Uncertainties in the values obtained by surface plasmon resonance

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Abstract. Surface plasmon resonance (SPR) is a suitable technique to optically characterize thin layers. It has often been stated that SPR cannot determine simultaneously both the thickness and the dielectric constant (possibly complex) of the layer. We demonstrate that this idea arises from an error caused by the method used in the simulation of the reflectivity curve. So we do not have to design complex systems to solve this problem as did previous authors. In this paper, we report on a simulation based on the Fresnel equations to calculate the reflectivity curve from the critical angle (θ_c) to cover a wider range of θ values. With a matrix formalism, we can pick the layers we want very easily. With our process, results are excellent for all kind of noise distributions even at high noise levels. A metallic layer was first characterized; then an ultrathin (12 Å) dielectric layer was added. We also calculated the standard deviations for all cases to prove that the SPR technique is a very sensitive probe. In all studies, the results showed very good agreement between the true values of the parameters and the simulated ones, as well as small standard deviations. [S0091-3286(00)03202-5]

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1 Introduction

The surface plasmon resonance (SPR) technique is widely used to characterize thin layers of materials in the three states of matter. Its performance has been found to be rather limited when noise is present, when the number of layers is more than three, when many pairs of the parameters (dielectric constant ϵ, thickness d) must be distinguished. If one looks at the chronology of the developments carried out by different groups, a recurrent problem appears: indeterminacy between several pairs of values (ϵ, d) characterizing the layer.

In the late eighties, this problem was encountered for the metallic layer;[1,2] the solution was to carry out a series of measurements either at different wavelengths or with different media to find out the set of values consistent with the various experiments. Later on, it was shown by Cowen[3] that there was in fact no indeterminacy. A few years later, the problem arise again, but this time for the characterization of a dielectric layer in contact with the metallic layer. In 1997, Peterlinz and Georgiadis[4–6] stated that the problem was only present for very thin layers ($d<20$ nm), and they thought that this indeterminacy had a physical origin. The stated problem is then still a reality and merits attention.

In this paper, we address this issue and show that very accurate quantitative characterizations of a very thin dielectric layer (unique and accurate determination of the optical constant and of the thickness) can be obtained from the analysis of a single SPR reflectance curve.

We carried out a series of simulations of reflectivity curves by using Fresnel equations. We first create a curve by applying the Fresnel equations, and this curve is considered as our ''experimental'' curve. The values of the parameters ϵ_r, ϵ_i, d used to calculate this reflectivity curve are then considered as ''true values.''

We then studied the fit of the curve to sense the sensitivity of the fit to the value of the parameter. The technique used was based on the minimization of the χ^2 by Bevington's[7] method using a nonlinear algorithm. We carried out the simulation and the fit in three steps:

1. We studied a reflectivity curve without noise and found that there was no indeterminacy in the set of parameters obtained by this method, whatever the number of layers examined or whatever the layer to be studied.
2. We added noise. Its amplitude and its distribution could vary.
3. We studied from a statistical viewpoint a set of 20 spectra in order to determine the uncertainty affecting our measurements. This last analysis was carried out with three unknown parameters, which might increase the uncertainty of the fitted parameters but would show the efficiency of the technique in a more difficult configuration.

All these tests were applied to systems with three media (including one thin layer, which was metallic) and on systems with four media (including two thin layers: one gold and one dielectric). We made calculations on many metallic layers (Au, Ag, Al) for the three-media system and on

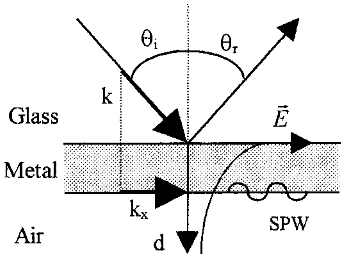

Fig. 1 Description of the physical process. θ_i: incident angle; θ_r: reflection angle; k: wave vector of incident light; k_x: wave vector of the surface plasmon wave (SPW). The electric field $\vec{E}$ decreases exponentially with increasing d.

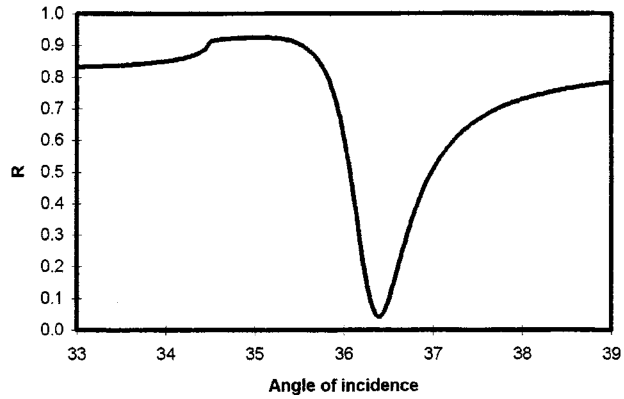

Fig. 2 Reflectivity curve of a typical surface plasmon resonance, plotted for the following system: $\epsilon_1 = 3.1195$, $\epsilon_2 = -11.694 + 1.3344i$ ($d_2 = 53.55$ nm); $\epsilon_3 = 1.0006$. Abscissa in degrees.

many dielectrics (absorbing or not) in the four-media system. This ensures that our conclusions are valid for any kind of system and any layer in the system, even though we show in this paper only two examples, one for a metallic layer and one for a dielectric one.

A discussion is given of the changes in sensitivity and uncertainty when the probing electric field is attenuated (far from the gold layer).

2 Theory

Surface plasmon resonance spectroscopy is an optical technique that is capable of monitoring chemical and physical processes at the second metal interface *in situ*. It is sensitive to small changes in the dielectric constant near a metal surface and has been used to characterize a number of different types of films. It is based on total internal reflection of light at the interface between two media. An evanescent wave is created. The wave propagates parallel to the interface with the amplitude of the electromagnetic field decreasing exponentially from the surface. If the second medium is a thin metallic layer (≈50 nm—a typical order of magnitude for the optimal thickness where the absorption peak yields zero reflectivity) and if the light is polarized in the TM mode, an evanescent wave can be generated on the metal, and for a particular incidence angle (resonance angle) an electronic oscillation called surface plasmon waves (SPW) will occur. The metals usually employed are gold, silver, and aluminum; for each metal the optical constants and the sensitivity of the method are different.

