Investigation of condensation of small portions of Ag at thermal evaporation in vacuum

D.G. Gromov¹, E.A. Lebedev¹, A.I. Savitskiy¹, A.Yu. Trifonov², V.V. Rubcov¹, N.I. Borgardt¹, Ya.S. Grishina¹
¹National Research University of Electronic Technology, 124498, Russia, Moscow, Zelenograd, Bld. 5, Pas. 4806
²Scientific Research Institute of Physical Problems named after F.V. Lukin, 124460, Russia, Moscow, Zelenograd, Bld. 6, Pas. 4806

E-mail: gromadima@gmail.com

Abstract. The formation of arrays of Ag nanoparticles from vapor phase on the unheated surface of the amorphous carbon by sequential evaporation of the two portions with decreasing masses has been studied using scanning electron microscopy. The dependence of particle size and their surface density on the amount of evaporated Ag was detected. The precipitate after condensation is in an unstable state: thermal treatment at low temperatures (200-250ºC) leads to significant changes and the array goes into a metastable state. This is manifested in the absence of further changes after repeated heat treatment at the same temperature or 100°C higher. It is shown that sequential evaporation of the two portions of the silver with a decrease in mass leads to bimodal distribution of particle sizes in the array.

1. Introduction

The objects whose dimensions are in the nanometer range are of particular interest recently. Such systems are attracting the attention of researchers due to their unexpected properties which are different from bulk materials. One of the representatives of such objects are metal nanoparticles. For example, the surface-enhanced Raman scattering on the array of Ag and Au nanoparticles was observed [1,2]. The enhancement factor can be as much as $10^{10}$ to $10^{11}$, which means the technique may detect single molecules.

The method of vacuum thermal evaporation is one of the techniques of forming an array of nanoparticles. Its attractiveness lies in the fact that, as has been shown, it allows to control the average particle size of Ag and Au on the substrate surface [3-12].

Nevertheless, there is still a number of phenomena that occur when small physical amounts are condensing in vacuum, which is not fully clear.

In the present study, we investigated the formation of arrays of silver nanoclusters by sequential vacuum thermal evaporation of two small amounts of the substance. The purpose was to enhance the understanding of this phenomenon in order to form arrays of nanoparticles of a given size.
2. Experimental

The investigated arrays of silver clusters were formed by vacuum thermal evaporation and condensation of small weight portions of the material from molybdenum evaporator at a distance from the evaporator to the substrate 20 cm. Preliminary experiments were conducted to determine the thickness of the thicker layers of silver deposited from weight portions 100-500 mg. The thickness of the layers was measured by atomic force microscopy. Using the results of measurements the calibration curves of the film thickness as a function of the silver weight portions were constructed. To determine the weight portions required to form the metal film with a thickness of a few nanometers, the calibration curves were extrapolated to the corresponding region of small thicknesses. According to this data, the silver weight portion of 0.6 mg was necessary to form 1 nm thick metal film. It should be noted that during evaporation of such small amounts of silver the condensate immediately turns into an array of clusters, so the specified film thickness in the range of 1-10 nm are hypothetical i.e. obtained as a result of extrapolation.

Thermally oxidized Si (100) was used as a substrate. The substrates were pre-washed in a standard way in Caro solution H$_2$SO$_4$:H$_2$O$_2$ (1:1) and then washed with deionized water and dried in isopropyl alcohol vapor. Then 20 nm thick layer of amorphous carbon was sputtered on the substrate by magnetron sputtering. The number of samples corresponds to the number of operations: one sample was withdrawn for investigation after each operation.

To produce the samples two weight portions of silver were subsequently vaporized: 4.5 mg and 2.7 mg. After each deposition vacuum annealing at 2 30°C for 30 minutes was performed. It should be noted that the heavier weight portion was evaporated first.

The resulting samples were examined using dual beam electron-ion microscope FEI Helios NanoLab 650. Images of nanoscale silver clusters were obtained in the immersion mode in secondary electrons at an accelerating voltage of 2 keV and a current of 100 pA. Then, images were analyzed and for each of the obtained samples the distribution histograms of the number of particles according to their size were constructed. This allowed to define the average particle size of the resulting array, as well as to determine the number of particles per area unit.

