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Aggregation kinetics of silver nanoparticles ensembles in sub-percolating state and its impact on memristive behaviour

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Abstract. The effect of coalescence and aggregation processes on the memristive properties of silver nanoparticle assemblies has been investigated. Nanoparticles were prepared by vacuum-thermal evaporation on silicon substrates with gold electrodes and quartz glasses for morphological control. The structure of the samples and size distribution of nanoparticles were studied using scanning electron microscopy (SEM) and UV-visible spectroscopy. Memristive properties were estimated using cyclic voltammetry. Due to Ostwald ripening and an increase in average nanoparticle size, the operating voltage required to switch the system into the memristive state decreased, while the conductivity dynamics changed. These findings are useful for ensuring the stability of memristive devices based on silver nanoparticle assemblies.

Keywords: coalescence, silver nanoparticles, surface plasmon resonance, memristive dynamics, surface diffusion

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Материалы конференции
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Кинетика агрегации ансамблей наночастиц серебра в субперколяционном состоянии и ее влияние на мемристивное поведение

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Аннотация. Исследуется влияние процессов коалесценции и агрегации на мемристивные свойства ансамблей наночастиц серебра. Системы наночастиц получены методом вакуум-термического испарения на кремниевые подложки с золотыми электродами и на кварцевые стекла для контроля морфологии. Морфологию частиц анализировали методами РЭМ и УФ-видимой спектроскопии, а мемристивные свойства с помощью циклической вольтамперометрии. Вследствие оствальдовского созревания и увеличения среднего размера наночастиц, снижается рабочее напряжение, необходимое для переключения системы в мемристивное состояние, при этом изменяется

динамика проводимости. Приведенные оценки полезны для обеспечения стабильности работы мемристивных устройств на основе ансамблей наночастиц серебра.

Ключевые слова: коалесценция, наночастицы серебра, поверхностный плазмонный резонанс, мемристивная динамика, поверхностная диффузия

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Introduction

Silver nanoparticles and nanowires are promising materials for the development of neuromorphic computing devices. Their main advantages include (1) the ability to scale, (2) the technological simplicity of application to various substrates, and (3) the presence of complex nonlinear dynamic characteristics [1–3]. In such systems, a self-organizing network of discrete memristive elements is formed, separated by nanometer gaps, where each nanoobject functions as an independent memristor [4]. The applied electric field induces the formation of atomically thin conductive filaments (filaments) between the nanoparticles, which is clearly detected by the characteristic hysteresis loops on the volt-ampere characteristics [5–7].

Experimental studies [8, 9] confirm the prospects of using nanoscale silver structures for processing time signals and solving predictive tasks. The main advantage of such systems is the implementation of the principle of reservoir computing, where learning affects only the output connections, while the internal network of nanoelements retains the same random configuration of connections. However, the key limitation of this technology is the temporary instability of silver nanostructures caused by the processes of coalescence (gradual particle enlargement) and aggregation (cluster formation), which leads to degradation of the original network architecture and deterioration of its functional characteristics. This work presents the results of a study of the temporal dynamics and the effect of coalescence and aggregation processes in an ensemble of silver nanoparticles on the memristive properties. It has been revealed that, in order to practically apply such systems, it is necessary to address the issue of nanoparticle stabilization, which can be accomplished by either modifying the surface of silver structures or by using additional materials that have increased resistance to structural changes [10].

Materials and Methods

Experimental samples were obtained by vacuum thermal deposition of silver onto a thermally oxidized silicon substrate, with a gap of either 2 or 20 microns (depending on the weight of the sample), between two gold electrodes. Silver weights of 0.62 mg, 1.18 mg, 3.34 mg, 4.71 mg, 6.06 mg, 10.05 mg, 15.06 mg, 17.2 mg, and 20.05 mg were selected for deposition. Simultaneously, deposition also occurred on quartz glass, for further investigation into the temporal dynamics of structural changes using optical spectroscopy (UV-VIS spectrometer, Thermo Fisher Scientific, US). After deposition, all samples underwent vacuum annealing at 230°C for 30 minutes.

The geometric dimensions of the nanoparticles were estimated from the SEM images obtained using the FEI Helios NanoLab 650i DualBeam electron-ion scanning microscope. To calculate the average values of nanoparticle diameters and distances between them, a Python program was developed, which uses the Delaunay method for distance calculation. Voltammograms were obtained for experimental samples using a probe station (Cascade Microtech Summit, US) and a B1500A parametric analyzer (Keysight, US). All samples were stored in a nitrogen-dry storage cabinet at 23 ± 2 °C and 14 ± 2% humidity.

