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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.