Simple modeling of plasmon resonances in Ag/SiO_2 nanocomposite monolayers

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Received 2 August 2010; revised 13 September 2010; accepted 14 September 2010; posted 14 September 2010 (Doc. ID 132711); published 8 October 2010

Normal incidence transmittance and reflectance spectra of sputtered nanocomposite monolayer films of Ag in SiO_2, buried and unburied, showed significant redshifted plasmon resonances from 410 to 455 nm, which could be well interpreted with a simple model that starts from the Maxwell Garnett theory and the Kreibig extension of the Drude–Lorentz equation, but with a further extension related to the dipolar interaction between the metal particles distributed on a surface. © 2010 Optical Society of America

OCIS codes: 310.6860, 240.6680.

1. Introduction

In the past few years, composite metal-dielectric media have been the object of several studies due to their peculiar optical properties. The main phenomenon governing these properties is the collective oscillation of electrons at wavelengths near the resonance frequency, the so-called plasmon resonance, which microscopically is responsible for the extraordinary increase of the optical field in the vicinity of metallic structures [1,2].

This kind of system has been used for a wide range of applications. The locally enhanced field has attracted interest to increase the Raman scattering signal of suitable molecules and other nonlinear phenomena [2,3]. The dependence of the plasmon resonance frequency on the refractive index of the surrounding dielectric media has enabled the design of sensors for several purposes (e.g., biosensing) [4]. Also, the ability of metallic particles to scatter light has been used to improve light coupling into solar cells, enhancing their performance [5]. In association with this application, special interest is devoted to understand and model the optical properties of thin films with plasmonic nanoparticles [6].

0003-6935/11/090C27-04$15.00/0

For three-dimensional composite metal-dielectric media, such as glasses doped with metallic inclusions, the Maxwell Garnett theory is well known for attempting to describe optical properties [1]. The model assumes spherical inclusions, with the dielectric function ε_i and dispersed in a host medium, with the dielectric constant ε_d. Those spheres have a radius much smaller than their average spacing, which is much smaller than the light wavelength. In this approach, the effective dielectric function of the composite material is given by

$$\frac{\varepsilon_{\mathrm{eff}} - \varepsilon_d(\omega)}{\varepsilon_{\mathrm{eff}} + 2\varepsilon_d(\omega)} = f\,\frac{\varepsilon_i(\omega) - \varepsilon_d(\omega)}{\varepsilon_i(\omega) + 2\varepsilon_d(\omega)}, \tag{1}$$

where f is the volume fraction of particles in the medium. The effective refractive index, usually complex, is given by $n_{\mathrm{eff}} = (\varepsilon_{\mathrm{eff}})^{1/2}$. The Maxwell Garnett model has also been applied to describe the optical properties of films with nanoparticles [7]. However, the model applies for a diluted composition ($f \ll 1$) or a symmetrically ordered arrangement of particles, in which interparticle effects can be neglected. The interaction between spherical particles of an arbitrary size embedded in nonabsorbing media has also been rigorously treated by solving the Maxwell equation [8]. This theory was later extended to take into account the effects of absorbing embedding media [9].

For noble metallic inclusions whose size allows a bulklike response, the dielectric function is usually well described by the Drude–Lorentz model [10]. However, in the frame of the Maxwell Garnett theory, the Drude–Lorentz model is no longer suitable when the diameter of the particle is reduced to below the mean free path of electrons in the material. In order to take this into account, Kreibig and co-workers proposed an extension to describe the optical response of the particles [1].

In this work, we investigate the applicability of the Kreibig extension with the Maxwell Garnett theory to calculate the optical properties of monolayer nanocomposite films, in which Ag particles are prepared, either buried or unburied, in a SiO_2 matrix. The need of a further extension to account for the observed plasmon resonance shifts is discussed and attributed to interparticle coupled oscillations.

2. Experimental

Radio frequency sputtering was used to fabricate films of Ag particles embedded in SiO_2. The films were produced on glass and silicon substrates to enable optical transmittance measurements around the visible spectrum and transmission electron microscopy, respectively. Film thicknesses, with mass equivalent to that of the set of silver particles, were monitored with a quartz crystal microbalance, which allowed precision better than 5%.

