Fabrication and optical properties of Au:SiO₂ nanostructured thin films

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Abstract. We demonstrate synthesis and theoretical study of the optical properties of Au:SiO₂ nanocomposite thin films. Localized surface plasmon resonance peak induced by Au NPs was clearly observed in optical spectra at wavelength range between 500 and 600 nm. Intensity and position of PL peak are demonstrated to depend on the Au NPs embedding depth.

1. Introduction

Noble metal nanoparticles (NPs) have been the subject of intense research in recent years due to their original structural, optical and electrical properties compared with their bulk counterparts [1]. Among them, Au NPs have drawn particular attention since they are capable of biological conjunction, as well as they demonstrate the nonlinear and broad absorption band in the visible range, which arise from localized surface plasmon resonance [2]. These properties make them highly suitable for the use in nanophotonics [2, 3]. For instance, there have been several demonstrations of chemical and biological sensing based on the plasmon absorption and scattering of Au NP [4] and their assemblies [5].

Typically, the realization of such devices relies on the deposition of NPs on a support, such as Al₂O₃, SiO₂ substrates, polymers, etc. [6-9]. There are several preparation techniques that can be employed for NPs deposition onto the substrates. Doing so with nano-lithographic techniques allows to fabricate well-defined NPs [10, 11], but at the same time it is difficult, time-consuming and inefficient to create sparse patterns of small particles. In turn, thermal annealing of thin Au films is the simplest and low-cost method, but there are the dispersion in the size of NPs forming [12]. Nowadays coloidal gold have become an important alternative because of stability, ease of synthesis [3] and deposition of NPs onto substrates. Furthermore, coloidal solution containing NPs with desired shapes are commercially available in a wide range of sizes from a few to tens of nanometers. Unfortunately, a common problem in the preparation of reliable sensors is poor adhesion between the Au NPs and oxide substrates, which may result in detachment of the NPs from the substrate and, subsequently, deterioration in detection efficiency [13].

Meanwhile, recent studies [14, 15] demonstrate that Au NPs could be thermally embedded into subsurface layer by the thermal annealing technique. Therefore, it can facilitate the better stability of Au NPs on oxide surfaces. However, it has been pointed out that the optical response of Au NPs during the annealing step can be changed due to the shape as well as dielectric environment variation. Therefore, establishing the correlation between the NPs morphology and optical properties is a prerequisite for both understanding metal supported systems and for creating future photonic devices.
In this work, we report on the fabrication and investigation of optical properties of SiO$_2$ thin films with embedded Au NPs.

2. Experiment

The investigations were carried out using Au colloidal solutions having 40 nm nominal diameter NPs. The deposition of Au colloidal solutions was performed onto the Si(100) substrates with preliminary created by thermal oxidation 190 nm thick SiO$_2$ layer. Prior to the deposition, the surface of the samples was modified by a short time Ar plasma treatment. Plasma treatment, as it was demonstrated previously [16], leads to a global improvement of the NP adhesion and the hydrophilic properties of the Si substrates. NP deposition time was equal to 150 s, afterwards the solution remnants were blown away with a dry N$_2$ gas.

The heat treatments of the samples with deposited Au nanoparticles were carried out in the horizontal quartz furnace at 1000°C under ambient air. After the annealing the samples were cooled down passively to room temperature inside the oven.

The morphological properties of samples were investigated using a scanning electron microscope (SEM) Zeiss Supra 25 operating at 20 kV.

The morphology of the nanowires was investigated using Zeiss Supra 25 field-emission scanning electron microscope (SEM).

Numerical simulations of PL spectra were carried out in COMSOL Multiphysics modelling environment.

3. Results

The SEM image of the sample surface with the deposited colloidal Au NPs is shown in Figure 1. Spherical 40 nm in diameters Au NPs are distributed randomly, but rather homogeneously across the whole sample surface. The average surface density of NPs is about 8×10$^8$ cm$^{-2}$.

![Figure 1. SEM image of the sample surface after Au NP deposition (a) and after the 25 min thermal annealing.](image)

After the thermal annealing for 25 min at 1000°C in a horizontal furnace under ambient air, the smaller diameter NPs surrounded by rims were observed (see Fig. 1b). The results obtained are attributed to the thermally-induced Au NPs embedding into silicon dioxide and the similar results were observed in other studies [14, 17-19]. It should be emphasized that despite the simplicity of the fabrication method, the mechanism of Au NPs embedding remains an open question.

Figure 2 illustrates the proposed kinetic of the Au NP embedding. The heating of the sample to the high temperatures leads to the formation of liquid gold NPs, which wets the sample surface (see Fig. 2b). At the same time Au NPs begins to penetrate into SiO$_2$ layer. This process is followed by the material transport from under the Au NP to the triple point (metal-vapor-oxide), leading to the ridge
formation. In addition, it should be pointed here, that gold atoms can be evaporate or be diffused into SiO$_2$, which can result in the NP size decreasing during the embedding process [14]. Thus, the thermal annealing can provide the controllable Au NPs embedding into SiO$_2$.

![Figure 2. Schematical representation of the proposed Au NP embedding in SiO$_2$ surface.](image)

The morphologies of the Au NPs demonstrated in Figure 2 were used for the simulations of optical properties of Au:SiO$_2$ nanostructured thin films obtained. Taking into account the size and the shapes of Au NPs, as well embedding depth and the ridge formation, numerical modelling of the spectra nanostructured films were performed. Numerical modelling studies were carried for the solid-state Au NPs having 40 nm diameter and surface density of $1 \times 10^9$ cm$^{-2}$. The model calculations assumed that the NPs preserve their volume during the annealing.

Figure 3 presents the calculated reflectivity spectra of obtained Au:SiO$_2$ nanostructured films. It is seen that the resonance peak of Au NPs deposited over SiO$_2$ surface is located near 500 nm. As the embedding depth increases, the peak shifts towards the red wavelengths. Simultaneously, since the NPs effective dielectric constant enhances, the reflectance intensity increases. It should be noted, this calculations did not take into account the formation of ridges. In turn, the formation of ridges, which were modeled by the addition of 5 nm height rims around the NP, leads to the increased reflection also.

![Figure 3. The calculated reflectance data of Au:SiO$_2$ nanostructured films. The right–hand panel shows the electric field distribution.](image)

The electric field patterns of Au NPs at the resonance wavelengths (Fig. 3) show that the Au NPs behave roughly as a dipole with accumulated electric field on the sides of the NPs. This confirms that the SiO$_2$ surrounding of Au NPs strongly influence the resonance.
4. Conclusion
In summary, the embedding of Au NPs, which can provide its better stability on the SiO$_2$ surface, was performed with applied by thermal annealing technique. The ability to control the embedding depth and, as a consequence, to tune the optical properties may provide new opportunities for the fabrication novel plasmonic materials.

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