

Surface plasmon resonance of metal nanoparticles sandwiched between dielectric layers: theoretical modelling

Maria L. Protopapa

Department of Advanced Physical Technologies and New Materials, Italian National Agency for New Technologies, Energy and the Environment (ENEA), CR Brindisi, SS. 7 Appia, 72100 Brindisi, Italy
(Lucia.protopapa@brindisi.enea.it)

Received 11 September 2008; revised 3 December 2008; accepted 11 December 2008; posted 11 December 2008 (Doc. ID 101407); published 26 January 2009

Composite films consisting of a ceramic matrix with embedded metal nanoparticles have received increased interest due to their numerous potential applications in the field of optics and optoelectronics. Numerous studies have been dedicated to the fabrication of these composite materials and it has been shown that nanocermet films can be obtained by successive deposition of alternate dielectric and metal films of thicknesses opportunely chosen. In this case, stacks of dielectric layers alternated with layers of metal nanoclusters (NCs) are obtained. However, until now, optical characterization of these kinds of multilayer stack has been used to retrieve mainly qualitative information on the dimension, shape, and geometric distribution of nanoparticles inside the dielectric matrix. An easy-to-handle model that quantitatively links the optical properties to the main features of the NCs embedded in the matrix is presented. This model can be applied to multilayer stacks of dielectric layers alternated with metal NC layers and is shown to be a valid alternative to a recently published model [Nanotechnology **19**, 125709 (2008)] that was applied to the case of a three-layer structure (dielectric/metal:dielectric/dielectric). © 2009 Optical Society of America

OCIS codes: 310.6860, 240.6680, 160.4236.

1. Introduction

Composite films consisting of a ceramic matrix with embedded metal nanoparticles have received increased interest due to their peculiar nonlinear optical properties with response times of a few picoseconds, making such material systems suitable for all-optical switching devices [1,2]. In the field of optics they have proved useful also as selectively absorbing optical coatings [3]. Moreover, noble metal-based nanoclusters (NCs) are promising candidates as nonlinear optical media for photonic nanodevice applications [4,5]. The linear and nonlinear optical properties of these materials are dominated by collective electron-plasma oscillations, the so-called

localized surface plasmons, induced on metal nanoparticles by the electric field associated with the incident electromagnetic wave.

This phenomenon produces a resonance called surface plasmon resonance (SPR) in the optical absorption spectra of nanocomposite materials. The main features of the resonance peak are related to the matrix refractive index and to the characteristics of the clusters: size, shape, and spatial distribution [6].

Numerous studies have been dedicated to the fabrication of nanocermets by chemical and physical techniques (see, e.g., [7]). In particular, it has been shown that nanocomposite materials can be obtained by depositing alternatively dielectric and metallic films of opportunely chosen thickness (see, e.g., [8–14]). In this way, nanocermets having the structure shown in the cross section in Fig. 1 can be obtained. It has to be noted that the interparticle

distance a in the x - y plane can be equal to the interparticle distance b along the z direction and, in this case, the NCs are uniformly distributed inside the sample volume. The theoretical approach useful to retrieve from the optical response of the sample information about the main features of the NCs (shape, dimension, geometric distribution) is well known when the NCs are uniformly distributed. In fact, the Mie theory in the case of low filling factors or, alternatively, effective medium theories like the Maxwell-Garnett (MG) theory when interacting effects among metallic clusters are not negligible, can be applied. However, the problem becomes much more complicated when distance a differs with respect to distance b . Therefore, the challenging problem that we try to solve is to find a suitable theoretical model to analyze the SPR spectra in the case of NCs distributed as in Fig. 1 with $a \neq b$.

Recently, several authors tried to explain the optical absorption spectra of metal NCs not uniformly distributed inside a dielectric matrix on the base of effective medium theories (see, e.g., [15–17]). The goal of calculations based on effective medium theories is to obtain an “effective dielectric function” ϵ_f . A hypothetical homogeneous medium, presenting ϵ_f as a dielectric function, has the same optical response as the inhomogeneous medium containing the metallic clusters. In particular, García *et al.* [15] proposed a simple model based on the MG theory

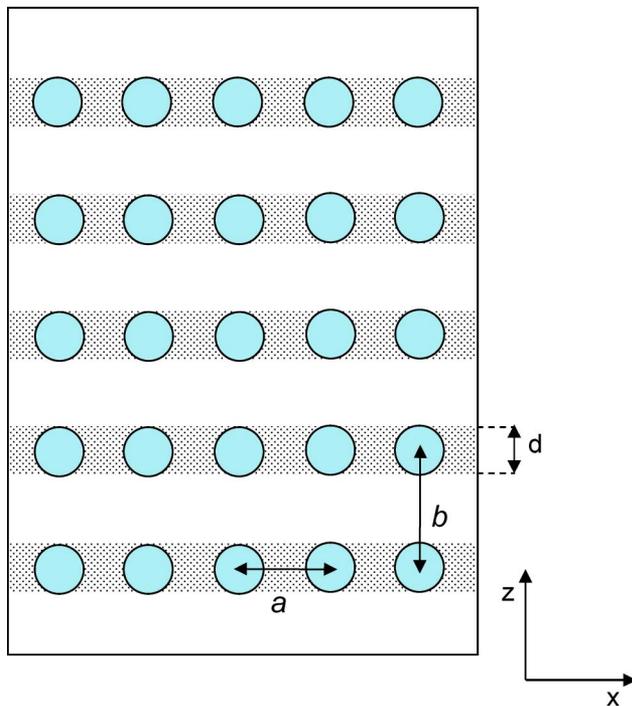


Fig. 1. (Color online) Scheme of the spatial arrangement of the silver NCs (cross section). In particular, the NCs lie on planes perpendicular to the direction of propagation of the spectrophotometer beam (z direction). The interparticle distance in the x - y plane is a , while the interlayer distance in the z direction is b . According to the Toudert *et al.* method [19], the shaded layers containing the NCs can be considered as effective-medium layers of thickness d equal to the diameter of the NCs.

