Ellipsometry of a thin film between similar media

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The conventional formula for the ellipsometric ratio $\rho = r_p/r_s$ diverges in the limit when the dielectric constants on either side of an inhomogeneous layer become equal, $\epsilon_1 = \epsilon_2$. The general case, including $\epsilon_1 = \epsilon_2$, necessitates going to second order in the layer thickness. A formula is derived that includes the $\epsilon_1 = \epsilon_2$ case without divergence; the predicted maximum in the imaginary part of ρ when $\epsilon_1 \approx \epsilon_2$ indicates that index matching (of the bounding media) can significantly increase the ellipsometric signal.

1. INTRODUCTION

Recent work of Beaglehole[1] has brought into focus a long-standing problem in the ellipsometry of thin films. This problem is that the first-order (in the film thickness) correction to the Fresnel formulas gives a divergent result for the ellipsometric ratio $\rho = r_p/r_s$ when the bounding media have equal dielectric constants. The equality of the dielectric constants ϵ_1, ϵ_2 of the bounding media was shown some years ago[2] to give a finite ρ, and, in fact, a zero $\bar{\rho}$ ($\bar{\rho}$ is defined as the value of the imaginary part of ρ at the principal angle, where the real part of ρ is zero). What has emerged from the calculations of Beaglehole of $\bar{\rho}$ for a uniform film is that as ϵ_2 tends to ϵ_1 the magnitude of $\bar{\rho}$ first increases before going to zero at $\epsilon_1 = \epsilon_2$, reaching a maximum for ϵ_2 close to ϵ_1. Because a maximum in the magnitude of $\bar{\rho}$ is of practical importance in polarization modulation ellipsometry,[3,4] we have developed a theory for the general case (encompassing all of $\epsilon_1 \neq \epsilon_2$, $\epsilon_1 \approx \epsilon_2$, and $\epsilon_1 = \epsilon_2$). This is given in Section 3. Before that, the conventional first-order theory is reviewed in Section 2.

2. THE FIRST-ORDER EXPRESSION FOR ρ, $\epsilon_1 \neq \epsilon_2$

Consider an inhomogeneous layer of thickness Δz, of dielectric function $\epsilon(z)$, bounded by media of dielectric constants ϵ_1 and ϵ_2. Light, of angular frequency ω and speed (in vacuum) c, is incident from medium 1. In the absence of the interfacial layer, the s and p polarization reflection amplitudes would be

$$r_{s0} = \frac{q_1 - q_2}{q_1 + q_2}, \qquad r_{p0} = \frac{Q_2 - Q_1}{Q_2 + Q_1}, \tag{1}$$

where q_1 and q_2 are the normal components of the wave vectors in media 1 and 2 and $Q_1 = q_1/\epsilon_1$, $Q_2 = q_2/\epsilon_2$. The q's are given by

$$q_1^2 = \epsilon_1 \frac{\omega^2}{c^2} - K^2, \qquad q_2^2 = \epsilon_2 \frac{\omega^2}{c^2} - K^2. \tag{2}$$

Here K is the (invariant) component of the wave vectors along the interface,

$$(cK/\omega)^2 = \epsilon_1 \sin^2\theta_1 = \epsilon_2 \sin^2\theta_2, \tag{3}$$

where θ_1 and θ_2 are the angles of incidence and transmission.

The presence of the layer modifies the Fresnel reflection amplitudes [Eq. (1)]. The modification can be expressed as a power series in the layer thickness,

$$r_s = r_{s0} + r_{s1} + r_{s2} + \ldots,$$
$$r_p = r_{p0} + r_{p1} + r_{p2} + \ldots, \tag{4}$$

where subscript n (=0, 1, 2, ...) denotes terms that are nth order in $\omega\Delta z/c$. Now

$$r_{s0} = \frac{q_1^2 - q_2^2}{(q_1 + q_2)^2} = \frac{\Delta\epsilon\omega^2/c^2}{(q_1 + q_2)^2}, \tag{5}$$

where $\Delta\epsilon = \epsilon_1 - \epsilon_2$; thus, provided that $\Delta\epsilon \neq 0$, $r_{s0} \neq 0$ and

$$\frac{r_p}{r_s} = \frac{r_{p0}}{r_{s0}} + \frac{r_{p1}r_{s0} - r_{p0}r_{s1}}{r_{s0}^2} + \ldots. \tag{6}$$