Results and Discussion

Figure 1 shows the results obtained for the experimental samples in their original form. For samples with an evaporated silver mass above 10 mg, the shape of the nanoparticles became distinct from spherical and represented arbitrarily oriented cluster-like elements. This was confirmed by both SEM images and the position of the surface plasmon resonance peak on optical spectra. The distance between nanoparticles was comparable to their diameter. Over time, coalescence and diffusion led to a characteristic Ostwald ripening process, accompanied by an increase in nanoparticle size due to the system's tendency to minimize surface energy.

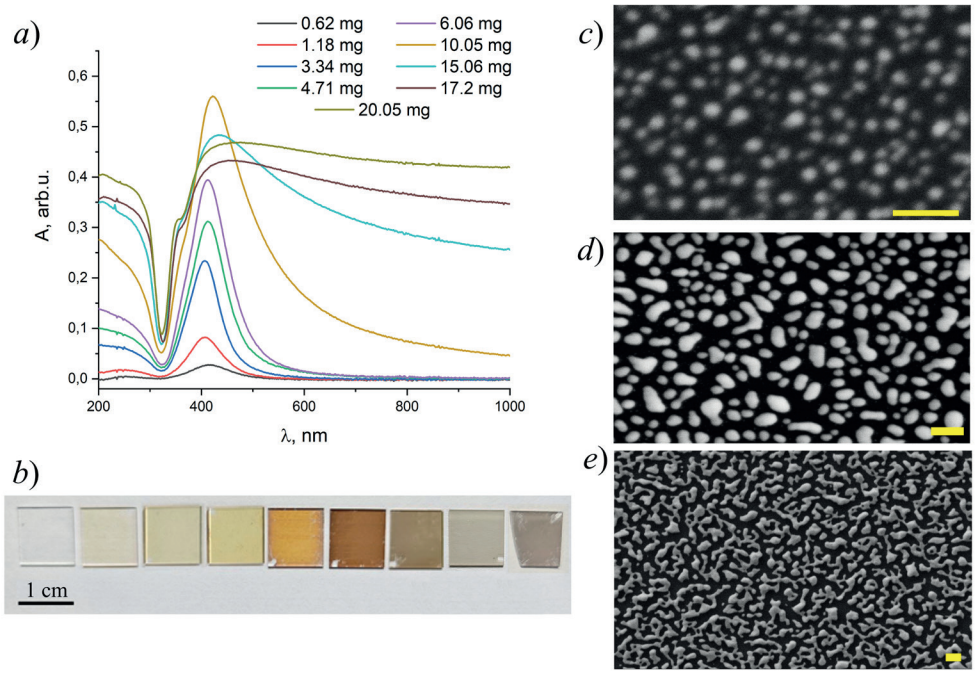

Fig. 1. Optical spectra of annealed experimental samples (*a*) and their photo (*b*) on quartz glass (mass increase from 0.62 mg to 20.05 mg from left to right), (*c*) – (*e*) SEM images for samples 3.34 mg, 10.05 mg and 20.05 mg respectively (from top to bottom). Scale bar for all SEM images is 100 nm

Figure 2 allows to estimate the rate of morphological change in nanoparticle ensembles over time based on the dynamics of the redshift of the absorption peak and its broadening. The results obtained confirm the general trend of nanoparticle enlargement over time. It is worth noting that for large silver sample masses, the rate of change in the geometric dimensions of nanoparticles is lower (for samples weighing 17.2 mg and 20.05 mg, the displacement was in the range of

