Ellipsometric determination of the thickness and the refractive index of superficial films deposited on metal mirrors

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Abstract. Ellipsometry is an optical method that allows very accurate determination of the optical constants of surfaces or determination of the thickness and optical constants of superficial films on solid substrates. If the determination of the optical characteristics of transparent superficial films is relatively simple, at least two ellipsometric measurements are required for optically absorbent films: at two different angles of incidence or using two different incidence media. This involves additional problems with errors related to the realignment of the ellipsometer. Ways to obtain the thicknesses and optical constants for thin or thick transparent or non-transparent superficial films are presented. A simple graphical method is presented to determine the thicknesses and optical constants of thin absorbent films with non-uniform thickness.

1. Introduction

When the external reflection of monochromatic radiation of wavelength λ occurs on the separation surface between the incidence medium of refractive index n_0 and a solid substrate with a complex refractive index $\tilde{n}_s = n_s - i \cdot k_s$, there is a change in the polarization state of incident radiation. This is expressed by ellipsometric parameters Δ and Ψ [1-6].

For solid substrates without superficial films, the fundamental equation of ellipsometry:

$$\tan \Psi_0 \cdot \exp(i\Delta_0) = f\left(n_0, \varphi_0, \lambda, \tilde{n}_s\right) \tag{1}$$

allows determining the complex refraction index of the substrate and the optical constants n_s and k_s of the substrate, from a single pair of experimental values Δ_0 and Ψ_0 measured at the incidence angle φ_0 and wavelength λ.

The thickness d_f and the complex refractive index of the superficial film can be determined if there is a superficial film on the solid substrate. One or two ellipsometric measurements are required as the superficial film is transparent or optically absorbent. The substrate on which the superficial film lies must be reflective, as in Figure 1.

The dispersive properties of the superficial film are expressed by the real part n_f (refractive index) and its absorbent properties are expressed by the imaginary part k_f (absorption index) of the complex refractive index $\tilde{n}_f$.

It is of theoretical and practical importance to measure the properties of superficial films only a few cases:

- thin transparent films of uniform thickness on reflecting substrate;
- thin optically absorbent films of uniform thickness, on reflecting substrate;
- thin optically absorbent films of non-uniform thickness, on reflecting substrate;
- thick optically absorbent films (of the order of microns);

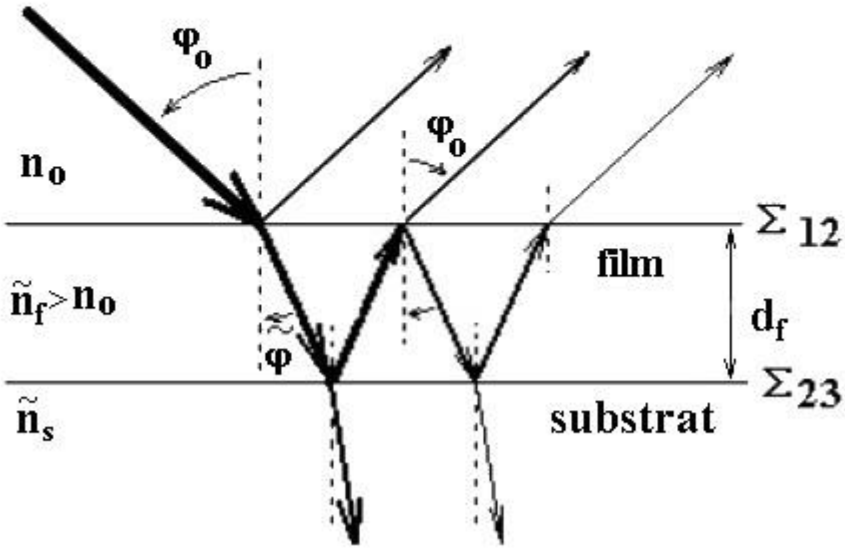


Figure 1. The external reflection of monochromatic radiation on a superficial film of uniform thickness deposited on a solid reflecting substrate

2. Experimental

The poly(methyl methacrylate) (PMMA) thin films on steel substrates were examined. The OLC-35 steel surface used as a substrate for the polymer film was obtained by grinding and polishing to obtain a mirror of good quality.

Thin films of PMMA were obtained by depositing a solution of polymer dissolved in benzene on the horizontal surface of steel samples. Commercial poly(methyl methacrylate) PMMA without any further purification was used [7].

Two methods were used for depositing the polymer film on the surface of the metal mirror.

In the first method, the metallic mirror on which the polymer solution was deposited was spinning during the evaporation of the solvent. The metal samples were centered on the horizontal surface of a turntable. On the freshly polished metal surface, at rest, lay the polymer solution and then start the centrifuge. In this way, the film of the polymer solution adhering to the metal surface is kept stretched during the evaporation of the solvent. The uniformity, thickness, and homogeneity of the polymer film depend on the concentration of the solution and the spin speed. By this method, the polymer films obtained may not have a constant thickness over the entire surface of the sample. Ellipsometric measurements showed a greater thickness of the polymer film to the edge of the sample relative to the center of the sample [8].