Two types of samples with a monolayer sequence of Ag particles were prepared: (i) the buried type, in which Ag particles are totally embedded in SiO_2, and (ii) the unburied type, in which Ag particles are not covered by silica. Figure 1 shows a representation of the buried type sample with its corresponding micrograph in the top view, whereas the unburied type sample is shown in the cross section in Fig. 2.

Optical transmittance and reflectance measurements were performed in a Cary 5000 spectrophotometer. Micrographs were obtained from a JEM-1220 transmission electron microscope.

3. Theory

As a first step, the effective dielectric function and hence the optical properties can be calculated by the Maxwell Garnett theory—whose input parameters are the filling factor, the dielectric function of the particles and of their surroundings—such as described in Eq. (1).

For the dielectric function of the surroundings, the experimental bulk dielectric function can be used. This is not always true for the particle inclusions, in particular when their size decreases to smaller than the mean free path of electrons (around 50 nm for Ag) [1]. In this case, it is very useful to apply the theoretical Drude–Lorentz model for the dielectric function with the bulk relaxation constant Γ_∞ replaced by the phenomenological approach proposed by Kreibig *et al.* [11],

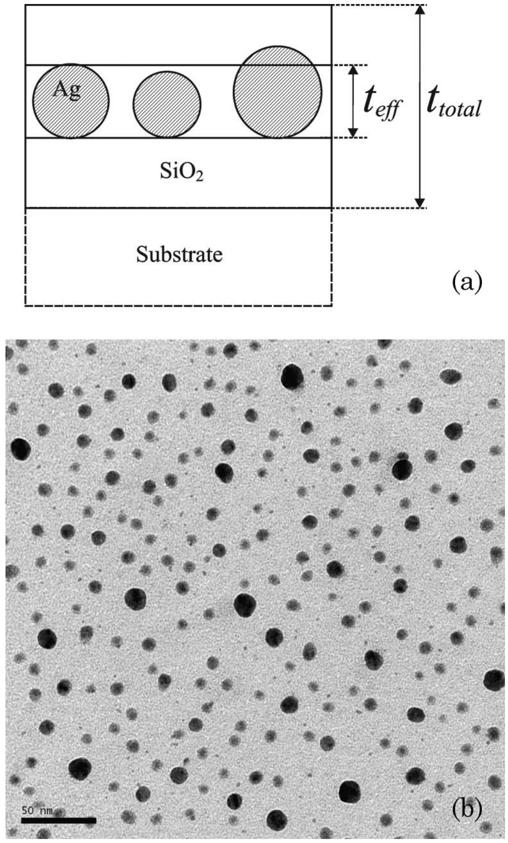

Fig. 1. (a) Cross-sectional scheme and (b) top-view micrograph of a sample with buried Ag particles in silica matrix; t_{eff} and t_{total} stand for effective medium and total thicknesses, respectively. A scale bar of 50 nm is shown in (b).

$$\Gamma = \Gamma_\infty + A\frac{v_F}{R}, \tag{2}$$

where v_F is the Fermi velocity of the electrons, R is the particle radius, and A is a parameter related to the strength of the electron-interface interaction within each particle [11,12].

At this point, it is worth remembering that the Drude–Lorentz dielectric function is given by

$$\varepsilon_{\text{DL}}(\omega) = \varepsilon_\infty + \frac{\omega_P^2}{(\omega_0^2 - \omega^2) + i\Gamma\omega}, \tag{3}$$

where ω_P is the bulk plasmon frequency and ω_0 is the natural frequency of oscillation from the Hooke law (see, e.g., [2,10]).