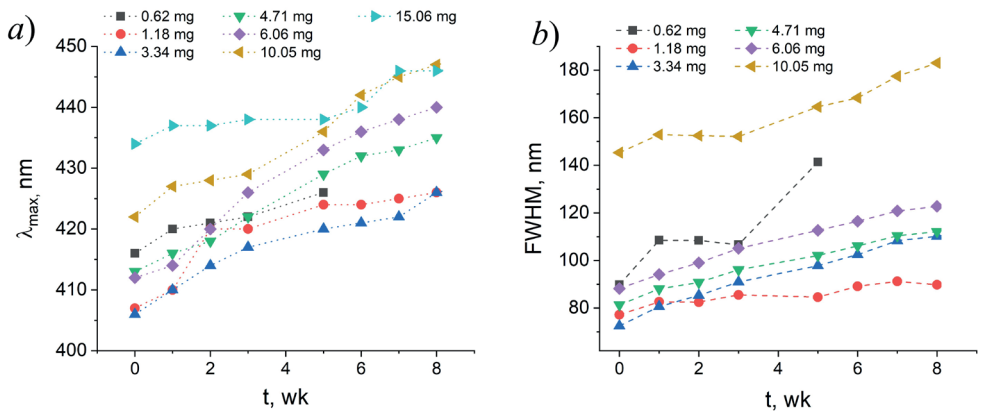

Fig. 2. Shift of the absorption maximum (*a*) and its broadening (*b*) for different masses of silver bulk

up to 5 nm during the presented time), which can be characterized as a more kinetically and thermodynamically stable structure due to a reduction in the surface area to volume ratio, which leads to a decrease in the driving force for minimizing surface energy. A more stable configuration is an important parameter in the development of architecture for practical applications.

Figure 3 also shows the unimodal diameter distribution obtained from analyzing the SEM image in the initial case, and the bimodal distribution after 2 months.

The decrease in the average diameter is explained by the appearance of many small nanoparticles in close proximity to large "nuclei", which is typical of Ostwald ripening. This result was observed in all samples up to a mass of 10 mg, as it reproduced the known mechanism of coalescence, including the stages of formation of a "neck" between adjacent nanoparticles, followed by "spherification" and gradual relaxation towards a thermodynamically stable structure. For elongated silver clusters with larger masses, it will take considerably longer to reach a spherical shape, as they initially have a larger surface area.

After the "molding" process, all experimental samples of silver nanoparticles exhibited characteristic memristive behavior and a hysteresis loop in their voltammograms. The less spherical the nanoparticles were in the ensemble, the lower the value of the switching voltage required to