In the second method, the steel surface sample coated by the polymer solution was covered with a Griffin glass beaker to allow very slow evaporation of the solvent [7].

Very slow evaporation of the solvent from the polymer solution occurs under the spout of Griffin beaker. Low concentrations of the polymer in the solvent allowed us to obtain thin films with thickness less than 2μm, without interference fringes. The absence of interference fringes can be explained by poor flatness and the parallelism between the substrate and the film surface and because of the beam divergence of the light source [9]. The middle part of the film was used in the tests to ensure uniform thickness.

3. Results and discussion

The results of ellipsometric measurements for several types of superficial films deposited on reflective steel mirrors are presented. Obtaining the thickness and optical constants of the superficial film can be solved in different ways depending on the nature of the superficial film (transparent or absorbent) and its thickness.

3.1. Thin transparent films of uniform thickness

For thin transparent films (k_f=0), of uniform thickness d_f, on reflective substrates the fundamental equation of ellipsometry has the form:

$$\tan\Psi \cdot \exp(i\Delta) = f\left(n_0, \varphi_0, \lambda, \tilde{n}_s, n_f, d_f\right) \tag{2}$$

A pair of measured values Δ and Ψ, allow the determination of n_f and d_f if known: the incident angle φ_0 of the radiation on the sample, the wavelength λ of the incident radiation, the refractive index n_0 of the incidence medium and the complex refraction index $\tilde{n}_s$ of the substrate. The optical constants n_s and k_s of the substrate on which the superficial film lies are obtained by a previous ellipsometric measurement of the film-free substrate. The result is obtained directly based on the McCrackin computing program [10].

The superficial film thicknesses can be correctly determined only if they have a thickness less than d_{min} due to the periodicity of the functions $\Delta = f(d_f)$ and $\Psi = f(d_f)$, as shown in Figure 2. [11]. The curves $\Delta = f(\Psi)$ shown in Figure 3 are repeated for thicknesses greater than d_{min}.

$$d_{min} = \frac{\lambda}{2\sqrt{n_f^2 - n_0^2 \sin^2\varphi_0}} \tag{3}$$

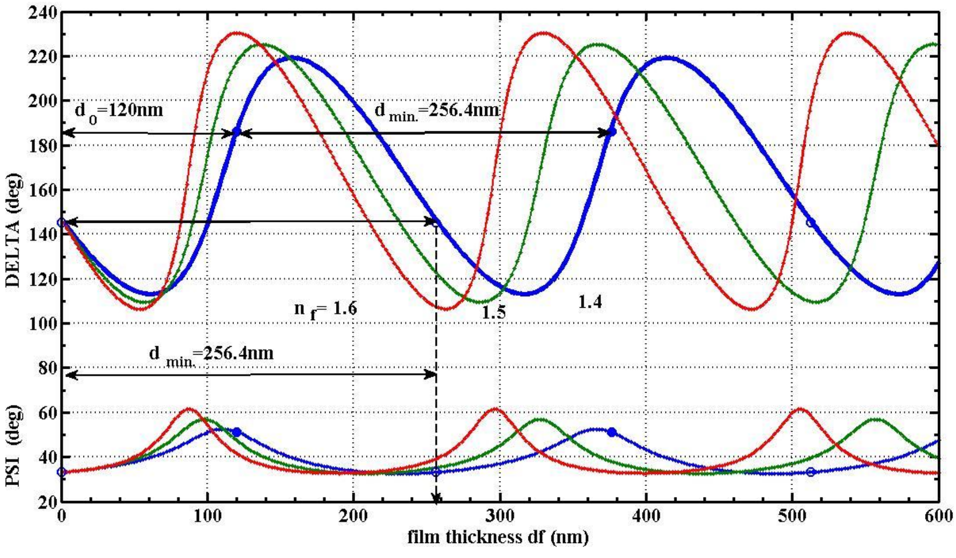


Figure 2. The periodic curves $\Delta = f(d_f)$ and $\Psi = f(d_f)$ for transparent film with $n_f = 1.4 \div 1.6$ on a steel mirror. $\tilde{n}_s = 2.67\ (1\text{-}1.18i)$; $\varphi_0 = 60^0$; $\lambda = 562.5$nm

For thicker films, the thickness shall be expressed by the relationship:

$$d_f = d_0 + m \cdot d_{min} \tag{4}$$

where d_0 is the thickness determined by the ellipsometric measurement and m is an integer. The value of d_{min} is usually of the order of 0.3÷0.5 μm. It depends on the incidence angle φ_0, the wavelength λ, the refractive index of the incidence medium n_0 and the refractive index n_f of the superficial film.