Long-wave perturbation theory,[5,6] which is reviewed in Chap. 3 of Ref. 7, gives the corrections r_{pn} and r_{sn} to the Fresnel reflection amplitudes. The first-order corrections are

$$r_{s1} = \frac{2iq_1\omega^2/c^2}{(q_1 + q_2)^2}\lambda_1, \tag{7}$$

$$r_{p1} = \frac{2iQ_1}{(Q_1 + Q_2)^2}\left(Q_2^2\lambda_1 - \frac{K^2}{\epsilon_1\epsilon_2}\Lambda_1\right), \tag{8}$$

where the integrals λ_1 and Λ_1 are the first in the sets

$$\lambda_n = \int_{-\infty}^{\infty} dz(\epsilon - \epsilon_0)z^{n-1}, \tag{9}$$

$$\Lambda_n = \epsilon_1\epsilon_2 \int_{-\infty}^{\infty} dz \left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon}\right)z^{n-1}. \tag{10}$$

Here $\epsilon_0(z)$ is the step function representing a sharp transition between media 1 and 2, $\epsilon_0(z) = \epsilon_1$ for $z < 0$, $\epsilon_0(z) = \epsilon_2$ for $z > 0$. From Eqs. (6)–(8) we find after some manipulation that

$$r_{s0}\frac{r_p}{r_s} = r_{p0} - \frac{2iQ_1K^2}{\epsilon_1\epsilon_2(Q_1+Q_2)^2} I_1 + \ldots, \tag{11}$$

where

$$I_1 = \Lambda_1 - \lambda_1 = \int_{-\infty}^{\infty} dz \frac{(\epsilon_1 - \epsilon)(\epsilon - \epsilon_2)}{\epsilon}. \tag{12}$$

The companion formula to Eq. (5) is

$$r_{p0} = \frac{\Delta\epsilon(\omega^2/c^2)}{\epsilon_1\epsilon_2(Q_1+Q_2)^2}\left[1 - \left(\frac{cK}{\omega}\right)^2\left(\frac{1}{\epsilon_1}+\frac{1}{\epsilon_2}\right)\right]. \tag{13}$$

On using Eqs. (5) and (13) in Eq. (11), we find that

$$\frac{r_p}{r_s} = \frac{(q_1+q_2)^2}{\epsilon_1\epsilon_2(Q_1+Q_2)^2}\left\{\left[1 - \left(\frac{cK}{\omega}\right)^2\left(\frac{1}{\epsilon_1}+\frac{1}{\epsilon_2}\right)\right] - 2iQ_1\left(\frac{cK}{\omega}\right)^2 I_1/\Delta\epsilon + \ldots\right\}. \tag{14}$$

The ellipsometric quantity $\bar{\rho}$ is the value of $\mathrm{Im}(r_p/r_s)$ at the angle where $\mathrm{Re}(r_p/r_s)$ is zero. To first order in the interface thickness, the real part is zero at the Brewster angle $\theta_B = \arctan(\epsilon_1/\epsilon_2)^{1/2}$, at which

$$\left(\frac{cQ_1}{\omega}\right)^2 = \left(\frac{cQ_2}{\omega}\right)^2 = \frac{1}{\epsilon_1+\epsilon_2}, \qquad \left(\frac{cK}{\omega}\right)^2 = \frac{\epsilon_1\epsilon_2}{\epsilon_1+\epsilon_2}, \tag{15}$$

$$\left(\frac{cq_1}{\omega}\right)^2 = \frac{\epsilon_1^2}{\epsilon_1+\epsilon_2}, \qquad \left(\frac{cq_2}{\omega}\right)^2 = \frac{\epsilon_2^2}{\epsilon_1+\epsilon_2}. \tag{16}$$

