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POWER REFLECTION SPECTROSCOPY FROM HOMOGENOUS AND INHOMOGENOUS LIQUID SYSTEMS

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ABSTRACT

The investigation of reflectance in sigma and pi polarisation from thin surface films is carried out with the admittance method due to Hild and coworkers. For a given dielectric loss of the surface liquid film power reflection coefficients are computed in pi and sigma polarisation, with the emergence of several useful features which depend strongly in shape and contrast on the film depth; the angle of incidence and reflection; and on an inhomogeneity in the system represented by a pure metal substrate (aluminium). The presence of the metal causes a potentially useful amplification of the pi reflectivity signal at the substrate Brewster angle from very thin surface films, down to one angstrom in thickness. The results obtained for the inhomogenous liquid film metal system using the admittance method are compared with those for the same dielectric liquid parameters from a perfectly homogenous liquid of the type used in the surface film. This allows a direct comparison of film and bulk reflectivity.

INTRODUCTION

The reflectance spectroscopy of thin films, coatings, composites and interfaces is an important analytical technique in industry, for optical thin film coatings. [1] The variable angle reflection from the surface of the film or coating is a technique which is widely used in quality control. Therefore it is important to have available a quantitative method of linking the dielectric properties of the material making up the surface film to the reflectance spectrum of the film substrate system in pi and sigma polarisation. This would allow the analysis of the properties of the low dimensional material and a direct comparison of the spectra of the bulk and of the film.

The film substrate system is inhomogenous and therefore it is not

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possible [2-5] to use Maxwell's equations analytically to compute the expected reflectance from the surface layer given its complex permittivity. In order to do this one must compute the pi and sigma reflectivity using the admittance method. This produces first order differential equations from the fundamental equations governing the process of interaction of electromagnetic radiation with condensed matter. The first order (Riccatti) equations can be integrated numerically with a Runge Kutta routine using a method developed originally by Hild [2] and described by Hild and Grofscik [3]. This paper shows that the reflectivity from a thin film/metal substrate system, for example, is dramatically different in both polarisations from that expected in the case where the radiation is incident on a homogenous sample consisting of the film material in the absence of substrate. In the latter case the pi and sigma reflectivity can be calculated analytically [6,7] from the complex permittivity of the homogenous sample using the Fresnel and Maxwell equations. Therefore, in order to interpret the reflectivity spectrum from a film substrate system it is necessary to resort to the numerical methods described in this paper. The results of this paper show that the pi and sigma waves reflected from the inhomogenous system may have no superficial resemblance at all to either the dielectric absorption/dispersion of the film material or indeed the reflectivity from a macroscopic (bulk) sample consisting entirely of the film material. A quantitative analysis of the spectrum from the surface film must therefore involve the admittance technique. It is not valid to use the simple Fresnel Laws and the basic Maxwell equations for inhomogenous media. The computations in this paper show that the reflectance is strongly dependent on the angle of incidence and the depth of the surface layer. Dramatic effects are observable, according to the computations reported here, near the Brewster angle of the substrate, defined by

$$\phi_B = \tan^{-1} \varepsilon_\infty^{\frac{1}{2}} \tag{1}$$

where ε_∞ is the infinite frequency permittivity of the substrate. For aluminium, the dielectric loss in the region up to approximately 200 cm^{-1} is approximately constant at 320,000 and the permittivity at 1.5. The Brewster angle is therefore defined almost entirely by the loss, and is, to a very good approximation:

$$\phi_B = \tan^{-1}(320{,}000^{\frac{1}{2}}) = 89.8987^\circ. \tag{2}$$

By looking at glancing angles therefore the pi beam is incident on the film/ metal system near the Brewster angle. The results described later in this paper show that the reflectivity in pi polarisation from the film / metal system is unrecognisably different in its rich frequency dependence from the equivalent reflectivity [6,7] from a homogenous, infinitely thick, sample of the film material. Furthermore there is a very useful amplification effect of the metal on the reflectivity from films of about 1000 Å (10^{-5} cm) and thinner. This makes possible the detection of such films by Brewster angle reflectivity across the whole electromagnetic spectrum.

