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Full Length Article

An original method to determine complex refractive index of liquids by spectroscopic ellipsometry and illustrated applications

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ABSTRACT

We present a method to characterize optical properties of liquids by spectroscopic ellipsometry. The experiments use a specific liquid cell that avoids disturbance of waves at air-liquid interface and allows the determination of the real and the imaginary part of the refractive index, with a sensitivity of the latter below 10^{-4}. The method is illustrated by results obtained with a spectroscopic phase modulation ellipsometer on several liquids such as deionised water, microscope oil and protein solution. Comparisons of the method with standard techniques are given.

1. Introduction

Ellipsometry has become a reference technique that provides optical properties which allow one to investigate or qualify material intrinsic properties. A survey of the scientific literature and industrial applications reveals that spectroscopic ellipsometry is applied mostly to characterize solids and generally thin film samples with a more or less complex structure [1]. Ellipsometry has also been applied to study solids in liquid ambients [2] and liquid-liquid or air-liquid interfaces [3–6] but to our knowledge, there has not been an application of ellipsometry to efficiently characterize real and imaginary parts of the complex refractive index of the actual liquids. There are several reasons for this, the most realistic one being that for liquids, transmission spectroscopy remains the reference technique, allowing reasonably good determination of the extinction coefficient. However transmission spectroscopy does not inform independently on the real part of the refractive index, for which Kramers-Kronig methods are required. On the other hand, ellipsometry is the only technique that gives access to both the real and the imaginary part of the optical indices of materials (N = n + ik) from measurement of the ellipsometric angles ψ and Δ at incidence angle Φ in air, simply by applying the two phases (bulk-air) semi-infinite model:

$$\rho = \tan\psi e^{i\Delta} \text{ and } N^2 = \sin^2\Phi[1 + \tan^2\Phi\frac{(1-\rho)^2}{(1+\rho)^2}]$$

2. Limitations of the bulk modelling approach

A difficulty met when measuring bulk materials by ellipsometry is the inevitable influence of overlayers, even at the nanometer scale because of the sensitivity of the technique. For bulk solids, this overlayer is often a combination of both roughness and contamination or oxidation. Its presence rules out the possibility to apply the semi-infinite direct inversion Eq. (1). For liquids, similar difficulty takes place with the overlayer being due to capillary waves. We illustrate in Fig. 1 what may be the most critical influence of these surface defects to ellipsometric analysis: it is impossible to distinguish between two systems such as a transparent liquid of pure real index covered by 1.2 nm overlayer (Fig. 1a) from a slightly absorbing liquid of complex index covered by 1 nm overlayer (Fig. 1b) because both systems generate nearly identical ellipsometric response (Fig. 1c) even at different angles of incidence. Inputs for these simulations are:

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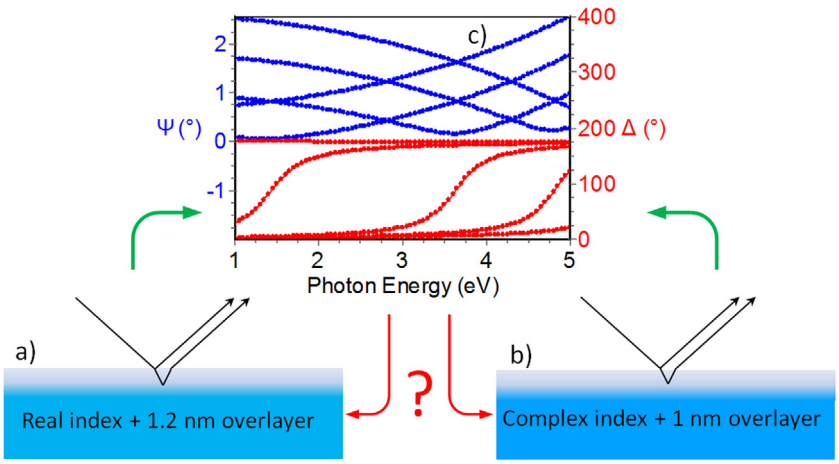

Fig. 1. Illustration for ambiguous ellipsometric inverse problem (red arrows). Two different models a and b having similar ellipsometric signature at angles of incidence varying between 52.5° and 54.5°(c). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

- n vary between 1.33 to 1.44 and k vary between 3.10^{-4} to 2.10^{-3} from near infrared to ultraviolet following an harmonic oscillator dispersion formula
- angles of incidence vary every 0.5° between 52.5° and 54.5°, on both sides of Brewster angle of the liquid, in order to improve the sensitivity of the ellipsometric data to the overlayer.