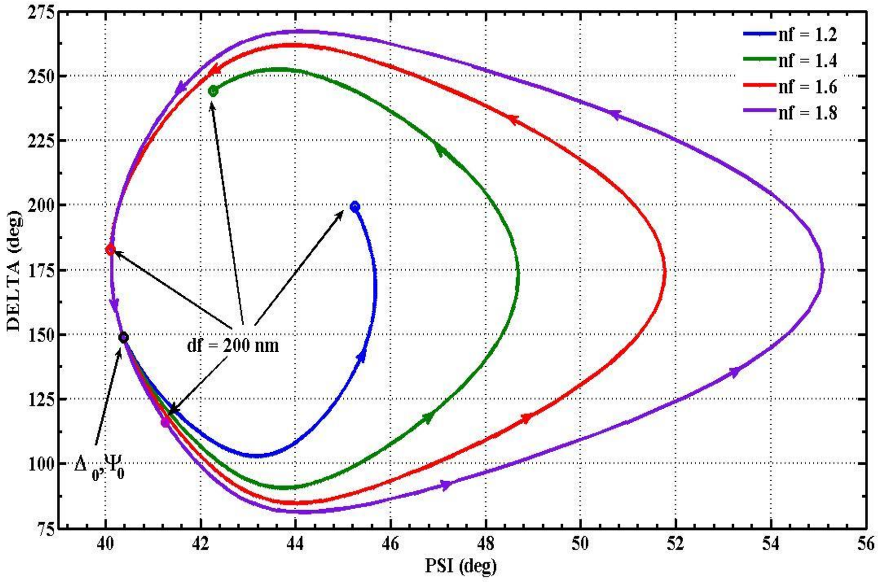


Figure 3. The curves $\Delta = f(\Psi)$ for transparent film with $n_f = 1.2 \div 1.8$ on a steel mirror. $\tilde{n}_s = 2.67(1\text{-}1.18i)$; $\varphi_0 = 60^0$; λ=562.5nm

For films with thicknesses greater than d_{min}, further measurements are needed to determine the thickness, due to the periodicity of the functions $\Delta=f(d_f)$ and $\Psi=f(d_f)$.

Usually, interferometer measurements are used to determine the order of magnitude of d_f, with a precision of 0.1 μm. Then, the ellipsometric measurement determines the exact thickness with a precision of the order of 0.1 nm [12].

3.2. Thin optically absorbent films of uniform thickness

If the superficial film is optically absorbent, having the complex refractive index $\tilde{n}_f = n_f - i \cdot k_f$ the fundamental equation of ellipsometry:

$$\tan\Psi \cdot \exp(i\Delta) = f\left(n_0, \varphi_0, \lambda, \tilde{n}_s, \tilde{n}_f, d_f\right) \qquad (5)$$

does not allow the determination of three unknowns: d_f, n_f and k_f from a pair of Δ and Ψ values of ellipsometric parameters measured at a single incidence angle. The curves $\Delta = f(d_f)$ and $\Psi = f(d_f)$ are not periodic and curves $\Delta = f(\Psi)$ are open [13]. Figures 4 and 5 show these curves.

For the determination of the three n_f, k_f and d_f sizes, at least two ellipsometric measurements shall be made at either two or more different angles of incidence or using two or more incidence media with different refractive indices [14].

Making ellipsometric measurements at the same point at two or more different angles requires the realignment of the ellipsometer at the respective angles of incidence. It is difficult to measure at the same point after realignment. The realignment of the ellipsometer can introduce large errors in determining n_f, k_f and d_f sizes [11].

The use of two or more different incidence media without changing the point of incidence of radiation on the sample is possible if we have a cell for ellipsometric measurements in various environments [15].