THEORETICAL METHODS

The electric and magnetic field vectors $\underset{\sim}{E}$ and $\underset{\sim}{H}$ of angular frequency ω obey the following differential equations [2-5] in an inhomogenous medium of relative permittivity $\hat{\varepsilon}$ and relative permeability $\mu(=1)$:

$$\Delta\underset{\sim}{E} + (\omega^2/c^2)\hat{\varepsilon}\underset{\sim}{E} - \mathrm{grad}\ \mathrm{div}\ \underset{\sim}{E} = \underset{\sim}{0} \qquad (3)$$

$$\Delta\underset{\sim}{H} + (\omega^2/c^2)\hat{\varepsilon}\underset{\sim}{H} + (1/\varepsilon)(\mathrm{grad}\ \hat{\varepsilon} \times \mathrm{rot}\ \underset{\sim}{H}) = \underset{\sim}{0} \qquad (4)$$

It is assumed that the system is infinite in the directions z and y and inhomogenous along the z axis:

$$\hat{\varepsilon} = \hat{\varepsilon}(z). \qquad (5)$$

The interfaces in the system are parallel to the xy plane and the surface layer is on a homogenous aluminium substrate of infinite thickness [4]. (When considering reflectivity from the material of the surface layer it is assumed that reflectivity is occurring from a homogenous, infinitely thick sample [6,7]) In the inhomogenous system the dependence of the field vector on z will be treated separately for σ and π polarisation. In π polarisation the electric field is parallel to the plane of incidence, whilst for σ polarisation it is perpendicular. σ polarisation corresponds to the TE (transverse electric) mode and, with $\underset{\sim}{E}$ in the direction y, and π polarisation to the transverse magnetic mode (TM) with $\underset{\sim}{H}$ in the direction y. The transverse field components Ey and Hy then obey the following differential equations

$$\frac{\partial^2 Ey}{\partial z^2} + \frac{\omega^2}{c^2}(\hat{\varepsilon} - \sin\phi_o)Ey = 0 \qquad (6)$$

$$\frac{\partial}{\partial z}\left(\frac{1}{\hat{\varepsilon}}\frac{\partial Hy}{\partial z}\right) + \frac{\omega^2}{c^2}\left(1 - \frac{\sin^2\phi_o}{\hat{\varepsilon}}\right)Hy = 0 \qquad (7)$$

If the admittance function is defined as

$$\hat{j}(z) = -\left(\frac{\mu_o}{\varepsilon_o}\right)^{\frac{1}{2}} \frac{H_t(z)}{E_t(z)} \qquad (8)$$

then according to the boundary conditions of Maxwell's equations, H_t and E_t are continuous transverse components and so $\hat{j}(z)$ is a continuous function of z unless $E_t = 0$ when the admittance function becomes infinite. The interaction of electromagnetic radiation with the inhomogeneous system can then be described by the following differential equations in the admittance function:

$$\frac{d\hat{j}_{TE}}{dz} = -\left(\frac{i\omega}{c}\right) [\hat{\varepsilon} - \sin^2\phi_o - \hat{j}^2_{TE}]; \qquad (9)$$

$$\frac{d\hat{j}_{TM}}{dz} = -\left(\frac{i\omega}{c}\right) [(1 - \frac{\sin^2\phi_o}{\hat{\varepsilon}})\, \hat{j}^2_{TM} - \hat{\varepsilon}]. \qquad (10)$$

These equations can be solved using the method of Hild and Grofscik [3], described in the context of epitaxials in a recent paper by Hild and Evans [4].

REFLECTIVITY FROM A HOMOGENEOUS MEDIUM

It is of interest to compare the reflectivity from the inhomogeneous system just described with that from the liquid alone. This will reveal the effect on the spectrum of the metal substrate.

