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Characterization of interfacial index gradients by spectroscopic ellipsometry at variable angle of incidence

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We discuss the characterization of inhomogeneous thin films by ellipsometry. We compare the sensitivity of ellipsometry measurements for different configurations – chromium mirror, total reflection prism and surface plasmon excitation – taking as an example the refractive index gradient of a polymer grafted layer. For thin layers (with a thickness much smaller than the wavelength), it is rather difficult in any configuration to analyze the details of the refractive index profile by a direct examination of the ellipsometric parameters. We thus propose an alternative treatment of the measured quantities, based upon the angular dependence of the effective thickness and refractive index of the inhomogeneous layer, calculated in the framework of the linear Born approximation.

1. Introduction

In recent years there has been an increased interest for the study of refractive index gradients, concerning both their elaboration and their characterization. In this work we develop a method of characterization of refractive index profiles by ellipsometry.

More specifically, we study the index gradient resulting from the concentration profile which settles down at the solid–liquid interface when end-functionalized polymers interact with a solid wall. Experimental confirmation of the index profiles predicted for interfacial polymer layers [1–3] has been attempted making use for instance of the fluorescence induced by evanescent waves [4], or of neutron diffusion [5] and neutron reflectivity [6]. For a long time, optical methods have also been used either by measuring the reflectivity as a function of the angle of incidence [7] or by ellipsometry [8–10]; in all these optical studies, it was assumed that the interfacial layer is a film with sharp interfaces and constant refractive index. However, when the index profile is slowly decreasing, the equivalent thickness and refractive index are found dependent on both the wavelength and the angle of incidence, as underlined by Charmet and de Gennes [11]. We explore this dependence below to extract further information on the index profile.

This paper presents calculated ellipsometric data for transparent media having a refractive index gradient, and discuss the ability to distinguish between two theoretical predictions for index profile of a grafted polymer layer from spectroscopic ellipsometry measurements at various angles of incidence. In the second section, we describe the models which we used to simulate the index profile in the interfacial layer and the method which we employed for the numerical calculation of the optical properties of an inhomogeneous layer. In the third section, we review several experimental configurations which could be adapted to the study of polymer layers and we discuss their sensitivity. In the fourth section, we use

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the spectral and angular dependence of the effective thickness and refractive index, in order to detect the existence of a profile gradient and to obtain the first moments of the profile.

2. Profile models for grafted polymer layers – Calculation of the ellipsometric parameters

We study grafted polymer layers obtained from end-caped copolymers. The functional end of the chain sticks to the surface and, when the density of the attached points is large enough, the chain extends towards the solvent, in a "brush" configuration.

A first model for the grafted chains [12] predicted a step-like concentration profile given by

$$\Phi(z)=N\sigma a/L\,,\quad \text{for } z\leqslant L\,,$$
$$\Phi(z)=0\,,\quad \text{for } z>L\,,\qquad (1)$$

where L is the layer thickness, N is the number of monomers in the chain, a is the characteristic size of a monomer and σ is the surface end-density.

Recently, it has been shown [3] that a more realistic model leads to a concentration profile which follows a parabolic law:

