

DIFFERENTIAL REFLECTION SPECTROSCOPY OF VERY THIN SURFACE FILMS

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The influence of thin adsorbed films on the reflectance properties of two-phase systems is discussed. It is shown that the linear approximation to the normalized reflectivity change $\Delta R/R$ reduces the complicated reflectivity expressions for multiphase stratified systems to a simple form which gives direct physical insight into the properties of these systems. Several interfacial systems of physical interest are examined in detail, and the results are generalized to include attenuated total reflection, fractional coverage, and interfaces with smoothly varying optical properties.

1. Introduction

Differential reflectance spectroscopy is currently employed to investigate the optical properties of solids, to study the formation and properties of thin films on their surfaces, and to detect intermediates and products of heterogeneous chemical and electrochemical reactions. In the latter applications, the sensitivity of detection is often comparable to that of ellipsometry. Further, since the reflectivity change can be measured rapidly during the actual course of an experiment, the surface coverage by an adsorbed species can be determined directly, even while another reaction takes place on the surface. The technique is thus of importance for studies of the mechanism of heterogeneous catalysis.

In the present communication, we consider the optical properties of very thin surface films whose thickness, d , is very much less than the wavelength, λ , of the monochromatic radiation incident on the surface. It is shown that by making simple linear approximations valid for $d \ll \lambda$, the complicated reflectivity expressions for multiphase stratified systems can be reduced to a simple form which gives direct physical insight into the properties of such systems. The reflectivity change produced by the formation of a thin film on a substrate surface is related to the film thickness, surface coverage, wavelength, and the dielectric constants of the ambient, film, and substrate phases. The range of validity of the linear-approximation theory is examined

and the sensitivities of film detection employing specular and internal reflection spectroscopy are compared.

2. Theory

As the simplest approximation to real systems we consider initially a two-phase system with a plane boundary consisting of a transparent ambient phase (e.g., a solution) and a bare substrate, both of which are assumed semi-infinite in extent. A three-phase system is formed when a thin film is generated between the original substrate and ambient phases. This film may consist of adsorbed chemical reactants, intermediates, or products; a surface film such as an oxide; or a thin surface layer of the substrate material itself, whose optical properties have been perturbed by the application of an external stress or field or by interaction with an adsorbed species.

A solution of the wave equation which describes the propagation of a plane electromagnetic wave through a medium is

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}^0 e^{i(\omega t - \mathbf{K} \cdot \mathbf{r})}, \quad (1)$$

where \mathbf{E} is the electric-field vector of amplitude E^0 , $\omega = 2\pi\nu$ is the angular frequency of the wave whose frequency is ν , \mathbf{K} is the wave vector and \mathbf{r} is the position vector referred to an arbitrary coordinate system.

The Fresnel reflection coefficient of the interface of two contiguous phases is defined as the ratio of the complex amplitudes of the electric-field vectors of the reflected and incident waves. Its value is a function of the polarization of the incident beam and the angle of incidence. For obliquely-incident radiation it is useful to define¹⁾ for any phase j , the angular-dependent quantity, ξ_j , as

$$\xi_j = \hat{n}_j \cos \varphi_j = (\hat{n}_j^2 - n_1^2 \sin^2 \varphi_1)^{\frac{1}{2}}, \quad (2)$$

where φ_1 and n_1 are the *real* angle of incidence and index of refraction of the transparent ambient phase (1), while \hat{n}_j is the *complex* refractive index of phase j . If phase j is absorbing, the angle φ_j is complex. The Fresnel coefficients of the interface between two phases j and k for perpendicular and parallel polarized radiation are then given by²⁾

$$r_{\perp jk} = \frac{\mu_k \xi_j - \mu_j \xi_k}{\mu_k \xi_j + \mu_j \xi_k}, \quad (3a)$$

$$r_{\parallel jk} = \frac{\hat{\epsilon}_k \xi_j - \hat{\epsilon}_j \xi_k}{\hat{\epsilon}_k \xi_j + \hat{\epsilon}_j \xi_k}, \quad (3b)$$

where μ_j , μ_k and $\hat{\epsilon}_j$, $\hat{\epsilon}_k$ are, respectively, the magnetic permeabilities and

complex dielectric constants of the two phases. At normal incidence ($\varphi_1=0$), $r_{\perp jk} = r_{\parallel jk}$.

The complex refractive index, \hat{n}_j , can be divided into its real and imaginary parts. If the time-dependence of the field is taken as $e^{+i\omega t}$, as in eq. (1), and the extinction coefficient $k_j \geq 0$, then

$$\hat{n}_j = n_j - ik_j, \quad (4)$$

where n_j is the index of refraction. With this convention, the real and imaginary parts of the complex dielectric constant are defined by

$$\hat{\epsilon}_j = \epsilon'_j - i\epsilon''_j = 1 + 4\pi\alpha_j - i4\pi\sigma_j/\omega, \quad (5)$$

where α_j is the complex electric polarizability and σ_j is the conductivity at the frequency ω . Since

$$\hat{n}_j = (\mu_j \hat{\epsilon}_j)^{1/2}, \quad (6)$$

and the magnetic permeability is in general real, then

$$\epsilon'_j = (n_j^2 - k_j^2)/\mu_j, \quad (7a)$$

$$\epsilon''_j = 2n_j k_j / \mu_j. \quad (7b)$$

The magnetic permeability can usually be taken as unity in the optical frequency range.