Since there is resonance between the parallel component (Fig. 1) of the wave vector of light ($\mathbf{k}$) and the wave vector of the electronic oscillations ($\mathbf{k}_x$), there is energy transfer between systems, which causes a dip in the reflectivity curve corresponding to an absorbing peak. This absorption band is located in the angular range of total reflection (Fig. 2). The characteristics of the resonance critically depend on the media in the layers and in particular on the properties of the metallic layer. This technique constitutes a local probe that can sense its environment on a length scale of the order of magnitude of the wavelength of the light, i.e., of the order of a micrometer if one uses a coherent source of visible light.

The crucial problem lies therefore in the exact modeling of the reflectivity curve, preferably over wider angular range than the vicinity of the minimum. If the model fits the experimental reflectivity curve, comparison between them can yield the characteristics of the layer: the real and imaginary parts of the dielectric constant, and the thickness. To simulate the reflectivity curve and avoid misinterpretation, the Fresnel equations will be used to calculate the changes in the light at each interface and between them.

If the simulation is only carried out in the vicinity of the absorption peak of the reflectivity curve (based on a Lorentzian curve) more than one consistent solution is possible. This has already been demonstrated by Cowen[3] on a three-media system. We propose to extend the study to a four-media system. Figure 3 illustrates the fact that the behavior near the minimum is not sufficient to characterize the system. Reflectivity curves of two sets of parameters are drawn in the vicinity of the minimum. Whereas in the limited range the two curves coincide, outside it they are different and one set of parameters fits better than the other.

This observation led us to investigate further the simulation of these reflectivity curves. To make easier the representation of the system, the matrix formalism introduced by Sprokel and Santo[8,9] will be used. This formalism allows the use of numerical calculation and a variable number of layers.

The minimization technique used to fit curves is based on a gradient-expansion least-squares algorithm introduced by Bevington.[7] The parameter χ^2 to be minimized is given by the following equation:

$$\chi^2 = \frac{1}{n_{\text{param}}} \sum_{i=1}^{N} [y_i - f(x_i)]^2,$$

where

N = number of data points $(x_i,\ y_i)$ in the spectrum

n_{param} = number of degrees of freedom

$f(x_i)$ = calculated value of y_i used to fit the spectrum.

The method consists in the search of minimum by the gradient method with a step size varying with the slope of the hypersurface χ^2. The aim of this algorithm can be seen from the flow chart in Fig. 4. As the first step is large, the first calculated values are always far from the input ones.

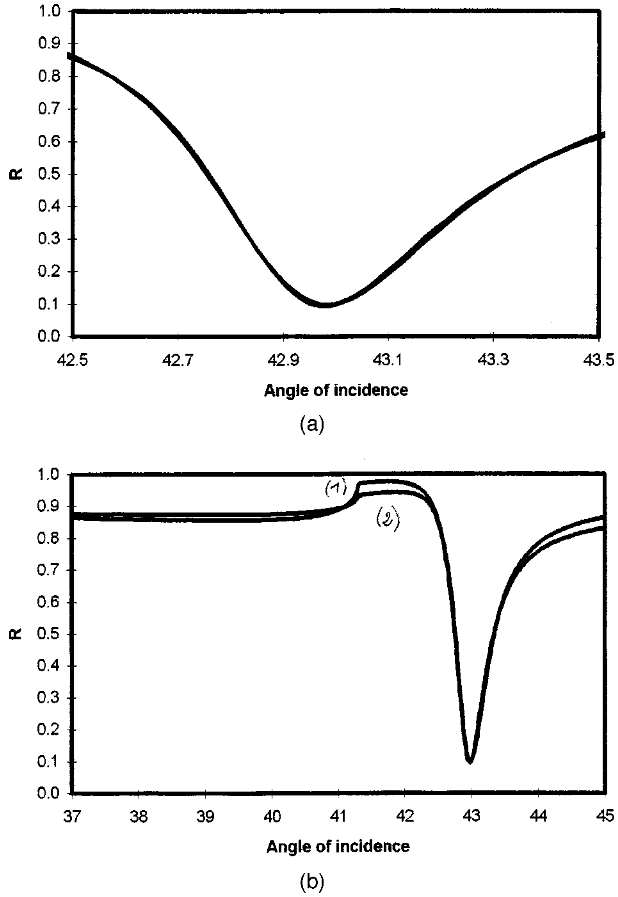

Fig. 3 (a) Coincidence of two sets of parameters in the vicinity of the minimum. (b) Difference between the two sets outside the minimum region. The two sets are: (1) $\epsilon_1=3.1195$, $\epsilon_2=-11.694+1.3344i$ ($d_2=53.55$ nm), $\epsilon_3=1.0006$; (2) $\epsilon_1=3.1195$, $\epsilon_2=-11.893+0.90337i$ ($d_2=47.10$ nm), $\epsilon_3=1.0006$.

The shift is at least about half of the input value. This means that even if we input the reference values, the first calculated ones will not be near the best ones. However, even if the input values are far from the reference ones, the algorithm converges very rapidly.

3 Study Without Noise

In this section we demonstrate that there is no indeterminacy of the set of parameters to be found, whatever the parameters and the number of layers are. We draw the χ^2 surface, for different combinations of ϵ and d [(ϵ_r,ϵ_i) or (ϵ_r,d) or (ϵ_i,d)]. The curves used are not obtained from an experiment, but are generated by computation. If an indeterminacy between two sets of values occurred, one would observe a valley-like minimum in the χ^2 surface, since two sets of values would give the same result and thus the same χ^2.