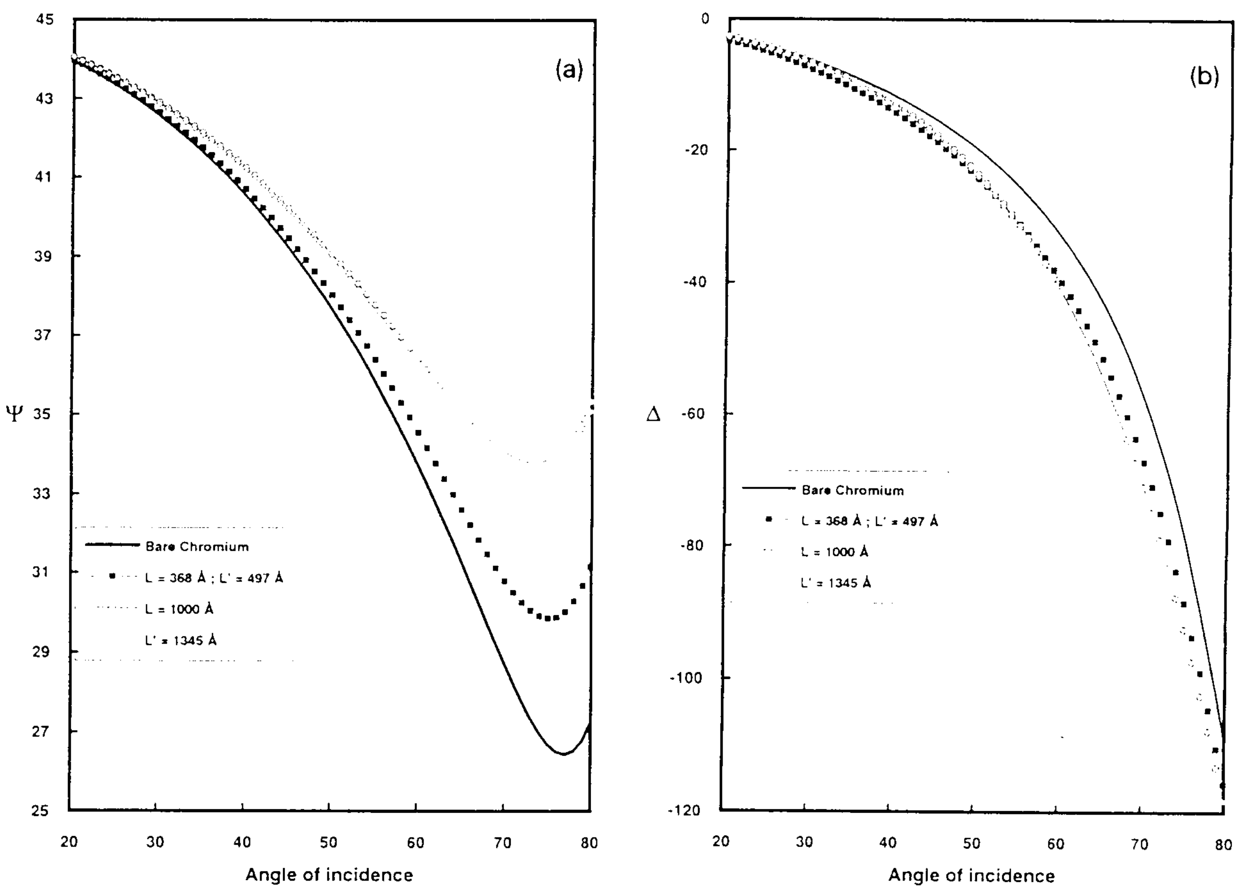

Fig. 1. Variation of the ellipsometric parameters Ψ (a) and Δ (b) with the angle of incidence, calculated at $\lambda=6000$ Å for: the bare chromium substrate (——); chromium coated with a polymer layer having a step-like index profile with thickness $L=368$ Å (—■—), $L=1000$ Å (– ○ –) and a parabolic profile with the corresponding thicknesses: $L'=497$ Å ((—■—), no distinguishable from $L=368$ Å), $L'=1345$ Å (– ◇ –). Figure c shows the differences $\delta\Psi$ and $\delta\Delta$ between the step-like and the parabolic index profile for the two chosen thicknesses.

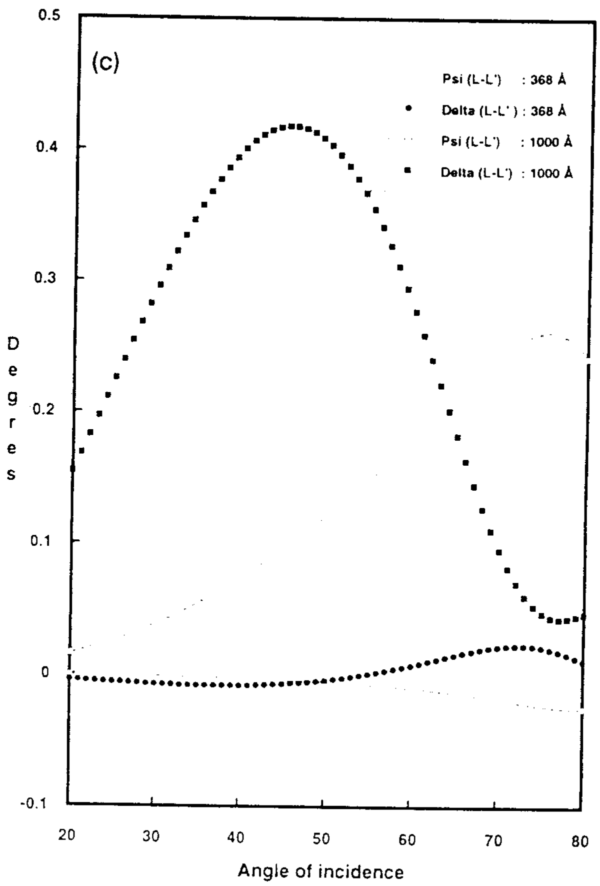

Fig. 1 (continued).

$$\Phi(z)=\frac{\pi^2}{8N^2}\left(\frac{L'^2}{a^2}-\frac{z^2}{a^2}\right), \quad \text{for } z\leqslant L',$$

$$\Phi(z)=0, \qquad \text{for } z>L'. \tag{2}$$

We compare these two profiles at fixed adsorbed amount $\Gamma=\int_0^\infty \Phi(z)\,dz$, which leads to the following relation between the two profile lengths

$$L'/L=(\pi/24)^{-1/3}=1.3447.$$

The optical properties of the grafted polymer layers, are thus described by the following two refractive index profiles.

Step-like:

$$n(z)=n_0, \quad \text{if } 0\leqslant z\leqslant L,$$

$$n(z)=n_s, \quad \text{if } z>L,$$

$$n(z)=n_2, \quad \text{if } z<0. \tag{3}$$

Parabolic:

$$n(z)=(n'_0-n_s)(1-z^2/L'^2)+n_s, \quad \text{if } 0\leqslant z\leqslant L',$$

$$n(z)=n_s, \quad \text{if } z>L',$$

$$n(z)=n_2, \quad \text{if } z<0, \tag{4}$$

where n_2 is the index of the substrate, n_s is that of the dilute polymer solution far from the wall (in our case n_s is the index of water), n_0 and n'_0 are the index values of the two profiles at the wall; we choose the index of the pure polymer equal to 1.60, the volume fraction of polymer at the surface ($z=0$) 0.3 for the parabolic profile and therefore 0.27 for the step-like index profile. This leads to the following numerical values for the refractive index:

$$n_s=1.33, \quad n_0=1.4033, \quad n'_0=1.4111.$$

We considered two different thicknesses for the step-like profile: $L=368$ Å and $L=1000$ Å. The corresponding characteristic lengths for the parabolic profile are then: $L'=497$ Å and $L'=1345$ Å. We calculated the ellipsometric response of the grafted polymer layer in different geometrical configurations for the two profile models.