to calculate the effective dielectric function ϵ_f to be assigned to a dielectric matrix with embedded metallic clusters. The model, presented in Refs [15,16], includes effects due to particle geometry and spatial homogeneity of the clusters' distribution but it is affected by some calculation errors and, for this reason, the expression given for ϵ_f does not reduce to the one expected by the MG theory [18] for spherical nanoparticles uniformly distributed inside a dielectric matrix.

More recently, Toudert *et al.* [19] presented a model that quantitatively links the nanostructure to the optical response of the film when considering the case of a three-layer structure (dielectric/metal: dielectric/dielectric). The central layer, formed by the metallic NCs embedded inside the dielectric matrix, is considered as an effective medium layer whose dielectric constant is calculated by fitting the ellipsometric response [$\tan(\Psi)$ and $\cos(\Delta)$ spectra] of the multilayer stack. In the fitting procedure, the thickness of the effective layer is fixed equal to the average height of the clusters, but, as is shown throughout this paper, this choice is not really correct. The dielectric constant of the effective-medium layer is related to the shape, dimension, and geometric distribution of the metallic NCs, as well as to the optical parameters of the NCs and the dielectric matrix. Therefore, the fitting of the ellipsometric spectra of the multilayer stack allows obtaining information on the main features of the NCs embedded in the dielectric matrix.

Here an alternative method, based on the corrected calculations of García *et al.* [15,16], is presented. It is a particularly easy-to-handle model. In fact, while the Toudert *et al.* [19] method requires the fitting of the ellipsometric spectra of the multilayer stack and the use of numerical codes that take into account the interference effect between the beams reflected and transmitted at each interface of the stack, the method presented in this paper is based on a simple equation linking the dielectric constant of the whole stack, considered as an effective medium, to the main features of the NCs.

The Toudert *et al.* method [19] is presented in detail and discussed in Section 2; Section 3 is dedicated to the description of the alternative method proposed in this paper. Finally, conclusions are given in Section 4.

2. Toudert *et al.* Method

The Toudert *et al.* method [19] has been applied to a three-layer system having a dielectric/metal: dielectric/dielectric structure, with the central nanocomposite layer being an effective medium. Therefore, the ellipsometric spectra of the three-layer system have been fit by numerical codes taking into account the interference of the beams reflected and transmitted at each interface of the three-layer stack. Because of the large amount of free parameters involved in the fitting procedure, some of them have been considered fixed. For example, the

thickness of the effective layer has been fixed equal to the average height of the clusters and the optical parameters of the dielectric and metal materials have been taken from the literature. In this way, the fitting procedure made it possible to obtain an effective dielectric function of the central metal:dielectric layer, which is related by the Yamaguchi theory [20,21] to the shape, dimension, and geometric distribution of the NCs. Therefore, the fitting of the ellipsometric spectra made it possible to determine the main features of the metallic NCs embedded in the dielectric matrix.

A simple test of the Toudert *et al.* method [19] can be performed by considering a uniform distribution of NCs inside a dielectric matrix. Let us suppose, for example, having Ag spherical NCs of 5 nm radius that are uniformly distributed inside a BaF₂ matrix, such as in Fig. 1 with $a = b = 30$ nm. The optical absorption spectra of this sample can be readily calculated by the MG effective medium theory. In fact, the optical absorbance α of the sample as a function of wavelength λ is given by

$$\alpha(\lambda) = \frac{4\pi k}{\lambda}, \quad (1)$$

where k is the extinction coefficient related to the effective dielectric function of the material ϵ_f by the formula

$$k = \left(\frac{|\epsilon_f| - \text{Re}(\epsilon_f)}{2} \right)^{1/2}. \quad (2)$$

According to the MG theory, ϵ_f is given by

$$\epsilon_f = \epsilon_m \left[1 + \frac{f(\epsilon - \epsilon_m)}{\epsilon_m + S(\epsilon - \epsilon_m)} \right], \quad (3)$$

where f is the filling factor given by $f = 4\pi R^3 / (3a^3)$, ϵ_m is the dielectric constant of the dielectric matrix, and parameter S is given by $S = L - f(1/3)$, where L is the depolarization factor equal to $1/3$ for spherical particles. Parameter ϵ in Eq. (3) is the complex dielectric constant of the metal clusters corrected for the variation of the electron mean free path with cluster radius R [22]:

$$\epsilon(\omega, R) = \epsilon_{\text{bulk}}(\omega) + \frac{\omega_p^2}{\omega^2 + i\omega\gamma_0} - \frac{\omega_p^2}{\omega^2 + i\omega(\gamma_0 + Av_f/R)}, \quad (4)$$

where $\omega_p = 13.8 \times 10^{15} \text{ s}^{-1}$, $v_f = 10^6 \text{ m/s}$, and $\gamma_0 = 2 \times 10^{12} \text{ s}^{-1}$, which are the plasmon frequency, the Fermi velocity, and the relaxation frequency of bulk silver, respectively. A is a phenomenological parameter of the order of 1 [22]. For the theoretical simulations presented in this work, the dielectric constant of bulk silver $\epsilon_{\text{bulk}}(\omega)$ were taken from [23]; the dielectric constant values $\epsilon_m(\omega)$ for BaF₂ were taken from [24]. The absorbance spectrum cal-

culated by the MG theory is shown in Fig. 2 as a solid curve.