3.1 *Three-Media Systems: Glass-Metal-Air*

In this example (Fig. 5), the unknown medium is the metal. We first generate a reference curve based on the following parameters:

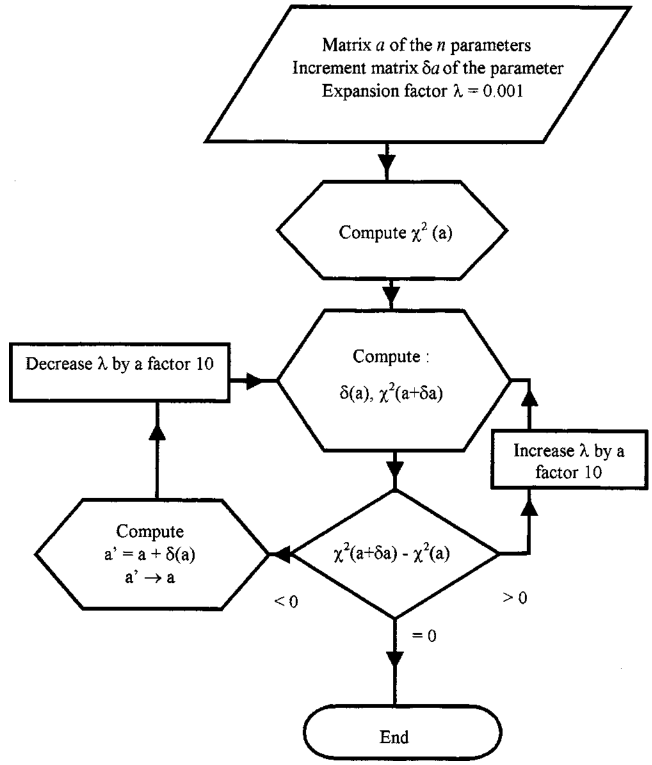

Fig. 4 Flow chart of the algorithm used for the least-squares minimization.

Glass: $\epsilon_0=2.2954977$

Au: $\epsilon_1=-11.6+1.5i,\quad d_1=50$ nm

Air: $\epsilon_\infty=1.0$

$\lambda=632.8$ nm

From these reference values, we plotted the hypersurface $\chi^2(\epsilon_r,\epsilon_i,d)$, keeping constant one parameter and changing the value of the others.

We first illustrated the computations by graphs with a wide range of the parameter values in order to have an overview of the surfaces. Since only one minimum was visible, we report only the graphs of that region.

We then used a smaller step to show the resulting valley. In Figs. 6–9, the surface is shown for values of ϵ_r varying from -12.2 to -11; in the previous simulation values from -15 to -10 had been tested. When some authors were confronted with the indeterminacy problem, the sets of values they found were included in the range $[-15,-10]$.[1,3,6] That explains our first choice. When we saw a single minimum, we focused on it and then used a smaller range $[-12.2,-11]$. We show in this paper results on this last

Fig. 5 Description of a three-media system.

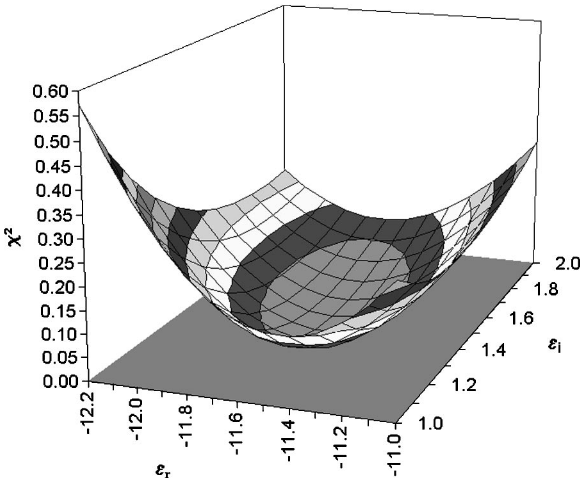

Fig. 6 3-D representation of $\chi^2(\epsilon_r,\epsilon_i)$.

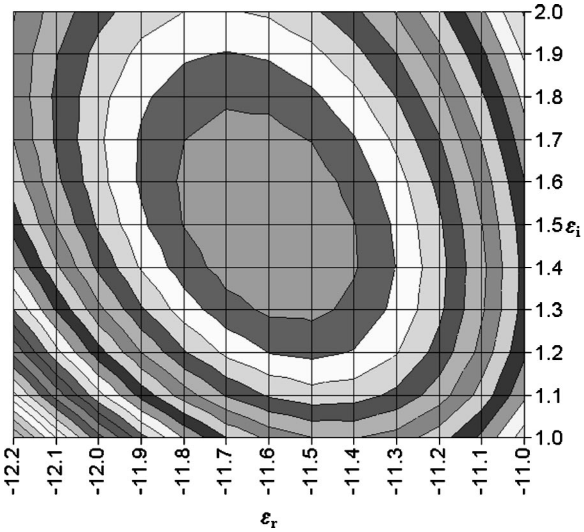

Fig. 7 Projection of $\chi^2(\epsilon_r,\epsilon_i)$.

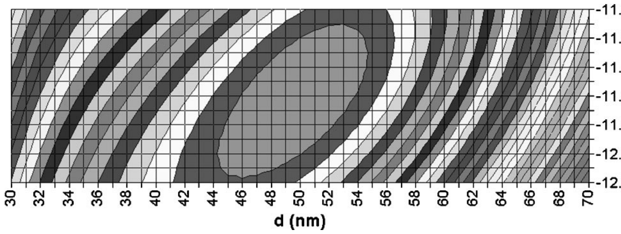

Fig. 9 Projection of $\chi^2(\epsilon_r,d)$.

range. The observed minimum was single in our case. The same procedure was also followed for all the other parameters.

Figures 6–11 illustrate the different χ^2 surfaces and their projections for different combinations of ϵ and d $[(\epsilon_r,\epsilon_i);\ (\epsilon_r,d);\ (\epsilon_i,d)]$. For Figs. 6 to 11 and 13 to 19, we plot χ^2, as defined previously, for the reference spectrum created with the reference values above and a test spectrum with test values. To get these test values, we divide the dielectric-constant range into steps of 0.1 and the thickness range into steps of 1 Å. Then we have an array of test values corresponding to the intersections in the graph grid. Each cell in this array will give a test spectrum and then a χ^2 value after comparison with the reference spectrum. Each graph is then plotted for an array of values.