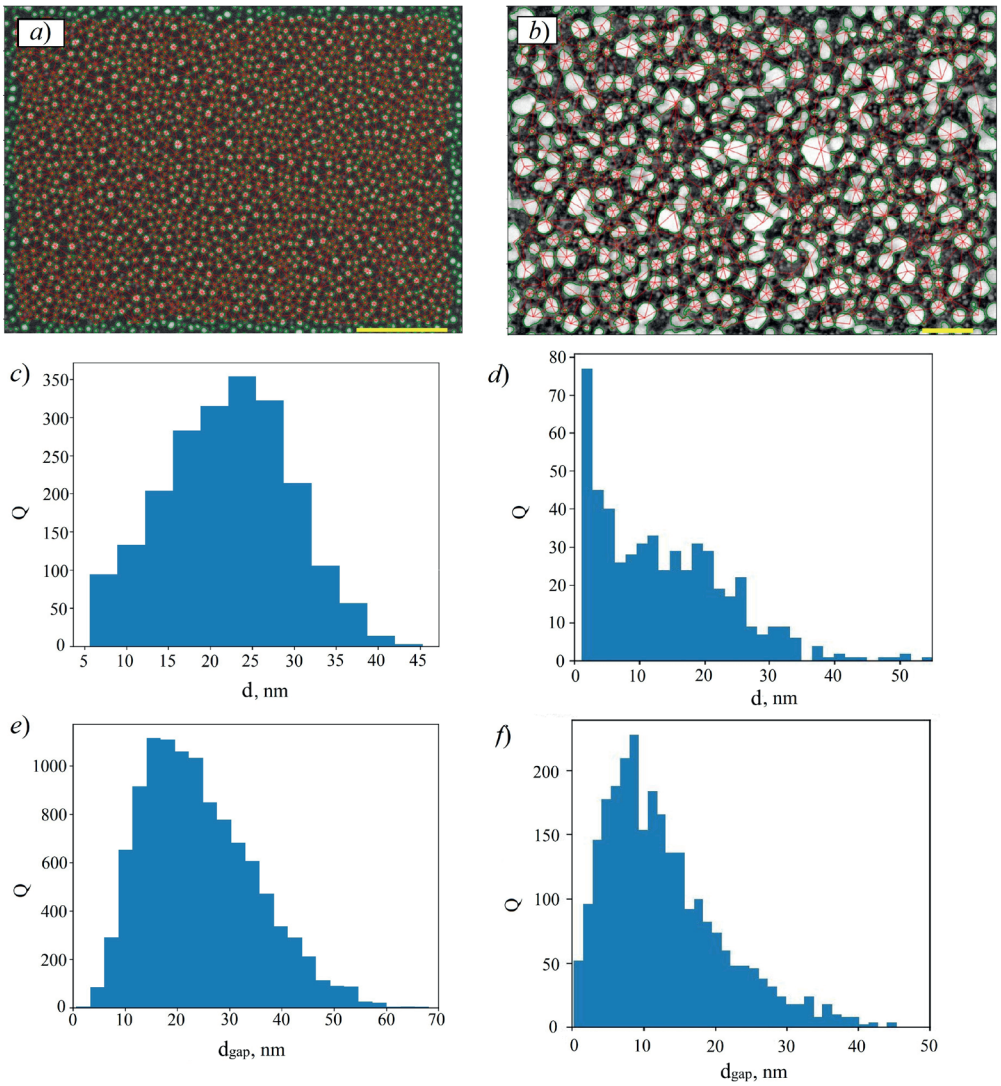

Fig. 3. The result of processing SEM images in the program for a 4.71 mg sample: (*a*) the initial ensemble, (*b*) after 2 months, (*c*) and (*d*) histograms of the diameter (d) size distribution via number of particles (Q), respectively, and (*e*) and (*f*) - a histogram for the gaps sizes (d_{gap}) between nanoparticles. The scale bar on the SEM is 200 nm, the boundaries of the nanoparticles are outlined in green, and the distances taken into account are in red

transition to the conductive state. This behavior can be explained by the presence of areas with higher electric field strength near elongated protrusions on the nanoparticles, which facilitate the formation of conductive pathways (filaments) in a more directed manner.

Over time, a gradual decrease in the "ON" voltage was observed, which is associated with the gradual formation of areas of large clusters, remaining after the incomplete destruction of the percolation cluster by voltages of different polarities. For small spherical nanoparticles, this is also due to their gradual enlargement. There was also an asymmetry of the hysteresis curve for small nanoparticles (Fig. 4) and a decrease in the number of intermediate "memory" states for large ones (a more rectangular loop shape).

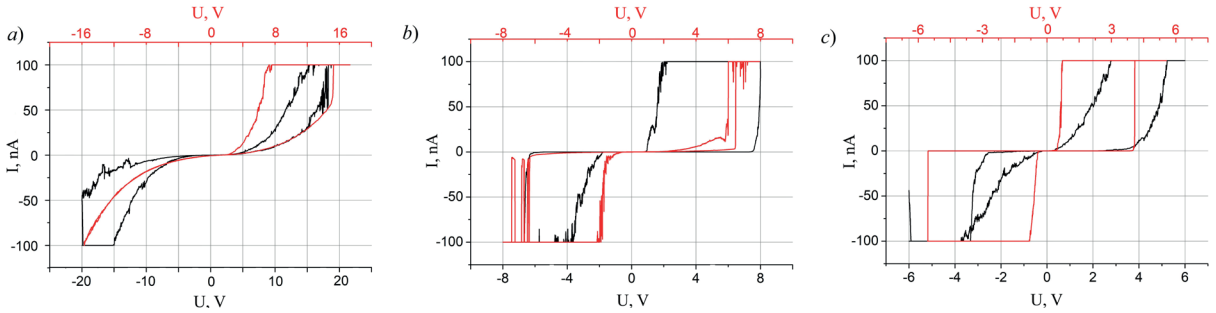

Fig. 4. Voltammograms for samples of 4.71 mg silver (*a*), 10.05 mg (*b*) and 17.2 mg (*c*). The curves for the initial state are highlighted in black, and after 8 weeks – in red

Conclusion

The paper presents the results of a study on the coalescence dynamics of ensembles of silver nanoparticles with various sizes (ranging from 5 nm to 200 nm, for evaporation masses of 0.62 mg and 20.05 mg, respectively), and its impact on the memristive properties. The observed slow relaxation of these systems towards a thermodynamically stable structure leads to changes in the morphology and geometric dimensions of the nanoparticles, which affects the control switching voltage and the operating characteristics. The smaller the nanoparticles are, the greater the ratio of their surface area to their volume, and therefore, the higher the mobility of surface atoms. Therefore, nanoparticles require external conditions for limiting coalescence to stabilize the system and reduce the frequency of tuning output connections.

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