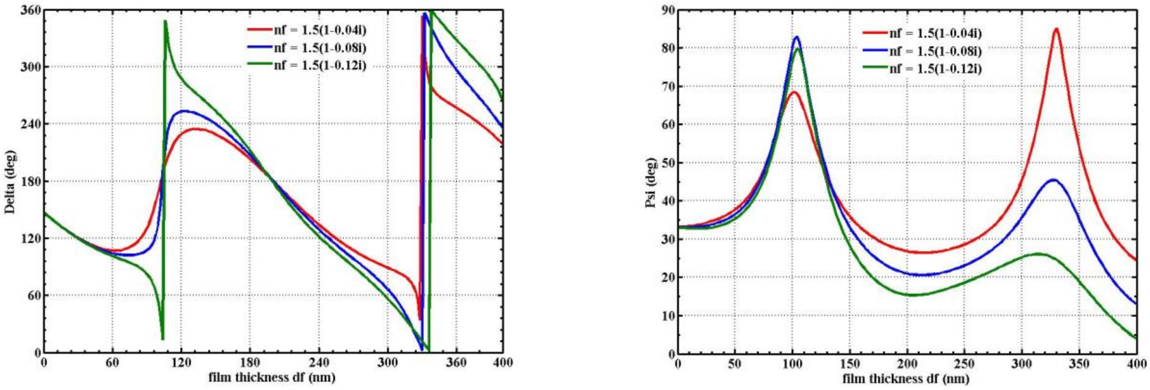


Figure 4. The curves $\Delta = f(d_f)$ and $\Psi = f(d_f)$ for optically absorbent (non-transparent) films deposited on metal mirrors; $\tilde{n}_s = 2.67(1\text{-}1.18i)$; $\varphi_0 = 60^0$; λ=562.5nm

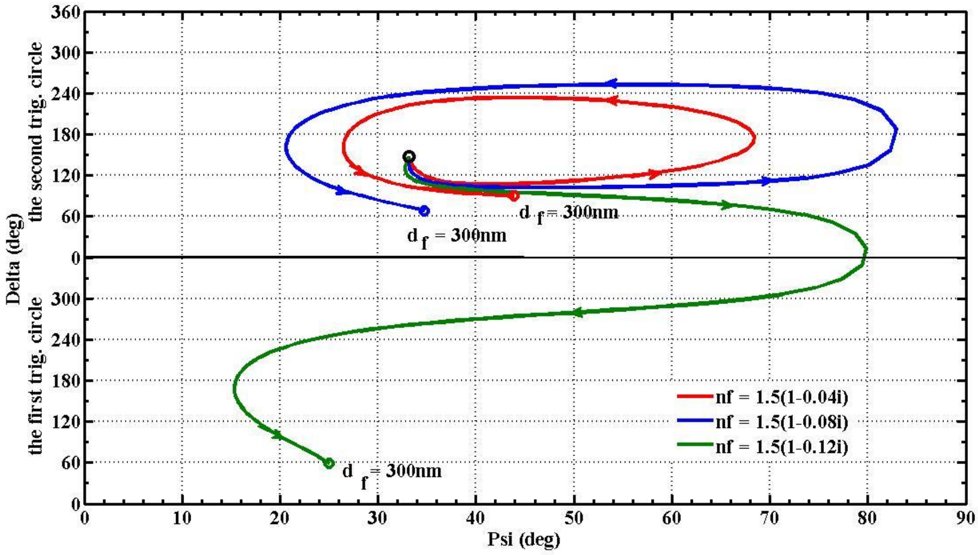


Figure 5. The curves $\Delta = f(\Psi)$ for optically absorbent (non-transparent) films deposited on metal mirrors; $\tilde{n}_s = 2.67(1\text{-}1.18i)$; $\varphi_0 = 60^0$; λ=562.5nm

3.3. Thin optically absorbent films of non-uniform thickness

If the absorbent film does not have the uniform thickness we propose a graphical method for determining the thickness and optical constants of the superficial film. It is assumed that the superficial film is homogeneous with the same values of the optical constants.

The same method can also be used when the thickness of the superficial film increases over time and the thickness of the film can be measured at different time points.

The non-uniform thickness films were typically obtained by the spin of the sample. The film obtained is thicker to the edge of the sample and thinner at its center. For absorbent films, the complex refractive index of the film and the optical constants n_f and k_f, as well as the thickness, can be readily determined by measuring the same sample in at least two different locations of different thicknesses, as in Figure 6. A measurement in the center of the sample (Δ_1, Ψ_1) and another measurement (Δ_2, Ψ_2)

in an area at the edge of the sample will be performed. The two thicknesses of the homogeneously analyzed film will thus be determined.

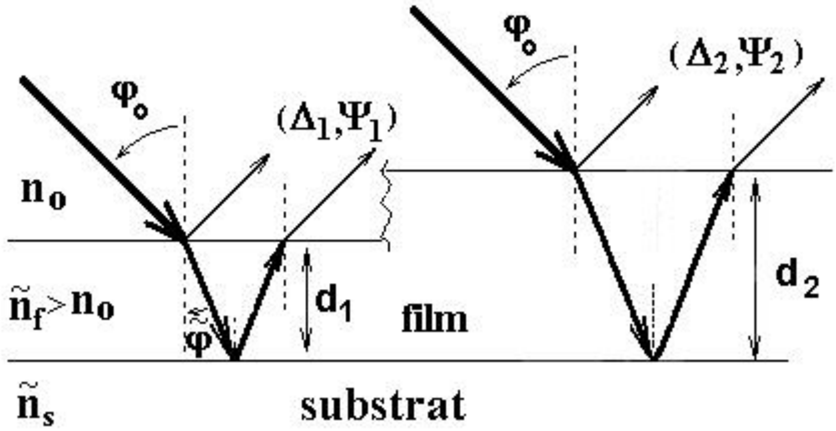


Figure 6. The external reflection of a monochromatic radiation on a superficial film of non-uniform thickness deposited on a solid reflecting substrate

Also, during the growth of film thickness, two ellipsometric measurements (Δ_1,Ψ_1) and (Δ_2, Ψ_2) are made at two time moments for two different thicknesses, as in Figure 6. It is assumed that the optical constants of superficial film n_f and k_f remain constant during film thickness growth.