The system in Fig. 1 can be decomposed into a stack of 11 layers. The shaded layers containing the Ag NCs can be considered effective medium layers, whose optical properties can be obtained by the Yamaguchi theory [20,21], which is valid for bi-dimensional distributions of NCs on dielectric substrates. The thickness d of the effective medium layers can be fixed equal to the diameter of the NCs (10 nm), as Toudert *et al.* did in [19]. Therefore, reflectance R and transmittance T of the multilayer stack can be calculated as interference between the beams reflected and transmitted at each interface of the stack. The optical response of the multilayer stack has to be the same as that of the sample considered as a single-layer film containing the nanoparticles. Therefore, optical absorbance α of the single-layer film can be calculated from R and T by the formula

$$\alpha(\lambda) = \frac{1}{D} [\ln(I_0 - R) - \ln(T)], \quad (5)$$

where D is the physical thickness of the stack and I_0 is the incident intensity of the spectrophotometer beam ($I_0 = 1$). It is worth mentioning that Eq. (5) is an approximation based on the hypothesis that the only contribution to the reflected intensity comes from the first reflection of the beam at the air-coating interface, i.e., interference effects between the multiply reflected beams at the air-coating and substrate-coating interfaces are neglected. Here, this approximation, generally valid only in the case of highly optically absorbing thin

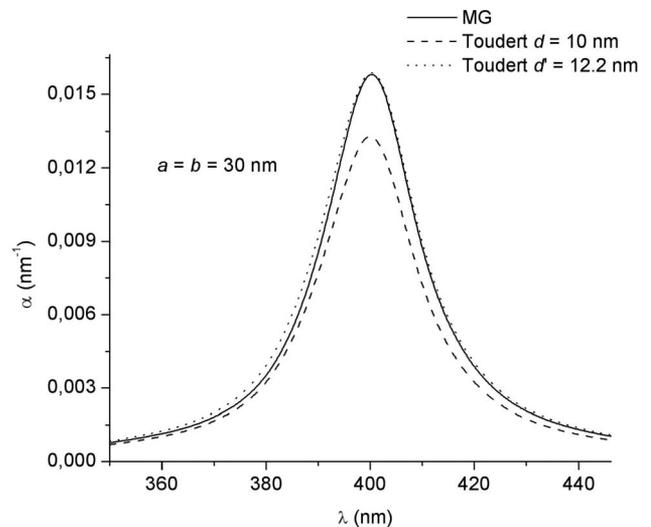


Fig. 2. Optical absorption spectra of the system shown in Fig. 1 with $a = b = 30$ nm and NCs' diameter equal to 10 nm. The optical absorption spectra have been calculated by the MG effective medium theory (solid curve), as well as by the Toudert *et al.* method [19] using as thickness of the effective medium layers diameter d of the NCs ($d = 10$ nm) (dashed curve) and a modified thickness $d' = 12.2$ nm (dotted curve).

films, has been tested for the sample under consideration.

The α spectrum of the stack obtained in this way is shown in Fig. 2 as a dashed curve. For a more precise comparison of the MG spectrum with the one obtained by the Toudert *et al.* method [19], the same approximated formula [Eq. (5)] was used to calculate the MG absorption spectrum (solid curve). In fact, the MG spectrum was obtained by considering the multilayer stack as a single layer of dielectric constant ϵ_f given by Eq. (3). Then, the reflectance and transmittance spectra of the single-layer film were calculated, and the optical absorption spectra were obtained by Eq. (5). The validity of the approximated Eq. (5) has been tested for the particular sample under consideration by comparing the α spectrum obtained by Eqs. (1)–(3) with the one obtained by Eq. (5). It was found that the two spectra are almost superimposable.

The absorbance spectra obtained by the Toudert *et al.* method [19] does not coincide with the one calculated by the MG formula since, although the SPR peaks of both spectra have the same spectral position, the peak intensity is higher for the MG spectrum with respect to the Toudert spectrum. The discrepancy can be ascribed to the thickness of the effective layers, which was arbitrarily chosen to be equal to the diameter of the silver NCs. In fact, by choosing a slightly higher value for the thickness of the effective layers, i.e., $d' = 12.2$ nm, and thus reducing the thickness of the dielectric layers as is

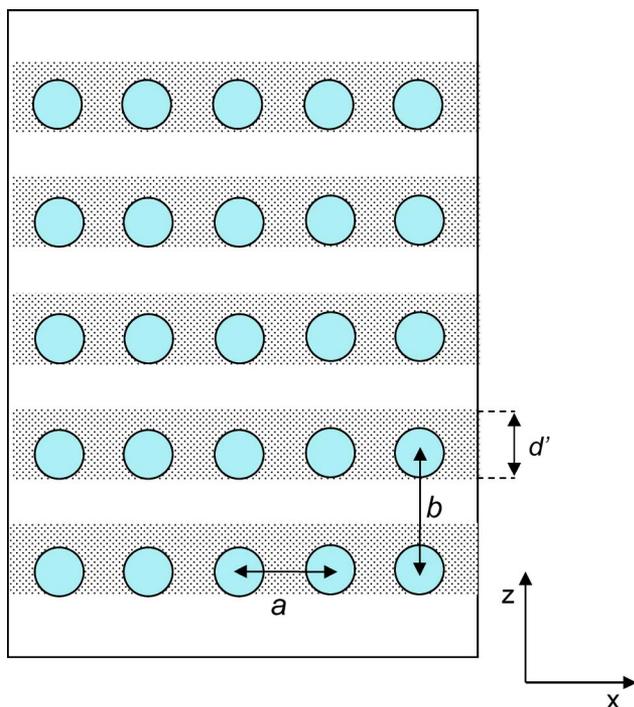


Fig. 3. (Color online) To obtain agreement between the optical absorption spectra calculated by the MG effective medium theory and the Toudert *et al.* method [19], it is necessary to consider the effective medium layers having thickness d' higher with respect to the NCs' diameter d .