The quantity measured by an ellipsometric experiment is the ratio ρ of the complex reflected amplitudes associated with the two polarization states s and p, respectively perpendicular and parallel to the plane of incidence.

$$\rho=r_p/r_s=\tan\Psi\exp(i\Delta).$$

The numerical calculation of the ellipsometric coefficients Ψ and Δ is straightforward in the case of an interface between two semi infinite media (Fresnel formulae) or in the case of a thin homogeneous layer [13]. However, the optical response of a medium presenting a refractive index gradient is not exactly known in general. We indeed have to integrate the equation of propagation of the electromagnetic wave in a region where the refractive index is a function of the position. An analytical solution can be found only in simple cases (linear profile, exponential profile, ...) at normal incidence [14]. Charmet and de Gennes [11] proposed a method of resolution for slowly varying profiles of the refractive index $n(z)$, valid in the Born approximation to first order in $(n(z)-n_s)$. This approach allows to express Ψ and Δ as a function of the Fourier transform of $n(z)$, thus offering a way to solve the inverse problem, namely to express $n(z)$ starting from the measurement of Ψ and Δ.

Our method of numerical calculation of Ψ and Δ, which divides the profile in elementary sub-layers of constant refractive index, is valid whatever the shape of the profile, provided that its thickness is small enough. Each elementary layer i is characterized by its thickness d_i and its complex index n_i; the characteristic matrix of the layer i is written as follows [13]:

$$\mathbf{M}_i = \begin{pmatrix} \cos\beta_i & (i/p_i)\sin\beta_i \\ ip_i \sin\beta_i & \cos\beta_i \end{pmatrix}, \tag{5}$$

where

$$\beta_i = (2\pi/\lambda_0) n_i d_i \cos\Theta_i ,$$

$$p_i = n_i \cos\Theta_i , \quad \text{in s polarization} ,$$

$$p_i = \frac{n_i}{\cos\Theta_i} , \quad \text{in p polarization} .$$

Θ_i is the angle of refraction in the region i and λ_0 the wavelength of light in the vacuum.

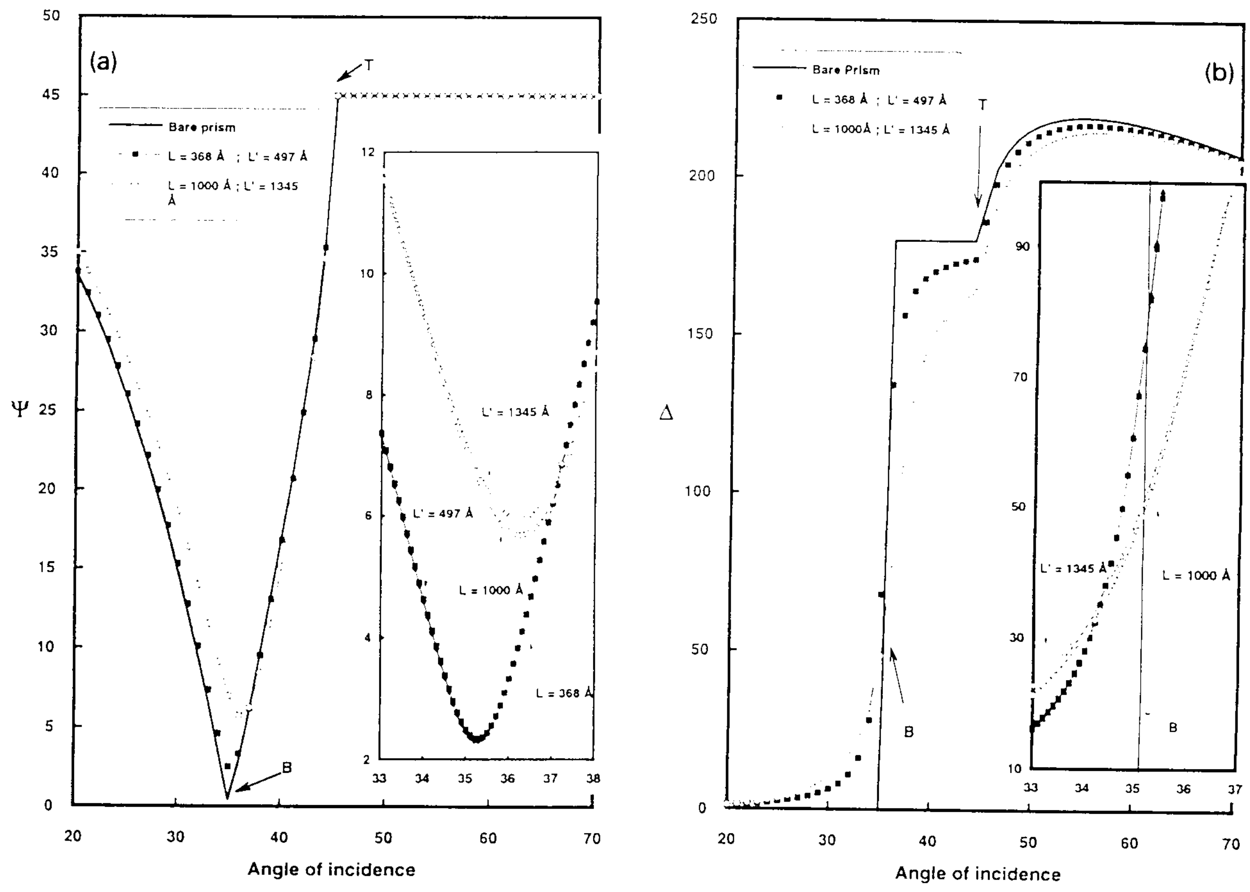

Fig. 2. Variation of Ψ (a) and Δ (b) as a function of the angle of incidence at $\lambda = 6000$ Å for a polymer layer adsorbed on a prism (index of the prism $n_p = 1.89$): bare prism (——); prism coated with a layer having a step-like profile $L = 368$ Å (—■—), $L = 1000$ Å (–○–); prism coated with a layer having a parabolic profile ($L' = 497$ Å (–◆–), $L' = 1345$ Å (–◇–)). B denotes the Brewster angle, and T the total reflection angle. The insert displays an enlargement around the Brewster angle and shows that the distinction between step-like and parabolic profile is possible for the thickest layer. Variation of Δ (c) in the total reflection region in the same conditions as (a) and (b).