The phase changes on reflection at the interface jk are

$$\delta_{\perp jk} = \tan^{-1} \left[\frac{\text{Im}(r_{\perp jk})}{\text{Re}(r_{\perp jk})} \right], \quad (8a)$$

$$\delta_{\parallel jk} = \tan^{-1} \left[\frac{\text{Im}(r_{\parallel jk})}{\text{Re}(r_{\parallel jk})} \right]. \quad (8b)$$

The equivalent Fresnel reflection coefficient of a multiphase system is defined by analogy to the two-phase system as the ratio of the amplitudes of the incident and reflected waves in the initial ambient phase (1). For a three-phase system the equivalent Fresnel coefficients are³⁾

$$r_{\perp 123} = \frac{r_{\perp 12} + r_{\perp 23} e^{-2i\beta}}{1 + r_{\perp 12} r_{\perp 23} e^{-2i\beta}}, \quad (9a)$$

$$r_{\parallel 123} = \frac{r_{\parallel 12} + r_{\parallel 23} e^{-2i\beta}}{1 + r_{\parallel 12} r_{\parallel 23} e^{-2i\beta}}, \quad (9b)$$

where β , the change in phase of the beam during one traversal of the thin film phase (2) of thickness d is given by

$$\beta = \frac{2\pi \hat{n}_2 d \cos \varphi_2}{\lambda}. \quad (10)$$

Phase (3) represents the substrate medium; λ is the *vacuum* wavelength.

Employing the identity

$$r_{13} = \frac{r_{12} + r_{23}}{1 + r_{12}r_{23}}, \quad (11)$$

the reflectivity of the two-phase system (13) can be expressed as

$$R_{13} = |r_{13}|^2 = \frac{R_{12} + R_{23} + 2R_{12}^{\frac{1}{2}}R_{23}^{\frac{1}{2}}\cos(\delta_{12} - \delta_{23})}{1 + R_{12}R_{23} + 2R_{12}^{\frac{1}{2}}R_{23}^{\frac{1}{2}}\cos(\delta_{12} + \delta_{23})}, \quad (12)$$

where R_{12} and R_{23} represent the reflectivities of the interfaces 12 and 23 in the three-phase system (123) and δ_{12} and δ_{23} are the corresponding phase changes on reflection. For the three-phase system, the reflectivity is

$$\begin{aligned} R_{123} &= |r_{123}|^2 \\ &= \frac{R_{12} + R_{23} e^{4\operatorname{Im}(\beta)} + 2R_{12}^{\frac{1}{2}}R_{23}^{\frac{1}{2}} e^{2\operatorname{Im}(\beta)} \cos[\delta_{12} - \delta_{23} + 2\operatorname{Re}(\beta)]}{1 + R_{12}R_{23} e^{4\operatorname{Im}(\beta)} + 2R_{12}^{\frac{1}{2}}R_{23}^{\frac{1}{2}} e^{2\operatorname{Im}(\beta)} \cos[\delta_{12} + \delta_{23} - 2\operatorname{Re}(\beta)]}, \end{aligned} \quad (13)$$

where $\operatorname{Re}(\beta)$ and $\operatorname{Im}(\beta)$ designate, respectively, the real and imaginary parts of β . The subscripts denoting the beam polarization are not indicated in eqs. (11)–(13) because the forms of the relations are identical for both modes. In applying these equations, the Fresnel coefficients, reflectivities, and phase changes appropriate to the plane of polarization under consideration must be employed. Since the reflectivity of the two-phase system is identical to that of a three-phase system with $d=0$, we can write

$$R_{13} = R(0), \quad (14)$$

$$R_{123} = R(d). \quad (15)$$

Although absolute measurement of the reflectivities $R(0)$ and $R(d)$ is very difficult in experimental systems, the ratio $R(d)/R(0)$ can be measured accurately with relative ease, owing to a cancellation of common errors. Unfortunately, the exact theoretical equations for $R(d)$ and $R(0)$ are too complicated [cf. eqs. (12) and (13)], even for normally-incident radiation, to give any direct insight into how the dielectric constant and film thickness of an intermediate phase and its coverage of the substrate surface affect the reflectivity of a real system. In many instances, however, the thicknesses of the films involved in surface studies are much less than the wavelength of the incident radiation. It is then possible to make first-order approximations, analogous to those employed by Drude⁴), which lead to simple general equations for the reflectivity ratio $R(d)/R(0)$. To our knowledge, these expressions have not been presented previously in a general functional form

which directly relates the fractional reflectivity change to the characteristic dielectric parameters of the system.

2.1. LINEAR-APPROXIMATION THEORY

The equivalent Fresnel coefficient of a three-phase system is

$$r_{123} = \frac{r_{12} + r_{23} e^{-2i\beta}}{1 + r_{12}r_{23} e^{-2i\beta}}. \quad (9)$$

When $d \ll \lambda$, this relation can be expanded to terms of first order in β to give

$$r_{123} = \frac{r_{12} + r_{23}(1 - 2i\beta)}{1 + r_{12}r_{23}(1 - 2i\beta)}. \quad (16)$$

From eqs. (11) and (16)

$$\frac{r_{123}}{r_{13}} = \frac{1 - 2i\beta[r_{23}/(r_{12} + r_{23})]}{1 - 2i\beta[r_{12}r_{23}/(1 + r_{12}r_{23})]}. \quad (17)$$

Expanding the denominator as a binomial series and neglecting terms higher than first order in β , we obtain

$$\frac{r_{123}}{r_{13}} = 1 + 2i\beta \left[\frac{r_{23}(r_{12}^2 - 1)}{(r_{12} + r_{23})(1 + r_{12}r_{23})} \right]. \quad (18)$$

Since the ambient phase (1) is transparent, ϵ_1 is real. Substituting from eq. (2) for the generalized Fresnel coefficients, we find for perpendicular polarization

$$\frac{r_{\perp 123}}{r_{\perp 13}} = 1 - \frac{4\pi i d n_1 \cos \varphi_1}{\lambda} \left(\frac{\mu_3 \hat{\epsilon}_2 \cos^2 \varphi_2 - \mu_2 \hat{\epsilon}_3 \cos^2 \varphi_3}{\mu_3 \epsilon_1 \cos^2 \varphi_1 - \mu_1 \hat{\epsilon}_3 \cos^2 \varphi_3} \right). \quad (19)$$