It is possible to obtain the power reflection coefficients from the homogeneous liquid (the material of the surface film) analytically [6,7]. For ease of reference the set of equations used is given below, starting with the dielectric loss

$$\varepsilon''(\omega) = \frac{(\varepsilon_o-\varepsilon_\infty)\omega\gamma\phi_o(o)\phi_1(o)}{\gamma^2(\phi_o(o)-\omega^2)^2 + \omega^2(\omega^2-(\phi_o(o) + \phi_1(o)))^2} \qquad (11)$$

and permittivity

$$\varepsilon'(\omega) = \varepsilon_o - \frac{(\varepsilon_o-\varepsilon_\infty)\omega^2(\gamma^2(\omega^2-\phi_o(o))+(\omega^2-\phi_1(o))(\omega^2-(\phi_o(o)+\phi_1(o))))}{\gamma^2(\phi_o(o)-\omega^2)^2+\omega^2(\omega^2-(\phi_o(o)+\phi_1(o)))^2} \qquad (12)$$

from Mori three variable theory [9]. Here γ, ϕ_o and ϕ_1 are the three coefficients of this formula, defined in terms of molecular parameters elsewhere. For $\gamma = 1.0 \times 10^{13}s^{-1}$; $\phi_o(o) = 1.0 \times 10^{25}s^{-2} = \phi_1(o)$ the dielectric loss and permittivity are illustrated in fig. 1.

The complex permittivity is the square of the complex refractive index

$$(\varepsilon' - i\varepsilon'')^{\frac{1}{2}} = n(1 - i\kappa) \qquad (13)$$

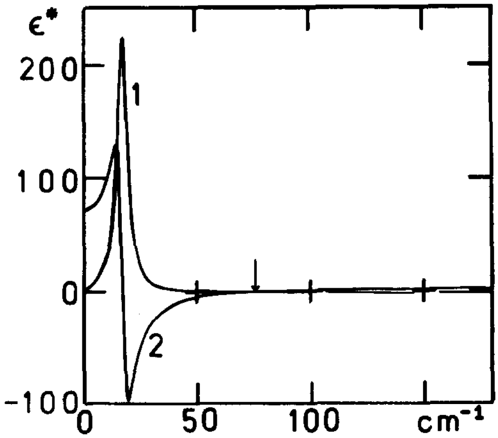

Fig. 1 Dielectric loss (I) and permittivity (2) of the surface liquid material. The arrow marks the wavenumber at which the permittivity cuts the abscissa on the high frequency side of the main dispersion.

The reflective power is then the ratio of the radiative energy reflected from the surface of the homogeneous material across the electromagnetic spectrum. It is dependent on the angle of incidence ϕ and on the state of polarisation. As for the inhomogeneous sample the direction of vibration is defined with respect to the plane of incidence with the liquid surface, and the component of the radiation vibrating parallel to this plane is the pi component, that perpendicular the sigma. The power reflection coefficient (or reflective power) for each component is given as a function of the angle of incidence and the angle of refraction χ by the Fresnel formulae:

$$R_\sigma = \frac{\sin^2(\phi - \chi)}{\sin^2(\phi + \chi)} \; ; \; R_\pi = \frac{\tan^2(\phi - \chi)}{\tan^2(\phi + \chi)} \qquad (14)$$

the angles being related by Snell's law:

$$\sin\phi = n' \sin\chi \tag{15}$$

where n' is the frequency dependent refractive index of the liquid. If at a given wavenumber the liquid absorbs, then n' becomes complex

$$\begin{aligned} n' &= n(1 - i\kappa); \\ n &= [\tfrac{1}{2}((\varepsilon'^2 + \varepsilon''^2)^{\frac{1}{2}} + \varepsilon')]^{\frac{1}{2}} \\ \kappa &= \frac{\varepsilon''}{2n}; \end{aligned} \tag{16a}$$

which implies that the process of refraction is complex:

$$n'\cos\chi = (n'^2 - \sin^2\phi)^{\frac{1}{2}} \equiv a - ib. \tag{16b}$$

It follows that:

$$R_\sigma = \frac{a^2 + b^2 - 2a\cos\phi + \cos^2\phi}{a^2 + b^2 + 2a\cos\phi + \cos^2\phi}; \tag{17}$$

$$R_\pi = R_\sigma \frac{a^2 + b^2 - 2a\sin\phi\tan\phi + \sin^2\phi\tan^2\phi}{a^2 + b^2 + 2a\sin\phi\tan\phi + \sin^2\phi\,tab^2\phi}; \tag{18}$$

where

$$a = \tfrac{1}{2}\left(\frac{x_1 + x_2}{2}\right)^{\frac{1}{2}}; \tag{19}$$

$$a^2 + b^2 = \frac{x_1 + x_2}{2} + \frac{2n^4\kappa^2}{x_1 + x_2} \tag{20}$$

with

$$\begin{aligned} x_1 &= n^2(1 - \kappa^2) - \sin^2\phi; \\ x_2 &= (x_1^2 + 4n^4\kappa^2)^{\frac{1}{2}} \end{aligned} \tag{21}$$

These relations generate the power reflection coefficients in sigma and pi polarisation from the frequency dielectric loss and permittivity of the homogeneous liquid [9].

