Clustering in thin silver films upon heating

V A Kazakov¹, A G Razina¹, A V Smirnov¹ and A I Vasilev¹

¹Department of Applied Physics and Nanotechnology, The Chuvash State University, Cheboksary 428015, Russia

e-mail: cossac@mail.ru

Abstract. The kinetics of the formation of silver clusters Ag from nanoscale continuous films of Ag on the surface of silicate glass and composite structures from films of Ag with carbon in the form of a continuous film and individual nanoparticles upon annealing in air at temperatures up to 670K is investigated. In the course of the work, the dependences of the surface morphology of silver clusters and absorption spectra in the visible wavelength range were obtained by the methods of atomic force microscopy and optical spectrophotometry.

1. Introduction

Plasmon resonance effects on silver and gold clusters are considered as an effective method for increasing the efficiency of photodiodes and thin-film photocells, a mechanism for increasing the capture of light in the visible and near infrared. An active search for nanomaterials with effects and various ways of their integration into real photovoltaic systems (photodiodes and solar cells). There are works [1,2], in which the formation of clusters Au and Ag on a transparent conducting contact (TCO) a-Si: H p-i-n structures and in as a return contact for tandem photocells. Silver [3] and gold [4] nanoparticles are used in surface-enhanced Raman spectroscopy or surface-enhanced Raman scattering (SERS) spectroscopy for the analysis of carbon structures and various biomedical applications.

Thin solid silver films less than 20 nm thick when heated than 500 K break up into separate clusters having the effect of a localized surface plasmon resonance [5,6]. During the annealing process, as a result of diffusion processes and the action of surface tension forces, the film is rebuilt, the cohesion is disturbed, the film becomes islet. Superficial plasma absorption occurs in the extrusion spectra, where the center of the absorption band determines the size of the silver nanoparticles. For silver nanoparticles this band is in the range of 300 500 nm. Cluster sizes and optical properties depend on substrate composition, annealing parameters, film thickness [7].

Various methods can be used for the deposition of nanoparticles: deposition from colloidal solutions, lithographic methods, or self-assembly of particles on the surface. Self-assembly into clusters during the deposition of silver can occur either during synthesis during heating of the substrate or during subsequent heat treatment as a result of diffusion processes and the action of surface tension forces. The sizes of silver nanoparticles depend on the composition and temperature of the substrate, annealing parameters, and film thickness [7]. In self-assembly, silver is deposited by thermoresistive evaporation with heating the substrate during deposition [8] or subsequent annealing after deposition [5] or ionic sputtering [9] followed by annealing. With an increase in the film thickness, the size distribution of clusters depends on the thickness and can have both unimodal and bimodal character.
The distribution pattern depends on the annealing temperature, substrate thickness, and material. For example, according to the data of [5], the bimodal character of the distribution is obtained for films with a thickness of more than 10 nm. In addition, with an increase in temperature in a film of the same thickness, the size distribution can change, an increase in the size of clusters, or crystallites, to 300°C, then a decrease from 300°C to 350°C, and again grow at a temperature from 350°C to 450°C with a corresponding change in the area of the occupied substrate surface. In addition, clustering can depend on the crystalline state of the resulting silver film: single-crystal, polycrystalline, or amorphous film. After annealing and clustering, the films exhibit the SPR effect in the range from 400 to 500 nm, which is easily controlled by optical spectrophotometry. According to the microscopic data from [5], as a result, for thin films, clusters have the shape of flattened spheroids; with a greater thickness, the film is partially destroyed with the formation of cracks. Annealing can be carried out both in vacuum and in any atmosphere. In this work, annealing was carried out in air and low vacuum.

The aim of this work is to trace the relationship between the morphology of silver particles formed as a result of annealing and optical transmission spectra.

2. Methodology
Pure silver films were prepared by thermoresistive evaporation in vacuum at a pressure of 10⁻³ Pa. Films of silver with carbon were prepared by cathode sputtering. Cover glasses for a microscope (optical transparency from 315 nm) were used as a substrate. Cathodic sputtering of silver-carbon films was carried out from a graphite-silver target in argon plasma at a voltage of 2 kV, a current of ~30 mA, and a pressure in the working chamber of 9-11 Pa. Changing the silver content on the surface of a graphite target makes it possible to control the carbon content in the film from tens to several percent. After obtaining, the films were annealed in air with heating from 140°C to 400°C and holding at this temperature for 10 minutes and subsequent cooling down to 350°C.