Multiplying by the complex conjugate and retaining only first-order terms in (d/λ) gives

$$\frac{R_{\perp}(d)}{R_{\perp}(0)} = 1 + \frac{8\pi d n_1 \cos \varphi_1}{\lambda} \operatorname{Im} \left(\frac{\mu_3 \hat{\epsilon}_2 \cos^2 \varphi_2 - \mu_2 \hat{\epsilon}_3 \cos^2 \varphi_3}{\mu_3 \epsilon_1 \cos^2 \varphi_1 - \mu_1 \hat{\epsilon}_3 \cos^2 \varphi_3} \right). \quad (20)$$

Similarly, for parallel polarization

$$\frac{r_{\parallel 123}}{r_{\parallel 13}} = 1 - \frac{4\pi i d n_1 \cos \varphi_1}{\lambda} \left(\frac{\mu_2 \hat{\epsilon}_3 \cos^2 \varphi_2 - \mu_3 \hat{\epsilon}_2 \cos^2 \varphi_3}{\mu_1 \hat{\epsilon}_3 \cos^2 \varphi_1 - \mu_3 \epsilon_1 \cos^2 \varphi_3} \right), \quad (21)$$

and

$$\frac{R_{\parallel}(d)}{R_{\parallel}(0)} = 1 + \frac{8\pi d n_1 \cos \varphi_1}{\lambda} \operatorname{Im} \left(\frac{\mu_2 \hat{\epsilon}_3 \cos^2 \varphi_2 - \mu_3 \hat{\epsilon}_2 \cos^2 \varphi_3}{\mu_1 \hat{\epsilon}_3 \cos^2 \varphi_1 - \mu_3 \epsilon_1 \cos^2 \varphi_3} \right). \quad (22)$$

It is convenient to express these results in terms of the normalized reflec-

tivity change defined as

$$\frac{\Delta R}{R} = \frac{R(d) - R(0)}{R(0)}. \quad (23)$$

It is this quantity which is usually measured experimentally. Further, since $\mu_1 = \mu_2 = \mu_3 = 1$ in the optical frequency range, these expressions simplify to

$$\frac{\Delta R_{\perp}}{R_{\perp}} = \frac{8\pi dn_1 \cos \varphi_1}{\lambda} \operatorname{Im} \left(\frac{\hat{\epsilon}_2 - \hat{\epsilon}_3}{\epsilon_1 - \hat{\epsilon}_3} \right), \quad (24a)$$

$$\frac{\Delta R_{\parallel}}{R_{\parallel}} = \frac{8\pi dn_1 \cos \varphi_1}{\lambda} \operatorname{Im} \left\{ \left(\frac{\hat{\epsilon}_2 - \hat{\epsilon}_3}{\epsilon_1 - \hat{\epsilon}_3} \right) \left[\frac{1 - (\epsilon_1/\hat{\epsilon}_2\hat{\epsilon}_3)(\hat{\epsilon}_2 + \hat{\epsilon}_3) \sin^2 \varphi_1}{1 - (1/\hat{\epsilon}_3)(\epsilon_1 + \hat{\epsilon}_3) \sin^2 \varphi_1} \right] \right\}, \quad (24b)$$

for perpendicular and parallel polarizations, respectively. At normal incidence these further reduce to

$$\frac{\Delta R}{R} = \frac{8\pi dn_1}{\lambda} \operatorname{Im} \left(\frac{\hat{\epsilon}_2 - \hat{\epsilon}_3}{\epsilon_1 - \hat{\epsilon}_3} \right) = - \frac{8\pi dn_1}{\lambda} \operatorname{Im} \left(\frac{\epsilon_1 - \hat{\epsilon}_2}{\epsilon_1 - \hat{\epsilon}_3} \right). \quad (25)$$

The relations for the Fresnel coefficients given in eqs. (19) and (21) are, in fact, mathematically equivalent to the relations originally derived by Drude^{5,6}) to account for the effects of a "transition layer" on the elliptic polarization of reflected light. Equivalent relations for the reflectivity ratios have been given by Francis and Ellison^{7,8}). Their derivation is based on the earlier work of Fry⁹) and employs Fry's notation, which is not readily interpreted on a physical basis. In the present communication, these relationships are expressed in terms of the fundamental physical parameters, μ_j and $\hat{\epsilon}_j$, which characterize the response of the system to elementary excitations. A normal incidence form (for $e^{-i\omega t}$ field time dependence), analogous to eq. (25), has previously been given by Axe and Hammer¹⁰).

3. Results

The simple form of eqs. (23) and (24) enables considerable insight to be gained into the optical properties of very thin film systems. We now discuss their application to several systems of physical interest.

3.1. RANGE OF VALIDITY

The range of validity of the linear-approximation theory is illustrated in fig. 1 for the formation of a strongly absorbing thin film (e.g., an oxide) on a metallic substrate immersed in an aqueous solution ($n_1 = 1.333$; $n_2 = 3.0$, $k_2 = 1.5$; $n_3 = 2.0$, $k_3 = 4.0$). The full curves show the values of $(\Delta R/R)_{\perp}$ and

$(\Delta R/R)_{\parallel}$ as a function of d/λ calculated from the exact expressions, while the dashed line show the values given by the linear-approximation theory. The angle of incidence is 45° . For perpendicular polarization, the approximation is valid ($\pm 20\%$) for $d/\lambda \leq 0.01$, while for parallel polarization the range of validity is $0 \leq d/\lambda \leq 0.03$.

Using a procedure similar to that employed for the linear approximation theory, the reflectivity ratio, $R(d)/R(0)$, can be expanded to terms of second order in d/λ . The resulting expression is too cumbersome to be of utility and is not given here. The range of validity of the second-order approximation for perpendicular polarization is illustrated in fig. 1 by the dash-dot curve. The second-order curve for parallel polarization is virtually coincident with the dashed line illustrating the first-order approximation.

