

Simulation of the optical properties of gold nanoparticles on sodium alginate

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Abstract. In this contribution, we report on the simulation of optical reflectance and transmittance (R&T) taken on a set of gold nanoparticles thin film, deposited on sodium alginate by magnetron sputtering. The gold layer is very thin, so that the films are not continuous and the material is arranged in nanostructured layers. R&T spectra are simulated using the Generalized Transfer Matrix method applied to the film-on-substrate model. The gold NP films are simulated using the Drude-Lorentz model, by taking into account that the optical function of nanostructured gold exhibits increased collision frequency and reduced relaxation time. Moreover, the signal of localized surface plasmon, evident in the spectra, is simulated by introducing a dedicated modified Lorentz oscillator. The experimental results are well reproduced by the applied model. All trends (amplitude and energy position of the plasmon oscillator, film thickness, relaxation time) are correlated with the deposition parameters. The procedure represents a useful tool in the characterisation of such nanoparticles thin films.

1 Introduction

Fabrication of thin conductive films on polymers is an important research field for the next generation of devices, where flexibility and lightweight are two main properties for the fabrication of wearable electronics and soft robotics.

Sodium alginate (SA) is a biopolymer extracted from marine algae, which is presently rising interest for applications in green electronics; its electrical functionalization by deposition of gold nanoparticles has already been proposed [1, 2].

Considerable attention has been paid so far to the description of the optical properties of gold nanoparticles (NP) [3] for their numerous applications in optics and electronics, also due to the possibility of introducing controlled enhanced absorption in specific devices and techniques, with applications in sensing, microscopy, nanophotonics, light harvesting, biomedicine, and many others [4–9]. Details on morphology, dispersion of the nanoparticle shape and size, and how these occurrences reflect on the optical spectra, are all argument of interest. The ability of performing quantitative simulation of experimental optical spectra is therefore an important tool to detect the details of the growing material at the nanoscale. In this paper, we report the optical properties of a set of several gold NP thin films on SA in the range 250-1100 nm, identify specific features, perform quantitative simulations, and show the trend of optical parameters.

2 Experimentals

Gold NP are deposited by magnetron sputtering at room temperature, using either 20 or 30 W Ar plasma power

and deposition time spanning from to 45 to 160 s, on free standing SA membranes of several tens of micron thickness, prepared by solution casting from 4% wt Alginic Acid Sodium Salt (Sigma-Aldrich) solution in water. The resulting films appear as an aggregate of NP, increasingly in contact to one another as thickness increases. SEM images of selected samples are reported in figure 1.

Optical spectra were obtained by a UV-visible Avantes spectrophotometer equipped with an integrating sphere, which was used because of the inherent roughness of the samples. Given the high reflectivity of gold, the T spectra were also corrected by accounting for the light back-reflected into the sphere. If this correction is neglected, erroneous negative absorption is measured.

3 Optical simulation

Reflectance and transmittance (R&T) spectra are simulated using the Generalized Transfer Matrix (GTM) method [10] applied to the film-on-substrate model. The dielectric function (DF) of the SA material used as a substrate for this specific set of samples was separately determined by R&T spectroscopy. The material shows some absorption in the UV and up to 400 nm; for longer wavelengths it is transparent with a refractive index of about 1.5 [11]. The DF of gold is described by a sum of three modified (see below) Lorentz oscillators with the addition of a Drude term, to account for both interband transitions and free carrier absorption. Starting from this formalism, the gold NP films are simulated by allowing the relaxation energy in the Drude term to vary as a free parameter [3, 12]. Moreover, an additional oscillator, described by four free parameters, was added to account for a strong absorption signal visible for thicknesses below about 7 nm, attributed