RESULTS AND DISCUSSION

Figs. (2) and (5) provide comparisons of the pi and sigma reflectivity computed for the inhomogeneous and homogeneous systems described above. In fig. (2) it is shown that the reflectivity from a surface film of 0.1 mm

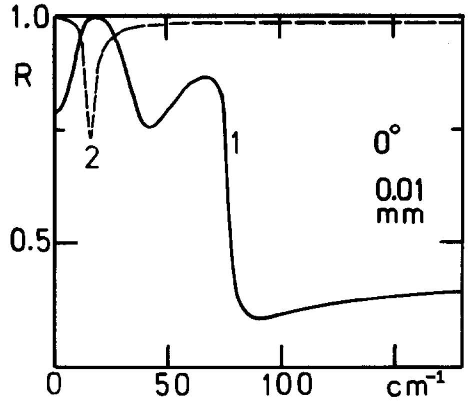

Fig. 2 Normal incidence reflectivity of a surface film of 0.01 mm on an aluminium substrate. (I) Equivalent reflectivity for a homogeneous liquid with the same properties as the surface liquid film (see text). Curve (2) reflectivity from the inhomogeneous system.

on aluminium substrate (the dielectric parameters of the film being described by eqns. (11) and (12)) consists of a single inverted peak at the same frequency as that of the dielectric loss peak in fig. (I). In contrast the reflectivity from a homogeneous sample of the surface film material is shown in fig. (I) as curve (1) and involves a band edge at about 76 cm^{-1}, the frequency at which the dielectric permittivity in fig. (I) cuts the abscissa on the high frequency side of the dispersion. Under the conditions of fig. (2) the reflectivity from the homogeneous sample is much more detailed than that from the inhomogeneous layer and at normal incidence the results in pi and sigma polarisations are identical.

It is already clear at normal incidence (fig. 2) that the results from the surface material in thin film deposited on the metal substrate and in homogeneous bulk are very different for the same dielectric permittivity (that of fig. (I)). Fig. (2) shows that it is clearly possible to use Maxwell's equations analytically in an inhomogeneous medium where there is reflection from more than one layer [4,5]. Another important result following from fig. (2) is that even for an intensely absorbing surface layer (we have used $\varepsilon_0 = \cdot 70.0$; $\varepsilon_\infty = 3.5$ for illustration) the nature of the substrate (in this case an almost perfect reflector) changes the nature of the composite reflectivity drastically (cf. curves 1 and 2 of fig. 2). This warns against the uncritical use of interferometric methods where a liquid film is placed in