Thus

$$\bar{\rho} = -\frac{(\epsilon_1+\epsilon_2)^{1/2}}{2\Delta\epsilon}\frac{\omega}{c} I_1 + \ldots. \tag{17}$$

Formulas (14) and (17), often attributed to Drude but in fact going back to Lorenz and Van Ryn (see Rayleigh[8] for a derivation and reference to earlier work), clearly fail when $\epsilon_1 = \epsilon_2$; the apparent divergence is due to the inadmissible division by zero in Eq. (6). When $\Delta\epsilon = 0$, both r_{p0} and r_{s0} are zero, and (see Ref. 2, Sec. 4)

$$\frac{r_p}{r_s} = \frac{r_{p1}}{r_{s1}} + \ldots = \cos^2\theta_0 - \frac{\Lambda_1}{\lambda_1}\sin^2\theta_0 + \ldots, \tag{18}$$

where θ_0 is the common value of θ_1 and θ_2 when $\epsilon_1 = \epsilon_2$. The value of $\bar{\rho}$ is thus *zero*, not *infinity*, to lowest order in the interface thickness. The fact that the simple theory gives a divergence as $\Delta\epsilon \to 0$, whereas the $\Delta\epsilon = 0$ value is zero, suggests the existence of a maximum for small $\Delta\epsilon$. This turns out to be true, as we will see in Section 3.

3. SECOND-ORDER THEORY FOR GENERAL $\Delta\epsilon$

We will calculate r_p/r_s, avoiding division by r_{s0} or r_{p0} so as to include the possibility of $\epsilon_1 = \epsilon_2$. We use the form

$$\frac{r_p}{r_s} = \frac{r_{p0} + r_{p1} + r_{p2} + \ldots}{r_{s0} + r_{s1} + r_{s2} + \ldots}. \tag{19}$$

The first-order terms r_{p1} and r_{s1} have been given above. The second-order terms are [Ref. 2, Eqs. (15) and (29)]

$$r_{s2} = \frac{-2q_1\omega^2/c^2}{(q_1+q_2)^2}\left(2q_2\lambda_2 + \frac{\omega^2/c^2}{q_1+q_2}\lambda_1^2\right), \tag{20}$$

$$r_{p2} = \frac{2Q_1Q_2}{(Q_1+Q_2)^3}\left\{\frac{K^4}{Q_2}\left(\frac{\Lambda_1}{\epsilon_1\epsilon_2}\right)^2 + K^2\left[(Q_1-Q_2)\frac{\lambda_1\Lambda_1}{\epsilon_1\epsilon_2} + (Q_1+Q_2)J\right] - Q_1Q_2^2\lambda_1^2 - 2(Q_1+Q_2)\frac{\omega^2}{c^2}\lambda_2\right\}, \tag{21}$$

where J is related to a second-order integral invariant j_2 [Ref. 2, Eq. (B7)] by

$$\Delta\epsilon J = j_2 + \left(\frac{1}{\epsilon_1}+\frac{1}{\epsilon_2}\right)\lambda_1\Lambda_1. \tag{22}$$

For nonabsorbing layers the first-order terms r_{s1} and r_{p1} are imaginary, and the second-order terms r_{s2} and r_{p2} are real. We multiply the numerator and denominator of Eq. (19) by the complex conjugate of the denominator. After a lengthy rearrangement of terms, the ratio r_p/r_s can be expressed in terms of the three integral invariants I_1, j_2, and i_2; i_2 is defined as

$$i_2 = 2\Delta\epsilon\lambda_2 - \lambda_1^2. \tag{23}$$

(These three integral invariants characterize the reflectivities $|r_p|^2$ and $|r_s|^2$ and the ellipsometric ratio r_p/r_s to second order in the layer thickness, for any layer. Their properties are discussed and their functional forms are tabulated for six profiles in Secs. 3–6 of Ref. 7.) The result is