The values of the parameters corresponding to the minimum are in perfect agreement with the reference values. Moreover, we can easily notice that there is no stability valley and hence no indeterminacy in the parameters. This study solves the indeterminacy problem encountered by some authors[1,2] with regard to the same metallic layer. Results shown here are for a gold layer, but they can be obtained as easily as here for any kind of metallic or dielectric layer.

3.2 *Four-Media System: Glass-Metal-Dielectric-Air*

In this system (Fig. 12), the unknown parameters belong to the dielectric layer deposited on the gold layer.

De Bruijn et al.[1,2] had suggested that an indeterminacy arose when one tried to find the metal parameters. As shown in the previous section, that is not correct; but after-

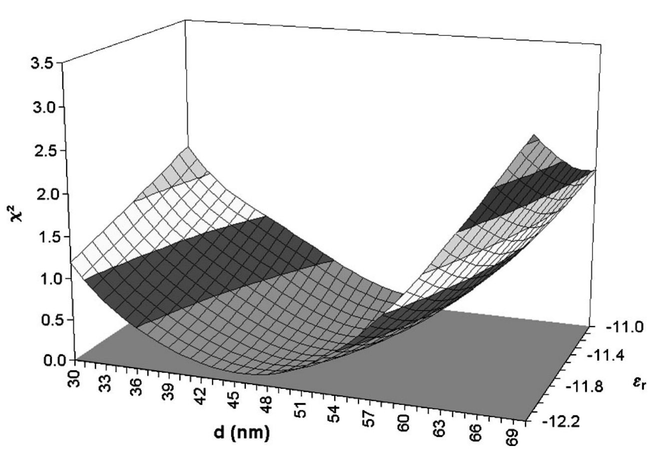

Fig. 8 3-D representation of $\chi^2(\epsilon_r,d)$.

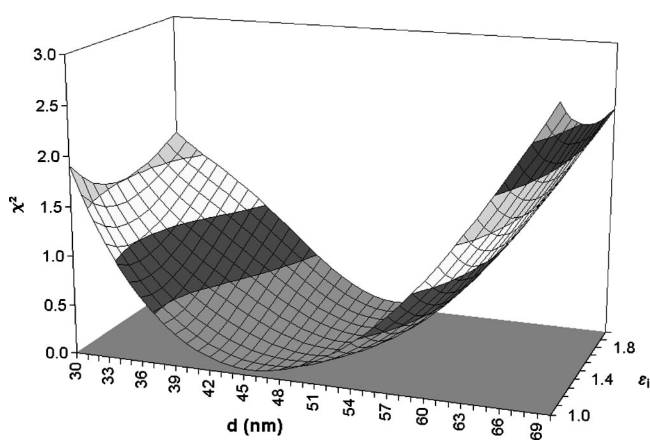

Fig. 10 3-D representation of $\chi^2(\epsilon_i,d)$.

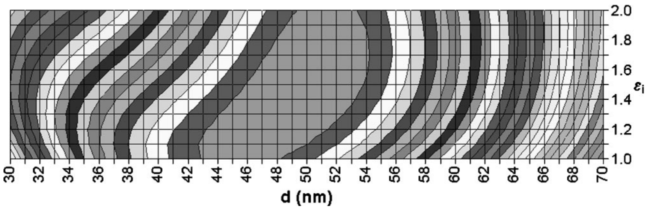

Fig. 11 Projection of $\chi^2(\epsilon_i, d)$.

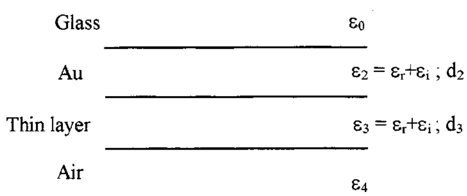

Fig. 12 Description of a four-media system.

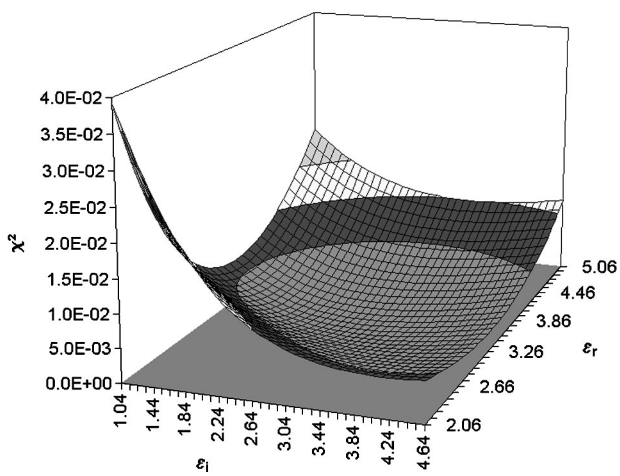

Fig. 13 3-D representation of $\chi^2(\epsilon_r, \epsilon_i)$.

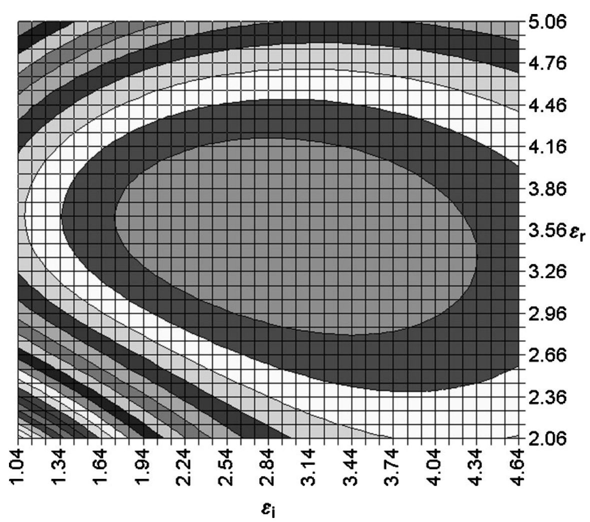

Fig. 14 Projection of $\chi^2(\epsilon_r, \epsilon_i)$.