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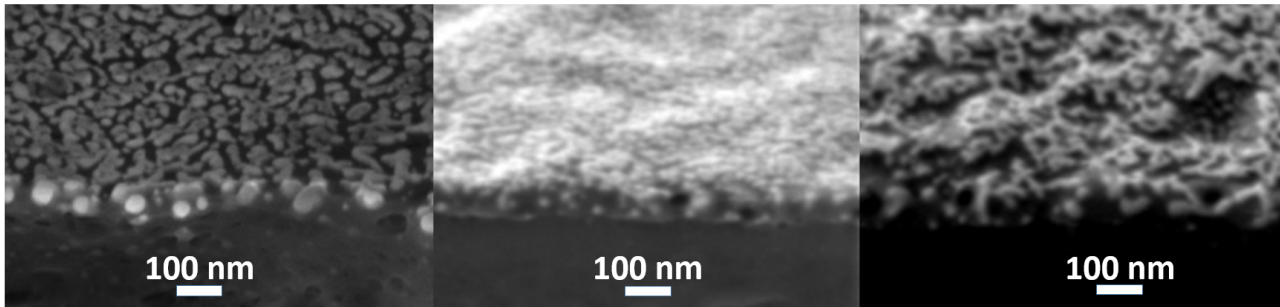


Figure 1. SEM images of selected gold/SA films. Thickness from simulation, from left to right: 4, 5, and 6 nm.

to the onset of the localised surface plasmon (LSP) that sets up in presence of gold NP [3]. The final form for the imaginary part of the dielectric constant of gold NP is therefore:

$$\varepsilon_2(E) = \sum_i \frac{(A_i - 1)E_{0i}^2 \Gamma_{Bi} E}{(E_{0i}^2 - E^2)^2 + (\Gamma_{Bi} E)^2} + \frac{E_P^2 E_T}{E(E^2 + E_T^2)} \quad (1)$$

In equation (1) the sum spans over four oscillators, three of which refer to bulk gold, and the fourth oscillator (LSP oscillator in the following) describes the LSP contribution. The second term on the right represents the Drude term, where E_P is the plasma frequency, and $E_T = h\nu_c$, where ν_c is the collision frequency and h is the Planck constant, is the relaxation energy. All oscillators, modified with respect to the three-parameter Lorentz oscillator, include an energy dependent broadening parameter Γ_{Bi} , which is given by:

$$\Gamma_{Bi} = \Gamma_i e^{-\alpha_i \left(\frac{E - E_{0i}}{\Gamma_i} \right)^2} \quad (2)$$

where α_i is the Gaussian broadening parameter, which has been introduced to limit the contribution of the oscillator to energies in the vicinity of the oscillator energy [13].

The parameters for bulk gold were obtained by fitting the gold DF in [14], and are reported in table 1. For the plasma frequency, $E_P = 8.78 \pm 0.02$ eV is obtained, similar to literature data [7–9, 15–17]. For E_{TB} , where “B” stands for “bulk”, the value 0.073 ± 0.005 eV is obtained. This value is in agreement with several results in the literature [4, 7, 9, 18] although not in agreement with the static collision frequency obtained from electrical measurements [19], because of its dependence on frequency [20]. In the simulation of the DF of gold NP, E_T is left as a free parameter, to account for the increased ν_c in that case [3, 4, 7, 12].

Table 1. Amplitude, energy, broadening, and energy dependent broadening parameter of Lorentz oscillators for bulk gold, obtained using equation (1) and equation (2) fitted over the experimental data in [14]. Moreover, $E_P = 8.78 \pm 0.02$ eV and $E_{TB} = 0.073 \pm 0.005$ eV.

Osc.	A	E (eV)	Γ (eV)	α
1	2.79 ± 0.04	6.25 ± 0.01	3.81 ± 0.05	2.00 (fixed)
2	3.18	3.97	1.80	1.48 ± 0.05
3	2.21	2.84	0.88	0.78

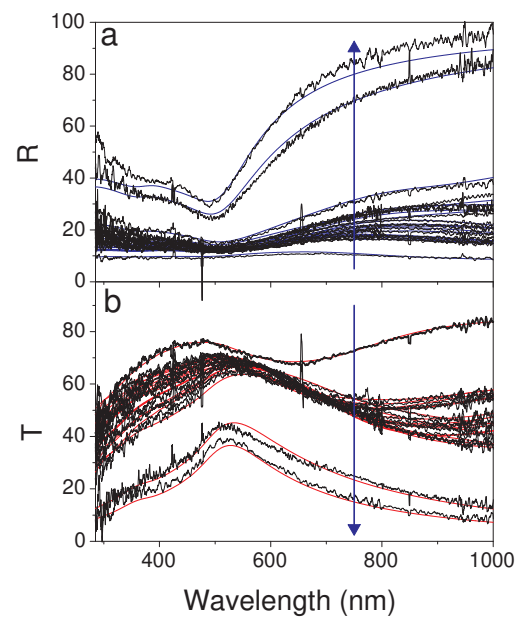


Figure 2. Reflectance (a) and Transmittance (b) of the whole set of samples. Black: experimental data. Color: simulation. The arrows indicate the direction of increasing overall deposited material.