shown in Fig. 3, the absorbance spectra given as a dotted curve in Fig. 2 is obtained. Therefore, the newly calculated Toudert spectrum can be almost perfectly superimposed upon the one obtained by the MG theory.

Let us now suppose that we vary the interparticle distance fixing $a = b = 40$ nm and leave the NCs' radii equal to 5 nm. Then, by using the MG theory, we obtain the absorbance spectrum shown as a solid curve in Fig. 4. The spectrum calculated by the Toudert *et al.* method fixing $d = 10$ nm is shown as a dashed curve in Fig. 4 and, as one can note, it does not coincide with the MG curve. In fact, it is necessary to increase the thickness of the effective layers to 12 nm to obtain agreement between the MG spectrum and the Toudert absorbance spectrum. The newly calculated Toudert spectrum with $d' = 12$ nm is shown in Fig. 4 as a dotted line, and it almost perfectly coincides with the MG curve.

As one can note, the thickness d , which has to be imposed to the effective medium layers, does not depend only on the radii of the NCs since, by leaving fixed radius R of the silver NCs equal to 5 nm, we obtained two different values of d' (12.2 and 12 nm) for the two values of the interparticle distance a (30 and 40 nm, respectively). By increasing the radii of the NCs from 5 to 7 nm, we obtained $d' = 17$ for the interparticle distance $a = b = 40$. Therefore, one can conclude that the thickness d' , which has to be imposed to the effective medium layers to obtain the correct SPR peak intensity, depends both on the interparticle distance as well as on radius R of the NCs.

In conclusion, if the Toudert *et al.* method [19] is used to retrieve from the absorbance spectrum the main features of the NCs, then it is not correct to impose the thickness d of the effective medium layers equal to the diameter of the NCs. Then, parameter

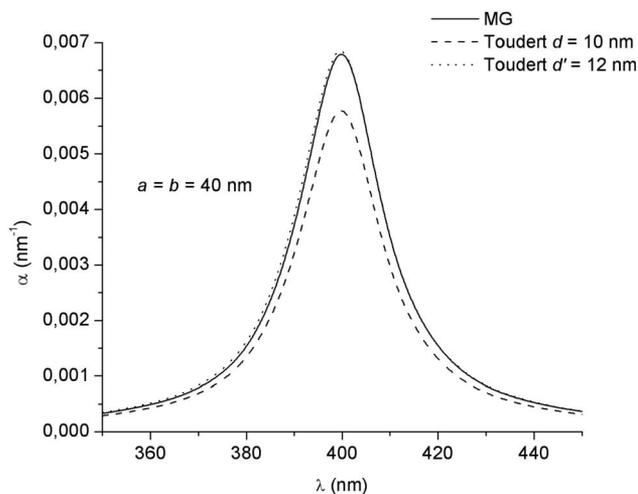


Fig. 4. Optical absorption spectra of the system shown in Fig. 1 with $a = b = 40$ nm and NCs' diameter equal to 10 nm. The optical absorption spectra have been calculated by the MG effective medium theory (solid curve), as well as by the Toudert *et al.* method [19] using as thickness of the effective medium layers the diameter d of the NCs ($d = 10$ nm) (dashed curve) and a modified thickness $d' = 12$ nm (dotted curve).

d remains one of the numerous free parameters of the fitting procedure and this represents the main limit of the Toudert *et al.* method [19].

3. Revised García *et al.* Method

The method suggested in this work for the optical characterization of nonuniform NCs distribution, similar to that shown in Fig. 1 with $a \neq b$, is based on the calculations presented by García *et al.* in [15,16]. However, since some errors were made in those papers, the correct calculations are presented here.

The local electric field on the i th metallic cluster is given by the sum of the external applied field \mathbf{E}_{ext} plus the field $\mathbf{E}_{\text{surr}}^i$ generated by the surrounding polarized metallic clusters at the i th cluster position:

$$\mathbf{E}_{\text{loc}}^i = \mathbf{E}_{\text{ext}} + \mathbf{E}_{\text{surr}}^i. \quad (6)$$

The electric field exerted on the i th particle by the surrounding particles can be expressed as the sum of two terms \mathbf{E}_1^i and \mathbf{E}_2^i :

$$\mathbf{E}_{\text{surr}}^i = \mathbf{E}_1^i + \mathbf{E}_2^i. \quad (7)$$

The first term, \mathbf{E}_1^i , is the contribution to the electric field acting on the i th particle due to the dipoles inside a hypothetical sphere (see Fig. 5) centered at the i th particle position and containing enough nanoparticles to be representative of the distribution of nanoparticles over the entire sample volume. It is worth mentioning that this theoretical approach remains valid in the case of nonuniform distributions of nanoparticles if \mathbf{E}_1^i is independent of radius R_L of the sphere. The second term, \mathbf{E}_2^i in Eq. (7), is the electric field exerted on the i th particle by the particles outside the sphere. Therefore, supposing that the external field \mathbf{E}_{ext} is oriented along the x axis (see Fig. 1), and that no preferential orientation of the individual dipoles is expected in the y or z direction, \mathbf{E}_1^i is given by