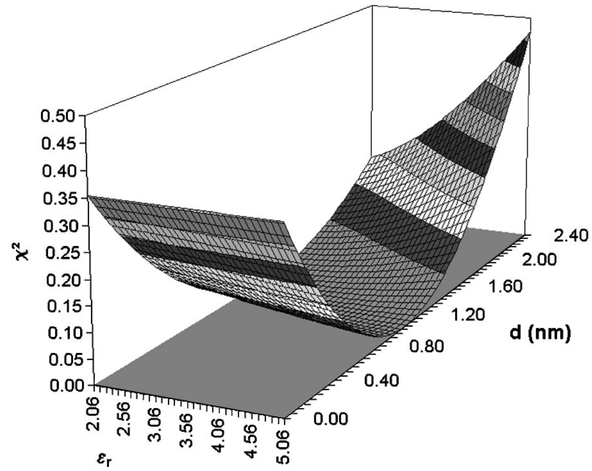

Fig. 15 3-D representation of $\chi^2(\epsilon_r, d)$.

ward it was argued that indeterminacy would still arise when the thickness of the layer in contact with the metallic one was very small ($d < 20$ nm).

We study now the case of the ultrathin layer. It seems to be more difficult in that even if the indeterminacy problem is solved for the metallic layer, it will persist for the other coating layers.

The parameters used to simulate the reference reflectivity curve were the following:

Glass: $\epsilon_0 = 2.2954977$

Au: $\epsilon_1 = -11.6 + 1.5i, \quad d_1 = 50 \text{ nm}$

Layer: $\epsilon_2 = 3.5578 + 2.8387i, \quad d_2 = 1.2 \text{ nm}$

Air: $\epsilon_\infty = 1.0$

$\lambda = 632.8 \text{ nm}$

The same procedure as the one previously described was followed. A wide range of values indicated a global minimum, which was studied by taking smaller steps in the fit. In Figs. 13–18, χ^2 surfaces and their projections versus (ϵ_r, ϵ_i), (ϵ_r, d), and (ϵ_i, d) are illustrated. They were made as described for the three-media system.

The minima are somewhat elongated, but the values obtained from them agree with the input values. Moreover,

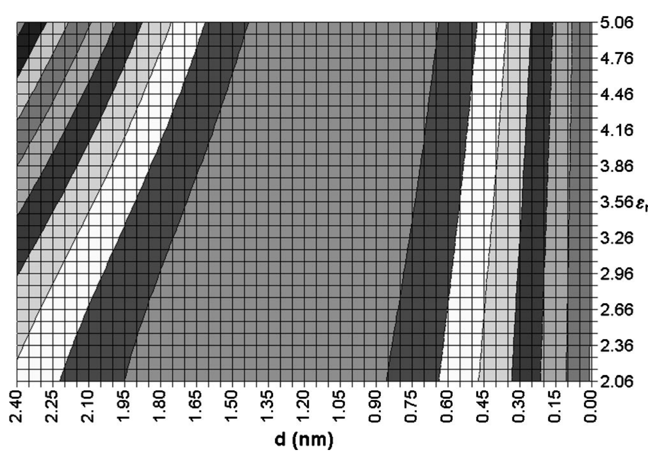

Fig. 16 Projection of $\chi^2(\epsilon_r, d)$.

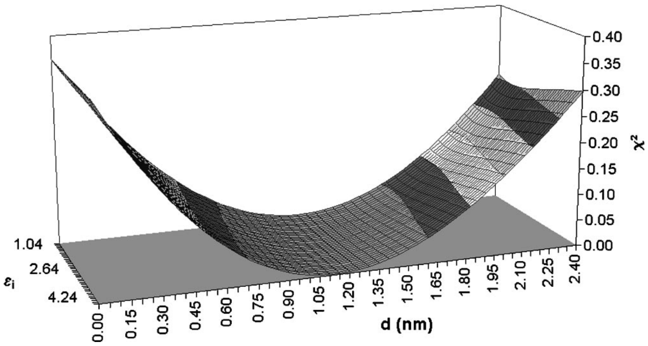

Fig. 17 3-D representation of $\chi^2(\epsilon_i, d)$.

from the expanded region of the minimum (Fig. 19), it is observed that no valley exists that could lead to an indeterminacy.

The indeterminacy that is referred to by some authors must therefore originate from a slower convergence or a less appropriate algorithm (such as a fit to a Lorentzian) that uses a smaller angular range. The minimum observed in our simulations is a global minimum, and if it is somewhat elongated, that is probably why some groups arrived at an indeterminacy. But that is due to numerical inaccuracy rather than a physical reason. This also provides a solution to the indeterminacy problem found by some other authors.[4–6] The same result is found for other systems, but we choose to show it for systems used in the literature.

4 Study with Noise

In this section, we discuss the uncertainty in the values of the set of parameters obtained when noise is present. We generated a reflectivity curve as described in the previous sections, to which we added noise. Different noise distributions were added, both independent of and dependent on the reflected intensity.

The noise is defined as a random variation of the reflected light intensity. This variation, ΔI, obeys a Gaussian distribution having mean zero. The general law is given by

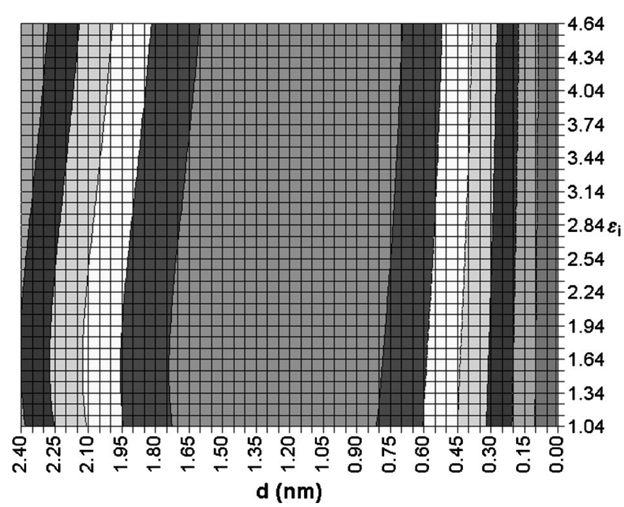

Fig. 18 Projection of $\chi^2(\epsilon_i, d)$.