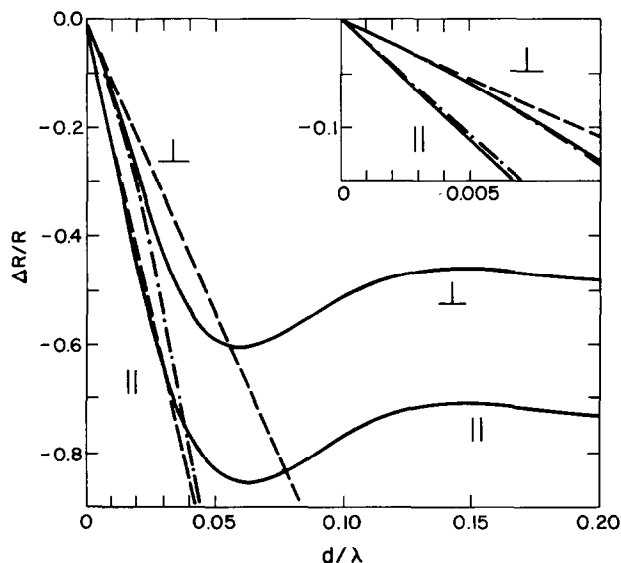


Fig. 1. Comparison of linear (---) and quadratic (---) approximations of $\Delta R/R$ to the exact (—) expression for an absorbing film on a metal substrate ($n_1 = 1.333$; $n_2 = 3.0$, $k_2 = 1.5$; $n_3 = 2.0$, $k_3 = 4.0$), for parallel and perpendicular polarizations. The angle of incidence is 45° . The portion of the curves near the origin is expanded in the inset.

In the above example, $\Delta R/R$ becomes constant for $d/\lambda > 0.3$ since all light transmitted into the film is absorbed before reflection at the rear surface occurs. Only the first front-surface reflection need be considered, therefore. The reflectivity of the three-phase system is then independent of film thickness and corresponds to that of the two-phase system, 12.

3.2. DETECTION SENSITIVITY

For constant or slowly varying values of ϵ_1 , $\hat{\epsilon}_2$ and $\hat{\epsilon}_3$, the sensitivity for film detection is linearly proportional to the film thickness and inversely proportional to the wavelength. Eq. (24) and (25) may be employed to estimate the sensitivity and signal-to-noise enhancement required of the detection system to obtain adequate resolution of the optical properties of the surface layer.

In general, greatest sensitivity can be attained by employing parallel-polarized radiation at oblique incidence. This is of particular importance in studying adsorbed films on metal substrates in the infrared wavelength region where metallic conductivities are very high. The component of the optical frequency electric field vector which is parallel to the surface plane is vanishingly small at the interface. Only the component of the field normal to the surface has sufficient amplitude to interact with the film and produce a measurable energy loss in wavelength regions where the film is absorbing. In the visible-UV wavelength region, the optical frequency conductivities of metals are generally much lower and the tangential field components are finite at the surface. This fact, combined with the enhanced sensitivity at shorter wavelengths, often permits absorbing films on metal substrates to be detected with normally incident radiation in this wavelength region. The characteristics of reflection at absorbing and dielectric substrate surfaces will be examined in detail in the following sections.

3.3. SPECULAR REFLECTION

Fig. 2 illustrates the dependence of the specular reflectivity of a film-free metal surface (solid curves) and that of a metal covered with approximately one monolayer ($d/\lambda = 10^{-3}$) of a strongly-absorbing substance (dash-dot curves) on the angle of incidence and polarization of the incident beam for radiation in the visible wavelength region. The optical constants of this system are the same as those employed in section 3.1. R_{\perp} increases monotonically from its minimum value at $\varphi_1 = 0^\circ$ to unity when $\varphi_1 = 90^\circ$. R_{\parallel} exhibits a minimum at the pseudo-Brewster angle. For unpolarized radiation, the reflectivity, R_N , remains nearly constant to large angles of incidence.

The variation of $\Delta R/R$ as a function of φ_1 and polarization is shown in fig. 3 for the same interface. With oblique incidence and perpendicular polarization, the sensitivity for film detection decreases monotonically as $\cos \varphi_1$ from its maximum value at normal incidence to zero at grazing incidence [cf. eq. (24a)]. With parallel-polarized radiation, the variation of $\Delta R/R$ is more complicated. Inspection of eq. (24b), however, reveals a similarity in form to eq. (24a). For the example illustrated here (strongly

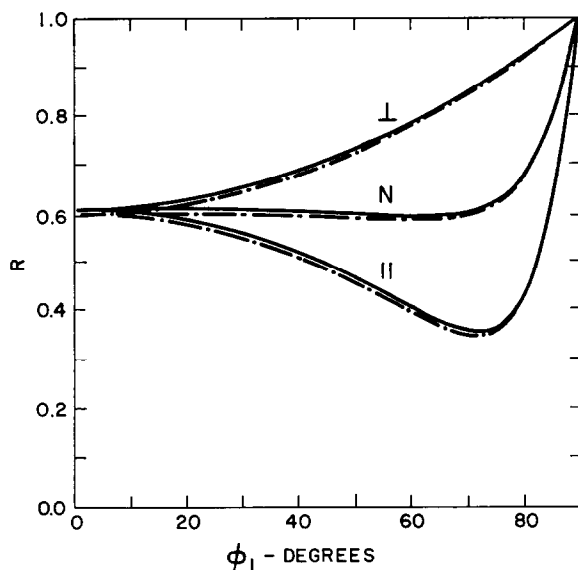


Fig. 2. The reflectivity of a bare metal substrate (—) and that of the substrate covered by approximately one monolayer of an absorbing film (----) as a function of the angle of incidence for parallel and perpendicular polarizations, and unpolarized light. The optical parameters are the same as in fig. 1, with $d/\lambda = 1 \times 10^{-3}$.

