OPTICAL PROPERTIES OF SILVER AND GOLD CLUSTERS IN SILICA MATRICES

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Abstract

Absorption and luminescence properties of silver and gold nanoclusters embedded in silica matrixes were studied experimentally. Thin SiO_2 films with different amount of silver and gold were produced by co-deposition of metal and SiO_2 onto the silica substrates in vacuum. Films with silver content possess three peaks in absorption spectra in near the UV range and two peaks in luminescence spectra in the visible range. We ascribed these spectral features to silver nanoclusters of different sizes that present in the film. Films containing gold particles have continuous absorption spectra in the visible and UV ranges. The luminescence was observed only in the samples with the silver content of less than 2.2%. Quenching of the luminescence in the films with larger silver content we associate with the nonradiative energy transfer between close-packed particles. Thermal annealing leads to the formation of lager particles and transforms both absorption and emission spectra of the films.

Keywords: Cluster, silver, gold, thin film, dielectric matrix

1. INTRODUCTION

Investigation of the size dependence of optical properties of nanoobjects is one of the most important research themes in the nanoscience. Spectral positions of the absorption and luminescence bands of nanoobjects can be tuning over the whole visible range by changing their size and shape [1,2].

Metal nanostructures with extremely small size (atomic or molecular clusters) can be distinguished in an individual group [3]. In contrast to the bulk metal or to metal nanoparticles their electronic structure is discrete and can significantly change with adding or removing just one atom. These changes are particularly pronounced in the clusters containing less than 12 atoms [4]. Due to discrete nature of the electronic structure their optical properties are closer to that of atoms and molecules, in particular, in very small clusters luminescence may be observe in the visible range [5-7].

In this paper metal clusters were created by the physical vapor deposition of metals in vacuum. However, at an ordinary deposition of the metal on the substrate surface small clusters cannot be obtained because even with a relatively small amount of deposited metal quite large metal nanoparticles having strong collective resonances (plasmon oscillations) are formed [8]. Besides that, the study of extremely small quantities of the deposited material is difficult to implement. In order to prevent the formation of large metal nanoparticles the dielectric material was deposited simultaneously with metal [9]. The samples produced in this way consist of the dielectric matrix with the metal particles included into it. Varying the ratio of the deposition rates of metal and dielectric one can change the clusters size, and hence their optical properties.

2. SAMPLE PREPARATION

Thin silica films containing silver or gold inclusions were obtained by simultaneous vacuum deposition of SiO_2 (99.99 %) and Ag (99.99 %) or Au (99.99 %) on the surface of the quartz substrate in the vacuum chamber PVD-75 (Kurt J. Lesker) at the residual vapor ~10^{-6} Torr. For the evaporation of metals, the resistive heated tungsten boat was employed and the electron-beam evaporator was used for SiO_2 deposition. The amount of the deposited material was monitored by the quartz crystal microbalance calibrated on silver. The mass-

thickness of the layer comprising silver or gold inclusions was set to 50 nm for all samples. Then, based on the ratio of the deposition rates, metal concentration in the film was calculated.

Series of samples with the silver content of 1.2, 1.6, 2.2 and 3.7 % and with gold content of 1.1, 1.6, 3.2 and 6.3 % were obtained. After the deposition the absorbance spectra (SF-56 LOMO) and fluorescence spectra (RF-5301 Shimadzu) of the samples were obtained. Then the samples were annealed at 200 °C for film with silver and at 500 °C for film containing gold for 1 h and spectral measurements were repeated.

3. RESULTS AND DISSCUSSION

Figure 1 plots the spectra of the optical density of the samples contains silver. After the deposition several absorption bands in the near UV region were observed - one broad peak at 3.08-3.11 eV (400 nm) and two narrow peaks at 3.72-3.78eV (330 nm) and 4.17 eV (297 nm). The spectral position of the first two peaks is shifted to the long-wavelength region of the spectrum with increasing amount of silver, and the wavelength of the third peak does not change. Thermal annealing of the film dramatically changes the absorption spectrum. Three UV bands melt together in a single broad peak with reduced optical density.

