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Correlations between microstructure of plasma-modified gold nanoclusters and their optical properties

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Abstract

Gold nanoclusters with diameters up to 50 nm were grown in sandwich structures consisting in 15 nm of plasma deposited silicon nitride, 1 nm of gold grown by sputtering and 15 nm of plasma deposited silicon nitride (SiN/Au/SiN). Previous to the last step, ammonia plasma treatments of the gold surface were carried out with time as the main variable. The resulting structures were analyzed by high resolution transmission electron microscopy and spectroscopic ellipsometry. As a result of plasma treatments, island-like structures of as-grown gold clusters evolve to near spherical-shape features with decreasing diameter as the plasma treatment time rises. Ellipsometric spectra were modeled based on the Bruggeman effective medium approximation and the influence of size and shape of nanoparticles on the optical properties were calculated.

Keywords: Spectroscopic ellipsometry; Gold clusters

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1. Introduction

The optical response of metallic nanoclusters embedded in a dielectric matrix arises from the excitation of surface plasmons, known as surface plasmon resonance (SPR), that induces a selective enhancement of the absorption [1]. The spectral position of the SPR depends on

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the optical properties of the metal and the dielectric matrix, as well as the cluster morphology and the cluster spatial arrangement [2,3]. Among the noble metals, gold is largely investigated because its excellent resistance to electromigration, high electrical and thermal conductivity and high temperature of operation [4]. The knowledge of the dielectric response of these materials at different energies is very important in a number of applications including nanoelectronics and nonlinear optics. In the range of the visible spectrum, this could be achieved by means of optical characterization such as absorption and spectroscopic ellipsometry (SE). In the former, the most common practice is to use the Mie theory combined with the discrete dipole approximation in order to fit the SPR peak, while in the later, ellipsometric data are fitted taking into account a complex dielectric function obtained by applying effective medium theories to the metallic particles–dielectric host system.

In this paper we implemented the Bruggeman effective medium approximation in order to study the dielectric response of gold nanoparticles embedded in silicon nitride thin film. The model takes into account not only the size, but also the particle shape, which plays an important role in the optical response.

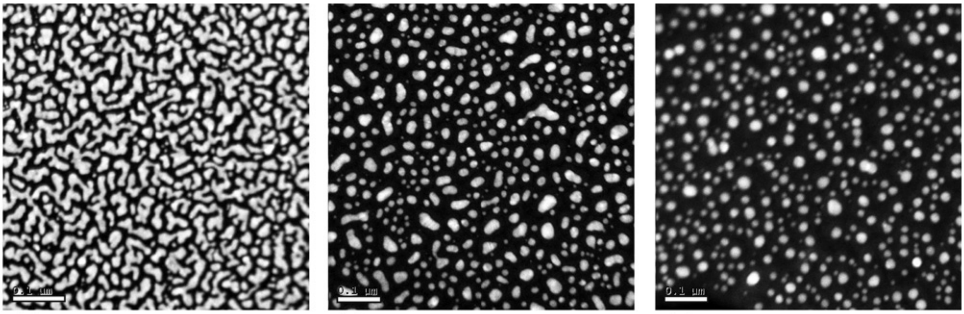
2. Experimental

Ammonia plasma-treated SiN/Au/SiN structures grown on crystalline silicon and NaCl substrates with total thickness of 30 nm were used for SE and high resolution transmission electron microscopy (HRTEM) characterization, respectively. Detailed information about the experimental parameters used is shown in Refs. [5,6]. The difference between the samples was the plasma treatment time, which was ranging from zero up to 600 s (0, 30, 60, 300, 600 s) and will be used as the main experimental variable throughout this work. The morphology of the resulting structures was studied by means of HRTEM using a JEOL-2010 FEG instrument with a point to point resolution of 0.19 nm. Optical characterization of the Au nanoclusters was performed by spectrometric ellipsometry using a Jobin Yvon Horiba (UVISEL) Spectroscopic Phase Modulated Ellipsometer from 1.5 to 3.0 eV. A merge configuration ($P - M = 45$; $M = 0$; $A = 45$ to obtain Δ and $P - M = 45$; $M = 45$; $A = 45$ for determining Ψ) was used in order to avoid indetermination in the ellipsometric angles. The ratio (ρ) of the total reflection coefficients of the two components of the light, R_P and R_S, polarized, respectively, parallel and perpendicular to the plane of incidence, is related with the ellipsometric angles according to the equation:

