Bimetallic clustered thin films with variable electro-optical properties

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Abstract The drop deposition of colloidal nanoparticles was performed from water-based colloidal solutions. The proposed procedure is based on the agglomeration of colloidal particles in laser-assisted evaporation processes. The evaporation process was resulted in the formation of clustered thin films on a glass substrate. In the experiments with bimetallic Au:Ag solutions, the clustered films are grown, the formation of the clustered films with the average height of 100 nm was achieved. Optical properties of the deposited structures were investigated experimentally. It is shown that the obtained films may become transparent and its properties are defined by its morphology.

1. Introduction
Efficient synthesis of thin films with controlled optical properties is a key issue in modern photonics. In particular, possibilities of plasmon-assisted light manipulations by using nanoparticles and nanostructures currently attract considerable attention enabling various applications and opening new research area [1]. Drop deposition of the colloidal particles on glass substrate represents, furthermore, a promising solution to this challenging problem. The optical properties of these films are dominated by a set of plasmonic effects and strongly depend not only on the composition of the film but also on its morphology. In the case of the structures composed of nanoparticles, such parameters as spacing and ordering of nanoparticles define the local field enhancement to be observed either for distinct resonance frequencies or in a much wider spectral ranges [2, 3]. Furthermore, if nanoparticle spacing is comparable with its sizes, optical properties of the random structures can considerably differ from that of the ordered ones. In the case of the thin bimetallic films, one can expect even more complicated optical properties [4].

2. Deposition of bimetallic thin films
Gold and silver particles were formed as a result of CW laser irradiation (power 30 W, laser spot diameter 100 μm) of a target in water [5]. The target was scanned by a laser beam with a velocity of 100 μm/s; the total exposure time was 30 min. After laser irradiation, the solution was exposed to ultrasound for 10 min and then separated on a CM-6M centrifuge. The particle sizes in the colloidal
solution was investigated by dynamic light scattering method with a Horiba LB-550 particle-size analyzer. They appear to be in the range from 5 to 10 nm. A mixture of silver and gold colloidal solution with the weight ratio of 1:1 was prepared by vigorous stirring. We have formed clustered films by method of drop deposition [6]. The basic concept of this method is the deposition of a small-radius (10 μm) drop of colloidal solution combining with the pinning effect. The particles are deposited on the contact area of the droplet with the substrate placed on the thermostabilized table at the temperature of about 80°C. The area of droplet doesn't change during the evaporation processes, because of an additional energy barrier, which impedes the interface displacement. In this case, the surface tension forces, which tend to make a drop spherical, dominate over the gravitational forces, which tend to flatten the drop. The dynamics of drop spreading is determined by the following factors: surface tension, wetting, viscosity, thermal conductivity, and ionic bonds [6]. Thus, when the particle concentration in a drop is relatively low, the particle deposition can be described similar to the behavior of an isotropic medium. As an example, Fig. 1 shows the deposited layers for different concentration of colloidal system.

For metal particles, we can control the cluster morphology at slow deposition process [6]. A more detailed analysis of the film morphology reveals a variety of aggregate shapes. Some of them gain typical fractal shapes which are shown in Figure 1.

3. The optical properties of deposited films

Transmittance spectra strongly depend on the aggregate shape. There is a periodical variation ranges in the transmission spectra of all films at the wavelength of the plasmon resonance of gold (500-540 nm) and silver (390-420 nm). The behavior of bimetallic films transmission spectra is more complicated at the wavelength of the plasmon resonance of silver nanoparticles. Additionally, Figure 2 illustrates this dependence for three typical fractal aggregate configurations shown in Figure 1.
4. Summary
We have presented an efficient method of the drop deposition of bimetal island films. The possibility of the formation of the clustered films of gold and silver nanoparticles with controlled morphology is demonstrated. The experimental data on optical properties of nanostructured bimetallic clustered films has been obtained. We have demonstrated that the properties of the island films depend on its morphology.

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