The film study was carried out by optical spectrophotometry on a Lambda 25 spectrophotometer in the range 300-800 nm and by atomic-force microscopy on a Solver Next atom in a semi-contact mode with frame sizes ranging from 1x1 µm to 30x30 µm. The thickness of the films prior to annealing was verified by an optical method, by measuring the transmission at a wavelength of 633 nm using the method described in [10] and comparing it with atomic force microscopy data. The accuracy of the thickness determination is limited to 5 nm due to some variability in the film and the error in the transmission method.

3. Experimental results
Figure 1 shows the transmission spectra of silver films obtained by thermoresic evaporation. The characteristic feature of such spectra is that the maximum position of absorption depends on the thickness of the film. At thicknesses greater than 20 nm, the film becomes transparent after annealing, but absorption occurs over the entire wavelength range. At thicknesses of less than 20 nm, an absorption peak is observed, the position of which is determined by Mi theory and depends on the diameter of the particles [11]. Such absorption [11] is characteristic of particles between 5 and 100 nm, and if the thickness increases above 30 nm or decreases below 10 nm the resonant absorption pattern disappears, Figure. 1. The most pronounced resonance is in the area of thicknesses from 15 to 25 nm. At the same time, there is a shift in the maximum absorption position from 468 to 480 nm, accompanied by a change in the mean particle size from 30 to 40 nm, Figure 2 and Figure 3. When the thickness of the films is reduced, in addition to deflection of the maximum position, there is an increase in the absorption peak, which is due to the fact that at such thicknesses clustering is observed with the formation of clusters in the more forked range of sizes from 20 to 100 nm.

When the thickness increases above 30 nm, the temperature is not sufficient to form clusters, or when the film is destroyed, the particles are larger than 100 nm and come into contact with each other, thus blurring the resonance according to Mi’s theory or the film does not break down.
Figure 1. Transmission spectra of silver films after annealing at 400°C at various thicknesses.

Figure 2 and Figure 3 show the surface morphology of the formed silver films.

Figure 2. Surface morphology and height profile of a 15-20 nm silver film after annealing at 400°C.

Figure 3. Surface morphology of a 20-25 nm silver film after annealing at 400°C.

In Figure 4 shows the transmission spectra of films of silver with carbon (the carbon content in silver is less than 5% by volume). As can be seen from the figure, the position of the absorption
maximum does not depend on the film thickness and is 420 nm, Figure 4. The morphology of the surface for films less than 5 nm and 10-15 nm is shown in Figure 5 and Figure 6. As can be seen, the presence of carbon leads to a significant decrease in the particle size.

![Graph showing transmission spectra of silver films with different thicknesses.](image)

**Figure 4.** Transmission spectra of films of silver with carbon of different thicknesses.

Figure 5 shows the surface morphology of carbon-containing silver film.

![Surface morphology images.](image)

**Figure 5.** Surface morphology of a silver film with carbon less than 5 nm thick after annealing at 400°C.

**Figure 6.** Surface morphology of a 10-15 nm thick silver / carbon film after annealing at 400°C.
On average, the surface roughness and particle size is less than 5 nm with individual particles less than 20 nm and does not strongly depend on the film thickness. The obtained images of nanoparticles in AFM cannot be explained by the deposition of dust or dirt, since foreign particles are usually much larger, and the results themselves were repeated in several areas of the studied samples. It should be noted that the presence of carbon in some cases leads to an increase in the temperature at which clustering begins. The results obtained with the formation of small nanoparticles less than 5 nm can be interpreted as the initial stage of film crystallization and grain formation.

4. Conclusion
The presence of carbon in thin silver films leads to a shift in the absorption peak towards shorter wavelengths from 460-480 nm to 420 nm, which is accompanied by a decrease in the size of the resulting particles.

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