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Determination of gold nanoparticle shape from absorption spectroscopy and ellipsometry

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ABSTRACT

A new methodology is developed to determine the shape distribution of gold nanoparticles (NPs) from optical spectroscopic measurements. Indeed, the morphology of Au colloids is deduced by fitting their absorption spectra with an effective medium theory which takes into account the nanoparticle shape distribution. The same procedure is applied to ellipsometric measurements recorded on photoresist films which contain Au NPs. Three spaces (L^2, r^2, P^2) are introduced to interpret the NPs shape distribution. In the P^2 space, the sphericity, the prolacity and the oblacity estimators are proposed to quantify the shape of NPs. The r^2 space enables the determination of the NP aspect ratio distribution. The distributions determined from optical spectroscopy were found to be in very good agreement with the shape distributions obtained by transmission electron microscopy. We found that fitting absorption or ellipsometric spectra with an adequate effective medium theory, provides a robust tool for measuring the shape and concentration of metallic NPs.

1. Introduction

Metallic nanoparticles (NPs) such as silver or gold NPs exhibit strong plasmon resonances whose characteristics depend on their size, shape and environment [1]. These unique optical properties give them great potentials as building blocks of photovoltaic devices and sensors [2–6]. These applications have motivated a sustained effort towards the control of NP size and shape distributions. Transmission electron microscopy (TEM) is usually used to estimate the NP radius and shape distribution. However, since TEM is a local characterization tool, the statistical analysis of NP distributions from TEM is too time consuming. In addition, TEM only gives a two dimensional projection of NPs. This could lead to a poor estimation of NP shape. Tomography mode is currently under development and is not implemented on conventional TEM. Moreover, the 3D observation of NPs in tomography mode is too time consuming to record their distribution over a huge number of NPs. Thus, the development of non-local alternative characterization tools is required to determine the NP shape distribution. Grazing incidence small angle X-ray scattering (GISAXS) was previously used to characterized the morphology of supported NPs [7–9]. The shape distribution can be estimated by comparing the measured GISAXS pattern with the simulated one. However, this technique requires some facilities such as synchrotron beam line. In addition, this technique cannot be used to characterize NPs in bulk solution or embedded in thick film.

Recent advances in optical modeling open new ways for quantitative optical characterization of metallic NPs. Garellie et al. [10] have introduced the NP size distribution into the Mie theory. However, Mie theory fails to describe the optical properties of non-spherical NPs [11]. As shown by Eustis et al. [12], the aspect ratio distribution of gold nanorods can be evaluated by fitting their longitudinal plasmon band by the Gans theory. Slyusarenko et al. [13] have validated this approach by comparing the NP volume fraction obtained from absorption spectroscopy to the one estimated by small angle X-Ray scattering measurement. However, Eustis et al. [12] neglect the influence of the aspect ratio distribution on the interband transitions and on the transversal plasmon band of NPs. In addition, this approach is limited to prolate NPs. Spectroscopic ellipsometry has been recently exploited to investigate the growth mechanism of metallic NPs [14–17]. As shown by Oates et al. [15,16], the NP size, orientation and organization can be characterized by spectroscopic ellipsometry. The analysis of ellipsometric data requires the modeling of the optical properties of nanomate-

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rials. Several approaches such as discrete dipole approximation [18] or boundary elements method [19] can be used to model the optical properties of complex NP shapes. However, these approaches are limited by computational resources and are too time consuming to take into account the NP shape distribution.

Effective medium theories which approximate the nanocomposite material as a homogeneous medium, enable the calculation of its effective dielectric function with few computational resources. Toudert et al. [20] have proposed an effective medium theory based on the Yamaguchi formalism which takes into account the NP interaction and their size distribution. However, this model requires a preliminary estimation of the pair correlation function of NPs by transmission electron microscopy. Another approach based on the mean field approximation was proposed by Bohren et al. [21] to extend the effective medium theory to ellipsoidal nanoparticles distributed in shape. This shape distributed effective medium theory (SDEMT) was used to design broadband epsilon-near zero composites [22] and to analyze ellipsometric measurements on gold nanoisland films [23] or absorption measurements on gold colloids [24–26]. However, the NP shape distribution is represented in a complex two dimensional space of depolarization parameters making the interpretation of the NP shape unclear.

In this paper, we determine the NP shape distribution of two gold colloidal solutions and two photoresist films which contain gold nanoparticles by fitting their absorption and ellipsometric spectra with the SDEMT, respectively. To make a quantitative analysis, we introduce two new spaces P^2 and r^2 derived from the space of depolarization parameter L^2 to interpret the shape distribution of NPs. The coordinates (P_o, P_p) in the P^2 space are assimilated as estimators of the oblate and prolate character of NPs, respectively. In addition, the coordinates (r_1, r_2) in the r^2 space correspond to the aspect ratio of ellipsoïdal NPs. Thus, by using SDEMT combined to an adequate space transformation, we demonstrate that the nanoparticle shape distribution can be directly extracted from optical spectroscopy.