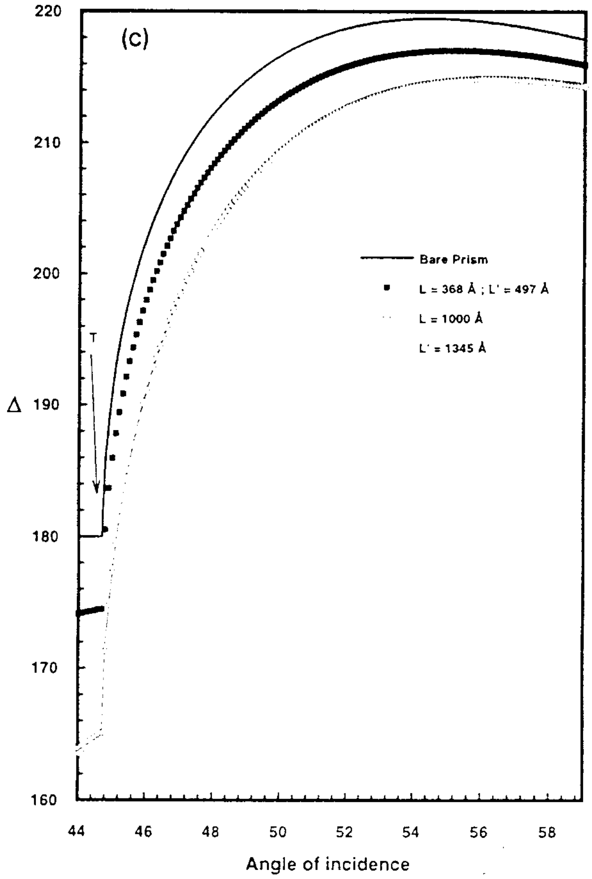

Fig. 2 (continued).

The characteristic matrix of a multilayer stack is obtained by multiplying the matrix of the elementary layers. We obtained r_p or r_s by writing

$$r_{s,p} = [p_0(m_{11} + p_s m_{12}) - (m_{21} + p_s m_{22})] \times [p_0(m_{11} + p_s m_{12}) + (m_{21} + p_s m_{22})]^{-1}, \qquad (6)$$

where p_0 and p_s correspond to the p_i's for the entrance and the exit medium for this angle of refraction and m_{ij} are the elements of the matrix **M** characteristic of the stack for the chosen polarization (s or p).

3. Sensitivity of ellipsometric measurements in various experimental configurations

The ellipsometric results reported in the literature were obtained on layers of polymers adsorbed from the solution onto chromium, gold or platinum mirrors, either in static [8] or under flowing conditions [9]. We calculated the ellipsometric parameters Ψ and Δ for a grafted polymer layer on a chromium mirror assuming a step-like profile and a parabolic profile.

The variations of Ψ and Δ as a function of the angle of incidence are drawn in figs. 1a, b. The calculation was made for a wavelength of 6000 Å. The (complex) refractive index of chromium at this wavelength is $n = 3.48 + \mathrm{i}\,4.36$, the other indices are those given in section 2. It is found that the difference between the bare substrate and the substrate coated by the grafted polymer is maximum at an angle of incidence of 75° for Ψ and 65° for Δ (the results reported in the literature were generally obtained at a fixed angle of incidence chosen between 70° and 80°). The ability of ellipsometry to distinguish between the two profiles is better shown in fig. 1c where we present the difference between the Ψ and Δ values obtained for the step-like profile and the parabolic profile for two different thicknesses ($L = 368$ Å and $L = 1000$ Å). It is clear from the figure that for the thinnest layer ($L = 368$ Å) it is not possible to decide between the two profiles from the Ψ and Δ measurements in this configuration; for the thicker layer ($L = 1000$ Å) the maximum Ψ and Δ differences between the two profiles are $\delta\Psi = 0.25°$ and $\delta\Delta = 0.4°$, therefore they become measurable. Notice however that they do not correspond to the same angle of incidence. This figure illustrates the necessity of performing ellipsometric measurements at variable angle of incidence.

The second experimental situation analyzed in our study is that in which the polymer is grafted on a total reflection prism, i.e. a glass prism with a refractive index n_p higher than the one of the solution (we choose $n_p = 1.89$). For a given wavelength, we considered two angular regions: the neighbourhood of the Brewster angle Θ_B and the domain of total reflection ($\Theta > \Theta_T$). With the chosen numerical values, the Brewster angle of the prism in presence of the diluted solution (index n_s) is $\Theta_B = 35.13°$, the angle of total reflection is: $\Theta_T = 44.72°$. The bare prism surface is supposed ideal, so that Δ changes from 0 to 180°, and Ψ goes through a null minimum, for $\Theta = \Theta_B$. For the prism coated with the polymer layer, the Brewster angle, defined as the angle of incidence for which $\Delta = 90°$, or which makes Ψ minimum, is moving towards higher angles of incidence with respect to the bare prism value. In that case the minimum Ψ value is not zero anymore, as we can see in figs. 2a, b, both corresponding to a wavelength of 6000 Å. We can differentiate the two profiles for the thicker brush ($L = 1000$ Å). The maximum difference between the two profiles is around 2° for Δ and 0.2° for Ψ. We notice an improvement on the sensitivity, as compared to the preceding case of the adsorption on a chromium mirror. Nevertheless the distinction between the step-like and the parabolic profile is still difficult for the thin profile.

When working at an angle of incidence $\Theta > \Theta_T$, Ψ stays constant and equal to 45° as expected (the whole light intensity is reflected). By contrast, the phase Δ varies strongly with the angle of incidence. The information brought by Δ was used to study the isotropic–nematic transition of liquid crystals [15] using an ellipsometer with a phase modulation. Despite the large Δ variation with the thickness of the grafted layer (fig. 2c), we do not see a real improvement on the sensitivity to the shape of the profile.