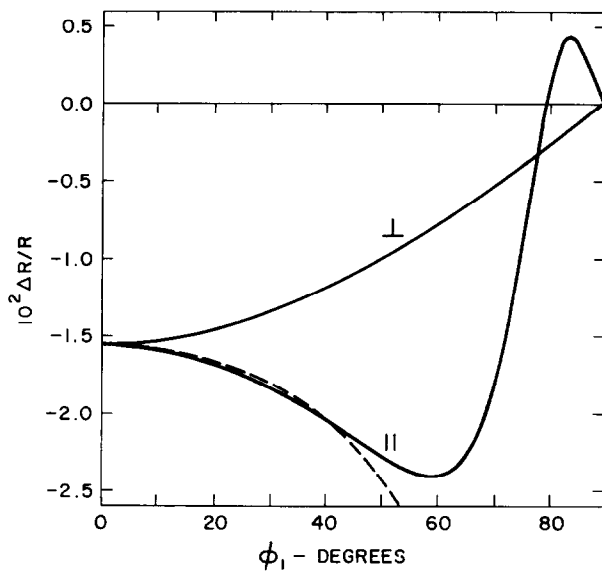


Fig. 3. The normalized change in reflectivity $\Delta R/R$ from fig. 2, caused by approximately one monolayer of an absorbing film ($d/\lambda = 1 \times 10^{-3}$). The change for perpendicular polarization varies as $\cos \phi_1$. The change for parallel polarization is more complicated but may be approximated by a $1/\cos \phi_1$ variation for small ϕ_1 (the dashed curve).

absorbing film on a metallic substrate), $|\hat{\epsilon}'_3| \gg \epsilon_1$ and $|\hat{\epsilon}'_2| \gg \epsilon_1$. As a result, the numerator of the square-bracketted term in eq. (24b) remains nearly real and close to unity for all values of φ_1 . The denominator of the square-bracketted term is nearly real and equal to $\cos^2 \varphi_1$ for small angles of incidence. The film-detection sensitivity using parallel-polarized radiation thus increases with φ_1 as $(1/\cos \varphi_1)$ and is greater than that for perpendicular polarization by the factor $(1/\cos^2 \varphi_1)$. As illustrated by the dashed curve representing $(1/\cos \varphi_1) (\Delta R/R)_{0^\circ}$ in fig. 3, this approximation is very good for the example considered when $\varphi_1 \leq 45^\circ$. For large values of φ_1 , the denominator of the square-bracketted term has approximately equal real and imaginary components. The cross-products of the real and imaginary parts of the terms in round and square brackets in eq. (24b) then combine in such a way as to produce a minimum, a maximum, and a sign change in $(\Delta R/R)_\parallel$ as shown in fig. 3. The value of $(\Delta R/R)_\parallel$ becomes zero when the sum of the cross-products equals zero. At grazing incidence $(\Delta R/R)_\parallel$ becomes zero again since $\cos \varphi_1 = 0$. While the anomalous behavior of $(\Delta R/R)_\parallel$ observed with the present example does not occur for all sets of optical constants, it is evident that measurements with angles of incidence greater than the pseudo-Brewster angle must be made with discretion. In general, maximum sensitivity can be obtained by employing parallel-polarized radiation and a value of φ_1 between 45° and the pseudo-Brewster angle.

Similar behavior is observed for external reflection from a dielectric surface, as illustrated in figs. 4 and 5 for the set of optical constants $n_1 = 1.333$; $n_2 = 3.0$, $k_2 = 1.5$; $n_3 = 4.0$, $k_3 = 0.0$. In this case, formation of a thin absorbing film ($d/\lambda = 10^{-3}$) on the transparent substrate produces a reflectivity increase for perpendicularly-polarized radiation when $0^\circ \leq \varphi_1 \leq 90^\circ$. For parallel-polarized radiation, ΔR is always finite but passes through zero and changes sign at the Brewster angle, $\varphi_B = \tan^{-1}(n_3/n_1)$. The value of R_\parallel also is zero when $\varphi_1 = \varphi_B$; as a result, the ratio $(\Delta R/R)_\parallel$ is discontinuous at this angle of incidence.

If ϵ_1 , $\hat{\epsilon}_2$, $\hat{\epsilon}_3$ are all real, $\Delta R/R$ is always zero [cf. eqs. (24a) and (24b)]. Hence to first order, the reflectivity of a two-phase dielectric system is unchanged by the deposition of a very thin dielectric film on the substrate surface. This results since interference effects, characteristic of reflection-enhancing and reflection-suppressing films, are of second order in d/λ and are negligible for $d \ll \frac{1}{4}\lambda$.

3.4. WEAKLY-ABSORBING FILMS

If the substrate is strongly absorbing (metallic) but the surface film is only weakly absorbing, such that $\epsilon''_2 \ll \epsilon''_3$, then for normal incidence

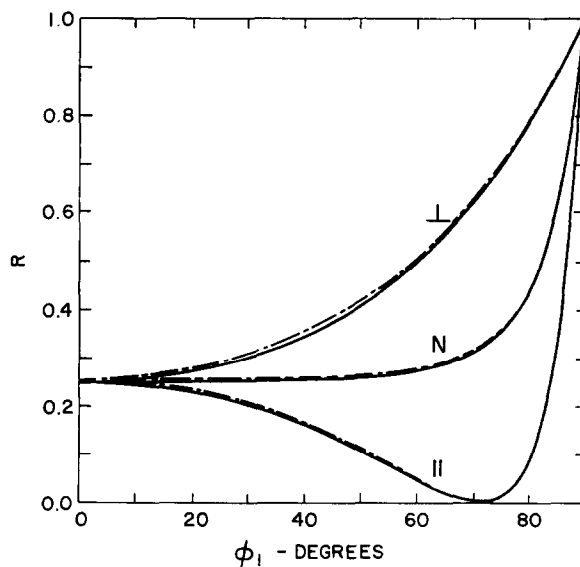


Fig. 4. The reflectivity of a bare dielectric (—) and that of the dielectric covered by approximately one monolayer of an absorbing film (----) as a function of the angle of incidence for parallel and perpendicular polarizations, and unpolarized light. The optical parameters are: $n_1 = 1.333$; $n_2 = 3.0$, $k_2 = 1.5$; $n_3 = 4.0$, $k_3 = 0$; $d/\lambda = 1 \times 10^{-3}$.