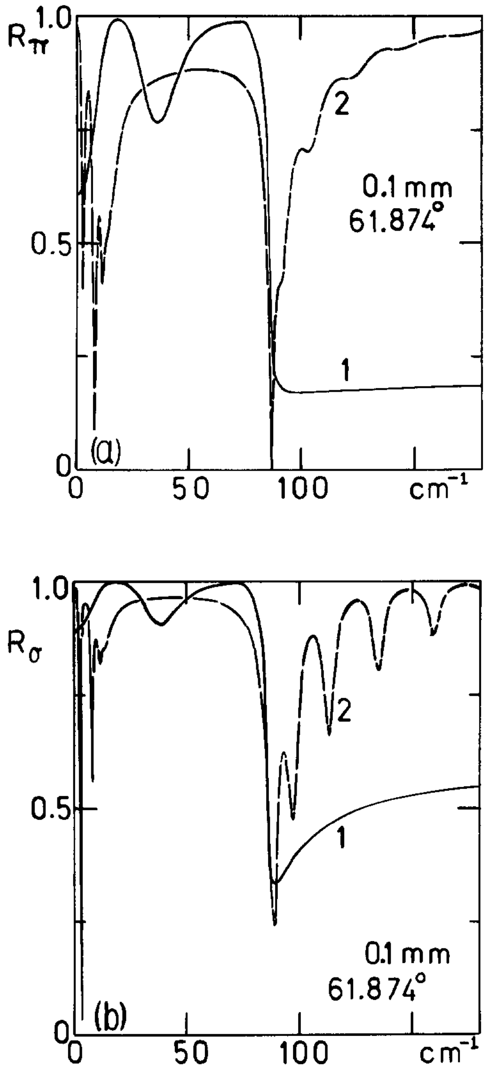

Fig. 3 Power reflection coefficients (a) in pi polarisation; (b) in sigma polarisation for (I) a homogeneous liquid system and (2) an inhomogeneous film/metal substrate system. Angle of incidence 61.874°, film thickness 0.1 mm.

one arm of the interferometer [10]. It is difficult in such methods to compensate for the effect of the aluminium mirror upon which the liquid is placed and for the resulting assymmetry in the interferogram.

For off-normal incidence as in fig. (2) the results for the reflected sigma ray and pi ray are different. In fig. (3a) there are fringes [3,4] observable in pi polarisation from the inhomogeneous system consisting of 0.1 mm of highly absorbing liquid on an Al substrate. The dielectric properties of the surface film material are again those of fig. (I). The 76 cm^{-1} band edge is identifiable both for the inhomogeneous and homogeneous systems and is strongly dependent (figs. (2) to (5)) on the angle of incidence, surface film depth, and polarisation, making it a useful feature for practical analysis of industrial samples. Both curves I and 2 of fig. (3a) are generated from the same dielectric properties (those of fig. (I))

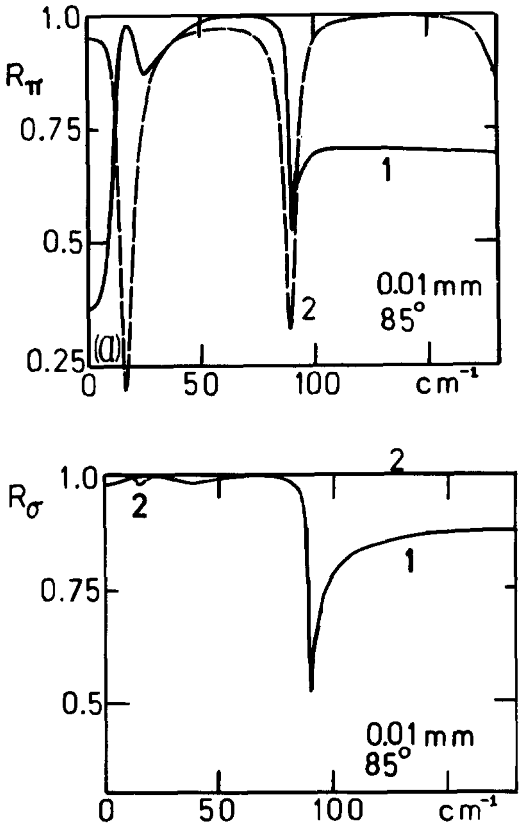

Fig. 4 As for figure (3), film thickness 0.01 mm, angle of incidence 85°

but the effect of the Al substrate is pronounced, introducing fringes, and distorting the homogeneous spectrum out of recognition.

The results equivalent to those in pi polarisation of fig. (3a) for sigma polarisation are given in fig. (3b), at the same incidence angle of 61.874°. This angle is $\tan^{-1}(3.5^{\frac{1}{2}})$ and is therefore the Brewster angle for the homogeneous medium (curve I). The fringes are more pronounced in sigma polarisation but otherwise the same distorting effect of the substrate is clearly apparent. It would not be obvious that both curves I and 2 of figs. (3a) and (3b) come from the same dielectric loss curves of fig. (I). This illustrates the importance of having available a method as in this paper of relating mathematically reflectance to dielectric loss and refractive index for both inhomogeneous and homogeneous media.