$$\frac{r_p}{r_s} = \frac{(q_1+q_2)^2}{\epsilon_1\epsilon_2(Q_1+Q_2)^2} \times \frac{(\Delta\epsilon)^2\left[1-\left(\frac{cK}{\omega}\right)^2\left(\frac{1}{\epsilon_1}+\frac{1}{\epsilon_2}\right)\right] - \Delta\epsilon 2iQ_1\left(\frac{cK}{\omega}\right)^2 I_1 + \frac{\Delta\epsilon 2Q_1K^2(cK/\omega)^2 I_1^2}{\epsilon_1\epsilon_2(Q_1+Q_2)} - 4q_1q_2\left[i_2 - \frac{1}{2}\left(\frac{cK}{\omega}\right)^2 j_2 + \left(\frac{1}{\epsilon_1}+\frac{1}{\epsilon_2}\right)i_2\right]}{(\Delta\epsilon)^2 - 4q_1q_2i_2}. \tag{24}$$

When $\Delta\epsilon \neq 0$ this ratio may be expressed in conventional form as a series of terms in increasing powers of the layer thickness, agreeing with Ref. 7, Eq. (3.52). However, because we want a theory applicable to small $\Delta\epsilon$, we will keep the form of Eq. (24).

We note some general properties of Eq. (24). All angular dependence is contained in the coefficients multiplying I_1, I_1^2, i_2, and j_2, the integral invariants depending only on the interfacial thickness and profile shape $\epsilon(z)$ and on the dielec-

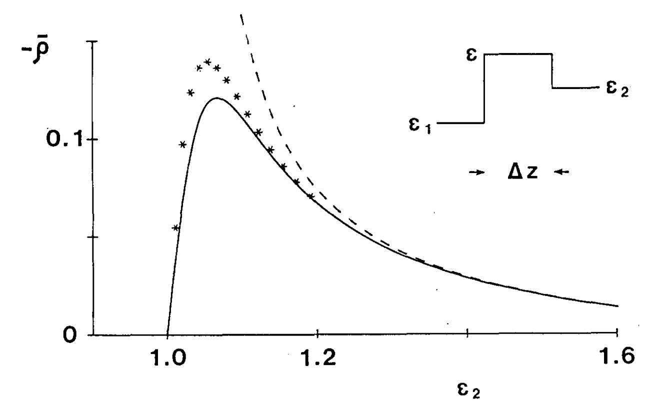

Fig. 1. The ellipsometric parameter $\bar{\rho}$ for a thin uniform film ($\omega\Delta z/c = 0.05$, $\epsilon = 2$) between media with dielectric constants $\epsilon_1 = 1$ and variable ϵ_2. The dashed curve is from Eq. (17), the conventional first-order theory, and diverges at $\epsilon_2 = \epsilon_1$. The solid curve is from expression (25), which is an approximate version of the second-order theory. The points are calculated from the exact reflection amplitudes. The $\bar{\rho}$ deduced from the second-order expression [Eq. (24)] is indistinguishable from the exact $\bar{\rho}$ for the small film thickness used here.

tric constants of the bounding media. At normal incidence ($K = 0$), we find $r_p/r_s \rightarrow 1$, as it must, since there is then no physical difference between the s and p waves. At grazing incidence ($q_1, Q_1 \rightarrow 0$), $r_p/r_s \rightarrow -1$, in accord with a general theorem of reflection (Ref. 7, Sec. 2-3). When $\Delta\epsilon = 0$ the invariants i_2 and j_2 take the values $-\lambda_1^2$ and $-2\lambda_1\Lambda_1/\epsilon_0$, respectively, and r_p/r_s reduces to the value given in Eq. (18). [We note in passing that Eq. (18) tends not to the correct value of -1 at grazing incidence but to $-\Lambda_1/\lambda_1$. This discrepancy arises from the divergence of perturbation theory at grazing incidence when $\epsilon_1 = \epsilon_2$, a difficulty that is discussed in Sec. 3-5 of Ref. 7. The divergence is removed in variational theory,[9] where for $\epsilon_1 = \epsilon_2$ and near grazing incidence,

$$r_s^{\text{var}} \rightarrow \frac{-1}{1 + \dfrac{2iq_0}{\lambda_1\omega^2/c^2}}, \qquad r_p^{\text{var}} \rightarrow \frac{1}{1 + \dfrac{2iq_0}{\Lambda_1\omega^2/c^2}}.$$