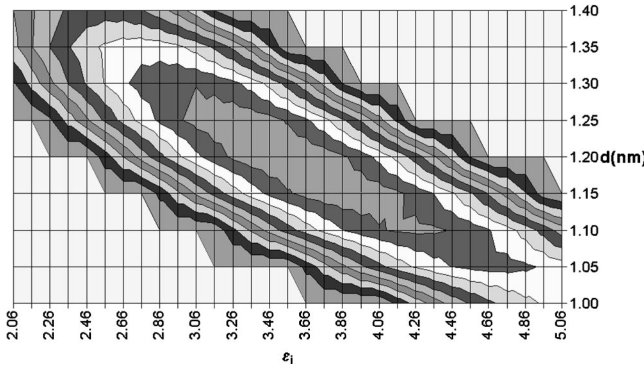

Fig. 19 Magnification of the region around the minimum of Fig. 18.

$$I = I_0 + \Delta I$$

Two noise distributions were studied:

1. The noise is random and independent of the intensity of the experimental value. Due to the sampling, we will get a discrete spectrum. Each data point will be called a *pixel*. It will correspond to a real pixel if, as in our experimental setup, a CCD camera is used. This technique enables us to avoid mechanical problems such as prism positioning and energy losses. The computed intensity of the pixel is then given by

$$I(\text{pixel}) = I_0(\text{pixel}) \pm \frac{x}{100} \quad \text{with}$$

$$x \in [0,100] \quad (\text{absolute noise}).$$

With this distribution, the reflectivity curve is shown in Fig. 20.

2. The law is

$$I(\text{pixel}) = I_0(\text{pixel}) \pm \frac{x}{100} I_0(\text{pixel}) \quad \text{with}$$

$$x \in [0,100] \quad (\text{relative noise}),$$

which is a relative noise depending on the light intensity. This case is close to the experimental conditions encountered, since a CCD is characterized by noise proportional to

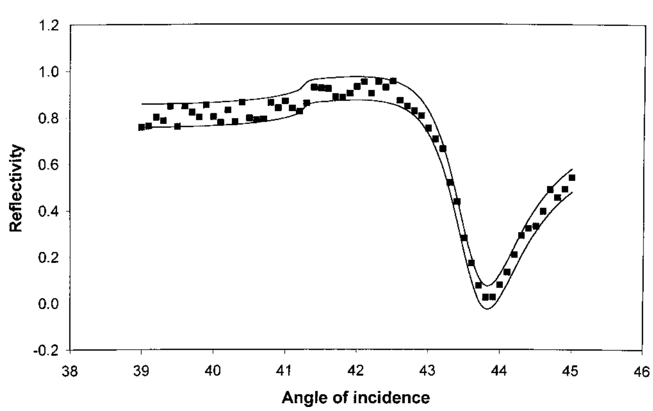

Fig. 20 Reflectivity curve with an absolute noise of 5% of the total reflectivity: $x = 5$.

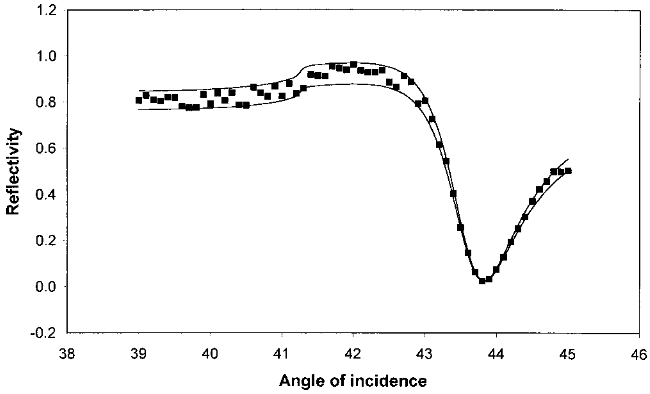

Fig. 21 Reflectivity curve with a relative noise of 5% of the total reflectivity ($x=5$).

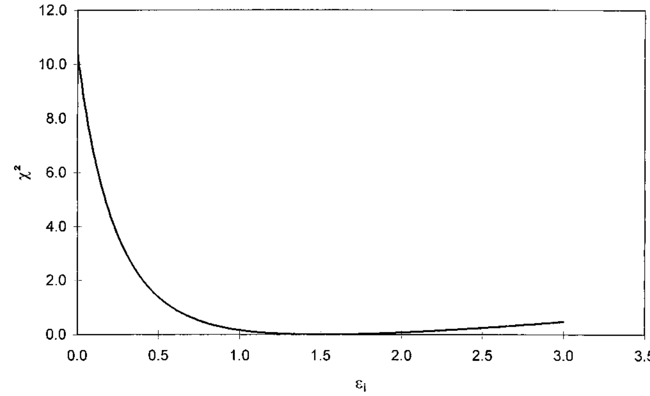

Fig. 22 One example of the nonsymmetrical variation of χ^2 for the parameter ϵ_i.

the light intensity. This distribution will emphasize the role of the slope of the reflectivity curve near the minimum. The curves are shown in Fig. 21.

The amplitude of the noise was chosen to be 5% of the total reflectivity. If it were smaller, as in the last section, the qualitative conclusion would be the same but the final uncertainty in the results would be smaller.

We fixed all the parameter values to the reference ones except one. In other cases, results are the same; only the time to reach them changes. One simple search of the minimum is then carried out, which leads to the result that the uncertainty on the parameter is equal to the value of the step used in the numerical simulation: 0.01 for the dielectric constant and 0.05 for the metal thickness. We chose these values because the evaluation of χ^2 does not need a smaller step size.

We will not try to characterize the noise distribution due to the rotating plate, because we have developed techniques for our setup so that it does not show that kind of noise.

4.1 *Three-Media System*

Table 1 shows values of the varying parameters corresponding to the χ^2 minimum. Also indicated are the two noise-distribution results for comparison with the reference values obtained from the curve without noise.