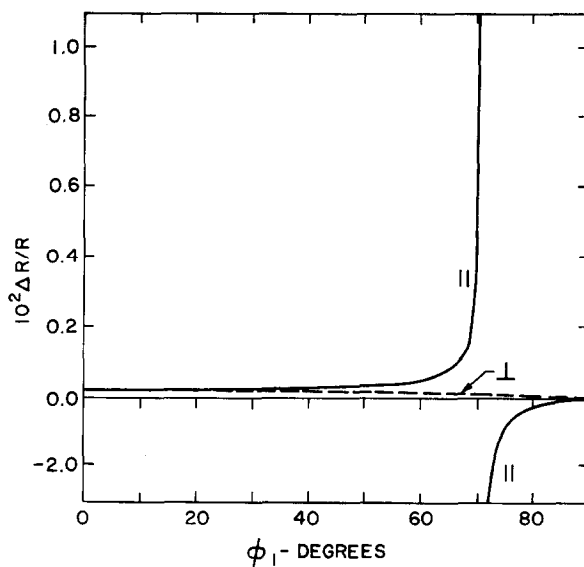


Fig. 5. The normalized change in reflectivity $\Delta R/R$ from fig. 4, caused by approximately one monolayer of an absorbing film ($d/\lambda = 1 \times 10^{-3}$).

$$\operatorname{Im} \left(\frac{\hat{\epsilon}_2 - \hat{\epsilon}_3}{\epsilon_1 - \hat{\epsilon}_3} \right) \approx \frac{\epsilon_3''(n_2^2 - k_2^2 - n_1^2)}{(\epsilon_1 - \epsilon_3')^2 + \epsilon_3''^2}. \quad (26a)$$

If the film is very weakly absorbing or transparent ($k_2 \approx 0$)

$$\operatorname{Im} \left(\frac{\hat{\epsilon}_2 - \hat{\epsilon}_3}{\epsilon_1 - \hat{\epsilon}_3} \right) \approx \frac{\epsilon_3''(n_2^2 - n_1^2)}{(\epsilon_1 - \epsilon_3')^2 + \epsilon_3''^2}. \quad (26b)$$

The reflectivity change for such cases is predicted to be very small and to be determined largely by the optical properties of the *substrate*. Little, if any, information can be gained concerning the absorptive properties of the film.

Alternatively, if the substrate is transparent, $\hat{\epsilon}_3$ is real and

$$\operatorname{Im} \left(\frac{\hat{\epsilon}_2 - \hat{\epsilon}_3}{\epsilon_1 - \hat{\epsilon}_3} \right) = -\frac{\epsilon_2''}{\epsilon_1 - \epsilon_3} = -\frac{2n_2k_2}{n_1^2 - n_3^2} \quad (26c)$$

The absorption coefficient, α_2 , of the thin film is related to the extinction coefficient, k_2 , by

$$\alpha_2 = 4\pi k_2/\lambda. \quad (27)$$

Hence, at normal incidence

$$\frac{\Delta R}{R} = -\frac{4n_1n_2\alpha_2d}{n_1^2 - n_3^2}. \quad (28)$$

The reflectivity change produced by the deposition of a thin absorbing film on a dielectric substrate can thus be either positive or negative, depending upon whether $n_3 > n_1$ or $n_3 < n_1$. If the substrate is optically more dense, greatest sensitivity is attained by employing the internal reflection mode.

On examination of eqs. (26) and (28), it is evident that the reflection spectra of thin films depend in a complicated way not only upon the optical constants of the film but also upon those of the substrate and ambient phases. If ϵ_1 and $\hat{\epsilon}_3$ are nearly constant over the wavelength range of interest, the reflectivity change can be related to the absorptive properties of the film. This relationship is obscured, however, by the fact that in the vicinity of a film absorption band, the refractive index, n_2 , exhibits anomalous dispersion. If this dispersion is strong, the reflection spectrum will be severely distorted as compared to a conventional transmission spectrum and the absorption maximum will be displaced. Finally, it may be noted that for absorbing substrates, ΔR is proportional to the real part, ϵ_2' , of the dielectric constant of a weakly absorbing film, while for dielectric substrates ΔR depends upon the imaginary component, ϵ_2'' .

3.5. INTERNAL REFLECTION

Although the linear-approximation theory has been discussed in the preceding sections primarily with regard to external reflection, it is equally

valid for the internal reflection mode. In this case, phase (1) corresponds to the internal reflection element which acts as the substrate, while phase (3) is the ambient medium and $n_1 > n_3$. If the ambient phase is transparent and the angle of incidence in the internal reflection element is equal to or greater than the critical angle, $\varphi_c = \sin^{-1}(n_3/n_1)$, total internal reflection occurs, such that $R_{\perp}(0)$ and $R_{\parallel}(0)$ are exactly unity. The value of the critical angle is independent of whether or not an absorbing layer is present on the surface of the substrate.

If phases (1), (2) and (3) are transparent, $\epsilon_1, \epsilon_2, \epsilon_3$ and $\sin \varphi_1$ are real. Inspection of eqs. (24a) and (24b) reveals that to first order there is no reflectivity change produced by deposition of a very thin dielectric film on the surface of an internal reflection element, i.e., $R(d) = 1$ and $\Delta R/R = 0$ for both polarization modes.

