

Effective dielectric function of mixtures of three or more materials: a numerical procedure for computations

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Abstract

A numerical procedure for solving the mathematical equations that define the effective medium for a mixture of materials is presented. The basic idea is to transform the inherent complex root-finding problem into a minimization task in real space so that the method can be implemented through a standard two-dimensional minimization algorithm. This leads to general, simple and useful procedures for ellipsometric and/or spectrophotometric data analysis in the optical characterization of materials and surfaces. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Heterogeneous media are usually modeled macroscopically by effective dielectric functions based on the assumption of different microscopic configurations for the material. There are several mathematical expressions available to represent various possibilities: the Lorentz–Lorenz equation for mixtures that are random at the microscopic level, the Maxwell–Garnett formulas for two separate phases or the related Bruggeman effective medium theory. The models can even take into account different types of mixture: spheres of both materials, spherical inclusions in a matrix, lamellae, lamellar inclusion, etc. It is also common to model the surface roughness by means of an effective layer consisting of a combination of the underlying material and air (having a volume

fraction each), fitting the thickness of the layer and allowing one or more extra parameters to differentiate between different roughness profiles. The different models can be considered as cases included within the effective medium approximation (EMA) [1,2].

In the case of mixtures of two components, the effective dielectric function ϵ is always deduced from the dielectric functions of the two phases (ϵ_a, ϵ_b) and the corresponding volume fractions (f_a, f_b). The equations are of the form

$$F(\epsilon_a, \epsilon_b, f_a, f_b, \epsilon) = 0, \quad (1)$$

where ϵ is defined implicitly by the preceding formula. The expression may be stated in terms of complex refractive indices as well.

Taking into account the fact that dielectric functions are complex numbers, in solving the previous expression for ϵ , one is faced with quadratic and cubic equations (or even higher powers depending on the number of materials considered),

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which require the selection of the proper branch from the corresponding multivalued complex solution. In spectroscopic ellipsometry, use of EMA theories requires calculation of the effective dielectric function at each single wavelength of the spectrum. Thus, any ellipsometric data analysis by EMA has to include a numerical procedure for solving Eq. (1) for each wavelength, elucidating what is the correct branch of the complex solution. This topic has been addressed recently and satisfactory procedures are deduced in Ref. [3] for two particular cases of Eq. (1) with two materials. When more than two materials have to be considered in the mixture, the EMA procedures may be easily generalized, from the theoretical point of view. The practical problems for solving the generalized version of Eq. (1) are similar to the previous ones. However, simple methods for solving numerically for ϵ are not available. Moreover, even with a fixed number of materials, different forms of Eq. (1) should be resolvable to cope with the different microscopic cases.

The aim of this paper is to present a numerical procedure for finding the effective dielectric constant when one has to solve (for each wavelength) any particular form of the EMA equations for mixtures of two or more materials. The capability and practical use of our procedures will be illustrated by a worked example where the complexity of the physical model will be gradually increased and by application to experimental measurements of an oxynitride thin film on silicon. The techniques presented can also be adapted to other physical situations, like the description of surface roughness by the EMA theories mentioned above.

2. Statement of the problem

We may include under the global denomination ‘EMA’ several theoretical approaches for modeling the dielectric properties of heterogeneous media. These theories are conceptually similar and differ basically in the consideration of the host medium [1,2]. Thus, the final mathematical expressions obtained for the different approaches are also similar. This is the starting point for the present work, since we are interested in the numerical

problem associated with the solutions of the equation which relates the effective dielectric constant with those of the component materials, their volume fractions and the parameters that describe the microstructure.

Some of the EMA equations where we can apply our procedures are:

the Lorentz–Lorenz equation for a mixture of several materials whose complex dielectric constants and volume fractions are ϵ_i and f_i

$$\frac{\epsilon - 1}{\epsilon + 2} = \sum_i f_i \frac{\epsilon_i - 1}{\epsilon_i + 2}; \quad (2)$$

the Bruggeman formula for computing ϵ in terms of ϵ_i and f_i

$$0 = \sum_i f_i \frac{\epsilon_i - \epsilon}{\epsilon_i + 2\epsilon}; \quad (3)$$

a more ‘general’ case, including the definition of a host material ϵ_h and a screening parameter y

$$\frac{\epsilon - \epsilon_h}{\epsilon + y\epsilon_h} = \sum_i f_i \frac{\epsilon_i - \epsilon_h}{\epsilon_i + y\epsilon_h}. \quad (4)$$

In fact, the last expression includes the two previous ones and the Maxwell–Garnett formula as a particular case [4]. The value 2 is usually taken for the screening parameter y (which corresponds to spherical inclusions); however, generally it may be written as

$$y = \frac{1}{l} - 1, \quad 0 \leq l \leq 1.$$

Other expressions like the Ping Sheng formulae [5] (another generalization of the Bruggeman theory) could be introduced at this point. It will become evident that our methods would be valid as well.

