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Abstract. In this work the results of a bimetallic Au-Ag structure deposition from the colloidal system by nanosecond laser radiation are presented. The formation of the extended arrays of gold and silver nanoparticles with controlled morphology is examined. We report the results of formation bimetallic islands films with various electrical and optical properties. The changes in the optical properties of the obtained thin films are found to depend on their morphology.

Introduction

The formation of transparent metal coatings is one of the promising fields in the modern nanotechnology. Particular attention is attracted by thin nanostructured metallic films demonstrating non-linear optical effects in the visible part of spectrum attributed to the surface plasmon resonance [1]. The optical properties of the films strongly depend on the composition and periodicity of the surface structures [2]. Such effects as local field enhancement can be observed either for distinct frequencies or in a wide diapason depending, for instance, on the structure spacing and ordering. In the case when the gap between the deposited particles is comparable with their sizes, randomly distributed structure properties can considerably differ from the periodically ordered ones [3]. When, furthermore, bimetallic thin films are deposited, one can expect even more complicated optical properties behavior [4] since they depend not only on composition, order and spacing, but also on their shape and morphology.

Thus, a considerable change in the optical properties can be observed upon laser-assisted deposition of fractal clustering thin films with respect to the continuos ones with the same composition [5,6]. Since traditional methods of the ordered deposition of the individual particles have a very low productivity and require more time [7], such new laser-assisted methods are of a considerable interest In this work, we investigated the influence of the film morphology (particle diameter in the colloid, the distance between the deposited particles, the number of layers, etc.) on the optical and elctrical properties of the deposited thin film of bimetallic clusters.

For the formation of a quasi-periodically spaced clusters of particles, we used a method of deposition of colloidal systems allowing nanoparticles deposition in colloids by the local laser heating and the following diffusion of particles towards the surface [8]. Changes in the optical properties of

the deposited bimetallic films are examined and the observed optical phenomena are explained based on a performed electromagnetic simulation.

1. Deposition of bimetallic thin films

1.1. Nanoparticle generation

The initial colloidal systems are prepared by continuous laser ablation of silver and gold targets in liquid environment (deionized water). As a result, the average particle size of 10 nm is obtained at a concentration of ~1mkg/ml [9]. The particle size is controlled by dynamic light scattering.

1.2. Pulse laser deposition of nanoparticle

For deposition of bimetallic structures, colloids were mixed in equal concentration proportions. KV8 glass substrate was placed in the cuvette with the solution and laser deposition method was applied to deposit particles from colloidal systems on the substrate [10].

For deposition, we used ytterbium fiber laser (λ = 1.06 microns) with a pulse duration of 100 ns, pulse repetition rate of 20 kHz, and a pulse energy of up to 1mJ. The diameter of the laser beam at the focal plane was 5 microns. Nanoparticle array formation on the substrate surface was performed by scanning the laser beam along the same direction (from five to twenty-five times) at a speed of 0.6 mm/s to 1.5 mm/s. The film deposition was obtained as a result of a step-by-step process, which is typical of the island structures.

In the proposed method, particle settlement/deposition occurs due to the local particle heating, so that the energy absorbed by the particles can be determined from the relation:

$$E_{abs} = \pi r_0^2 Q_{abs} \int I(t)dt\,, \qquad (1)$$

where $I(t)$ is laser intensity distribution; r_0 is particle radius; and Q_{abs} is the effective parameter.

To calculate the Q_{abs} classical Mie theory is used [11,12] for spherical particles of 10 nm diameter as follows

$$Q_{abs} = \frac{8\pi r_0}{\lambda} Im\left(\frac{\varepsilon^2-1}{\varepsilon^2+2}\right), \qquad (2)$$

where $\varepsilon = n + ik$ and the calculation parameters of gold and silver at the laser wavelength λ = 1064 nm are given in [13]. Depending on the conditions of laser exposure for a single pulse, the value of the absorbed energy is 10^{-6}-10^{-9} J.

During laser irradiation of a colloidal system, it is necessary to take into consideration the amount of heat transferred to nanoparticles from the laser field. Taking into account small size of particles relative to laser wavelength (1064 nm), the temperature of a particle can be found from relation [14]:

$$T_{max} = \frac{I_p k_a d}{8\chi} \qquad (3)$$

where I_p is the peak laser power, x is the thermal conductivity of liquid phase of the colloid, coefficient k_a takes into account the small size of the particle relative to the wavelength, and

$$k_a = e^{(-0.2[\sqrt{n^2+k^2}-1])}\left(1-e^{\left(-\frac{4\pi kd}{\lambda}\right)}\right) \qquad (4)$$

Taking into account that coefficients *n* and *k* for gold and silver are close to each other for radiation with a wavelength of 1064 nm and that we are using particles of equal diameters, we can assume that they reach close temperatures. Substituting laser parameters typical of our experiments (average power 20W, pulse width 100 ns, pulse-repetition rate 20 kHz, and beam diameter 5 mkm), we find that the temperature of nanoparticles in a colloid calculated from (3) can reach 600 K.