Equations (1)–(3) are used to determine numerically the optical transmittance of the system in which sputtered silver nanoparticles were buried in silica, shown in Fig. 1(a). Transmittance and reflectance curves are calculated through the characteristic matrix approach for multilayer films [13]. These results are used as inputs to the merit function

$$F = \sum_j [T_{\exp}(\lambda_j - T_{\text{calc}})(A, \lambda_j)]^2, \tag{4}$$

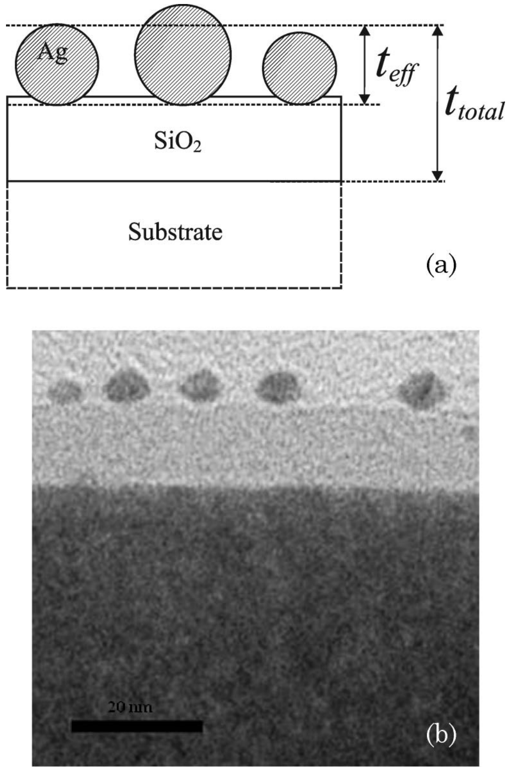

Fig. 2. Cross-sectional (a) scheme and (b) micrograph of a sample with unburied Ag particles in silica matrix; t_{eff} and t_{total} stand for effective medium and total thicknesses, respectively. A scale bar of 20 nm is shown in (b).

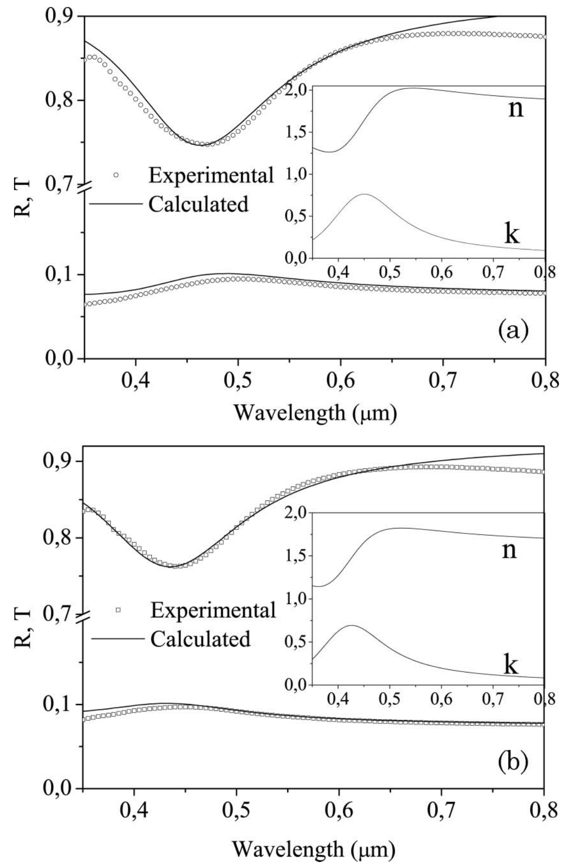

Fig. 3. Experimental and theoretical data for samples with (a) buried and (b) unburied Ag particles. At the insets, the recovered real and imaginary parts of the refractive index are shown in the measured spectral range, with a vertical scale from 0 to 2.0.

where T_{exp} is the experimentally measured transmittance [14]. The merit function is minimized in order to find the best fit as a function of A.

A similar procedure is used for the film with unburied Ag particles. In this case, by taking into account that one part of the particles was exposed to air and another was in contact with silica, the dielectric function of the host medium is taken as

$$\varepsilon_{\mathrm{diel}} = n_{\mathrm{diel}}^2 = [1/2(n_{\mathrm{SiO_2}} + n_{\mathrm{air}})]^2. \qquad (5)$$

4. Results and Discussion

In Fig. 3, results are shown for the buried and unburied Ag cases. In each picture, the transmittance is shown in the upper portion, whereas the reflectance appears at the bottom. Corresponding values of parameter A are $2.917 + 0.908i$ and $3.354 + 1.304i$, respectively.

