -1$ will be very small, owing to the cancellation evident in relation (27). On the other hand, if a film is adsorbed on one side only (say, the illuminated side a), measurements of ρ at $Z = 1$ and $Z = -1$ determine I_a/l_a and I_a, and thus both characteristic integrals can be found.

In general, ρ moves on a complicated path in the complex plane as $Z = \exp(2iq\Delta z)$ moves on the unit circle. Measurements at general thicknesses (at least two in the case of one film, at least four in the case of two films) are needed to extract the integrals I and l by fitting relation (23) to the experimental results. Our experience in comparing relation (23) with exact results for a simple model (discussed in Section 4) indicates that measurements are easiest in the region near $Z = -1$, since there the ellipsometric ratio is least sensitive to the thickness Δz of the uniform layer and to the angle of incidence θ_a. Experimentally, Δz and θ_a can be known only to a certain precision, and it is best to work in a region where small changes in these variables produce zero or small changes in the measured result. Near $Z = 1$ the signal is largest, but most sensitive to the precise value of Z, since the denominator of relation (23) rapidly changes in magnitude as Z passes through 1. Near $= Z - 1$ the magnitude of the denominator of relation (23) is maximum, and although the signal is small, it is stable.

4. EXAMPLE

We compare the theoretical expression (23) with exact calculations for the simple case of uniform thin films attached to either side of a uniform layer. In this example we take dielectric constants corresponding to films of water on glass (with refractive indices 4/3 and 3/2), the system being in air. The water film thicknesses are $(\omega/c)\delta z_{a,b} = 0.05, 0.01$ or vice versa, which corresponds to water layers about 5 and 1 nm thick when $\lambda_a = 633$ nm. The glass thickness Δz is variable in Fig. 2, and the angle of incidence θ_a is variable in Fig. 3.

The exact ρ for this problem can be found by multiplying together the three layer matrices corresponding to the three uniform layers, water–glass–water, as given in Sec. 12-2 of Ref. 3. (An equivalent matrix method, but with imaginary off-diagonal elements, is given in Sec. 1.6.2 of Ref. 7.) For the s and p waves the layer matrices have the form

$$\begin{bmatrix} \cos q\delta z & \dfrac{\sin q\delta z}{q} \\ -q \sin q\delta z & \cos q\delta z \end{bmatrix}, \quad \begin{bmatrix} \cos q\delta z & \dfrac{\sin q\delta z}{Q} \\ -Q \sin q\delta z & \cos q\delta z \end{bmatrix}, \tag{28}$$

and the product $M_3M_2M_1$ of three such matrices has the elements

$$\begin{aligned} m_{11} &= c_1c_2c_3 - p_1r_2c_3 - c_1p_2r_3 - p_1c_2r_3, \\ m_{12} &= r_1c_2c_3 + c_1r_2c_3 + c_1c_2r_3 - r_1p_2r_3, \\ m_{21} &= p_1r_2p_3 - c_1c_2p_3 - c_1p_2c_3 - p_1c_2c_3, \\ m_{22} &= c_1c_2c_3 - r_1p_2c_3 - r_1c_2p_3 - c_1r_2p_3, \end{aligned} \tag{29}$$

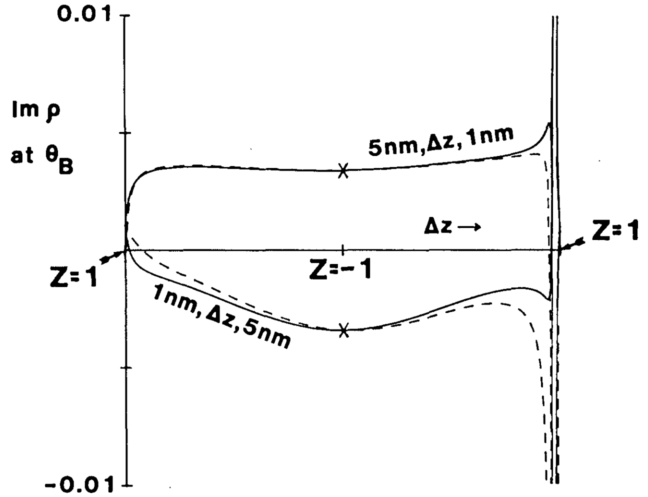

Fig. 2. Imaginary part of $\rho = r_p/r_s$ at $\theta_B = \arctan(\epsilon_u/\epsilon_a)^{1/2}$, for a three-layer system. The central layer is glass; the outer layers are water. The central-layer thickness Δz varies through one period [defined by Eq. (24)], during which $Z = \exp(2iq\Delta z)$ moves once around the unit circle in the complex plane, from $Z = 1$ to $Z = 1$. Solid curves show the exact values; dashed curves show the perturbation-theory values given by relation (23); asterisks give the $Z = -1$ values, approximated by relation (27).