Using this microscope by in-situ lift-out method [13] the cross-section samples of silver clusters deposited on the ~20 nm thick amorphous carbon film at various stages of formation, were prepared.

The resulting samples less than 50 nm thick were investigated in the transmission electron microscope Philips CM 30 with lanthanum hexaboride cathode at an accelerating voltage of 200 kV.

3. Results and discussion

Fig. 1 shows micrographs of the obtained arrays of clusters and cluster size distribution histogram. Condensate resulting from the first evaporation has "insular" structure where the "islands" have an elongated serpentine shape, but are completely separated and are tightly arranged relative to each other (Fig. 1). The length of some of them is 80 nm and the width generally ranges from 10 to 20 nm. In this structure, on an area of 1 μm$^2$ there are ~3000 of such particles, and the average spacing is about 4 nm. Measurements have shown that the electrical conductivity in such a layer is missing.
Figure 1. SEM image of the sample obtained by evaporation of 4.5 mg weight portions

Subsequent annealing at quite low temperature of 230°C leads to significant changes in the array: particles of various shapes form an array of clusters, the shape of which is close to the spherical (Fig. 2). Moreover the surface density of the particles markedly reduces. In this case this value is about 1500 pcs/μm², and the average distance between particles is ~8 nm. The diameter of the largest one of the clusters is ~40 nm whereas the smallest are in the range from 4 to 8 nm. Although somewhere one can find the smaller clusters whose diameter is estimated to be about 2 nm. The average size of the particles in the formed array is ~21 nm.

Figure 2. SEM image (a) and the cluster size distribution histogram of silver particles of the sample obtained by evaporation of 4.5 mg weight portions after annealing for 30 min at 230 °C (b)

Subsequent evaporation of the finer silver weight portion leads to the fact that there is a large amount of small particles on the surface of amorphous carbon. These particles are located between the clusters which were already formed at the previous step (Fig. 3). Thus, the density of particles on μm² now is ~3000 pcs. Furthermore, bimodal size distribution of the particles begins to emerge. Preferred diameters are 5 and 21 nm.
Figure 3. SEM image (a) and the cluster size distribution histogram of silver particles of the sample with consecutive evaporation of 4.5 and 2.7 mg weight portions (b)

Despite the fact that in general, after the annealing the total number of particles decreased (now 2000 pcs/μm²), which is directly related to their enlargement, the clusters size distribution still is bimodal (Fig. 4). Predominant sizes shift to the area of larger values: 11 and 24 nm after annealing versus 5 and 21 nm before this heat treatment, respectively.

Figure 4. SEM image (a) and the cluster size distribution histogram of silver particles of the sample with consecutive evaporation of 4.5 and 2.7 mg weight portions after annealing at 230 °C during 30 min (b)

Repeated heat treatment of already annealed samples was carried out at a higher temperature of 300°C. Additional annealing has not led to any noticeable changes: for the samples with both unimodal and bimodal distributions, the average particle size and surface density of the particles remained unchanged.

Thus, investigation of the samples after sequential evaporation of the two small portions of silver when the second weight portion is smaller than the first, demonstrate the following features:
1. The initial state of silver condensate is extremely unstable. Insignificant thermal impact causes a change in it and leads the system to a state where clusters are more separated from each other;
2. At repeated evaporation, the formation of smaller particles occurs both between and over previously formed clusters;
3. After the second evaporation bimodal size distribution of the particles is observed;
4. Repeated thermal impact onto previously annealed array of clusters at even higher temperatures does not lead to any noticeable change in it.
Upon substance evaporation from a point source in vacuum, evaporated atoms retain high temperature, because their trajectories diverge, and the atomic concentration is small. This makes the exchange of energy between them unlikely. In case of silver evaporation, we expect that the temperature of the vaporized atoms corresponds to the evaporation temperature of silver ~1300 K. Therefore, during the condensation we actually deal with the impact of hot steam onto the deposition surface. For this reason, the dependence of the size of nanoparticles on quantity of evaporated substance is observed: the larger silver weight portion, the more intensive steam action on the surface, and as a consequence, larger the average size of the nanoparticles in the array, as it has been previously demonstrated in a number of papers [3,5,11,12].