In the calculation, starting from $t_{\mathrm{eff}} = 8\,\mathrm{nm}$ in accordance with the observed average particle size, optimized A parameters were pursued for best fitting to the measured transmittance curves.

By substituting the Γ parameter of Eq. (2) in the Drude–Lorentz model [Eq. (3)], it is easy to verify that $\mathrm{Im}\{A\}$ is responsible for shifting the bulk natural frequency of oscillation, whereas only $\mathrm{Re}\{A\}$ accounts for a true new relaxation constant for the particles. In Fig. 3, although the theoretical curves overestimate the transmittance tails above 650 nm, a very good fit was reached in the region around the absorption dips caused by surface plasmon resonance, in either case of buried or unburied Ag particles.

In addition, agreement was obtained between the theoretical curves and the measured reflectance data, well within their experimental uncertainties, for both types of composite film.

But what does $\mathrm{Im}\{A\}$ physically mean?

Consider that when the wave electric field is parallel to the plane of the particles, which is the case for normal incidence of light, coupling of charge oscillation in the particles occurs, as shown qualitatively in Fig. 4. The isolated particle natural frequency of oscillation $\omega_0 = (K_0/m)^{1/2}$ is then reduced, due to the attractive force between charges in adjacent particles, to $\omega_C = [(K_0 - 2K_C)/m]^{1/2}$, giving rise to a

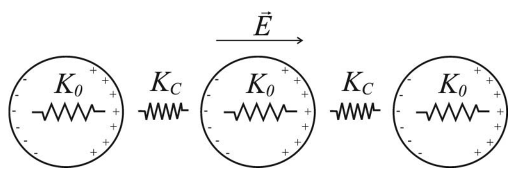

Fig. 4. Scheme for description of the coupling between particles when the exciting electric field is parallel to the plane of particles.

redshift in the resonance frequency of oscillation, as experimentally determined from 410 to 455 nm. Also the deviation of the real part of A from unity, whose value was theoretically predicted [1], may be attributed to the component of the damping frequency Γ due to the interparticle coupled oscillation of electrons in the particles.

From Eqs. (2) and (3), correspondence between $\mathrm{Im}\{A\}$ and the coupling constant K_C can be established:

$$\mathrm{Im}\{A\} = \left(\frac{R}{\omega v_F}\right)\frac{2K_C}{m}, \tag{6}$$

with frequency ω taken at resonance. This indicates the role of interparticle coupling in the observed plasmon resonance redshift.

5. Conclusions

For monolayer films composed of almost spherical silver nanoparticles in a silica matrix, simple modeling was shown to accurately and simultaneously match the measured optical transmittance and reflectance data around the surface plasmon resonance region, in cases of covered and uncovered Ag particles. This indicates suitability to both cases of the Maxwell Garnett theory and of the Drude–Lorentz equation with the Kreibig extension with parameter A (related to the strength of the electron-interface interaction within each metal particle), with a further extension that accounts for the interaction between particles distributed on a surface.

This interaction is responsible for the measured redshifted plasmon resonances and for the associated role of the complex A parameter in this work. $\mathrm{Re}\{A\}$ accounts for a modified relaxation constant for the particles, whereas $\mathrm{Im}\{A\}$ is responsible for shifting the bulk natural frequency of oscillation. This imaginary part was shown to be directly related to the interparticle coupling constant K_C, and thus its physical meaning was here related to the coupled oscillation of electrons, beyond the Maxwell Garnett theory and the Kreibig relaxation constant extension in the Drude–Lorentz equation.

The results are also encouraging to the continuity of this work with multilayer nanocomposite films, because they open the possibility of their analytical treatment in a similar manner.

This research was partially supported by the Brazilian agencies Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES).

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