Thus, when $(\epsilon_0)^{1/2}\cos\theta_0$ is much less than $\lambda_1\omega/c$ and $\Lambda_1\omega/c$ respectively, $r_s \rightarrow -1$ and $r_p \rightarrow 1$, as required. For thin films this limit is reached, however, only for θ_0 close to 90°. When $\epsilon_1 = \epsilon_2$ the formula $r_p/r_s \approx \cos^2\theta_0 - (\Lambda_1/\lambda_1)\sin^2\theta_0$, derived as in Eq. (18) or from Eq. (24), is correct to lowest order in the film thickness and accurate away from grazing incidence.]

Of particular interest is the value of $\bar{\rho}$. From Eq. (24) we see that the real part of r_p/r_s is zero at an angle θ_p that differs in second order in the film thickness from the Brewster angle $\theta_B = \arctan(\epsilon_2/\epsilon_1)^{1/2}$. Approximating θ_p by θ_B and using Eqs. (15) and (16) in Eq. (24), we find that

$$\bar{\rho} \approx \frac{-\dfrac{1}{2}\Delta\epsilon(\epsilon_1 + \epsilon_2)^{1/2}\dfrac{\omega}{c}I_1}{(\Delta\epsilon)^2 - \dfrac{4\epsilon_1\epsilon_2}{\epsilon_1 + \epsilon_2}\dfrac{\omega^2}{c^2}i_2}. \tag{25}$$

This tends to zero as $\Delta\epsilon \rightarrow 0$, as required. The exact $\bar{\rho}$ (to second order, but not assuming $\theta_p = \theta_B$) is also zero when $\Delta\epsilon = 0$ because the functional form $\Delta\epsilon I_1/[(\Delta\epsilon)^2 - 4q_1q_2i_2]$ is retained.

For a uniform layer,

$$I_1 = \frac{(\epsilon_1 - \epsilon)(\epsilon - \epsilon_2)}{\epsilon}\Delta z, \qquad i_2 = (\epsilon_1 - \epsilon)(\epsilon - \epsilon_2)(\Delta z)^2,$$

$$j_2 = \frac{2(\epsilon_1 - \epsilon)(\epsilon - \epsilon_2)}{\epsilon}(\Delta z)^2. \tag{26}$$

Figure 1 shows $\bar{\rho}$ calculated exactly [or from Eq. (24)], from expression (25) and from Eq. (17) for a thin uniform layer ($\epsilon = 2$) between media with $\epsilon_1 = 1$ and variable ϵ_2. The thickness parameter $(\omega/c)\Delta z$ is 0.05, which corresponds to a film thickness of approximately 5 nm for $\lambda_1 = 632.8$ nm.

From expressions (25) and (26) and by using the fact that the maximum magnitude of $\bar{\rho}$ occurs for ϵ_1 near ϵ_2, we find that the maximum magnitude occurs at

$$\epsilon_2 - \epsilon_1 \approx (2\epsilon_1)^{1/2}(\epsilon - \epsilon_1)\frac{\omega}{c}\Delta z \tag{27}$$

and takes the value

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and takes the value

$$\bar{\rho}_m \approx \frac{\epsilon_1(\epsilon_1 - \epsilon)}{4\epsilon}. \tag{28}$$

Note that $\bar{\rho}_m$ is *independent of the film thickness:* index matching (ϵ_2 close to ϵ_1) can give the large ellipsometric signal [expression (28)] even for very thin films.

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