The aim of the present work was to provide a simple, fast and stable numerical algorithm for solving any of the above EMA equations, in order to find ϵ in terms of the set of ϵ_i and f_i (and parameters y , etc.). The procedure will be valid for more than two materials ($i > 2$) and will have to be used for each single wavelength of the range of interest.

The basic idea we propose is to use a standard downhill-simplex minimization algorithm (DS), adapted to our problem. This requires: defining the space of the variables (where to move the simplex figure), defining the merit function to be minimized and providing the initial point in the space to start the DS. We shall develop our procedure in detail for the Bruggeman formula with three materials, written in terms of complex refractive indices. In case of other mathematical expressions, the only difference will be the definition of the merit function (see below).

Let us assume that the explicit form of Eq. (1) is Eq. (3), expressed in terms of the complex refractive index N ,

$$\sum_{i=1}^3 f_i \frac{N_i^2 - N^2}{N_i^2 + 2N^2} = 0, \quad (5)$$

where f_i and N_i are the volume fraction and complex optical constant for component i , and N is the effective value to be computed. In terms of numerical procedures our problem may be stated as a complex root-finding case [6], where N is the complex variable. Certainly, given f_i and N_i and a guess $n' + jk' = N'$ for the effective complex refractive index, the problem is to find $n + jk = N$ which fulfils Eq. (5). This is to find the root of the complex function of a complex variable $\underline{F}(N)$

$$\underline{F}(N) = \sum_{i=1}^3 f_i \frac{N_i^2 - N^2}{N_i^2 + 2N^2} \quad (6)$$

(in fact more than one root exists; the discussion on the choice is postponed).

The standard numerical technique for root finding in more than one dimension is the Newton–Raphson method [6], which requires the computation of derivatives of the merit function. To simplify things a little, we can also formulate our problem as a two-dimensional minimization of a real merit function whose variables are the real and imaginary parts (n, k) of N . This merit function is

$$F(N) = \left| \sum_{i=1}^3 f_i \frac{N_i^2 - N^2}{N_i^2 + 2N^2} \right|. \quad (7)$$

Certainly the minimization we propose now is

numerically simpler than the complex root-finding described before. For example, one may use the widespread DS technique, which does not even need computation of derivatives of the function. The simplification we are proposing requires only a final check to guarantee that is giving us the required root: since we minimize a function that is the modulus of a complex number, if the minimum found is zero so is the complex number. Only in the case that the DS stops at a minimum different from zero will the couple (n, k) not be a solution of the EMA equation. We have not observed this problem in any of the cases we have studied. This is due to the very nature of the physical case we deal with, where the knowledge of the refractive indices of the component materials and their volume fractions always provides good starting points for the DS, which lead to the right solution.

Thus, for solving numerically Eq. (5) we propose the DS method. As commented, a key point is the choice of the starting point. In our case this is an initial estimation of the complex refractive index of the mixture. We have seen that using $n' = \sum f_i n_i$ and $k' = \sum f_i k_i$ as the starting point for the DS algorithm leads to fast and accurate convergence to the right branch of the solutions. In fact, our choice is common sense and, moreover, is justified by the theoretical analysis of the problem [7,8], where the allowed limits for mixtures of separate phases are established.

The application of our method to Eqs. (2) and (4) is straightforward. For expression (2), the merit function would have to be

$$F(\epsilon) = \left| \frac{\epsilon - 1}{\epsilon + 2} - \sum_{i=1} f_i \frac{\epsilon_i - 1}{\epsilon_i + 2} \right|. \quad (8)$$

In the case of Eq. (4), the corresponding merit function is

$$F(\epsilon) = \left| \frac{\epsilon - \epsilon_h}{\epsilon + y\epsilon_h} - \sum_{i=1} f_i \frac{\epsilon_i - \epsilon_h}{\epsilon_i + y\epsilon_h} \right|. \quad (9)$$

Multiple solutions for the EMA equations always exist, but there is only one that is physically meaningful. In terms of our procedure, the facts that: (1) the DS stops the minimization with a zero value for the merit function, and (2) the

ending point for the variable is an acceptable value for ϵ or N , are enough to guarantee the validity of the method. The ending point has to fulfil the conditions:

- in terms of dielectric constant: $\epsilon_i > 0$ (imaginary part);
- in terms of optical constants: $n > 0$ and $k > 0$.