If the thin film phase is absorbing, ϵ_2 is complex and the evanescent wave from the internal reflection element suffers a power loss, such that $R(d) < 1$ and $\Delta R/R \leq 0$ for *all* values of the optical constants n_2 and k_2 when $\varphi_c \leq \varphi_1 \leq 90^\circ$. The solid curves in fig. 6 illustrate the dependence of the reflectivity of a film-free dielectric internal reflection element ($n_1 = 4.0$, $k_1 = 0.0$) in contact with an aqueous solution ($n_3 = 1.333$, $k_3 = 0.0$) on the angle of incidence and polarization of the incident beam. R_{\parallel} exhibits a minimum value of zero at the principal angle, $\varphi_p = \tan^{-1}(n_3/n_1) = 18.4^\circ$,

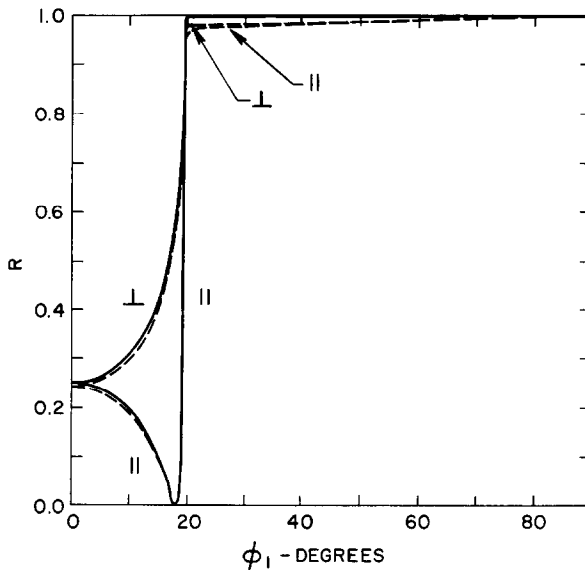


Fig. 6. The internal reflectivity of a bare dielectric (—) and that of the dielectric covered by approximately one monolayer of an absorbing film (---) as a function of the angle of incidence for parallel and perpendicular polarizations. The optical parameters are $n_1 = 4.0$; $n_2 = 1.333$, $k_2 = 1.5$; $n_3 = 1.333$, $k_3 = 0$; $d/\lambda = 1 \times 10^{-3}$.

which is the complement of the external polarizing angle, φ_B . R_{\parallel} then rises abruptly to unity at the critical angle, $\varphi_c = 19.5^\circ$. The dashed curves show the reflectivity when a thin film ($d/\lambda = 10^{-3}$, $n_2 = 1.333$, $k_2 = 1.5$) is present on the surface, for perpendicular- and parallel-polarized radiation, respectively. Fig. 7 shows the corresponding plots of $\Delta R/R$ versus φ_1 . The value

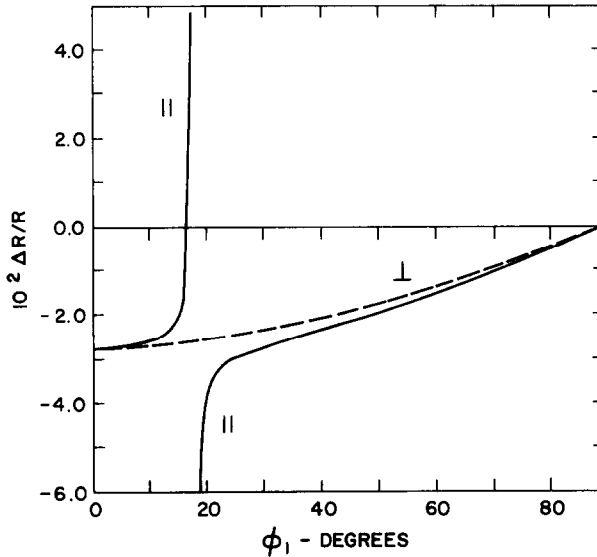


Fig. 7. The normalized change in reflectivity $\Delta R/R$ from fig. 6, caused by approximately one monolayer of an absorbing film ($d/\lambda = 1 \times 10^{-3}$).

of $|\Delta R/R|$ decreases monotonically with $\cos \varphi_1$ from normal to grazing incidence, independently of whether $\varphi_1 \leq \varphi_c$. The value of $(\Delta R/R)_{\parallel}$ is discontinuous at the principal angle.

In the present example, the sensitivity for film detection using attenuated total reflection (ATR) with $\varphi_1 > \varphi_c$ is greatest for parallel polarization. This is not universally true, however; the opposite behavior is observed for films with slightly larger values of n_2 . Examination of eqs. (24a) and (24b) reveals that for all angles of incidence greater than φ_p , $|\Delta R/R|_{\parallel} < |\Delta R/R|_{\perp}$ if $|\hat{\epsilon}_2|^2 > \epsilon_1 \epsilon_3$.

3.6. SURFACE COVERAGE

If the surface is fractionally covered, a mean film thickness can be defined as

$$\bar{d} = \frac{1}{A} \sum_i^n d_i \delta A_i, \quad (29)$$

where d_i is the local thickness, δA_i the area of a small patch or island of film on the substrate surface, and A is the area of the completely bare substrate surface (*not* the total film area). If the film forms with a uniform thickness, d_i is constant and equal to an integral multiple of the monolayer thickness, d_0 . Hence the effective thickness is

$$\bar{d} = md_0\theta \quad (m = 1, 2, \dots), \quad (30)$$

where the surface coverage, θ , is defined by

$$\theta = \frac{\sum \delta A_i}{A}. \quad (31)$$

In the region of validity of the linear-approximation theory, we may replace the quantity, d , in eq. (24) by \bar{d} . Then, for normal incidence

$$\frac{\Delta R}{R} = \frac{8\pi n_1 m d_0 \theta}{\lambda} \operatorname{Im} \left(\frac{\hat{\epsilon}_2 - \hat{\epsilon}_3}{\epsilon_1 - \hat{\epsilon}_3} \right). \quad (32)$$

At a fixed wavelength, $\Delta R/R$ is linearly proportional to the surface coverage, provided $\hat{\epsilon}_2$ and $\hat{\epsilon}_3$ are invariant. The optical properties of the film and substrate may vary, however, according to the variation of the heat of adsorption with surface coverage. Such changes will perturb the values of $\hat{\epsilon}_2$ and $\hat{\epsilon}_3$. When these changes are negligibly small, we can denote the reflectivity of the fully-covered three-phase system ($\theta=1$) as

$$R_{\text{III}} = R(1). \quad (33a)$$

Similarly the reflectivity of the two-phase system with $\theta=0$ is

$$R_{\text{II}} = R(0). \quad (33b)$$

The reflectivity change as a function of surface coverage is then given by

$$\frac{\Delta R(\theta)}{R_{\text{II}}} = \theta \frac{R_{\text{III}} - R_{\text{II}}}{R_{\text{II}}}. \quad (34)$$