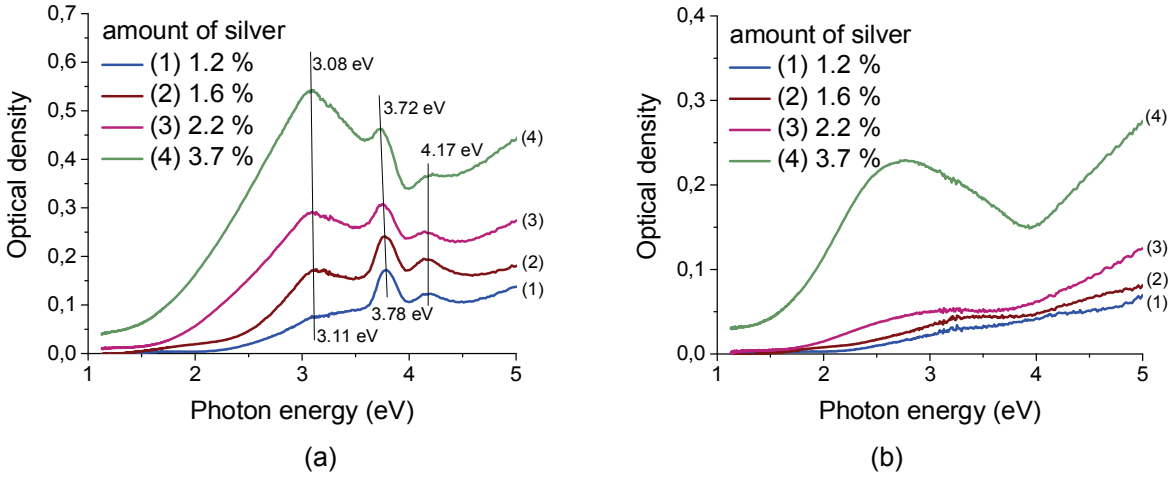

Figure 1 Optical density of thin SiO_2 films with different amount of silver after the deposition (a) and after thermal annealing (b)

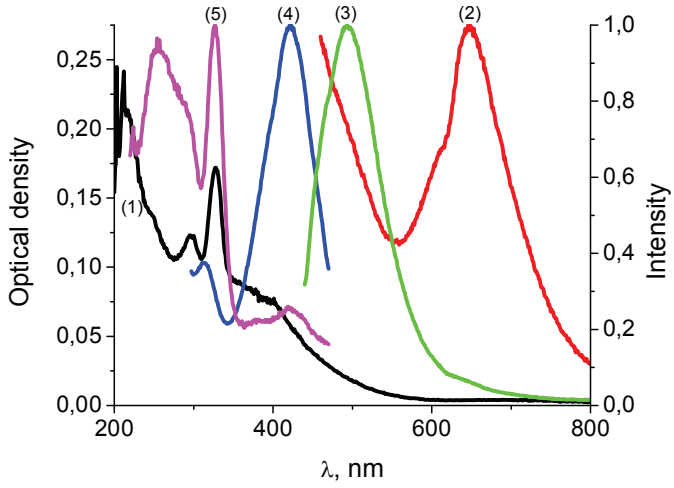

Figure 2 Optical density (1), luminescence at λ_{ex}=330 nm (2) and λ_{ex}=420 nm (3), and luminescence excitation at λ_{em}=490 nm (4) and λ_{em}=645 nm (5) spectra of thin SiO_2 films with 1.2 % of silver after deposition

Figure 2 shows normalized luminescence spectra, luminescence excitation spectra, and the optical density spectra of the sample with the silver content of 1.2 %. Excitation at 330 nm leads to the intense luminescence band with the maximum at the wavelengths of 648 nm. Excitation at 420 nm leads to the intense luminescence band with the maximum at the wavelengths of 492 nm. Hence, the red shift of the excitation wavelength leads to the blue shift of the luminescence band.

The luminescence excitation spectra are in accord with the absorption spectra, but they are very different for the luminescence recorded at wavelength 490 and 645 nm. So the highest luminescence intensity at the wavelength 645 nm was observed at 330 nm excitation wavelength, which coincides with the central peak in the absorption spectrum. The highest intensity of the luminescence at a wavelength 490 nm was observed upon excitation by radiation with 420 nm.

After thermal annealing (**Figure 3**) the structure in the absorption spectra disappeared almost completely. The luminescence bands lose their dependence on the excitation wavelength and stabilize at 507 nm with a shoulder at 634 nm. The luminescence excitation spectra related to luminescence at 510 and 640 nm are virtually identical and the expressed maxima observed before annealing disappear.

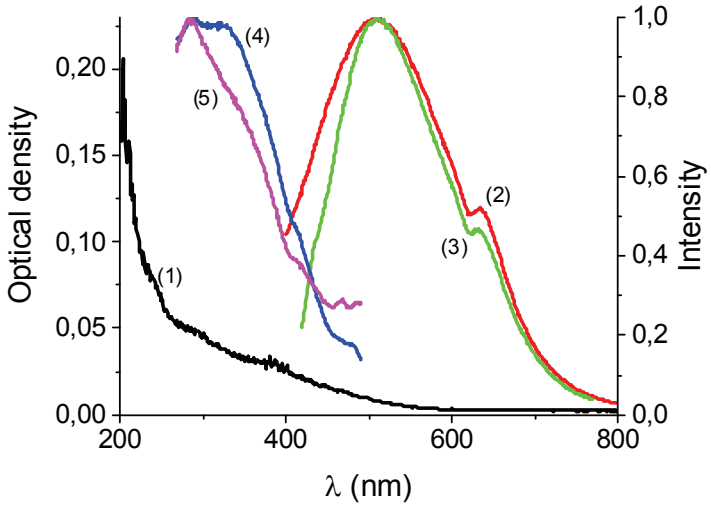

Figure 3 Optical density (1), luminescence at λ_{ex}=330 nm (2) and λ_{ex}=420 nm (3), and luminescence excitation at λ_{em}=510 nm (4) and λ_{em}=640 nm (5) spectra of thin SiO_2 films with 1.2 % of silver after thermal annealing

A slight redshift of the luminescence band was observed in the films with larger silver content. Simultaneously, luminescence intensity was reduced. Results are presents in **Table 1**. It is to be mentioned that the luminescence was undetectable for silver content of more than 2.2 % and for the film with 2.2 % of silver the luminescence was observed only after thermal annealing.