As commented, we have observed no problems in finding the right solution in all the cases we have analyzed with computer-generated (theoretical) data, probably because of the appropriate determination of the starting point for the DS.

3. Results and discussion

To test the procedure, we have simulated (by computer) the ellipsometric characterization of a structure consisting of two layers (separated by an interface region) on silicon. The innermost layer is SiO₂, 0.455 μm thick, and the outer layer is a-Si:H (hydrogenated amorphous silicon), 0.385 μm thick. We assume an interface region, 70 nm thick, where SiO₂, a-Si:H and voids are mixed with equal volume fractions. In terms of the computation scheme, our structure consists of three layers with physical thicknesses (from inside to outside) of 0.42 μm /0.07 μm /0.35 μm (see Fig. 1). The optical data for the three materials that we are using, in the range 600–850 nm, are taken from Ref. [9] and we assume that the interface region can be described by EMA, according to Eq. (3) for three materials. This is Eq. (5) for SiO₂, a-Si:H and voids.

We have computed the ellipsometric data ($\cos \Delta$, $\tan \Psi$) at 70° which ideally would be measured

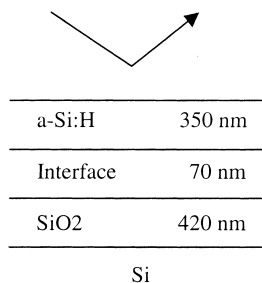


Fig. 1. Sketch of the layered structure to be studied.

for this sample. These values are presented in Fig. 2 as the solid line. In the same figure we also show the values corresponding to two other similar configurations:

- two layers (SiO₂ and a-Si:H) without an interface and with thicknesses of 0.455 μm /0.385 μm (dashed line);
- three layers of thickness 0.42 μm /0.07 μm /0.35 μm where the interface is formed by a 50% mixture of both materials without voids (dashed–dotted line).

This plot shows the significant differences that could be expected in the measured data in a real case, showing the potential utility of ellipsometry for the proposed characterization of the configuration.

The characterization of the sample is done by fitting the simulated experimental data with a model consisting of three layers on a substrate whose adjustable parameters are the thicknesses of the layers and the volume fractions of the components of the interface layer. The merit function for the fitting is a chi-square sum defined by the differences between the simulated experimental data and those computed with the set of adjustable parameters that we are considering. Its lower limit is zero, but physically acceptable minima should be around 1 under well-defined experimental conditions [6]. When working with simulated data (with unlimited precision) very low values (unrealistic) may be obtained. Nevertheless, the validity of the minimization algorithms is independent of the value of the merit function at the minimum. For the minimization of this chi-square merit function we use a DS algorithm, which will be referred to as the ‘global’ DS. It must be pointed out that there are two DS algorithms in the whole fitting procedure: the global DS is responsible for the fitting of the simulated experimental data (the unknowns are the adjustable parameters) and this global DS uses, as a tool for determining the complex refractive index of the interface, a second DS algorithm for solving the EMA equations (as explained in the previous section). The unknowns of this second DS are (for each wavelength) the real and imaginary parts of the index of the interface layer.

In the following figures we illustrate the ability of our procedures for the fitting of ellipsometric