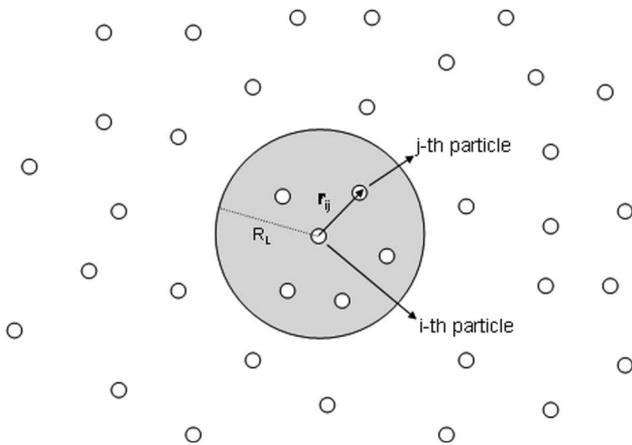


Fig. 5. Scheme of the imaginary sphere used for the calculation of the electric field exerted on the i th particle located at the center of the sphere.

$$\mathbf{E}_1^i = \frac{1}{4\pi\epsilon_m} \sum_j \left[\frac{3x_{ij}^2 p_{jx}}{r_{ij}^5} - \frac{p_{jx}}{r_{ij}^3} \right] \hat{\mathbf{x}}, \quad (8)$$

where p_{jx} is the x component of polarization vector \mathbf{p}_j of the j th particle and x_{ij} is the x component of position vector \mathbf{r}_{ij} of the j th particle with respect to the i th particle.

\mathbf{E}_2^i can be calculated as the electric field inside a uniformly polarized sphere, and it is given by

$$\mathbf{E}_2^i = \frac{\mathbf{P}}{3\epsilon_m}, \quad (9)$$

where \mathbf{P} is the polarization density vector given by

$$\mathbf{P} = \epsilon_m \sum_i n_i \alpha_i \mathbf{E}_{\text{loc}}^i, \quad (10)$$

with n_i indicating the number per unit volume of particles having a polarizability α_i and subject to the electric field $\mathbf{E}_{\text{loc}}^i$.

The polarizability α_i of the i th metallic nanoparticle can be written as

$$\alpha_i = \frac{V_i(\epsilon_i - \epsilon_m)}{\epsilon_m + L_i(\epsilon_i - \epsilon_m)}, \quad (11)$$

where parameter V_i is the volume of the i th particle, while parameter L_i is a depolarization factor which is equal to $1/3$ for spherical nanoparticles, while it assumes values close to zero for flat metallic plates whose normals are perpendicular to the external electric field and values close to $1/2$ for prolate spheroids with the long axis perpendicular to the external electric field.

By defining parameter K_i as

$$K_i = \sum_j \left[\frac{3x_{ij}^2}{r_{ij}^5} - \frac{1}{r_{ij}^3} \right] \frac{p_{jx}}{P},$$

and substituting Eq. (7) into Eq. (6), once the terms \mathbf{E}_1^i and \mathbf{E}_2^i have been explicated, we obtain

$$\mathbf{E}_{\text{loc}}^i = \mathbf{E}_{\text{ext}} + \frac{\mathbf{P}}{3\epsilon_m} + \frac{1}{4\pi\epsilon_m} K_i \mathbf{P}. \quad (12)$$

Substituting $\mathbf{E}_{\text{loc}}^i$ from Eq. (12) into Eq. (10) we obtain

$$\mathbf{P} = \epsilon_m \left[\frac{\sum_i n_i \alpha_i}{1 - \frac{1}{3} \sum_i n_i \alpha_i - \frac{1}{4\pi} \sum_i n_i \alpha_i K_i} \right] \mathbf{E}_{\text{ext}}. \quad (13)$$

Moreover, the polarization density \mathbf{P} for the effective medium, characterized by dielectric constant ϵ_f , is given by

$$\mathbf{P} = \varepsilon_m \left(\frac{\varepsilon_f}{\varepsilon_m} - 1 \right) \mathbf{E}_{\text{ext}}. \quad (14)$$

Therefore, substituting Eq. (14) into Eq. (13), we obtain

$$\varepsilon_f = \varepsilon_m \left[1 + \frac{\sum_i n_i \alpha_i}{1 - \frac{1}{3} \sum_i n_i \alpha_i - \frac{1}{4\pi} \sum_i n_i \alpha_i K_i} \right]. \quad (15)$$

It is worth mentioning that parameter K_i is strongly sensitive to the spatial arrangement of the nanoparticles around the i th particle. In particular, it assumes zero value when the nanoparticles are disposed at the vertices of a cubic lattice, e.g., when they are uniformly distributed inside the sample volume.

It is worth noting that, substituting Eq. (11) into Eq. (15), and supposing, for the sake of simplicity, a uniform distribution of the NCs' dimensions and, therefore, a uniform distribution for the dielectric constant $\varepsilon_i(\omega)$ of the metal NCs [i.e., $\varepsilon_i(\omega) = \varepsilon(\omega)$ for all the NCs], and assuming K_i and L_i are uniformly distributed over the ensemble of nanoparticles ($K_i = K$ and $L_i = L$ for all the nanoparticles), one obtains

$$\varepsilon_f = \varepsilon_m \left[1 + \frac{f(\varepsilon - \varepsilon_m)}{\varepsilon_m + S'(\varepsilon - \varepsilon_m)} \right], \quad (16)$$

where S' is given by $S' = L - f(1/3) - f(K/4\pi)$.