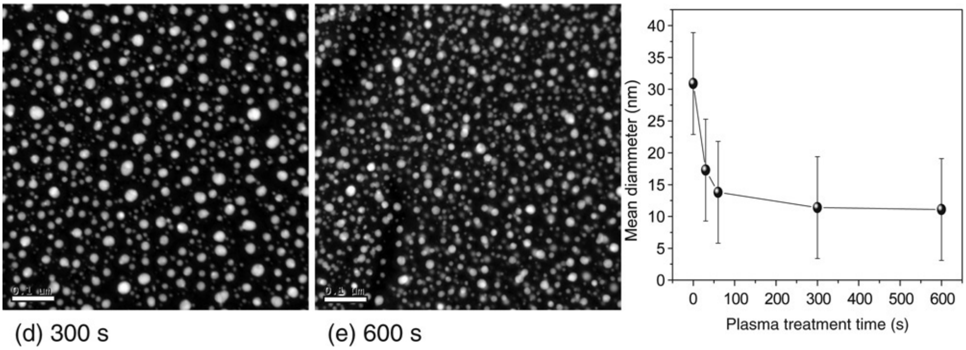
$$\rho = \frac{R_P}{R_S} = \tan \Psi \exp(\mathrm{i}\Delta) \tag{1}$$

where Ψ and Δ are the ellipsometric angles.

The spectra were analyzed in terms of an optical model based on the Bruggeman effective medium approximation (BEMA), considering the *c*-Si substrate and a composite layer of SiN containing the Au clusters. The optical response of the Au particles was modeled adjusting the complex dielectric function of the bulk material in order to take into account the particle size effect [7]. The refractive index and extinction coefficient were extracted from the dielectric function of the effective medium. Then, the Fresnel coefficients for both interfaces were calculated. These values allow the determination of the total reflection coefficients, which are directly related with ρ through Eq. (1). Calculated and experimental values of ρ were compared quantitatively by evaluating the mean-square deviation using the Levenberg–Marquardt algorithm.



(a) As grown (b) 30 s (c) 60 s



(d) 300 s (e) 600 s

Fig. 1. Dark field HRTEM images of the structures for each of the ammonia plasma treatment times (white rectangles at the left bottom corner of the HRTEM images represent 100 nm). Behavior of the mean particle diameter calculated from HRTEM images as a function of plasma treatment time (error bars take into account the standard deviation of the particle size distributions).

3. Results and discussion

The results of the HRTEM measurements are shown in Fig. 1, where a morphological evolution of the gold particles with the plasma treatment time is evident. The as-grown structure shows a typical behavior of the initial stages of a growing film, where the clusters begin to diffuse and grow by connecting each other, filling out a large fraction of the available surface. After 30 s of ammonia plasma exposure, gold islands begin to acquire a particle-like geometry, increasing the distance between them, but there is still a fraction of clusters with enlarged shapes. From 60 up to 600 s of plasma treatment, the clusters depicted a near-spherical geometry with decreasing radius.

The main changes in gold dielectric function were observed in the range of energies between 1.5 and 3.0 eV that contains the SPR peak (∼2.5 eV) of gold nanoparticles [6]. By this reason this range was used in calculation and experiments. Fig. 2 shows the variation of the real part of the theoretical values of ρ with the nanoparticle diameter and the polarization factor (K). The imaginary part has a similar behavior.

As can be seen in Fig. 2(a), the value of ρ rises as the nanoparticle size increases; however the curves remain with the same shape. At values of particle radius higher than 20 nm the simulated spectra don't show any changes. This behavior agrees well with a large number of works published (see for example Ref. [1] and references there in). The value of K, related to the shape of nanoparticles, introduces a change in the shape of the curves (Fig. 2(b)). K has a value of two for spherical particles, equals one for long nanorods oriented with their axes parallel