2. Theory

2.1. Shape distributed effective medium theory (SDEMT)

The effective dielectric function ε_{eff} of a medium composed of ellipsoidal NPs distributed in shape and randomly oriented in a matrix is defined as the ratio between the spatial averages of displacement <**D**> and electric <**E**> fields:

$$\varepsilon_{\text{eff}} = <\mathrm{D}><\mathrm{E}>^{-1}. \tag{1}$$

In the mean field approximation, the spatial averages of electric <**E**> and displacement <**D**> fields in the material are the sum of two contributions [21]:

$$\langle \mathbf{E} \rangle = (1-f)\langle \mathbf{E_m} \rangle + f\langle \mathbf{E_{np}} \rangle, \tag{2}$$

$$\langle \mathbf{D} \rangle = (1-f)\varepsilon_m \langle \mathbf{E_m} \rangle + f\varepsilon_{np}\langle \mathbf{E_{np}} \rangle, \tag{3}$$

where ε_{np} and ε_m are the complex dielectric function of NPs and the matrix, respectively. f is the NP volume fraction of NPs while <$\mathbf{E}_m$> and <$\mathbf{E}_{np}$> are the spatial average electric field inside the matrix and NPs, respectively.

In the quasi-static limit i.e. for NP size smaller than the wavelength, we derive a linear relationship between the electric field inside NPs and the electric field inside de matrix. For small NP volume fraction, the electric field inside the matrix is homogeneous and the spatial average electric field inside the NPs is related to the spatial average electric field inside the matrix by:

$$\langle \mathbf{E_{np}} \rangle = \langle \beta \rangle \langle \mathbf{E_m} \rangle. \tag{4}$$

The slope <β> is given by [26]:

$$\langle \beta \rangle = \frac{\varepsilon_m}{3} \int\int P(L_1, L_2) \sum_{i=1}^{3} \frac{1}{\varepsilon_m + L_i\left(\varepsilon_{np}(l) - \varepsilon_m\right)} dL_1 dL_2. \tag{5}$$

L_1, L_2, L_3 are the depolarization parameters of ellipsoïdal NPs along their three principal axis. These parameters which depend on the NP shape, vary in the 0–1 range and must respect the following sum rule:

$$1 = L_1 + L_2 + L_3 \tag{6}$$

Note that this equation fails for NPs located on an interface. In this case, dipole images must be taken into account. Other theories such as the Yamaguchi theory [27] or the Bedeaux and Viegler theory [28,29] must be considered to take into account dipole image effects. The distribution of the depolarization parameters ($P(L_1, L_2)$) is introduced into Eq. (5) to take into account the distribution of NP shape. The effective dielectric function of a medium composed of ellipsoidal NPs embedded in a dielectric matrix can be calculated by combining Eqs. (1)–(4):

$$\varepsilon_{eff} = \frac{(1-f)\varepsilon_m + f\varepsilon_{np}\langle\beta\rangle}{(1-f) + f\langle\beta\rangle}. \tag{7}$$

This effective dielectric function respects the Wiener limits and Hashin-Shtrikman bounds. In the following, we assume that the distribution of depolarization parameters is described by a sum of Gaussian distributions [24,26]:

$$P(L_1, L_2) = C\sum_{k=1}^{N} C_k e^{-0.5\left(\frac{(L_1-\bar{L}_{1k})^2}{\sigma_{1k}^2} + \frac{(L_2-\bar{L}_{2k})^2}{\sigma_{2k}^2} + \frac{(L_3-\bar{L}_{3k})^2}{\sigma_{3k}^2}\right)}. \tag{8}$$

Note that other distributions can be used. C is a constant used to normalize the distribution. $\sigma_{i,k}$ and $\bar{L}_{i,k}$ are the standard deviation and the mean value of L_i of the k^{th} Gaussian term, respectively. $\bar{L}_{1,k}$, $\bar{L}_{2,k}$ and $\bar{L}_{3,k}$ are linked together by Eq. (6). The relative volume fraction f_k attributed to the k^{th} Gaussian term is defined by:

$$f_k = fCC_k. \tag{9}$$

2.2 L^2, P^2 and r^2 spaces

By considering the Bohren convention [21] ($L_1 \le L_2 \le L_3$), we can define a two dimensional depolarization space (L^2) in which each NP shape is represented by an unique point $M(L_1, L_2)$ (Fig. 1a). In this space, the normalized distribution of NP depolarization factors $P(L_1, L_2)$ is correlated to the NPs shape distribution. As an example, the locus of spherical, oblate and prolate NPs are $L_1 = L_2 = 1/3$, $L_1 = L_2$ and $L_2 = 0.5–0.5L_1$, respectively. However, the quantitative description of nanoparticle shape distribution and the numerical calculation of the integral of Eq. (5) remain difficult in this physical space. As shown in Fig. 1a, each point M of the L^2 space is included in a ABC triangle. Thus, the vector **AM** must respect the following relationship:

$$\boldsymbol{AM} = \left(1-P_p\right)\boldsymbol{AB} + (1-P_o)\left(1-P_p\right)\boldsymbol{BC}. \tag{10}$$

Where $0 \le P_o \le 1$ and $0 \le P_p \le 1$. Each point $M(L_1, L_2)$ can be represented by a new set of coordinates (P_0, P_p) in a two dimensional orthonormal space (P^2) (Fig. 1b). The (L_1, L_2) coordinates are related to the (P_1, P_2) coordinates thanks to the following transformations:

$$L_1 = \frac{(1-P_o)\left(1-P_p\right)}{3}. \tag{11}$$

$$L_2 = \frac{\left(1-P_p\right)}{2} - \frac{(1-P_o)\left(1-P_p\right)}{6} \tag{12}$$

The locus of oblate, prolate or spherical NPs in P^2 are $(0, P_p)$, $(P_o, 0)$ and $(0, 0)$, respectively. In other words, P_o and P_p traduce