The four sizes of the superficial film to be determined: the refractive index n_f, the absorption index k_f and the two thicknesses of the film d_1 and d_2 are obtained from the system of the equation:

$$\begin{cases} \tan\Psi_1 \cdot \exp(i\Delta_1) = f\left(n_0, \varphi_0, \lambda, \tilde{n}_s, n_f, k_f, d_1\right) \\ \tan\Psi_2 \cdot \exp(i\Delta_2) = f\left(n_0, \varphi_0, \lambda, \tilde{n}_s, n_f, k_f, d_2\right) \end{cases} \tag{6}$$

From the first ellipsometric measurement (Δ_1,Ψ_1) we obtain the set of values (n_f,k_f,d_1) based on the McCrackin computing program [10]. The curve k_f = $f_1(n_f)$ for the different thicknesses d_1 of the superficial film is shown in Figure 7a and the curve $k_f = g_1(d_1)$ for the different values of n_f is shown in Figure 7b.

From the second ellipsometric measurement (Δ_2,Ψ_2) we obtain the set of values (n_f,k_f,d_2) based on the same computing program. The curve k_f = $f_2(n_f)$ for the different thicknesses d_2 of the superficial film is shown in Figure 7a and the curve $k_f = g_2(d_2)$ for the different values of n_f is shown in Figure 7b.

The curve equations are determined by fitting experimental curves as second-order polynomials and are expressed by relations (7÷9). The coefficient of determination (R squared) R^2 is also calculated.

The curve equations are determined by fitting experimental curves as second-order polynomials and are expressed by the relations (7 ÷ 9). The coefficients of determination R^2 are also calculated.

For the example shown in Figure 7, the curve intersection k_f = f_1 (n_f) and k_f = f_2 (n_f) allows the determination of the optical constants n_f and k_f of the superficial film by solving the system:

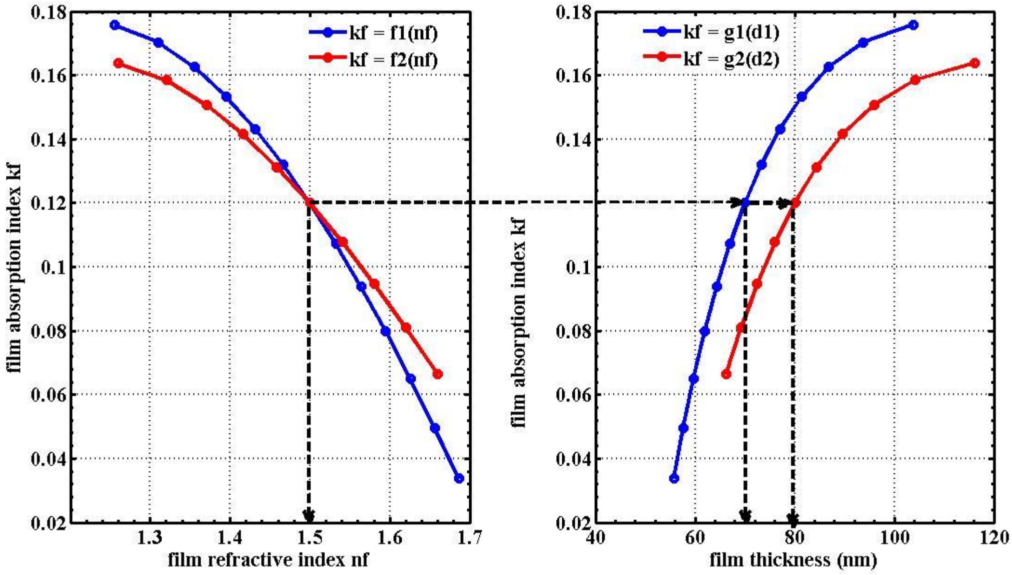
$$\begin{cases} k_f = f_1(n_f) = -0.5551 \cdot n_f^2 + 1.298 \cdot n_f - 0.5779 \qquad R^2 = 0.9998 \\ k_f = f_2(n_f) = -0.3972 \cdot n_f^2 + 0.912 \cdot n_f - 0.3543 \qquad R^2 = 0.9996 \end{cases} \tag{7}$$

The values obtained are: $\mathbf{n_f = 1.4963}$; $\mathbf{k_f = 0.1215}$.