It is worth mentioning that the theoretical approach discussed above can be considered still valid in the case of nanoparticles lying on parallel planes, despite the strong nonuniformity of this geometric distribution. In fact, by defining the parameter σ_i as the summation

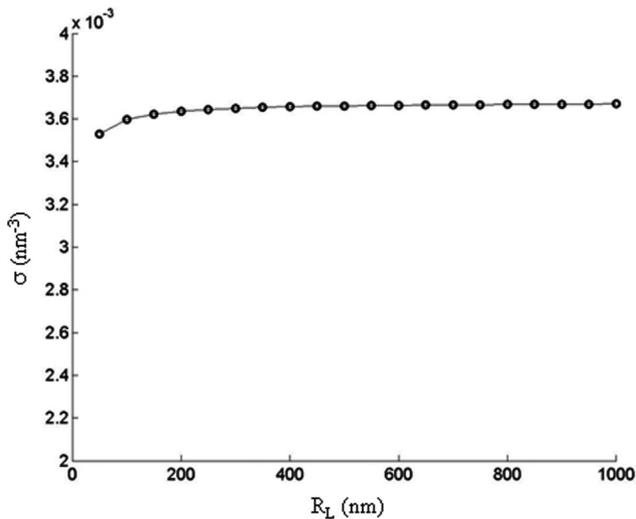


Fig. 6. σ value as a function of the Lorentz sphere radius R_L for NCs lying on layers spaced 50 nm apart perpendicular to the beam direction. The interparticle distance along the x as well as the y directions has been taken equal to 10 nm.

$$\sigma_i = \sum_j [(3x_{ij}^2)/(r_{ij}^5) - 1/(r_{ij}^3)],$$

and assuming, for the sake of simplicity, all the NCs have the same component $p_{jx} = p_x$ and the same volume V , and supposing each of the nanoparticles is surrounded by approximately the same geometric distribution of NCs (i.e., $\sigma_i = \sigma$ for each nanoparticle), the electric field due to the nanoparticles inside the Lorentz sphere E_1^i can be written as

$$E_1^i = \frac{\sigma p_x}{4\pi\varepsilon_m}. \quad (17)$$

Figure 6 shows the dependence of the summation σ on the Lorentz sphere radius R_L in the case of nanoparticles lying on layers spaced 50 nm apart. The interparticle distance along the x as well as the y directions has been taken equal to 10 nm. As one can note, summation σ remains close to $3.6 \times 10^{-3} \text{ nm}^{-3}$ independent of radius R_L . Therefore, since E_1^i given by Eq. (17) is almost independent of the R_L of the Lorentz sphere, the theoretical approach presented above remains valid in the case of NCs distributed on parallel layers.

It is worth mentioning that, in the case of NCs uniformly distributed inside the dielectric matrix ($K = 0$), Eq. (16) reduces to the MG formula [Eq. (3)] since $S = S'$.

It is important to note from Eq. (16) that the effective dielectric function ε_f depends on $\varepsilon(\omega)$ and $\varepsilon_m(\omega)$, as well as on parameters f and S . Therefore, one can infer that it is not possible to univocally determine parameters L and K from the fitting of the $\alpha(\lambda)$ curve. In fact, the only parameters that can be univocally determined are S and f , besides the NCs' radii R , which appears in the expression for the metallic NCs' dielectric constant ε [see Eq. (4)]. This means that the fitting procedure of the SPR curve, through the theoretical model hereby presented, allows determining the K parameter only if the depolarization factor L is known. In other words, the fitting procedure of the SPR curve makes it possible to obtain information on the spatial arrangement of the metallic NCs only if their shape is determined through other characterization techniques. It is worth mentioning that even using the Toudert *et al.* method it is not possible to univocally determine the shape and the geometric distribution of the NCs. In fact, according to the Yamaguchi theory [20,21], the effective dielectric constant of the layers containing the NCs is given by

$$\varepsilon_f = \varepsilon_m \left[1 + \frac{f(\varepsilon - \varepsilon_m)}{\varepsilon_m + F(\varepsilon - \varepsilon_m)} \right], \quad (18)$$

where F is given by $F = L - \frac{K}{4\pi}f$ with the parameter K calculated now on the plane. Therefore depolarization factor L and parameter K cannot be univocally determined.

A good check of the revised Garcia *et al.* [15,16] model can be obtained calculating the absorption spectra in the case of geometric distributions with $a \neq b$ and comparing it with the one obtained by the Toudert *et al.* method [19] using the modified thickness d' as the thickness of the effective medium layers. Therefore, let us suppose having parallel layers of Ag NCs of 5 nm radius embedded inside a BaF₂ matrix with interparticle distance a in the x - y plane (see Fig. 1) equal to 40 nm and interlayer distance b equal to 60 nm. In this case, the K parameter is equal to 1.72. Therefore, substituting the K , L (equal to 1/3 for spherical particles), and f values inside Eq. (16), we directly obtain the effective dielectric function ϵ_f of the whole stack. It is worth mentioning that the definition of the f parameter is problematic in the case of nonuniform distributions of NCs. In fact, it could be calculated as the total volume of the metallic NCs over the volume of the sample. However, since the absorption spectra is sensitive to the filling factor locally met by the spectrophotometer beam when it crosses the layers of NCs, we calculated the filling factor as $f = 4\pi R^3 / (3a^3)$. In this way, f represents a "local filling factor" met by the spectrophotometer beam along its path. The optical absorption spectrum of the whole stack can be calculated directly from Eqs. (1) and (2), using as ϵ_f the effective dielectric function relative to the whole stack calculated by the García *et al.* method [Eq. (16)]. However, for a comparison with the Toudert *et al.* method [19], we used the same method described in Section 2: we calculated the reflectance and transmittance spectra of the whole stack considered as a single layer of dielectric function ϵ_f and then we used the same approximated formula used by the Toudert *et al.* method [19] [Eq. (5)] to calculate the absorbance spectrum. The optical absorption