In all cases the real part of the dielectric constant is obtained from the imaginary part by means of Kramers-Kronig transformation. All calculations are performed using the code GTB [13].

The total number of parameters in the simulation of the DF of gold NP is therefore 5: four for the modified LSP oscillator, plus the relaxation energy E_T . Film and substrate thicknesses were also left as free parameters in the simulation.

4 Results and discussion

The entire set of R&T spectra, both experimental and simulated, is reported in figure 2. The arrows indicate the direction of increasing material (increasing deposition time, or plasma power). The sample with highest

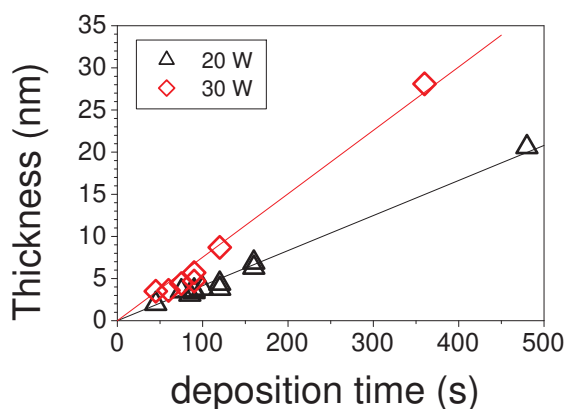


Figure 3. Thickness of all samples, obtained from the simulation.

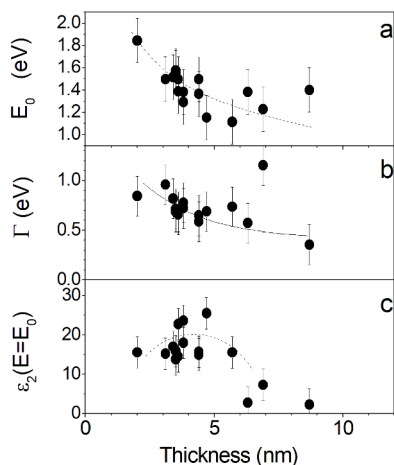


Figure 4. Energy of the oscillator describing the LSP (a); broadening of the oscillator (b); peak value of the associated contribution to the imaginary part of the dielectric constant (c). The lines are a guide to the eye.

R and lowest T refers to a 26 nm thick Au sample, which resulted to be best simulated using the optical constant of bulk gold, namely, E_T practically unaltered and the amplitude of the fourth oscillator vanished.

The good quality of the simulation confirms the choice of the optical model. The samples exhibit a broad minimum in T at about 650 nm for the thinnest sample, then shifting to the red for thicker samples. Less evident is the corresponding maximum in R, because it is superimposed to the increase associated to FC absorption. Both occurrences are due to the presence of the additional absorption signal, which can be attributed to the onset of a localized surface plasmon [5, 6].

The thickness of Au films obtained from the simulations is reported in figure 3. The growth of Au layer follows a linear process, with higher slope for higher plasma power. In the simulation the gold layer was simulated by a continuous film; an effective medium comprising voids

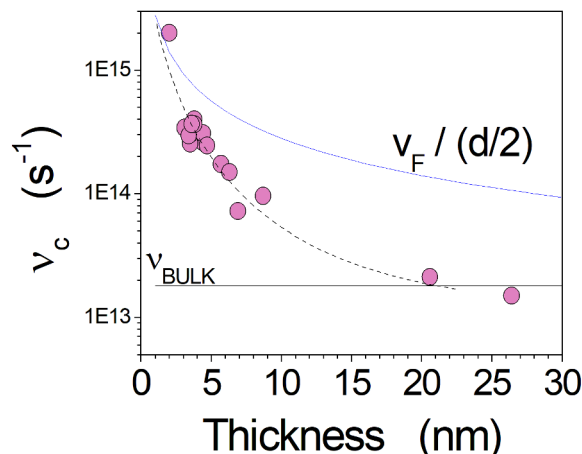


Figure 5. Collision frequency versus sample thickness. The value for bulk gold obtained from the simulation is also indicated. The continuous line represents the condition of mean free path equal to half the film thickness. The dashed line is a guide for the eye.

has not been considered. This was done because in this range of thickness, thickness and void fraction are correlated parameters and the determination of both of them is not possible. In other words, the obtained thickness is the “equivalent” thickness, *i.e.*, the thickness of a dense film containing the same amount of material.