The value of the absorption index k_f thus obtained is then introduced into the equations:

$$k_f = g_1(d_1) = -7.96E^{-5} \cdot d_1^2 + 0.01545 \cdot d_1 - 0.5742 \qquad R^2 = 0.9949 \tag{8}$$

$$k_f = g_2(d_2) = -4.75E^{-5} \cdot d_2^2 + 0.01052 \cdot d_2 - 0.42 \qquad R^2 = 0.9967 \tag{9}$$



a) b)

Figure 7. A graphical method for determining the thickness d_f and the optical constants n_f and k_f of a PMMA non-uniform thickness absorbent film deposited on a steel mirror; $\tilde{n}_s = 2.67(1\text{-}1.18i)$;$\varphi_0 = 60^0$; λ=562.5nm

The quadratic equations have two solutions. The solutions of the two equations are: d_1 = 69.8nm and 124.2nm respectively d_2 = 79.6nm and 141.8nm. The solutions that fall within the scope of the experimental points in Figure 7 are correct.

Thus, the thicknesses of the superficial film at the two points determined are **d_1=69.8nm** respectively **d_2=79.6nm**.

You can write the equations $k_f = g_1(d_1)$ and $k_f = g_2(d_2)$ as order 3 polynomials:

$$k_f = g_1(d_1) = 1.268E^{-6} \cdot d_1^3 - 0.00038 \cdot d_1^2 + 0.0388 \cdot d_1 - 1.164 \qquad R^2 = 0.9999 \tag{10}$$

$$k_f = g_2(d_2) = -6.21E^{-7} \cdot d_2^3 - 0.0002167 \cdot d_2^2 + 0.02563 \cdot d_2 - 0.8607 \qquad R^2 = 1 \tag{11}$$

In this case, three roots are derived from each equation, two of which are complex and only one (the correct one) is real. The values obtained are: **d_1=69.84nm** respectively **d_2=79.65nm**.

If the value of the absorption index obtained **k_f = 0.1215** is introduced into the order 3 polynomials described by equations (10) and (11), the thickness of the superficial film is obtained at the two points: **d_1=70.14nm** and **d_2=80.44nm**. Using the equations $k_f = g_1(d_1)$ and $k_f = g_2(d_2)$ as order 3 polynomials results in better values for d_1 and d_2.

3.4. Thick optically absorbent films

However, for thick absorbent films, it is found that over a certain thickness of the film the optical constants Δ and Ψ remain constant and the film-substrate system ceases to behave as being composed of two phases. The system behaves like a bulk with a refractive index equal to the superficial film. In this case, the thickness can no longer be determined and the optical constants n_f and k_f are obtained from the final values Δ_{final} and Ψ_{final}. Curves $\Delta = f(d_f)$ and $\Psi = f(d_f)$ are non-periodic and the curves $\Delta=f(\Psi)$ are open curves. Figures 8 and 9 show these curves.

The thickness of the film from which Δ and Ψ remain constant is even smaller as the superficial film is more absorbent as seen in Figure 8.

In this case, a single ellipsometric measurement (Δ_{final}, Ψ_{final}) is sufficient to determine the complex refractive index of the superficial film.

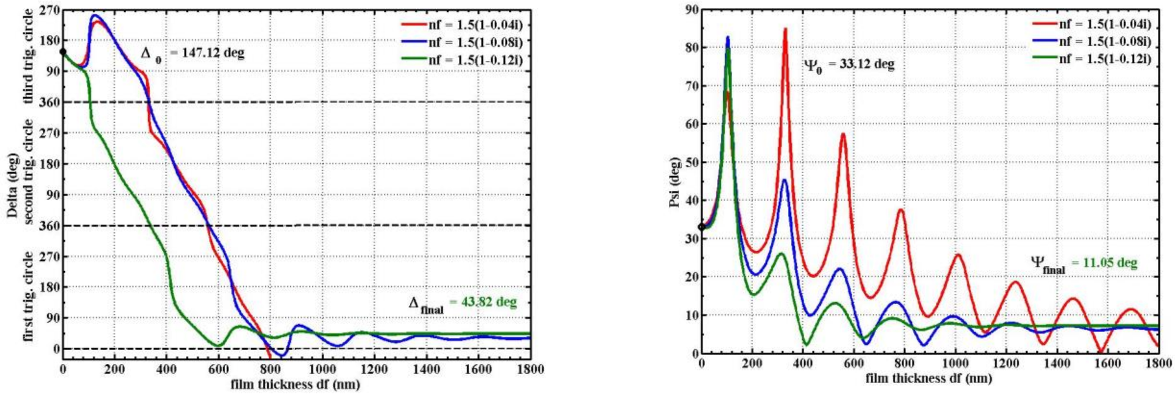


Figure 8. The curves $\Delta = f(d_f)$ and $\Psi = f(d_f)$ for optically absorbent (non-transparent) films deposited on metallic mirrors; $\tilde{n}_s = 2.67(1\text{-}1.18i)$; $\varphi_0 = 60^0$; λ=562.5nm