However, under conditions of multi-pulse exposure local heating may occur, leading to the stability loss of the colloidal system [10, 15]. In addition, agglomerates can be formed due to particles heating, that will absorb a larger fraction of laser energy and will be able to move thermally in the colloid. The local heating of the liquid will, furthermore, result in the formation of convective currents also ensuring particle motion of to the substrate surface.

The proposed deposition method allows one to change the morphology of the deposited structures depending on the laser exposure conditions. In what follows, we describe the consecutive stages in the formation of bimetallic island films depending on the number of passes in the deposition area.

After 10 skans, islands significantly increase their area (Figure 1a), and the average height of the relief becomes 18nm.

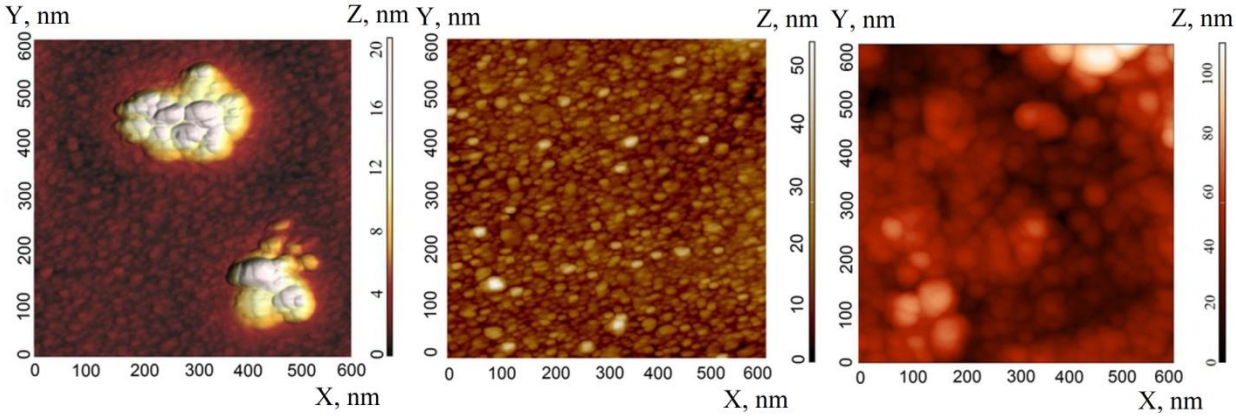

Figure 1. AFM images of bimetallic nanostructures deposited on a glass substrate. The power of the laser radiation formed is 2.5W, scanning speed is 1.2 mm/s for different number of laser pas passes: (a) - 10 scans, and (b) -25 scans, (c) – 35 scans.

With further scans the surface of the substrate islands completely fused and formed the structure of quasi-periodically arranged nanoparticles, the total height of the deposited topography increases monotonically with increasing number of passes of the laser beam in the same area. As a result, after 25 scans a granulate film is formed with an average height of the relief 52nm (Figure 1b), and after 35 scans the film with average height 112nm is formed (Figure 1c).

2. Measured optical properties of the depositing structures

The optical properties of the formed thin films are studied in the spectral range from 300 nm to 800nm by using SF -2000 spectrophotometer (Figure 2) .

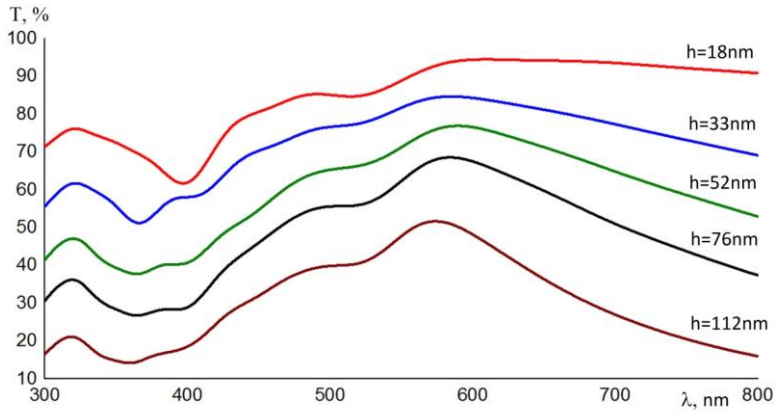

Figure 2. Transmission spectra of bimetallic films deposited with an average height of 18 to 112 nm .

Type transmission spectrum depends strongly on the structure of the deposited layer. The regions of plasmon resonance for silver (340-420nm) and gold (520-580nm) slightly stand out depending recorded. However, as the number of layers is increased, significant changes in the spectrum are

observed. In the plasmon resonance region for silver, a system of local minima and laxima is observed, while the absorption maximum experiences the "red", the "blue" shifts. For all the films, an enhancement of transmission is observed between 550 and 600 nm. In all multilayer films, there is a periodic variation in transmittance between 400 and 500nm , which can be explained by the formation of the colloidal alloys of silver and gold nanoparticles [6], and by the interference –based antireflection of thin film.