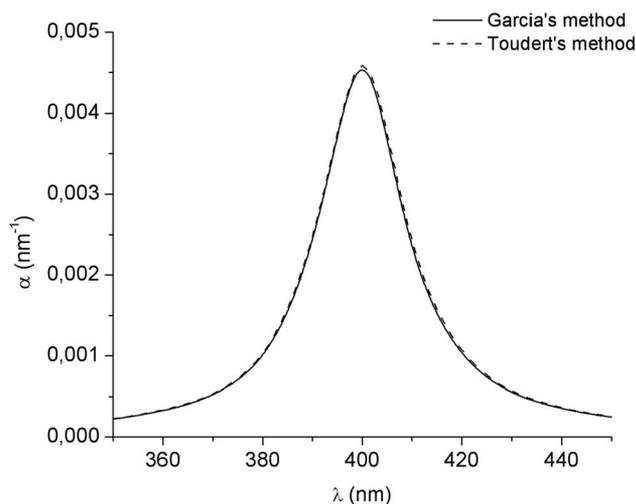


Fig. 7. Optical absorption spectra of the system shown in Fig. 1 with $a = 40$ nm and $b = 60$ nm, calculated by the García method [15,16] (solid curve) and by the Toudert *et al.* method [19] using the modified thickness $d' = 12$ nm (dashed curve) for the effective medium layers. The NCs' diameter is 10 nm.

curve obtained in this way is shown as a solid curve in Fig. 7.

Let us now compare this spectrum with the one obtained by the Toudert *et al.* method [19]. Let us use as the thickness of the effective medium layers the value $d' = 12$ nm obtained in Section 2 for $a = 40$ nm and $R = 5$ nm (we are supposing d' to be independent of the interlayer distance b). The $\alpha(\lambda)$ obtained in this way is shown as a dashed curve in Fig. 7 and, as one can note, it is perfectly superimposed to the one obtained by the García *et al.* method [15,16].

It is worth mentioning that the García *et al.* method [15,16] represents an easier to handle method with respect to the Toudert *et al.* method [19]. In fact, the latter method requires the use of numerical codes that take into account the interference effect between the beams reflected and transmitted at each interface of the stack to retrieve from the optical spectra [e.g., reflectance and transmittance, or $\tan(\Psi)$ and $\cos(\Delta)$] the dielectric function of the effective layers. In contrast, the method presented here can be easily applied to calculate the optical absorption spectrum from reflectance and transmittance through Eq. (5). Then, using Eqs. (1), (2), and (16), it is possible to retrieve the main features of the NCs. On the other hand, for a more precise calculation, the numerical codes considering interference effects can be used to obtain the effective dielectric constant of the whole stack considered as a single effective layer, and then Eq. (16) can be used to retrieve the NCs' features.

4. Conclusions

The aim of this work is to determine the theoretical model that has to be applied in the case of multilayer stacks formed by layers of metallic NCs sandwiched between dielectric layers, such as the one shown in Fig. 1 with $a \neq b$, to retrieve from the optical absorption spectra the main features of the metallic NCs (shape, dimension, and geometric distribution). A possible approach to the problem was recently presented by Toudert *et al.* [19] who considered the stack as a multilayer coating, composed of dielectric layers alternated with effective medium layers. It has been shown that the Toudert *et al.* method [19] is able to reproduce the absorbance spectrum given by the MG effective medium theory in the case of uniform distributions of metallic NCs embedded inside a dielectric matrix, provided that the thickness of the effective medium layers d' is opportunely chosen. It has been shown that the thickness d' depends on both the radius R of the NCs as well as on the interparticle distance a but, since a correlation that links d' to a and R has not been found, d' remains one of the numerous free parameters of the fitting procedure.

An alternative method, based on the calculations presented by García *et al.* in [15], has been proposed here and has been shown effective to obtain the optical absorption spectra in agreement with those obtained by the Toudert *et al.* method [19], provided that the corrected thickness d' is used for the

effective medium layers. It has been pointed out that this method, as well as the Toudert *et al.* method, does not allow determining separately the depolarization factor L and the K parameter, related to the shape and the geometric distribution of the NCs, respectively. Therefore, due to the large amount of parameters involved in the theory, some of them have to be fixed equal to those determined by other microstructural characterization techniques. In this way, it is possible to retrieve from the optical absorption spectra information about the spatial arrangement (or shape) and dimension of the NCs, as well as the effective filling factor locally met by the spectrophotometer beam along its path.

This work has been done within the framework of the PONAMAT project "Development of polymer nanocomposite materials for optical, electronic and sensor applications," CIP PS_016, financially supported by Regione Puglia, Italy.