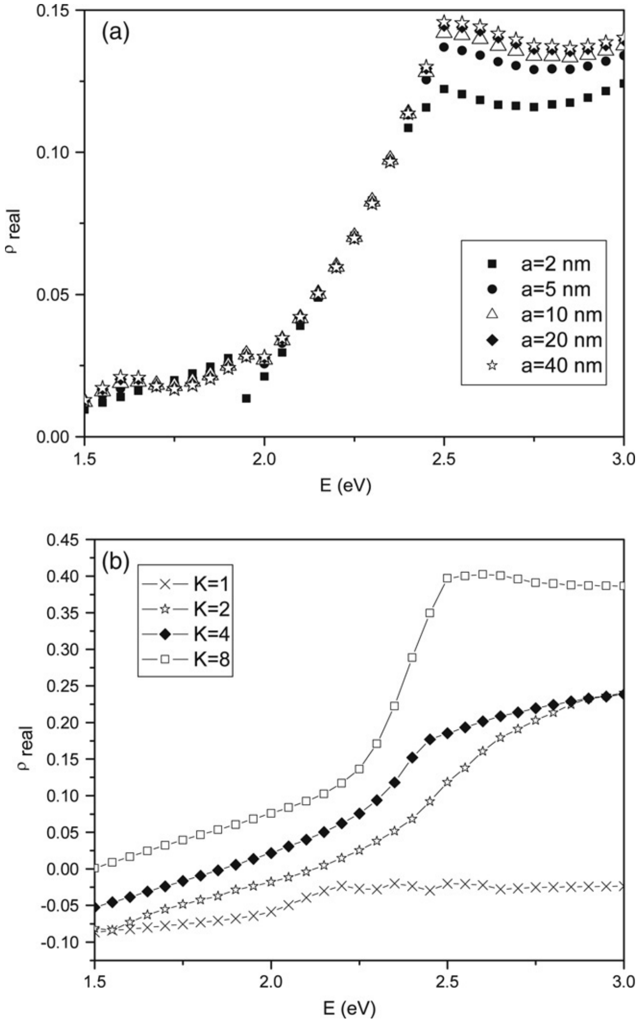


Fig. 2. Variation of the real part of ρ with (a) the radii of nanoparticles and (b) K.

to the direction of the incident light, and its value approaches infinity for a flat disc oriented perpendicular to the incident light [1].

In Fig. 3(a) it can be observed that different shapes and values of the real part of ρ are obtained in each case as a function of energy. It is consistent with the differences obtained in size and shape (Fig. 1) and the previous analysis in the model. In this way both K and a were varied in simulation for adjusting the experimental data. Fig. 3(b) shows the result of adjusting for the sample without treatment and with treatment of 30 s. The value of χ^2 was smaller than one in all cases. Table 1 shows the values obtained in each case with the fit.

4. Conclusions

The optical properties of the grown structures were directly related to the size and shape of the gold nanoclusters. As the plasma treatment time increases, the particle main diameter decreases

Table 1
Results of fitting according to the model

Sample	a (nm)	K	χ^2
As-grown	50.4	10	0.51
30 s	18.1	8.5	0.36
60 s	12.3	7.2	0.37
300 s	10.2	2.0	0.36
600 s	9.8	2.0	0.34

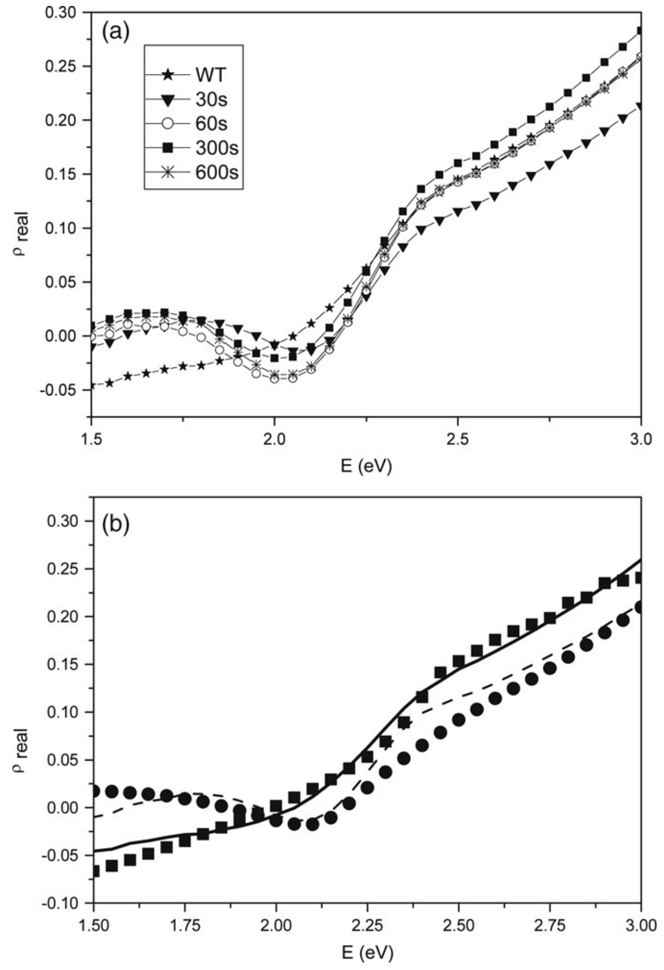


Fig. 3. Variation of real part of ρ in (a) the experimental samples and (b) fitted spectra for sample without treatment and with treatment of 30 s.

and their shapes approach that of the spherical geometry. Good agreement between HRTEM and SE measurements was demonstrated by using the Bruggeman effective medium model.

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