The characterization of interfacial layers can be achieved in a very sensitive way by the optical excitation of surface electromagnetic waves. Such an excitation is possible in a spectral range where the dielectric constant is negative; this condition is satisfied if we have: $\epsilon_1 < 0$ and $\epsilon_2 \ll |\epsilon_1|$ ($\epsilon = \epsilon_1 + i\epsilon_2$) [16]. An easy way to generate surface plasmons is to use a glass prism covered by a thin Ag layer at the

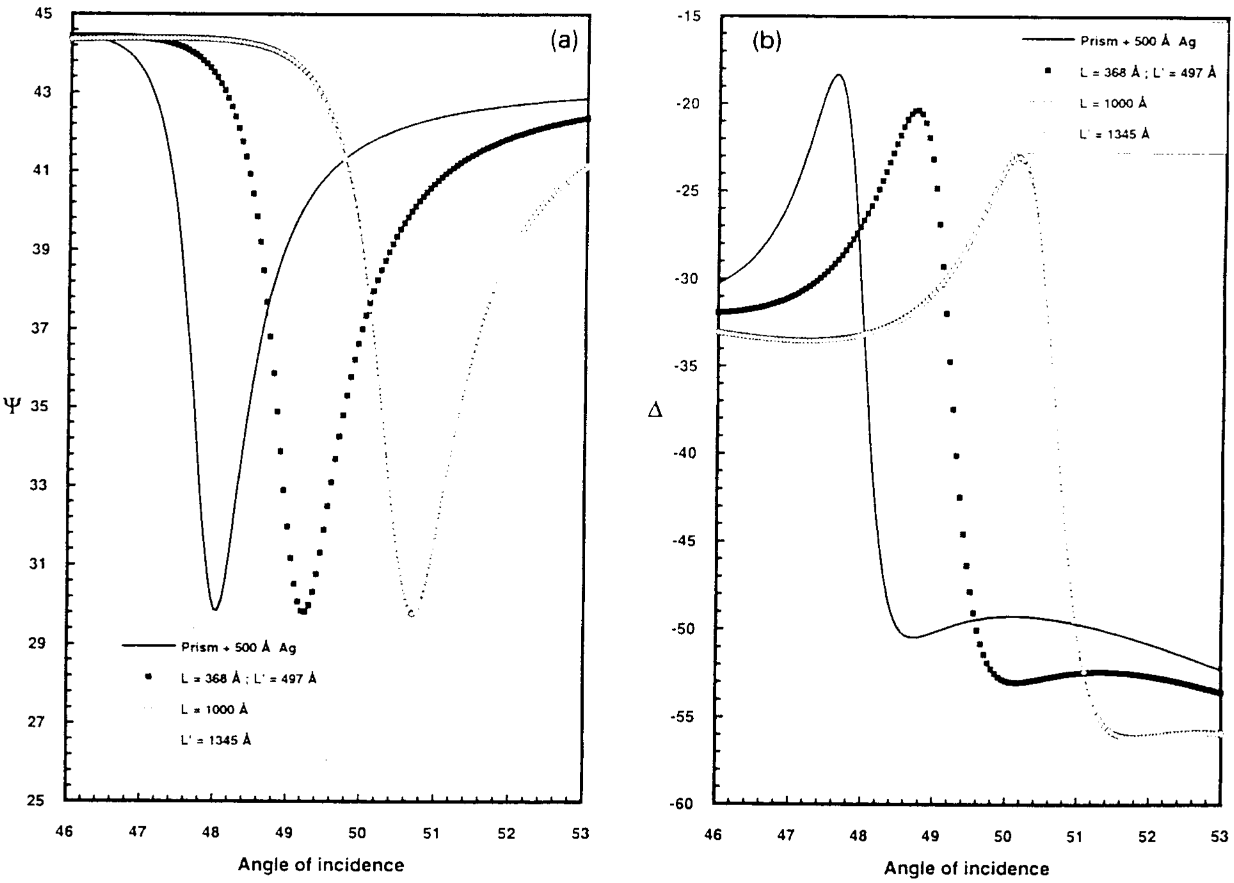

Fig. 3. Variation of Ψ (a) and Δ (b) as a function of the angle of incidence at $\lambda = 6000$ Å in the configuration of surface plasmon excitation: prism coated with a 500 Å thick Ag film (——), adsorption of a polymer layer on the prism coated with Ag: assuming a step-like index profile ($L = 368$ Å (—■—), $L = 1000$ Å (–○–)) and a parabolic profile ($L' = 497$ Å (—■—), $L' = 1345$ Å (–◇–)).

surface of which the polymers will be adsorbed. We can observe a resonance in Ψ and Δ, the angular position of which varies with the thickness of the profile. Figs. 3a, b show the ellipsometric parameters Ψ and Δ calculated in the case of a glass prism of index $n_p = 1.89$, covered by a Ag layer of 500 Å ($\epsilon = -16.5 + i\ 0.22$) on which polymer layers of increasing thicknesses are adsorbed. We point out the extreme sensitivity of the method to the thickness of the profile, the position of Ψ minimum shifting by 1.5° when L increases from 368 Å to 1000 Å. The shift is of the same order of magnitude for Δ. The sensitivity to the shape of the profile is not so large; for $L = 1000$ Å the shift of the minimum of Ψ and of the point of inflexion of Δ is as small as 0.05° and 0.1° when changing the profile from step-like to parabolic.

4. Experimental evidence for the existence of a gradient of index – Discussion

The experimental determination of the actual form of the refractive index profile is a rather difficult problem: even when one has a few theoretical forms to test, it may be experimentally impossible to discriminate between these theoretical models from Ψ and Δ measurements, as suggested in section 3 with our a priori calculation.