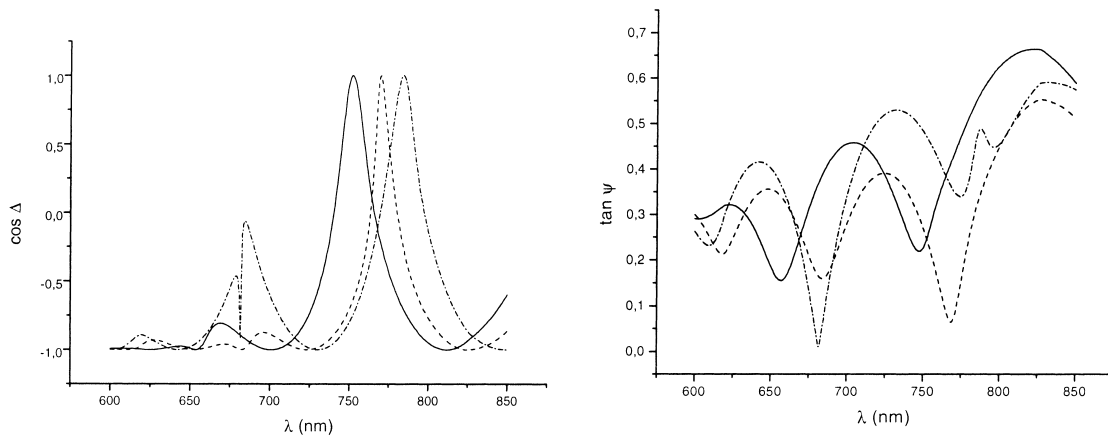


Fig. 2. Ellipsometric spectra corresponding to three different configurations of the interface layer (see text).

data. Assuming we have measured an ellipsometric spectrum given by the continuous line (our target), and supposing we have an initial guess about our physical configuration whose spectrum is the dashed line, our numerical procedures are able to fit the target perfectly, finding the right values for the sample configuration. To be precise, in the example of Fig. 3, we start a global DS algorithm from an initial guess of adjustable parameters as follows. Thickness of the interface: 100 nm; composition: 45% (SiO_2), 10% (voids), 45% (a-Si:H). These suppositions correspond to the dashed spectrum. We may consider our initial guess as a poor estimation of the interface composition since the two ellipsometric spectra (target and starting

point) are quite different. Nevertheless, the global DS algorithm is able to find the right solution (to the third decimal digit) in a short time (less than 30 s on a personal computer).

Similarly, Fig. 4 illustrates a more difficult case, since our target spectrum is now found starting from an initial configuration where, apart from the same previous values for the interface thickness and composition, also the thicknesses of the other two layers were taken as unknown. The external layer was assumed to be 335 nm thick and the internal one 405 nm. Again, the initial ellipsometric spectrum is the dashed line and the global DS is able to find the physical configuration of the target.

To illustrate the influence of the screening

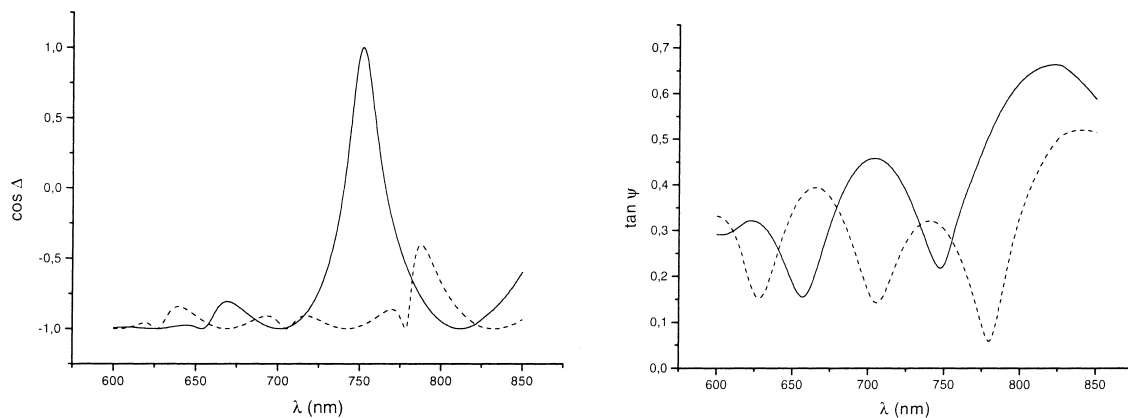


Fig. 3. Ellipsometric spectra corresponding to the starting point of the first global DS described in the text (dashed line) and to the layered structure of Fig. 1 (continuous line).