References

- C. N. Afonso, J. Solis, R. Serna, J. Gonzalo, J. M. Ballestros, and J. C. G. de Sande, "Pulsed laser deposition of nanocomposite thin films for photonic applications," *Proc. SPIE* **3618**, 453–464 (1999).
- A. Polman, E. Snoeks, G. N. van den Hoven, M. L. Brongersma, R. Serna, J. H. Shin, P. Kik, and E. Radius, "Ion beam synthesis of planar opto-electronic devices," *Nucl. Instrum. Methods Phys. Res. B* **106**, 393–399 (1995).
- R. Joerger, R. Gampp, A. Heinzel, W. Graf, M. Kohl, P. Gantenbein, and P. Oelhafen, "Optical properties of inhomogeneous media," *Solar Energy Mater. Sol. Cells* **54**, 351–361 (1998).
- M. J. Bloemer and J. W. Haus, "Versatile waveguide polarizer incorporating an ultrathin discontinuous silver film," *Appl. Phys. Lett.* **61**, 1619–1621 (1992).
- A. Podlipensky, J. Lange, G. Seiffert, H. Graener, and I. Cravetchi, "Second-harmonic generation from ellipsoidal silver nanoparticles embedded in silica glass," *Opt. Lett.* **28**, 716–718 (2003).
- U. Kreibig and M. Vollmer, *Optical Properties of Metal Clusters* (Springer, 1995).
- H. Takele, H. Greve, C. Pochstein, V. Zaporozhchenko, and F. Faupel, "Plasmonic properties of Ag nanoclusters in various polymer matrices," *Nanotechnology* **17**, 3499–3505 (2006).
- J. Toudert, S. Camelio, D. Bobonneau, M. F. Denanot, T. Girardeau, J. P. Espinos, F. Yubero, and A. R. Gonzalez-Elipe, "Morphology and surface-plasmon resonance of silver nanoparticles sandwiched between Si_3N_4 and BN layers," *J. Appl. Phys.* **98**, 114316 (2005).
- S. Camelio, J. Toudert, D. Bobonneau, and T. Girardeau, "Tailoring of the optical properties of Ag: Si_3N_4 nanocermet by changes of the cluster morphology," *Appl. Phys. B* **80**, 89–96 (2005).
- S. K. Mandal, R. K. Roy, and A. K. Pal, "Effect of particle shape distribution on the surface plasmon resonance of Ag- SiO_2 nanocomposite thin films," *J. Phys. D* **36**, 261–265 (2003).
- J. Gonzalo, R. Serna, J. Solis, D. Bobonneau, and C. N. Afonso, "Morphological and interaction effects on the surface plasmon resonance of metal nanoparticles," *J. Phys. Condens. Matter* **15**, S3001–S3010 (2003).
- J. P. Barnes, A. K. Petford-Long, R. C. Doole, R. Serna, J. Gonzalo, A. Suarez-Garcia, C. N. Afonso, and D. Hole, "Structural studies of Ag nanocrystals embedded in amorphous Al_2O_3 grown by pulsed laser deposition," *Nanotechnology* **13**, 465–470 (2002).
- U. Schurmann, H. Takele, V. Zaporozhchenko, and F. Faupel, "Optical and electrical properties of polymer metal nanocomposites prepared by magnetron co-sputtering," *Thin Solid Films* **515**, 801–804 (2006).
- V. S. K. Chakravadhanula, M. Elbahri, U. Schurmann, H. Takele, H. Greve, V. Zaporozhchenko, and F. Faupel, "Equal intensity double plasmon resonance of bimetallic quasi-nanocomposites based on sandwich geometry," *Nanotechnology* **19**, 225302 (2008).
- M. A. García, J. Llopis, and S. E. Paje, "A simple model for evaluating the optical absorption spectrum from small Au-colloids in sol-gel films," *Chem. Phys. Lett.* **315**, 313–320 (1999).
- J. C. Pivin, M. A. García, H. Hofmeister, A. Martucci, M. Sendova Massileva, M. Nikolaeva, O. Kaitasov, and J. Llopis, "Optical properties of silver clusters formed by ion irradiation," *Euro. Phys. J. D* **20**, 251–260 (2002).
- M. Quinten, A. Leitner, J. R. Krenn, and F. R. Aussenegg, "Electromagnetic energy transport via linear chains of silver nanoparticles," *Opt. Lett.* **23**, 1331–1333 (1998).
- Z. Q. Sun, D. M. Sun, and T. N. Ruan, "Microstructural and optical absorption properties of Cu-MgF₂ nanoparticle cermet film," *Chin. Phys. Lett.* **19**, 1365–1368 (2002).
- J. Toudert, D. Bobonneau, L. Simonot, S. Camelio, and T. Girardeau, "Quantitative modelling of the surface plasmon resonances of metal nanoclusters sandwiched between dielectric layers: the influence of nanocluster size, shape and organization," *Nanotechnology* **19**, 125709 (2008).
- T. Yamaguchi, S. Yoshida, and A. Kimbara, "Optical effect of the substrate on the anomalous absorption of aggregated silver films," *Thin Solid Films* **21**, 173–187 (1974).
- V. A. Fedotov, V. I. Emel'yanov, K. F. MacDonald, and N. I. Zheludev, "Optical properties of closely packed nanoparticle films: spheroids and nanoshells," *J. Opt. A* **6**, 155–160 (2004).
- H. Hovel, S. Fritz, A. Hilger, U. Kreibig, and M. Vollmer, "Width of cluster plasmon resonances: bulk dielectric functions and chemical interface damping," *Phys. Rev. B* **48**, 18178–18188 (1993).
- P. B. Johnson and R. W. Christy, "Optical constants of the noble metals," *Phys. Rev. B* **6**, 4370–4379 (1972).
- E. D. Palik, *Handbook of Optical Constants* (Academic, 1985).