We propose hereafter a method which allows to demonstrate the *existence* of a gradient of refractive index in an interfacial layer, using spectroscopic measurements at variable angle of incidence.

As in the last section the following calculations

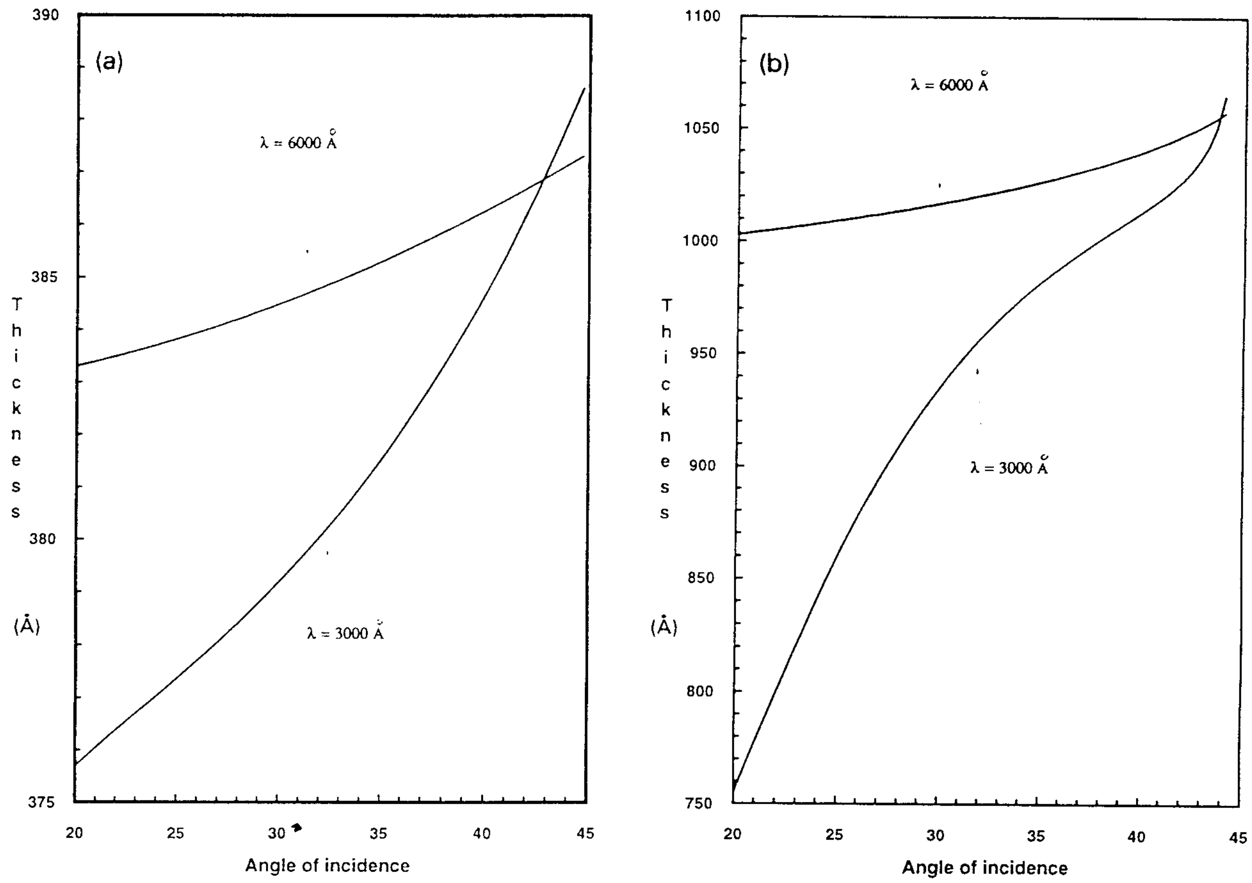

Fig. 4. Equivalent thickness d_{eq} as a function of the angle of incidence calculated as explained in the text at two wavelengths, for the thicknesses of a parabolic index profile: $L' = 497$ Å (a) and $L' = 1345$ Å (b).

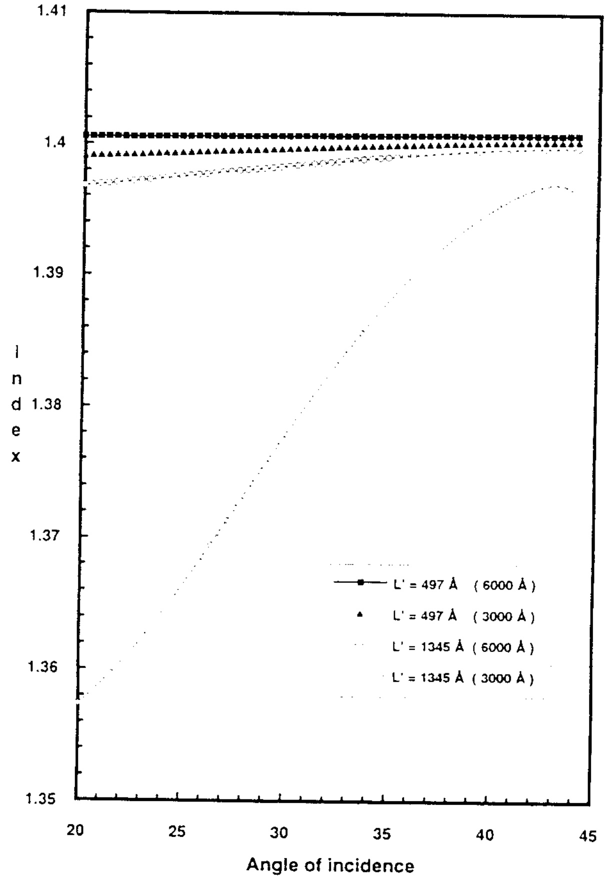

Fig. 5. Equivalent index n_{eq} as a function of the angle of incidence calculated as explained in the text at two wavelengths, for two thicknesses of a parabolic index profile.

correspond to a grafted polymer layer on a total reflection prism. This configuration is of practical interest, because the angle of incidence can easily be varied, which is not the case for the cells normally used for the adsorption on a metallic mirror.