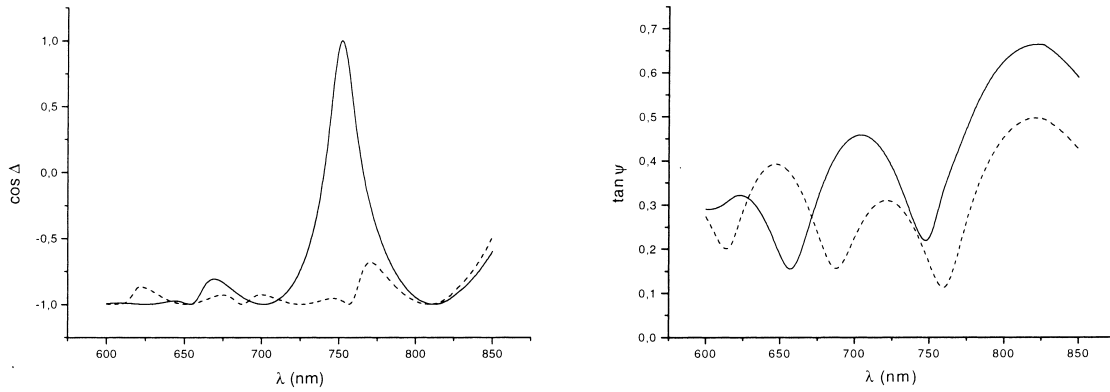


Fig. 4. Ellipsometric spectra corresponding to the starting point of the second global DS described in the text (dashed line) and to the layered structure of Fig. 1 (continuous line).

parameter in the ellipsometric spectra, we have also included this microstructural factor in the example considered. In terms of the formulas (2), (3) and (4) presented in Section 2, we now have to use Eq. (4) with $\gamma \neq 2$ and host material $\epsilon_h = \epsilon$ (this is the generalization of the previous Bruggeman formula). In Fig. 5 we show the effect of considering $\gamma = 1.0$ (dashed line) instead of $\gamma = 2.0$ (continuous line) in the theoretical spectrum.

In Fig. 6 we present as a dashed line the starting point for a global DS fitting procedure when assuming initially $\gamma = 1.5$, besides all the remaining initial configuration values of Fig. 4. In summary, the dashed line in Fig. 6 is the ellipsometric spectrum corresponding to the following configuration:

- thickness of the innermost layer: 405 nm;
- thickness of the interface: 100 nm;
- composition of the interface: 45% (SiO_2), 10% (voids) and 45% (a-Si:H);
- screening parameter of the interface: 1.5;
- thickness of the outermost layer: 335 nm.

The continuous line in Fig. 6 is our target, which corresponds to Fig. 1, with $\gamma = 2$. Our procedures are able to virtually reproduce the target starting from the approximate values just presented. In fact, we get for the fitted configuration $\gamma = 1.95$, 34% voids and 32% SiO_2 (instead of $\gamma = 2.0$, 33.3% voids and 33.3% SiO_2). The differences in the spectra are not noticeable.

As a last simulated example, Fig. 7 shows the computed spectral reflectance (at 0° incidence) of

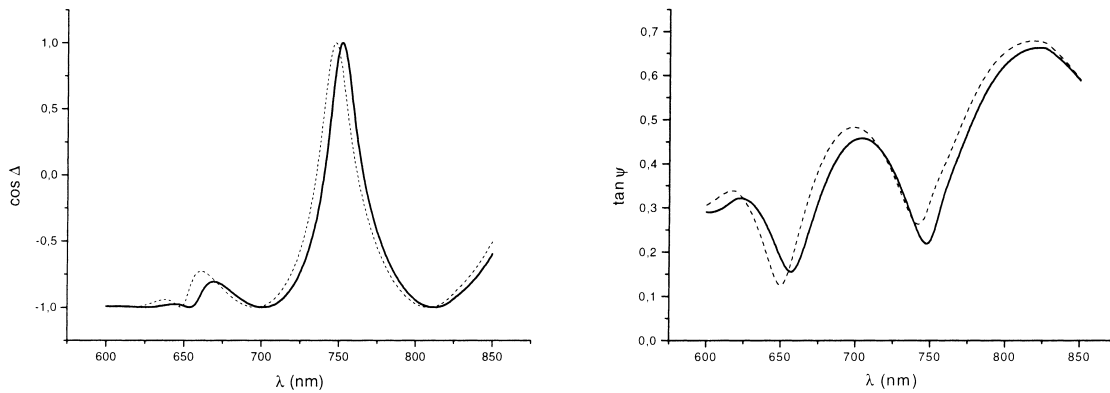


Fig. 5. Effect of having a value of 1.5 for the screening parameter in the interface (dashed line) as compared with a value of 2, originally assumed in the layered structure of Fig. 1 (continuous line).