When we first vaporize a larger weight portion and larger clusters are formed, and then re-evaporate a smaller number of substance, this smaller amount of substance is not able to heat larger clusters to a high enough temperature. Therefore, we observe features 2) and 3): smaller clusters are formed between the previously formed large clusters and over them, and as a result, there are two predominant particle sizes.

The cross-sectional images obtained by transmission electron microscope allowed to determine the height of the nanoparticles (Fig. 5).

![TEM cross-sectional images of the samples obtained by evaporation of 4.5 mg weight portions before annealing (a) and after annealing for 30 min at 230 °C (b)](image)

Figure 5. TEM cross-sectional images of the samples obtained by evaporation of 4.5 mg weight portions before annealing (a) and after annealing for 30 min at 230 °C (b)

Using electron-microscopic images of silver clusters shown in Fig. 1 and 2, a comparative evaluation of the amount of substance in the array of nanoparticles after deposition and after heat treatment was carried out. Because the shape of the particles obtained after deposition is complex and not spherical, the volume of silver was calculated as the product of the surface area occupied by silver particles to their height (Fig. 5a). For the annealed sample, the particle shape is close to spherical, but nevertheless there are some deviations (Fig. 5b). Given these nuances, the estimate calculations showed that the mass of silver was ~ 3.2*10^{-14} g/μm² and ~ 4.6*10^{-14} g/μm² for the initial and annealed samples, respectively. This evaluation showed that after annealing the total amount of matter in an array of nanoparticles is larger than before annealing. This, of course, in no way means that there is a violation of the mass conservation law, or large calculation error, because the calculations were carried out repeatedly and in various samples. We are more inclined to think that this is due to the resolving power of the electron-ion microscope we used, and we just do not see on the original sample any part of the deposited silver, which is not in the form of clusters. Obviously, this part of the material is the cause of feature 1): when the initial condensate is in an unstable state and a small thermal impact leads system into a more stable state. This explains why the re-annealing does not lead to any change (feature 4).
4. Conclusions

Thus, our investigation of condensation of small amounts of Ag during thermal evaporation in vacuum showed that Ag condensate after the deposition is in an unstable state, and a relatively small thermal impact leads to the formation of an array of separated from each other clusters. It is important to note that, despite the small size of the clusters in the array, and consequently, the high surface energy of the system, this state is sufficiently stable. One would expect that repeated annealing of such a system would lead to coalescence into larger particles, but after repeated annealing no changes were observed. Moreover, second deposition of smaller weight portion of silver allows to form new particles with another characteristic size without noticeable enlargement of existing particles.

Acknowledgments

This work was financially supported by the Ministry of Education and Science of the Russian Federation within the state program "Organization of research" (code 486). The equipment of the center for collective use "Diagnosis and modification of microstructures and nano-objects" was used in this work.

References

[1] Sanles-Sobrido M et al 2009 Journal of the American Chemical Society 131 7 pp 2699-2705
[2] Shen C et al 2008 Chemistry of Materials 20 22 pp 6939-6944
[3] Hamilton J F et al 1973 Thin Solid Films 16 pp 49-63
[4] Goldby I M et al 1996 Appl. Phys. 69 19 pp 2819-2821
[5] Schmidt A A et al 1996 Surf. Sci. 349 3 pp 301-316
[6] Carrey J et al 2002 Surf. Sci. 504 pp 75-82
[7] Gatel C et al 2006 Surf. Sci. 600 pp 2650-2662
[8] Sui M et al 2013 Nanoscale Res. Lett. 8 pp 525
[9] Gromov D G et al 2013 Physics of the Solid State 55 3 pp 619-623
[10] Belov A N et al 2014 Calphad 44 pp 138-141
[11] Gromov D G et al 2015 Appl. Phys 118 4 pp 1297-1303
[12] Gromov D G et al 2015 Physics of the Solid State 57 pp 173-180
[13] Giannuzzi L A et al 1998 Microscopy Research and Technique 41 4 pp 285-290