We assume a parabolic refractive index profile and calculate the values of Ψ and Δ as a function of the angle of incidence Θ for two different thicknesses: $L'=497$ Å and $L'=1345$ Å and for two different wavelengths easily available in ellipsometry: $\lambda_1=6000$ Å and $\lambda_2=3000$ Å. For this calculation, we did not take into account neither the dispersion of the refractive indices of the prism and of the polymer nor a possible optical absorption of the solution at 3000 Å.

These calculated Ψ and Δ values were then considered as experimental data and analyzed by assuming that the adsorbed layer was a homogeneous layer with refractive index n_{eq} (constant over the depth of the layer) and a thickness d_{eq}. These equivalent quantities n_{eq} and d_{eq} were determined as a function of the angle of incidence ($\Theta<\Theta_T$) (figs. 4a, b and 5). If the layer were homogeneous, d_{eq} and n_{eq} would be independent of λ and Θ. In fact, as a consequence of the presence of a parabolic gradient of the refractive index, we found that the values of d_{eq} are always smaller than L', and vary with the angle of incidence, the variation depending of both the wavelength and the thickness of the profile. Except in the vicinity of Θ_T, the equivalent thickness measured at $\lambda_2=3000$ Å is always smaller than the one measured at $\lambda_1=6000$ Å. For the largest L' value the variations of d_{eq} and n_{eq} with the angle of incidence are definitely noticeable and therefore very easy to determine experimentally. For the thinner profile n_{eq} is not very sensitive to the angle of incidence or to the wavelength.

These results clearly show that a convenient way to detect the presence of a gradient of refractive index through an interfacial layer is to perform ellipsometric measurements at different wavelengths and angles of incidence and to verify whether the effective thickness and index present significant variations with λ and Θ. We now examine if more information about the profile can be extracted from the variations of n_{eq} and d_{eq}.

Charmet et al. [11] calculated the reflectance of a diffuse layer for a plane wave travelling from a medium with index n_s to a medium with index n_2 throughout an interfacial region of spatially varying refractive index. They gave expressions of the ellipsometric parameters as a function of the Fourier transform of the profile in the Born approximation. Marques et al. [17] worked out this approximation in more detail and extended this model to the total reflection geometry. Moreover, they were able to write expressions of the effective thickness $d_{eq}(q)$ and index $n_{eq}(q)$ as a function of the sine and cosine Fourier transforms of the profile (in the following part of the paper, the index eq will be dropped).

$$\delta n(q)\{1-\cos[2q\,d(q)]\}=2q\int_0^\infty \mathrm{d}z\,\delta n(z)\,\sin(2qz)\,,$$

$$\delta n(q)\,\sin[2q\,d(q)]=2q\int_0^\infty \mathrm{d}z\,\delta n(z)\,\cos(2qz)\,. \tag{7}$$

In these expressions $n(z)=\delta n(z)+n_s$, and for the parabolic profile $\delta n(z)=(n_0'-n_s)(1-z^2/L'^2)$, q is the component of the wavevector normal to the interface. In the total reflection geometry:

$q=(2\pi/\lambda)\sqrt{n_s^2-n_p^2\sin^2\Theta}$,

where Θ is the angle of incidence in the prism.

In the total reflection geometry, q vanishes for a finite angle Θ_T (the angle of total reflection), allowing in practice a precise scanning of the small q region. Using the above eqs. (7), it is in principle possible to extract the profile from ellipsometric data when an inverse Fourier transform can be accurately performed. This condition is generally fulfilled when the profile extends over a distance many times larger than the light wavelength. In the opposite cases (thin profiles), we can expand the arguments of the sine and cosine Fourier transforms for small q vectors. The successive coefficients of the expansion are related to the successive moments of the profile Γ_i defined by