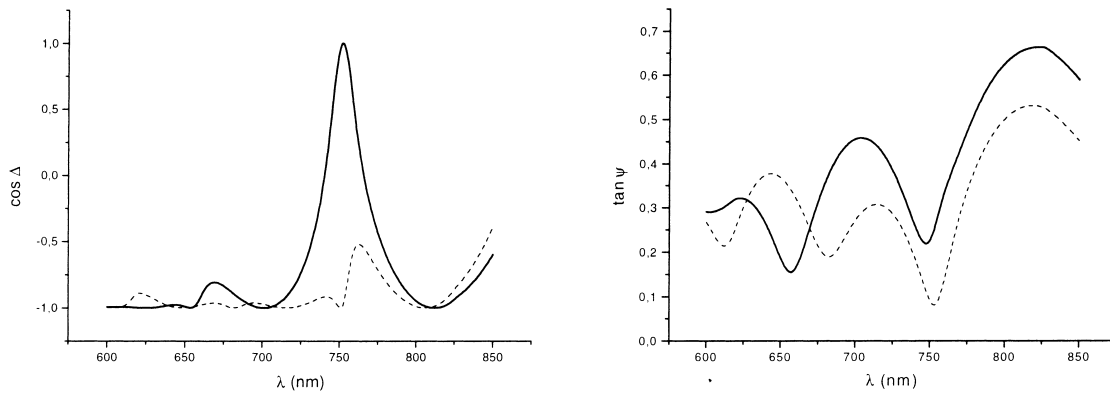


Fig. 6. Ellipsometric spectra corresponding to the starting point of the more complicated global DS described in the text (dashed line) and to the layered structure of Fig. 1 (continuous line).

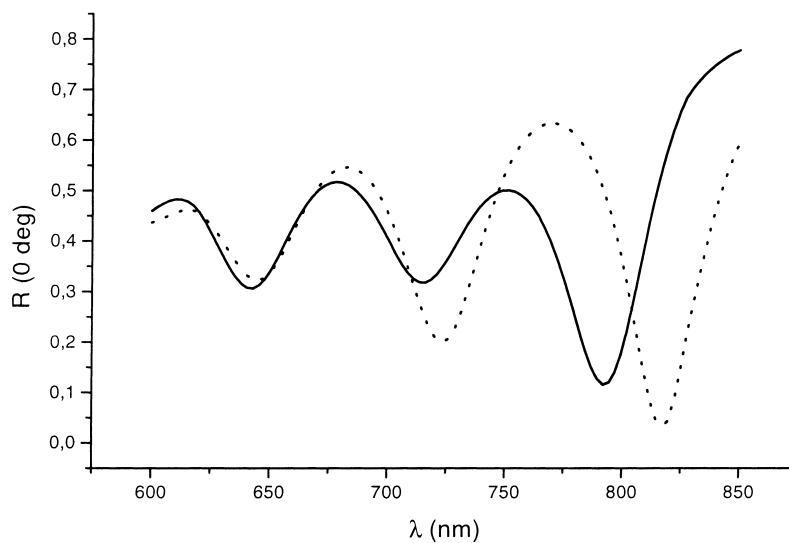


Fig. 7. Comparison between the 0° incidence reflectance spectra corresponding to the layered structure of Fig. 1 with an interface containing voids (continuous line) and without voids (dashed line).

our theoretical sample (continuous line) as compared with the case of an interface without voids (50% upper-layer material plus 50% lower-layer material). This reflectance has been computed on the assumption of a semi-infinite silicon substrate (no backsurface reflection). This comparison illustrates the fact that spectrophotometric data are also sensitive to the interface composition and our procedures could also be used for this kind of spectrum.

To evaluate the performance of our numerical

procedure with experimental data we have considered a measured spectrum corresponding to an oxynitride thin film deposited on a crystalline silicon (c-Si) substrate. The film was grown in a plasma-enhanced chemical vapor deposition reactor by radio-frequency glow discharge decomposition of a gas mixture of SiH_4 (5%), NH_3 (70%) and N_2O (25%). Ellipsometric measurements were performed with a spectroscopic phase-modulated ellipsometer [10] using the autocalibrated method [11] to increase the accuracy in the determination

of the measured quantities: $\cos(2\Psi)$ and $\cos(\Delta)$. Spectra were obtained in the energy range from 1.6 to 5.0 eV with an angle of incidence of 69.45° .