In the first case, the values of the parameters obtained are equal to those used for simulating the reference reflectivity curve. One can however notice that the values of χ^2 for both dielectric constants of air are large compared with the χ^2 for the other parameters. This is due to the fact that the functions are discontinuous. This difficulty can be solved by the choice of a smaller step size in the numerical calculations. Nevertheless, the values of the dielectric constants are correct.

If we compare the results in the noisy system, we see that the χ^2 are larger than in the case of the spectrum without noise, but the values of the obtained parameters are in excellent agreement with the reference values.

It must be noticed that even if the added noise is on the average symmetrical around the reference value, the parameters obtained are not characteristic of the average spectrum. It is observed that the χ^2 variation is in fact never symmetrical around its minimum value (Fig. 22). Therefore, if noise is added, χ^2 will increase and the range where the parameter will lie will be shifted towards the smaller slope. Although the idea of evaluating a parameter in a noisy spectrum by averaging the spectrum before computing the parameter is thus not valid as far as the mathematics is concerned, it is nevertheless observed that the numerical results are close to the minimum of the spectrum without noise.

We must concede that we are not certain to find the global minimum. However, if another minimum were present, the results obtained would be better for the parameter sought, since we compute the χ^2 minimum with re-

Table 1 Results for the characterization of a three-media system.

			With noise			
	Without noise		Absolute		Relative	
Param.	χ^2	Value	χ^2	Value	χ^2	Value
ϵ_r(glass)	1.027E−17	2.2954977	0.04665	2.2954977	0.02868	2.2954977
ϵ_r(Au)	4.085E−19	−11.6	0.04649	−11.62	0.02865	−11.61
ϵ_i(Au)	6.412E−21	1.5	0.04641	1.48	0.02827	1.47
d (nm)	2.555E−18	50	0.04658	49.9	0.02866	50.05
ϵ_r(air)	6.293	1	6.4697	1	6.3395	1
ϵ_i(air)	6.501	0	6.6806	0	6.5481	0

Table 2 Results for the characterization of a four-media system.

	Without noise		With noise: Absolute		With noise: Relative	
Param.	χ^2	Value	χ^2	Value	χ^2	Value
ϵ_r (glass)	7.68E−18	2.2954977	0.04665	2.2954977	0.02867	2.2954977
ϵ_r (Au)	6.28E−20	−11.6	0.04665	−11.6	0.02867	−11.6
ϵ_i (Au)	1.76E−21	1.5	0.04592	1.5	0.02808	1.45
d_2 (nm)	4.34E−20	50	0.04665	50	0.02867	50
ϵ_r (diel.)	2.24E−21	3.5578	0.04653	3.4078	0.02864	3.4578
ϵ_i (diel.)	1.14E−21	2.8387	0.04658	2.6387	0.02851	2.6887
d_3 (nm)	7.39E−22	1.2	0.04648	1.15	0.02867	1.2
ϵ_r (air)	0.1033	1	0.1376	1	0.1248	1
ϵ_i (air)	0.4049	0	0.4891	0	0.4534	0

spect to only one parameter. If two parameters were used, they would share the residual uncertainty (value of the χ^2 compared with zero) and the uncertainties should be lower (the more parameters we use, the less the residual error is). In the case of only one parameter, it will support all the residual error and as a consequence will be affected by a higher uncertainty.

If the different noise distributions are now compared, the χ^2 minimum is seen to be smaller for the relative noise than for the absolute noise. Finally, when only one parameter is fitted, the noise distribution does not influence the values of the compared parameters.

4.2 *Four-Media System*

In this subsection, the same procedure is applied to a dielectric layer in contact with the metal. Table 2 illustrates the results for the reference spectrum as well as for spectra with two distributions of the noise.

The numerical steps were 0.01 for air and glass, 0.05 for the dielectric constants, and 0.5 and 0.05 for the thicknesses. We do not need smaller steps, as previously explained.

As in the previous case, the values of the dielectric constants for the infinite medium show significant residual value, because the functions are discontinuous. The accuracy depends on the step width used for the calculation. The curve without noise gives a minimum χ^2 value that can be considered as negligible. In the other spectra, with noise, the first medium, the metal, and the infinite medium can be easily characterized, and the values obtained are equal to the reference values. For the ultrathin layer, only the dielectric values are given with a higher uncertainty; the thickness is obtained with good accuracy. The observed shift in ϵ_i is always toward a lower value. This can be explained by the fact that when noise is added to the reflected intensity there is more scope for the width of the absorption peak to be reduced and the depth to be increased, which leads to a smaller value of ϵ_i.

5 Statistical Study

In this last part of the study we estimate the theoretical uncertainty on the parameters. Moreover, all three parameters of the unknown layer (the metal in the three-media system, and the ultrathin layer in the four-media system) are varied simultaneously. We thus have three unknowns to calculate: ϵ_r, ϵ_i, and d—respectively, the real and imaginary parts of the dielectric constant and the thickness.

Let us recall that even in the case of only two unknown parameters, the authors in the references cited above[1,2,4–6] claimed that it was not possible to distinguish between two sets of parameters without designing another experiment.

We have simulated a series of twenty spectra without noise with the same parameters characteristic of the media. Then we added noise obeying the same distribution but sampling the value of the noise at random for one spectrum without reference to the other. Then we computed the values of the parameters corresponding to the minimum χ^2 and we considered these results as random variables, for which we estimated a mean and a standard deviation. We did all the calculations for the three parameters in each of the two distributions. Let us recall that the noise amplitude was 5%, which is larger than in generally encountered experimental conditions.

For these studies, initial values are reference values for all parameters. But let us recall that the first calculated values used by the fitting program are different from the input ones, as described at the end of Sec. 2. Moreover, due to noise, the best values are not reference values of the noise-free spectrum. As previously explained, input values do not have any influence on the results. This has been verified in tests.

5.1 *Three-Media System*

We examine two confidence levels: 90% and 99%. These intervals will enable us to estimate error bars centered on the mean value. By using the twenty spectra, we obtained the results in Table 3. We have reported in the table the name of the computed parameter, its mean, the standard

Table 3 Statistical results for three-media system.