Table 1 Position and intensity of the short-wavelength luminescence peak at 420 nm excitation wavelength

Silver content	λ_{em} (nm)	Intensity (arb. un.)
1.2 %	493	74
1.2 % annealed	507	58
1.6 %	497	78
1.6 % annealed	512	51
2.2 % annealed	525	33

The presence of several peaks in the absorption and luminescence spectra of the films after deposition can be explained by strong dispersion of particle size, i.e. by the presence in the film of the two kinds of particles [6,10]. Presumably the smallest clusters have absorption bands at 3.75 eV and 4.17 eV which is typical for the clusters with number of atoms less than 12 [4]. These clusters have a long wavelength luminescense band with the exitation efficiency maximum at 3.75 eV. For larger spherical particles, one absorption band is observed [11]. In our case, the absorption band at 400 nm and the luminescence peak at about 500 nm correspond to such clusters.

When the silver content in the film rises the average particle size rises as well. This leads to the increase of the absorption of long wavelength peak with it slight redshift. Along with the rise of the average particle size, their concentration may increase too, that can lead to the increased nonradiative energy transfer between particles. In this case, the luminescence intensity decreases in the samples with higher concentration of silver.

Thermal annealing also leads to the formation of larger particles due to coalescence of the smallest clusters. As a result, the short-wavelength absorption bands and long-wave luminescence band disappear and the short-wave luminescence band shifts to the red. Reduction of the optical density of the samples may be due to the decrease of the clusters concentration in the film.

Similar results was obtained for silica films with gold inclusions. **Figure 4** shows absorption spectra of samples with different amout of gold after the deposition and after the thermal annealling at 500 °C for 1 hour. It should be noted that at 200 °C spectra were not changed. In contrast to the films with silver the samples with gold after deposition have a continuously rising absorption spectrum from the visible range to UV range. Thermal annealing leads to increasing of the optical density in the long-wavelength region and decreasing in the UV-region. The plasmon resonance of gold nanoparticles at 2-2.5 eV was observed in the annealed samples with gold concentration more than 3.2 %. The luminescence signal was not observed for this samples which is most likely due to the lower mobility of gold atoms and the formation of closely spaced particles like in samples with high concentration of silver.

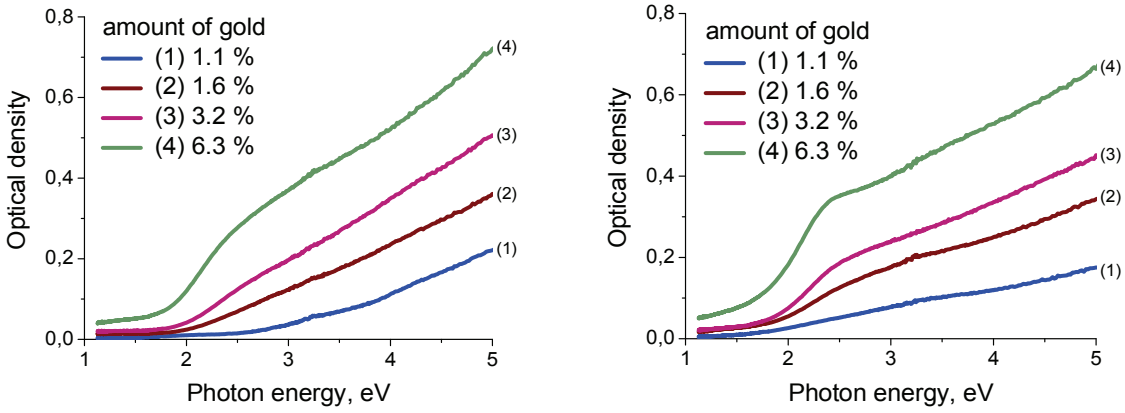

Figure 4 Optical density of thin SiO2 films with different amount of gold after the deposition (a) and after thermal annealing (b)

4. CONCLUSION

A simple method of producing of Ag and Au cluster in dielectric matrix was presented. For films with silver content less than 2.2 % the luminescence in visible range was observed. The process of self-organization of the films leads to a broad size distribution of metal particles with different absorption and luminescence properties. Thermal annealing leads to formation of lager particles (including plasmonic nanoparticles) with redshifted absorption and luminescence bands. The absence of the luminescence in the samples with a high

silver content and in all samples with gold content can be explained by non-radiative energy transfer between the particles.

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