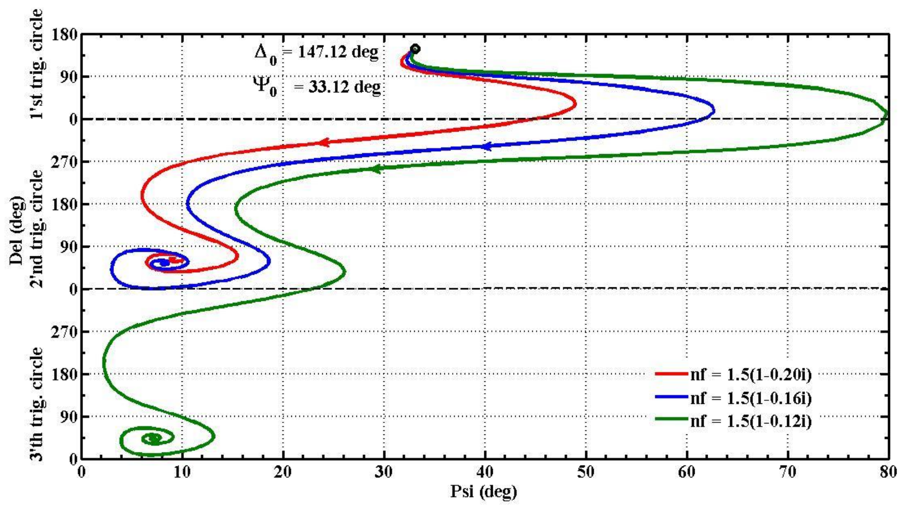


Figure 9. The curves $\Delta = f(\Psi)$ for optically absorbent (non-transparent) films deposited on metal mirrors; $\tilde{n}_s = 2.67(1\text{-}1.18i)$; $\varphi_0 = 60^0$; λ=562.5nm

For films whose thickness increases over time, it is found that starting from a certain thickness of the film Δ and Ψ remain constant. These values correspond to a film-free substrate whose optical constants are those corresponding to the bulk film.

When the thickness of the superficial film rises above a certain value, the exponential term:

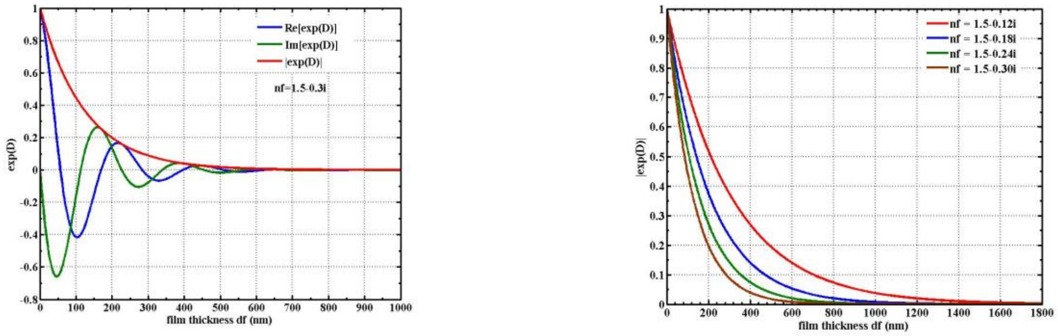
$$\tilde{D} = -\frac{4 \cdot \pi \cdot i \cdot d_f}{\lambda} \sqrt{\tilde{n}_f^2 - n_0^2 \cdot \sin^2 \varphi_0} \tag{12}$$

of the expressions of the reflection coefficients $\tilde{R}_p$ and $\tilde{R}_s$:

$$\tilde{R}_p = \frac{\tilde{r}_p^{12} + \tilde{r}_p^{23} \cdot \exp\tilde{D}}{1 + \tilde{r}_p^{12} \cdot \tilde{r}_p^{23} \cdot \exp\tilde{D}} = \mathrm{Re}(\tilde{R}_p) + i \cdot \mathrm{Im}(\tilde{R}_p) = R_p \exp(\varphi);\ R_p = |\tilde{R}_p| = \sqrt{\mathrm{Re}^2(\tilde{R}_p) + \mathrm{Im}^2(\tilde{R}_p)} \tag{13}$$

$$\tilde{R}_s = \frac{\tilde{r}_s^{12} + \tilde{r}_s^{23} \cdot \exp\tilde{D}}{1 + \tilde{r}_s^{12} \cdot \tilde{r}_s^{23} \cdot \exp\tilde{D}} = \mathrm{Re}(\tilde{R}_s) + i \cdot \mathrm{Im}(\tilde{R}_s) = R_s \exp(\varphi);\ R_s = |\tilde{R}_s| = \sqrt{\mathrm{Re}^2(\tilde{R}_s) + \mathrm{Im}^2(\tilde{R}_s)} \tag{14}$$

tends to zero as seen in Figure 10. R_p and R_s are reflectances [16].