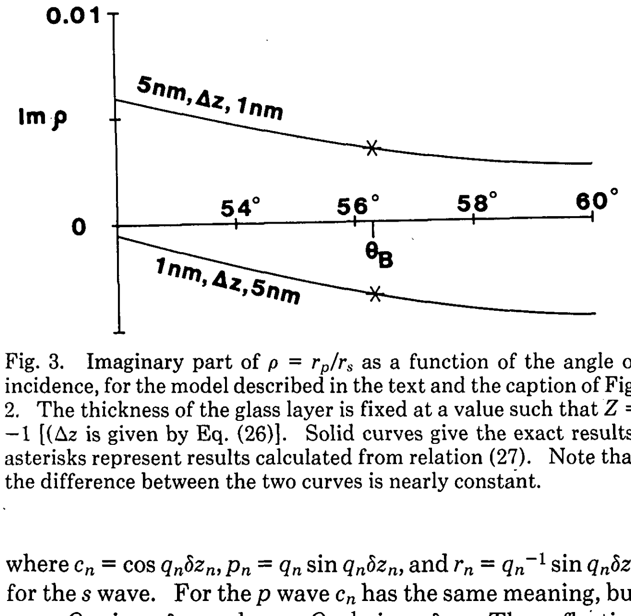

Fig. 3. Imaginary part of $\rho = r_p/r_s$ as a function of the angle of incidence, for the model described in the text and the caption of Fig. 2. The thickness of the glass layer is fixed at a value such that $Z = -1$ [(Δz is given by Eq. (26)]. Solid curves give the exact results; asterisks represent results calculated from relation (27). Note that the difference between the two curves is nearly constant.

where $c_n = \cos q_n\delta z_n$, $p_n = q_n \sin q_n\delta z_n$, and $r_n = q_n^{-1} \sin q_n\delta z_n$ for the s wave. For the p wave c_n has the same meaning, but $p_n = Q_n \sin q_n\delta z_n$ and $r_n = Q_n^{-1} \sin q_n\delta z_n$. The reflection amplitudes r_s and r_p are found from Eqs. (12.48) and (12.52) of Ref. 3.

In Fig. 2 the exact and approximate [relation (23)] values of Im ρ at θ_B are shown as a function of Δz, which varies through one period [from $Z = 1$ to $Z = 1$, as given by Eq. (24)]. We see that there is slow variation in Im $\rho(\theta_B)$ near $Z = -1$, that is, for thicknesses given by Eq. (26). In this region the accuracy of the perturbation theory is also best. Near the end points, where $Z = \exp(2iq\Delta z) = 1$, there is rapid variation in Im $\rho(\theta_B)$, and the perturbation-theory expression (23), which predicts the entirely real signal (25), fails to give the imaginary part of ρ. The real part is given accurately (not shown in Fig. 2) but would be difficult to measure, since it too varies rapidly with Z.

Figure 3 shows the sensitivity of the imaginary part of ρ to the angle of incidence θ_a, at a value of Δz given by Eq. (26), where $Z = -1$. We see that there is a steady variation of Im ρ but that this can largely be eliminated by illuminating the sample alternately from one side and then from the other and taking the difference between the Im ρ values.

5. DISCUSSION

We have derived general expressions for the s- and p-wave reflection amplitudes off a uniform layer with adsorbed thin films on one or both sides. The general formulas predict a complicated variation of the ellipsometric ratio, which is difficult to interpret experimentally except in the special case of like media on either side of the sample, illuminated at the Brewster angle for the uniform layer. At this angle of incidence, and provided that the thickness of the layer is not such that the s-wave reflection for the layer is near zero, the theory indicates that ellipsometry of adsorbed thin films on finite layers is possible, at least in the sense that r_p/r_s is free of rapid variation with the thickness of the uniform layer or with the angle of incidence.

It is interesting that the predicted ellipsometric ratio [relation (27)] is of similar form and of the same order of magnitude as in the case of a transition layer between semi-infinite media a and u, where the imaginary part of ρ at the angle where the real part is zero is given by

$$\mathrm{Im}\,\rho = \frac{(\epsilon_a + \epsilon_u)^{1/2}}{2(\epsilon_u - \epsilon_a)} \frac{\omega}{c} \int dz \frac{(\epsilon - \epsilon_a)(\epsilon_u - \epsilon)}{\epsilon}. \tag{30}$$

When $I_b = 0$, this is equal to Im ρ as given by relation (27), multiplied by $(\epsilon_u + \epsilon_a)^2/(\epsilon_u^2 + \epsilon_a^2)$. A qualitative correspondence of this kind was noted by Beaglehole.[1]

ACKNOWLEDGMENT

I am indebted to David Beaglehole for suggesting this problem and for stimulating discussions.

REFERENCES

1. D. Beaglehole, "Ellipsometry of thin substrates and intruding layers," J. Opt. Soc. Am. A (to be published).
2. J. Lekner, "Reflection of long waves by interfaces," Physica A **112**, 544–556 (1982).
3. J. Lekner, *Theory of Reflection* (Nijhoff, Dordrecht, The Netherlands, 1987), Sec. 2-1.
4. R. M. A. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light* (North-Holland, Amsterdam, 1977).
5. J. Lekner, "Second-order ellipsometric coefficients," Physica A **113**, 506–520 (1982).
6. J. Lekner, "Invariant formulation of the reflection of long waves by interfaces," Physica A **128**, 229–252 (1984).
7. M. Born and E. Wolf, *Principles of Optics* (Pergamon, New York, 1965).