3. Investigation of the electrical properties of the depositing structures

The current-voltage characteristics of the films were investigated using four contact setups. Two outer contacts are the pinch point contacts and are located at a distance of 1 mm from each other. The two other (central) are tips of an atomic force microscope coated with a conductive coating, and could move to a distance of up to 100 μm in the XY plane. The observed deviations from linearity (Figure 3) can be explained by the fact that the deposited layer was a nanoparticle conglomerate; the schema is not uniform and is an ensemble of ohmic contacts [10, 16].

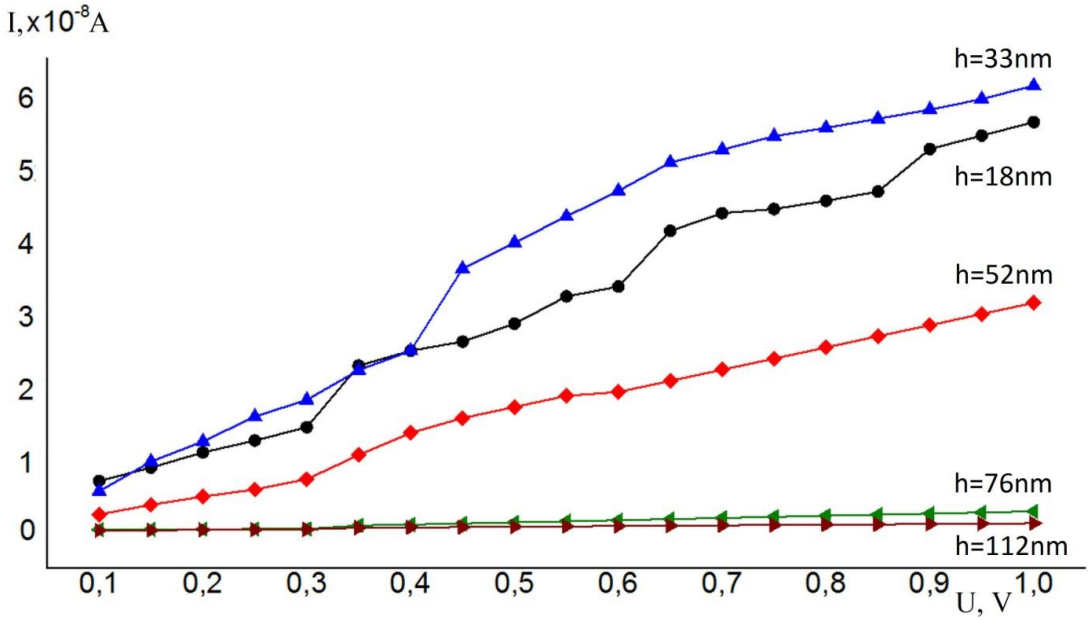

Figure 3. Current-voltage characteristics of deposited layers with different heights.

Changing current in the film can be described using the following equation:

$$j \propto U\sqrt{\frac{E_a}{kT+{}^{2eUd}/_{L}}}\exp\left(\frac{{}^{eUd}/_{L}-E}{kT}\right) \qquad (5)$$

U – potential difference between macrocontacts, E_a – ionization energy, e – electron charge, d – average distance between neighboring clusters, L – length of conductive layer between macrocontacts, k – Boltzmann constant, T - temperature

In deposited “islands” structures electrons move in unniform systems and the increasing of the voltage results in the opening of the new canal of the conductance. The obtained distribution in such system is shown in Figure 3. This system can be considered as a capacitor with capacitance C (tunneling between two metal contacts). "Coulomb blockade" is possible during the passing/tunneling like-charged particles across the border barrier/potential well, i.e., absence of the current in the structure when the external voltage owing to the Coulomb repulsion of the particles.

An estimation of the required minimum value of the energy (one-electron tunneling) for the overcoming of the "Coulomb barrier" can be done as follows:

$$\Delta E_K = hG/C, \qquad (6)$$

where h - Planck's constant, G – the conductivity of tunnel transition.

The island films occurs electron scattering at the grain boundaries, this may change in the total resistance of the film depending on the ratio of the grains area (S_g) to the volume (V_f):

$$R = R_0 + \rho_g \left(\frac{S_g}{V_f}\right), \quad (7)$$

where R_0 – resistance of monocrystalline material , ρ_g – resistivity of grains border.

In our case, we have seen competition increase conductivity while opening new channels and increase the resistance by increasing the area of the grain. At the same time due to thermal activation also changes the current strength in the formed island films. Thus, the possibility of forming films of gold and silver nanoparticles for which the ability to control change in their electrical resistance by changing the morphology.

Conclusions

We demostrate the method of laser deposition of bimetal island films. The possibility of the formation of the surface array of gold and silver nanoparticles with controlled morphology is demonstrated.We have presented both the experimental data on the optical and electrical properties of nanostructured bimetallic films. We demosntrate what the properties of the films are found to depend on the film morphology.

Acknowledgments

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