For a better insight on the material properties, we have a look to the features of the LPS oscillator (figure 4). We note that the LSP is located between 1.2 and 1.8 eV, increasing for decreasing thickness (figure 4a). Such energies are lower than what expected for monodispersed, isolated NP’s, for which a value about 2 eV, decreasing only slightly for increasing NP diameter [12], also depending on shape, dielectric environment, and separation [3, 4, 8, 9], is expected. We attribute the result to the specific NP arrangement, with no fully isolated structures, yet not continuous, still showing resonance effects. Besides all non-idealities, according to [6] the shift of the LSP signal to the red (900 nm and beyond) is favoured by a high deposition rate that hinders the formation of isolated NP’s.

We also observe (figure 4c) that the peak intensity increases for thicknesses about 5 nm, then it decreases, to fully disappear for about 10 nm. Since the LSP signal is expected to persist to much higher diameters [12], the result indicates that for this thickness, under our experimental conditions a continuous film is formed.

An indication on NP aggregation comes from the relaxation energy, which is markedly altered with respect to the “bulk” value. In case of isolated NP’s, the collision frequency is related to NP radius as $1/r$ [12], possibly through a fitting factor [4, 7]. In figure 5 we report the collision frequency determined from E_T for our samples. The “bulk” value $v_{BULK} = E_{TB}/h$, is indicated. The curve v_F/d , where $v_F = 1.4 \times 10^{15}$ nm/s is the Fermi velocity for gold [19] and d is the film thickness, is also indicated. This would be the curve expected for isolated NP with diameter $2r$ equal to film thickness. The figure shows that only

for the very initial stages of the deposition is the collision frequency controlled by film thickness; for higher thicknesses, ν_c rapidly decreases and reaches the “bulk” value for about 20 nm, thus indicating that in-plane aggregation and rapid interconnection of the deposited material takes place. Similar conclusions were previously obtained by means of electrical measurements [2].

By comparing the results of figure 4 and figure 5, we observe that the LSP signal is strictly related to the non-continuous morphology of the films; it decreases and eventually vanishes as soon as sufficient material is deposited so that a continuous film is obtained, as detected by optical measurements, and in agreement with previously obtained electrical results [2]. This is in agreement with the observation that such band is possibly associated to the presence of islands and holes in low quality films [20]. In fact our material markedly differs from the ideal case, due to an inhomogeneous, granular organization, where, although self arrangement on the substrate surface occurs, physical separation is not guaranteed, and the material is to be regarded as an aggregation of particles somewhat in contact among one another, evolving to a continuous film as the total amount of material increases. In this context, the observed remarkable broadening of the LSP oscillator (figure 4b) it is likely to reflect the convolution of a family of signals that arise from such an articulated structure, and to the multidispersed shape and size of NP's.

5 Summary and conclusions

The optical properties of very thin films of gold NP deposited by sputtering on SA substrates have been studied by means of simulation of optical properties. For low thickness, we observe the presence of an absorption band, which reaches the maximum intensity at about 5 nm, associated to a peak energy of 1.3 eV. For higher thickness, both intensity and peak energy decrease. The band eventually vanishes for thicknesses larger than 10 nm. The band is attributed to the onset of the local surface plasmon in conditions of highly disordered material and limited separation of the gold NP's.

For low thickness, we observe a high collision frequency which is to be expected given the low mean free path of such an articulated material. For increasing thickness the collision frequency rapidly decreases, which indicates aggregation of the deposited NP's. The results indicate that on this kind of substrate the initial stages of the deposition result in the formation of non-continuous material aggregates. Continuous film are formed for 20 nm deposition. The analysis is suitable to be applied to the study

of the formation of the material on different substrates of different morphology and nature.

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