We assume that the sample consists of an ambient/film/native oxide/c-Si substrate structure and that the film is isotropic and homogeneous. The native oxide layer is 3 nm thick as revealed by a previous spectroscopic ellipsometry measurement. The dielectric function of the film is modeled by an EMA mixture of fused silica (SiO_2), non-crystalline silicon nitride (Si_3N_4) [9] and voids. Thus, the fitting parameters are the thickness of the film and the volume fraction of its constituents.

The numerical procedure was tested by using different sets of initial values, for example: assuming no voids present and 50% for both of the other components; assuming 10% of voids, 40% of Si_3N_4 and 50% of SiO_2 ; assuming 20% of voids, 40% of Si_3N_4 and 40% of SiO_2 ; etc. For the thickness, one can start with 80 or 120 nm. It is important to note that, for all of these starting points, the same minimum was found, with a χ^2 value of 4.7. Fig. 8 compares the measured and fitted spectra, with the best fitting parameters obtained being summarized in Table 1.

All the computation programs have been implemented using the numerical procedures and C functions taken from Ref. [6]. The computation times for spectra of around 200 points (wave-

Table 1

Best-fit parameters corresponding to the measured ellipsometric spectra

	Thickness (nm)	SiO_2 (%)	Si_3N_4 (%)	Voids (%)
Film	96.3	57.8	39.7	2.5
Interface	3	100	–	–

lengths or energies) are of the order of 1 min, using a Pentium II processor under Windows 98.

4. Conclusions

We have presented a numerical method for computation of the effective optical constants of layers consisting of mixtures of three or more materials from ellipsometric or spectrophotometric data. The theoretical model for the mixture may be defined by any of the existing EMA expressions, including also variations in the microstructure of the layer defined through a screening parameter. The practical procedure is illustrated first by means of a worked example consisting of a characterization of an ideal sample which includes an intermediate layer that can be described by an EMA model. The characterization is able to find the correct values of the volume fraction of the compo-

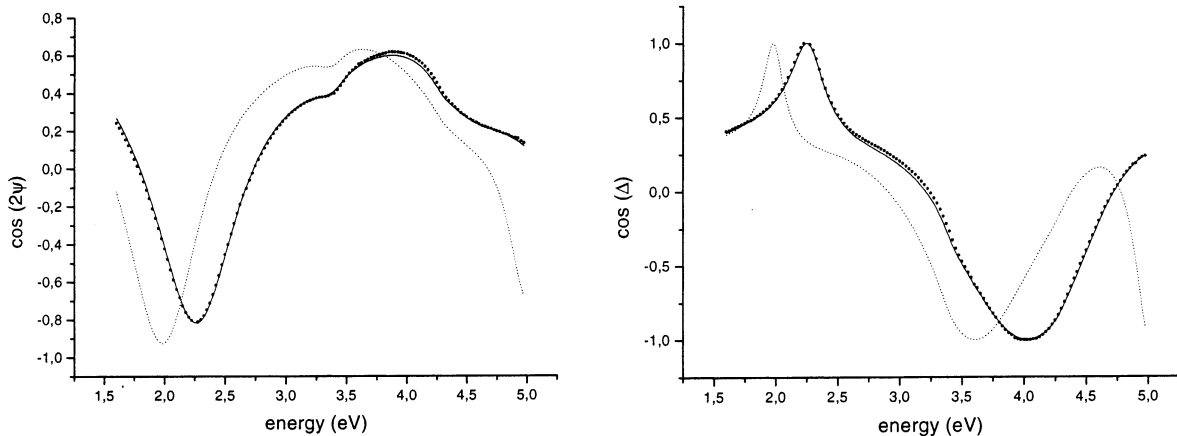


Fig. 8. Measured ellipsometric spectra (dots) of the oxynitride sample, compared with the best fitting found (continuous line, for the parameters of Table 1) and with the spectra (dashed) of the starting point defined by: 120 nm film thickness, 20% voids, 40% Si_3N_4 and 40% SiO_2 .

nents of the EMA layer, from simulated ellipsometric spectra. In the example the complexity of the configuration is gradually increased by increasing the number of unknowns in the characterization. To evaluate the performances of the method with experimental data, we have considered a two-layer (interface plus film) structure where the film is a mixture of three materials. In this case, particular emphasis was placed on testing and proving the independence of the results obtained with respect to the starting point of the fitting procedure. We also point out that the present methods are also valid for modeling surface roughness by EMA.

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