In figs. (4) the depth of the surface film has been reduced to 0.01 mm and the incidence angle increased to 85°. The result is the emergence of several features in both polarisations that could prove useful in practice. In the pi polarisation of fig. (4a) the amplification effect of the Al substrate begins to be visible in the lower frequency inverted peak of curve (2), that from the inhomogeneous system. This shows that even for a layer as thin as 0.01 mm the spectrum of the composite system is nearly full scale. Fig. (5) shows that this continues to be the case down to 1000 Å of surface material and less. The inverted peaks at 76 cm^{-1} in fig. (4) are useful analytical features both for the inhomogeneous and inhomogeneous systems. Both these curves are again generated from the dielectric parameters of fig. (I) but again the results for the homogeneous and inhomogeneous systems in fig. (4a) are very different. This difference is emphasised to a much greater degree in fig. (4b) where the reflectivity in sigma polarisation for the inhomogeneous system is dominated almost completely by the metal, so that it is unity for all frequencies except for a very small residual peak at the original peak frequency of dielectric loss (cf. fig. (I)). In great contrast the reflectivity with the metal removed (curve I) is dominated by a strong half scale 76 cm^{-1} inverted peak, at the frequency (cf. fig. (I)) where the dielectric permittivity cuts the abscissa on the higher frequency side of the overall dispersion process.

Finally fig. (5) illustrates strong contrast between homogeneous and inhomogeneous systems, but this time in a sense opposite to that of fig. (4b). The result in fig. (5) is for pi polarisation again from the same dielectric curves of fig. (I). The depth of surface film is now 1000 Å (10^{-5} cm) and the incidence angle is $\phi_B = 89.8987^{\circ}$, the Brewster angle of the aluminium substrate. Under these conditions the reflectivity of the homogeneous system

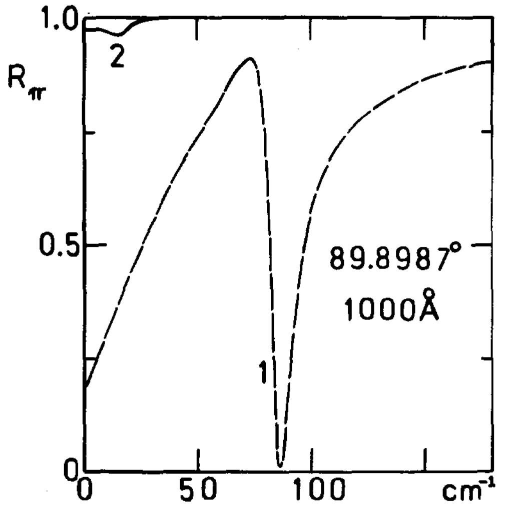

Fig. 5 As for figs (3) and (4), pi polarisation only. Film thickness 1000 Å; angle of incidence 89.8987°.

(liquid only with the metal missing) is curve 2. It can be seen that it is unity for nearly all frequencies with a small amount of residual spectral feature at low frequency. This is easily understandable in terms of mechanical analogies like skimming a stone, i.e. at such low angles nearly all the light is reflected from the inhomogeneous medium both for the sigma and pi rays. What is not so easily forecast intuitively is the result from the film/ metal system (fig. I)). It is seen from fig. (5) that the 76 cm^{-1} feature familiar from figs. (2) to (4) has been amplified to full scale even for a film as thin as 1000 Å. In an addition there has appeared in curve I of fig. (5) a new feature around zero frequency which is about 0.75 scale. All this occurs at the precise Brewster angle of the substrate. Apart from the practical usefulness of such full scale features in analysing optical films and polymers deposited on metals, oxide films on metals, alloys and so on it is clear that the contrasts between the homogeneous and inhomogeneous system is at a maximum under the conditions of fig. (5) i.e. at the Brewster angle of the Al and for very thin films. Clearly it would be impossible to guess that the two curves of fig. (5) shared in common the dielectric properties illustrated in fig. (I) without the intervention of the admittance method to solve the relevant governing equations, under all conditions. It is abundantly clear from fig. (5) that the interaction of electromagnetic radiation with homogeneous and inhomogeneous media is strikingly different, especially at low angles.

We have verified that the feature for the inhomogeneous system in fig. (5) persists to film thicknesses of only 1.0 Å thus making it possible to detect monolayers using the metal amplification technique. Alternatively the technique could be useful in the design of reflectors of surface coatings, and anti-reflector devices.

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