$$\Gamma_i=\int_0^\infty \mathrm{d}z\,z^i\,\delta n(z)\,. \tag{8}$$

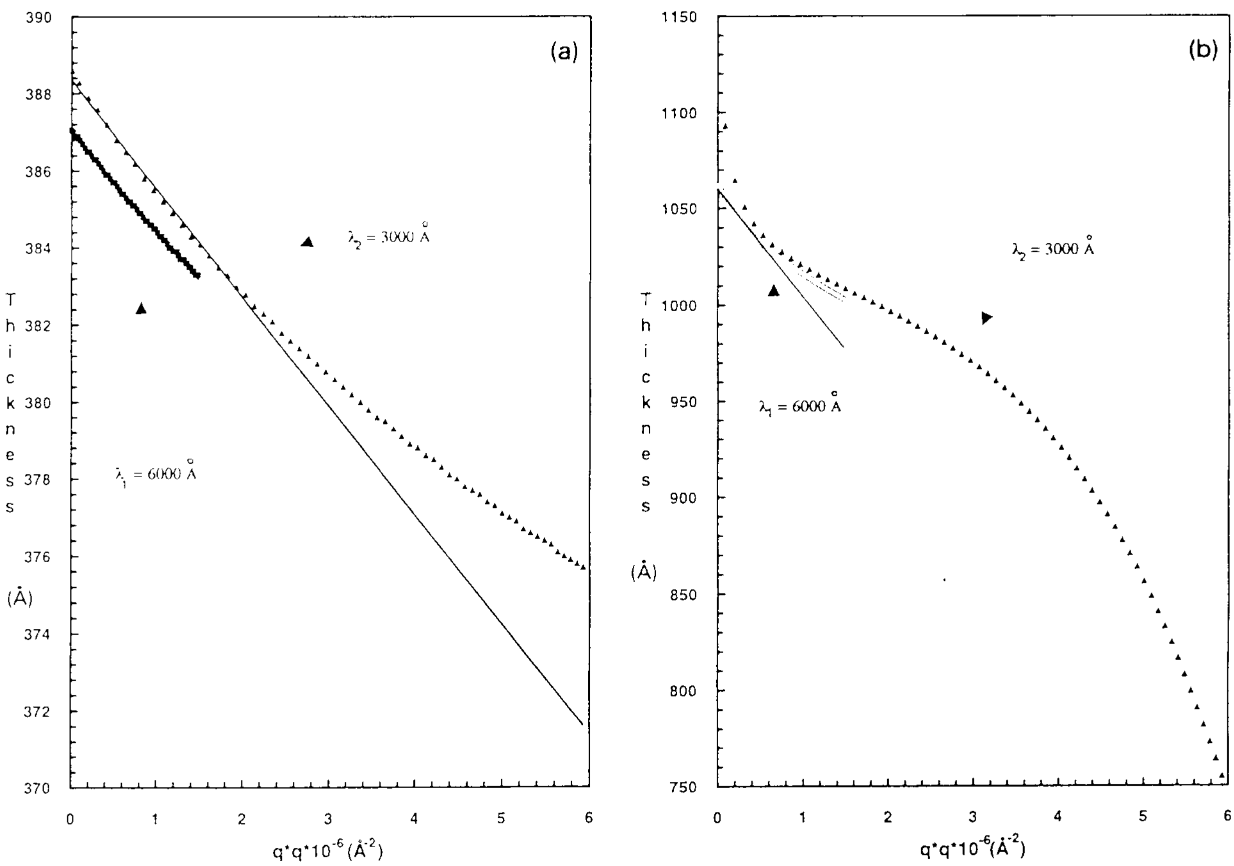

Fig. 6. Variation of the equivalent thickness d_{eq} as a function of q^2, q being the component of the wavevector normal to the surface of the polymer layer at two wavelengths, for two thicknesses of a parabolic index profile: $L'=497$ Å (a) and $L'=1345$ Å (b).

Table 1
Values of the coefficients d_0 and d_2 obtained by fitting the equivalent thickness d_{eq} with expression (9) for small q values.

	$L'=497$ Å $\lambda_1=6000$ Å	$L'=497$ Å $\lambda_2=3000$ Å	$L'=1345$ Å $\lambda_1=6000$ Å
d_0 (Å)	387	388	1058
d_2 (Å^3)	-2.579×10^6	-2.823×10^6	-54.55×10^6
L'_{exp} (Å)	516	517	1411

For thin profiles it is convenient to expand $d(q)$ and $\delta n(q)$ in powers of q by setting

$$d(q)=d_0+qd_1+q^2d_2+\ldots,$$

$$\delta n(q)=\delta n_0+q\delta n_1+q^2\delta n_2+\ldots. \quad (9)$$

The coefficients d_i and δn_i are combinations of the Γ_i's, more exactly of the Γ_i/Γ_0 ratios (only the even coefficients have non-zero values).

In the case of our parabolic profile, it can easily be shown that [17]

$$d_0=\tfrac{3}{4}L', \quad d_2=-\tfrac{7}{960}L'^3. \quad (10)$$

As explained in ref. [17] there results are only exact in the limit of zero contrast; i.e., when δn_0 goes to zero. A proper handling of the method thus requires a set of data for different δn_0 small values and a consecutive extrapolation to $\delta n_0=0$. In this paper we compare our (non-extrapolated) results at $\delta n_0=n'_0-n_s=0.08$ to the predictions of eqs. (10). In order to perform such a comparison we plot in figs. 6a, b the values of d_{eq} obtained for two thicknesses at λ_1 and λ_2 as a function of q^2. We notice that for the thinner profile at λ_1 and λ_2, the variation of d_{eq} with q^2 is linear for small q values, in contrast to the variation of d_{eq} with q^2 for the thicker profile ($L'=1350$ Å) which is very different at $\lambda_2=3000$ Å; indeed in this case the ratio L'/λ cannot be considered as small any more. By fitting the curve of d_{eq} versus q with the quadratic law for small q values (eqs. (9)), we are able to determine d_0 and d_2; these values are reported in table 1. From d_0 we can deduce the thickness of the parabolic profile L'_{exp}. The error on L'_{exp} due to the use of the approximate expression is about 4–5%, but the error on d_2 is, as expected, much larger.

5. Conclusion

We tested the ability of three different ellipsometric methods to finely analyze the refractive index profile of an inhomogeneous interfacial layer. We took as an example the parabolic profile which occurs in grafted polymer layers. For each of the tested methods – chromium surface, glass prism and surface plasmons – we numerically calculated the expected ellipsometric parameters Ψ and Δ for the parabolic profile and for the step profile having the same first integral (corresponding thus to the same surface coverage). In any case it is almost impossible in practice to distinguish the two profiles from the bare ellipsometric parameters at any angle of incidence.

It is however possible to demonstrate the existence of a refractive index gradient by analyzing the ellipsometric data in terms of an equivalent step-function profile: when such a gradient exists the equivalent thickness and refractive index are angle dependent. In our case this method unambigously shows the difference between the two tested profiles.

Moreover the angle dependence of the ellipsometric thickness and refractive index provides some information on the first moments of the index profile, as show in ref. [17]. In the case of the parabolic profile we verified that the layer thickness extracted from the data with this method is fairly close to the actual value, even without using a proper extrapolation to zero contrast.

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