Treatments of partial monolayer coverage have been presented which are based on scattering¹¹⁾ and microscopic atomic polarizability¹²⁾ models. These theories, whose applicability has recently been discussed by Bootsma and Meyer^{13, 14)}, predict reflectivity changes proportional to the fractional amount of surface coverage if the polarizabilities of the isolated atoms are not too different from collections in the bulk phase, as is assumed in eq. (32). Berreman has shown that a correction to the dielectric function of the film, of boundary condition origin, may also arise depending on the surface concentration of scattering centers and the microscopic surface topology¹⁵⁾.

It should be pointed out that the treatment of isolated atoms as a uniform intermediate phase, as in eq. (32), is legitimate as long as the average separation distance is much less than the wavelength of incident light. This is always the case for concentrations of adsorbed atoms which are sufficiently large to be detected by optical means.

3.7. GRADUAL TRANSITION REGIONS

For simplicity, we have discussed three-phase systems where the boundaries are sharp. Under certain circumstances, the sharp boundary restriction can be relaxed and the results can be applied to systems where the optical properties change uniformly over a small region, which for example occurs in electroreflectance measurements on metals¹⁶.

Wave propagation in a material with a one-dimensional inhomogeneity in the propagation direction (which is also assumed to be normal to the surface) can be described approximately by the wave equation with a spatially-dependent dielectric function¹⁷)

$$\left[\frac{d^2}{dz^2} + \frac{\omega^2}{c^2} \hat{\epsilon}(z) \right] E^0 \exp \{ i[\omega t - Kz - \varphi(z)] \} = 0, \quad (35)$$

$$\hat{\epsilon}(z) = \hat{\epsilon}_3 + \Delta\hat{\epsilon}(z) = \hat{n}_3^2 + \Delta\hat{\epsilon}(z),$$

where $\hat{\epsilon}_3$ is the uniform dielectric constant of the substrate, $\Delta\hat{\epsilon}(z)$ is the spatially-dependent change in the interfacial region (corresponding to $(\hat{\epsilon}_2 - \hat{\epsilon}_3)$ in the previous sections), and $\varphi(z)$ is a variable phase which is zero for $\Delta\hat{\epsilon}(z)=0$ and represents the influence of $\Delta\hat{\epsilon}(z)$ on wave propagation. E^0 is taken independent of z . Although eq. (35) cannot be solved exactly, a linear approximation can be obtained using the same approximations inherent in eq. (25). Rewriting eq. (35) in terms of $\varphi(z)$ gives

$$i\varphi''(z) + 2K\varphi'(z) = -[\varphi'(z)]^2 - \frac{\omega^2}{c^2} \Delta\hat{\epsilon}(z),$$

where

$$K = \hat{n}_3\omega/c = 2\pi\hat{n}_3/\lambda.$$

The term $[\varphi'(z)]^2$ is of second order in $\Delta\hat{\epsilon}(z)$. If $\Delta\hat{\epsilon}(z)=0$ except within a distance d from the surface where $d/\lambda \ll 1$, then $[\varphi'(z)]^2$ is of second order in d/λ and may be dropped. It follows that

$$\varphi'(z) \cong iK^2 \int_{z_s-d}^{z_s} dz' e^{2iK(z_s-z')} \frac{\Delta\hat{\epsilon}(z')}{\hat{\epsilon}_3}. \quad (36)$$

It is apparent from the integration limits in eq. (36) that φ' is of order d/λ .

By analogy to eq. (25), the exponential can be replaced by 1 to yield

$$\varphi' \cong \frac{iK^2 d}{\hat{\epsilon}_3} \langle \Delta \hat{\epsilon} \rangle, \quad (37)$$

where $\langle \Delta \hat{\epsilon} \rangle$ is defined as the local change $\Delta \hat{\epsilon}(z)$ averaged over its depth d :

$$\langle \Delta \hat{\epsilon} \rangle = \frac{1}{d} \int_{-d}^0 dz' \Delta \epsilon(z_s + z'). \quad (38)$$

Eqs. (37) and (38) define an effective intermediate phase for a sharp-boundary three-phase system which gives the same reflectance properties as the uniformly varying layer. Using the reflection equation in the form

$$R = \frac{|K_3 - i\varphi' - K_1|^2}{|K_3 - i\varphi' + K_1|^2}, \quad (39)$$

and expanding to first order in (d/λ) completes the derivation; the result, equivalent to eq. (25), is

$$\frac{\Delta R}{R} = \frac{8\pi n_1 d}{\lambda} \operatorname{Im} \frac{\langle \Delta \hat{\epsilon} \rangle}{\epsilon_1 - \hat{\epsilon}_3}, \quad (40)$$

where $\langle \Delta \hat{\epsilon} \rangle$ is defined by eq. (38). From eqs. (38) and (40) it is apparent that, to first order, the value of $\Delta R/R$ is independent of the thickness of the surface layer. It is evident that these results can be extended to non-normal incidence by the replacement of $(\hat{\epsilon}_2 - \hat{\epsilon}_3)$ with $\langle \Delta \hat{\epsilon} \rangle$ in eqs. (24). Owing to the symmetry between ϵ_1 and $\hat{\epsilon}_3$ in eq. (25), we note that $\langle \Delta \hat{\epsilon} \rangle$ can also be defined with respect to ϵ_1 in order to describe a uniform variation in the optical properties from ϵ_1 to $\hat{\epsilon}_3$ at the interface of a two-phase system. Such a treatment is of interest for studies of liquid-vapor interfaces, for example.

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