Parameter	Mean m	Std. dev. σ	Absolute error	Relative error (%)	Interval width 90%	Interval width 99%
(a) Absolute noise						
ϵ_r	−11.6118	0.0577	−0.0118	0.1017	0.0229	0.0379
ϵ_i	1.5126	0.0546	0.0126	0.84	0.0217	0.0359
Thickness (nm)	50.1020	0.6107	0.1020	0.204	0.2423	0.4009
(b) Relative noise						
ϵ_r	−11.6008	0.0197	−0.0008	0.0068	0.0078	0.0129
ϵ_i	1.5132	0.0309	0.0132	0.88	0.0123	0.0204
Thickness (nm)	50.0362	0.3133	0.0362	0.0724	0.1243	0.2057

deviation, the absolute error (obtained value − reference value), the relative error, and finally, the width of the intervals with a confidence level of 90% and 99%.

It is observed that for all the noise distributions the relative error is lower than 1%. The absolute error values are lower than the standard deviations, which indicates that the values we obtained are not one set among others but a unique solution corresponding to the true set of values.

The less affected spectra are those with a relative noise; this kind of noise affects more the slope of the minimum, leaving unchanged the minimum position of the reflectivity curve (ϵ_r is not affected), but the bandwidth is affected, which leads to a greater error in ϵ_i. The spectrum with absolute noise gives worse results, since the noise has the same amplitude everywhere on the curve.

5.2 *Four-Media System*

The results for the four-media system are illustrated in Table 4. One can observe that compared with the previous table, the relative errors are increased (being 2% to 3%). The precision of the probe decreases as the medium is placed farther from the metal. But the error of 2% is without any doubt very reasonable. We must not forget that the amplitude of the noise is rather important.

6 Study With 1% Noise

In this section we report calculations with only 1% noise, which we believe are conditions closer to the experimental ones.

6.1 *Three-Media System*

The unknown parameters are those of the metal layer. The results are summarized in Table 5.

6.2 *Four-Media System*

The unknown parameters are those of the dielectric layer in contact with the metal. The results are summarized in Table 6.

In these fits, one can conclude that due to the observed small values of the standard deviation there is no possibility of confusion between two (or more) different sets of parameters. The greatest relative error is of the order of 1.5%, which is less than the standard deviation, and it is found for ϵ_i. This result is understandable, since ϵ_i is related to the width of the absorption band that is most affected by the noise.

Table 4 Statistical results for four-media system.

Parameter	Mean m	Std. dev. σ	Absolute error	Relative error (%)	Interval width 90%	Interval width 99%
(a) Absolute noise						
ϵ_r	3.6123	0.2837	0.0545	1.53	0.1126	0.1863
ϵ_i	2.8402	0.2541	0.015	0.052	0.1008	0.1568
Thickness (nm)	1.1911	0.0579	0.0089	0.0074	0.023	0.038
(b) Relative noise						
ϵ_r	3.5194	0.1933	−0.0384	−1.07	0.0767	0.1269
ϵ_i	2.9160	0.1577	0.0773	2.72	0.0626	0.1035
Thickness (nm)	1.1942	0.0276	−0.0058	−0.48	0.011	0.0182

Table 5 Statistical results for three-media system.

Parameter	Mean m	Std. dev. σ	Absolute error	Relative error (%)	Interval width 90%	Interval width 99%
			(a) Absolute noise (1%)			
ϵ_r	−11.6018	0.0115	−0.0018	0.0155	0.0046	0.0076
ϵ_i	1.5025	0.0115	0.0025	0.16	0.0045	0.0075
Thickness (nm)	50.0268	0.6107	0.0268	0.0536	0.0504	0.0833
			(b) Relative noise (1%)			
ϵ_r	−11.6004	0.0042	−0.0004	0.0034	0.0017	0.0028
ϵ_i	1.5024	0.0067	0.0024	0.16	0.0027	0.0044
Thickness (nm)	50.0177	0.0465	0.0177	0.0354	0.0184	0.0305

Table 6 Statistical results for four-media system.

Parameter	Mean m	Std. dev. σ	Absolute error	Relative error (%)	Interval width 90%	Interval width 99%
			(a) Absolute noise			
ϵ_r	3.5316	0.0706	−0.0262	−0.73	0.0767	0.1269
ϵ_i	2.8807	0.0706	0.042	1.47	0.0626	0.1035
Thickness (nm)	1.1970	0.0134	−0.003	−0.25	0.011	0.0182
			(b) Relative noise			
ϵ_r	3.5535	0.0427	−0.0043	−0.120	0.017	0.0281
ϵ_i	2.8666	0.0570	0.0279	0.982	0.0227	0.0375
Thickness (nm)	1.1934	0.0081	−0.0066	−0.55	0.0033	0.0054

7 Conclusions

In this paper, we have shown that the surface plasmon resonance technique is very suitable for the characterization of optical properties of thin dielectric layers. In the first section, it was shown that using an efficient nonlinear algorithm, it is possible to make a unique determination of ϵ_r, ϵ_i, and d of a thin layer. So there is no indeterminacy in the set of parameters when the entire reflectivity curve is used for the fit. It is then concluded that the difficulties encountered by some authors are due to either incomplete modelling or a less efficient algorithm.

These studies were performed on several kinds of metallic layers and on several kinds of coating layers (absorbing or not) in contact with the metallic one. We also used characteristics from papers that encountered indeterminacy problems. These conclusions are found to be valid for any kind of system and for any layer in the system.

We then estimated the performance of our fitting method in extreme conditions, using a noise amplitude 5% of the reflectivity and using different distributions. We were able to show that the different parts of the reflectivity curve are sensitive to noise, which leads to uncertainties affecting the different parameters, depending on the angular range. In all cases the dispersion of the values is small and the absolute error is smaller than the standard deviation.

Finally, we fitted the curves with 1% noise, which is considered as a more realistic experimental condition, in order to estimate the uncertainties affecting the computed parameters.

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