This correlation can explain the lack of studies on liquids by standard reflection ellipsometry. It also illustrates the general limitation of the technique to detect small absorptions of bulk phases. The reason why this theoretical example is given is because the technique described in the next section takes advantage of a new principle to overcome the difficulties encountered with liquid overlayers or weak absorptions.

3. Experimental principle and background for modeling

We propose an ellipsometric setup to characterize the liquids that combines several specific aspects which are summarized in Fig. 2.

The liquid under study is sandwiched between the base of an isosceles prism and a bulk mirror. This ensures the absence of surface waves at both interfaces of the liquid. The thickness of the liquid under study is mechanically fixed by spacers with thicknesses in the range of 50–200 μm. The incident ellipsometric beam enters the prism under normal incidence and the angle of the prism and its material are so that light is partially reflected and transmitted at the prism-liquid interface. This method should not be confused with the total reflection technique. Finally, light is reflected at the liquid-mirror interface. A regime of multiple reflections takes place into the liquid layer when it is sufficiently transparent. The thickness of the liquid between spacers makes the optical path of multiple reflections at oblique incidence in the range of 200 μm and more. Such a transmitted path of light through the liquid enables a very significant improvement of sensitivity to the small absorption of the liquid compared to the one obtained during the bulk studies.

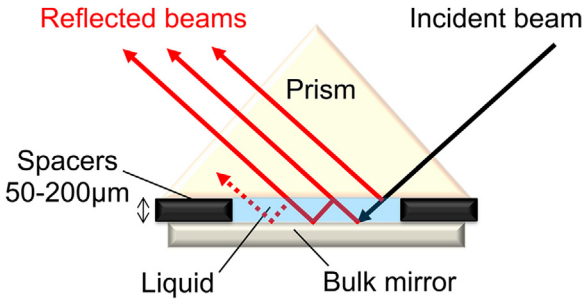

Fig. 2. Principle of the method. Multiple reflected beams become negligible after the third one.

In such a regime of multiple reflections into the liquid, given the typical range of thicknesses, there are no interferences as the path difference between multiple emerging beams is larger than the coherency length of the optical setup, which is given by the spectral resolution of the detection system, typically in the range of 4 nm. Thus, regarding thin film optics, the modeling for such experiments consists of the incoherent summation of multiple reflected beams, adding their contributions in terms of intensities. The estimation of the related intensities between each beam shows that one can neglect the contributions of beams after the third one as illustrated in Fig. 2. The modeling process comparing measured data and calculated one relies on the approach developed in Ref. [7]. Measured data are m_{33} and m_{34}, 2 elements of the Mueller matrix of the system, often mentioned as variable Is and Ic. With brackets <> denoting products averaged over spectral resolution, the ellipsometric parameters Is and Ic have the following form:

$$m_{33} = \mathrm{Ic} = \frac{2Re\langle r_p r_s^* \rangle}{\langle r_p r_p^* \rangle + \langle r_s r_s^* \rangle} \text{ and } m_{34} = \mathrm{Is} = \frac{2Im\langle r_p r_s^* \rangle}{\langle r_p r_p^* \rangle + \langle r_s r_s^* \rangle} \quad (2)$$

Calculated data come from the geometric serie summation of partial beam decomposition. When neglecting any overlayer surrounding the liquid, they take the form:

$$\langle r_x r_y^* \rangle = r_{01x} r_{01y}^* + \frac{t_{01x} t_{01y}^* t_{10x} t_{10y}^* r_{12x} r_{12y}^* e^{-4\mathrm{Im}(\beta)}}{1 - r_{10x} r_{10y}^* r_{12x} r_{12y}^* e^{-4\mathrm{Im}(\beta)}} \quad (3)$$

where r (resp. t) stands for Fresnel reflection (resp. transmission) coefficient and the index x or y for either p or s polarization mode. The asterisk stands for complex conjugate, the indices 0, 1, 2 denote interfaces between media, respectively, prism, liquid and mirror. The film phase thickness **β** depends on the thickness of the liquid d and the wavelength λ:

$$\beta = 2\pi \frac{d}{\lambda} \left(n_1^2 - n_0^2 \sin^2 \Phi \right)^{1/2} \quad (4)$$

A special device holding the prism, the liquid, the spacer and the mirror was developed in order to achieve the work shown here. The prism is made of fused silica with an isosceles angle smaller than critical angle, typically 55°. The cell is made of PVC and the bulk mirrors in the present studies are bare silicon wafers. Spacers are

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