a) b)

Figure 10. The dependence of exponential term on superficial film thickness; $\tilde{n}_s$=2.67(1-1.18i); φ_0= 60^0; λ=562.5nm

Also, the reflectance values $\tilde{R}_p$ and $\tilde{R}_s$ tend towards the Fresnel reflection coefficient values $\tilde{r}_p^{12}$ and $\tilde{r}_s^{12}$ corresponding to the reflection of light only at the superficial air-film interface

$$\tilde{R}_p = \frac{\tilde{r}_p^{12} + \tilde{r}_p^{23} \cdot \exp\tilde{D}}{1 + \tilde{r}_p^{12} \cdot \tilde{r}_p^{23} \cdot \exp\tilde{D}} \rightarrow \tilde{r}_p^{12};\ \tilde{R}_s = \frac{\tilde{r}_s^{12} + \tilde{r}_s^{23} \cdot \exp\tilde{D}}{1 + \tilde{r}_s^{12} \cdot \tilde{r}_s^{23} \cdot \exp\tilde{D}} \rightarrow \tilde{r}_s^{12} \tag{15}$$

as can be seen in Figure 11.

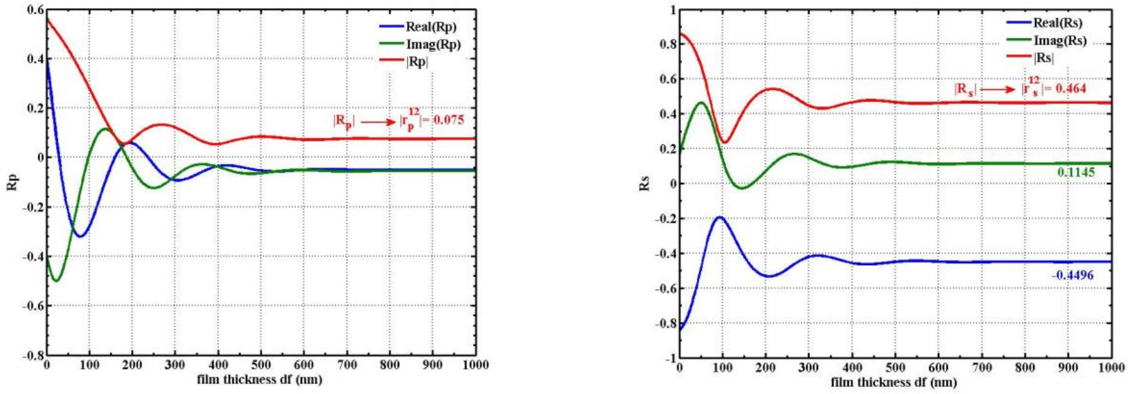


Figure 11. The dependence of the reflectances $\tilde{R}_p$ and $\tilde{R}_s$ on superficial film thickness; $\tilde{n}_s$=2.67(1-1.18i); n_f=1.5(1-0.2i);φ_0 = 60^0; λ=562.5nm

The Δ_{final} and Ψ_{final} values correspond to the Fresnel reflection coefficients of a substrate with optical constants equal to the superficial film. The exponential term depends on the incidence angle φ_0, the wavelength λ, the refractive index n_0 of the incidence medium and the refractive index n_f of the superficial film. The dependence of the exponential term on the refractive index of superficial film is significant. The exponential term tends to zero more quickly when the absorption index of the film is higher, as can be seen in Figure 10b.

4. Conclusions

For transparent superficial films, its thickness can be obtained by direct measurement only if its thickness is less than a certain d_{min} value.

For thin optically absorbent films of uniform thickness, it is not possible to determine the thickness and optical constants in a single ellipsometric measurement at a single incidence angle. At least two measurements are required at two different incidence angles or using two different incidence media.

The proposed graphical method, to obtain the thicknesses and optical constants of thin optical absorbent films with uneven thickness, is very simple and precise.

The ellipsometric parameters Δ and Ψ remain constant for optically absorbent superficial films with thicknesses greater than a certain value $d_{max.}$ Only the optical constants of the film can be determined. The film behaves like a volume phase of undeterminable thickness.

Both the d_{min} value and the d_{max} value depend on the incidence angle φ_0, the wavelength λ, the refractive index of the incidence medium n_0 and the refractive index n_f of the superficial film.

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