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Memristive behavior of the system comprising Ag nanoparticles coated by HfO_x layer

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Abstract. Memristive systems promise energy-efficient computing and accelerated machine learning tasks by enabling simultaneous storage and processing of information within single device architecture. The research focuses on the analysis of percolation memristive systems based on silver nanoparticles in a hafnium oxide dielectric matrix. Conductivity in the nanoparticle network is achieved through atomic filament connections between adjacent particles. The systems exhibit hysteresis in I-V curves when a sawtooth electric voltage is applied. The hafnium oxide coating was used to provide sample stability and also to reduce the formation voltage due to the proposed additional mechanism of valence change during subsequent filament formation.

Keywords: silver nanoparticles, filament, percolation, neuromorphic computing

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Мемристивная динамика системы наночастиц серебра с покрытием HfO_x

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Аннотация. Исследование сосредоточено на анализе перколяционных мемристивных систем на основе наночастиц серебра в диэлектрической матрице оксида гафния, где проводимость достигается за счет атомных связей между частицами. Системы демонстрируют гистерезис на кривых I-V при приложении пилообразного электрического напряжения. Покрытие оксидом гафния используется для стабилизации образца и снижения напряжения формирования.

Ключевые слова: серебряные наночастицы, филамент, перколяция, нейроморфные вычисления

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Introduction

Memristive systems offer the potential for energy-efficient computing and accelerated machine learning thanks to their unique ability to store and process information simultaneously within a single device architecture [1]. In some studies, memristive networks of nanoparticles (NPs) near the percolation threshold are investigated for their potential to exhibit brain-like activity related to critical dynamics [2, 3]. The percolation threshold refers to the point at which NPs begin to connect and form a continuous network. The functional synaptic plasticity, nonlinear dynamics, and decaying memory inherent in these systems make them suitable for neuromorphic computing [4]. The potential of metal oxide-based resistive random access memory (RRAM) offers new opportunities for creating more efficient memory devices due to its low power consumption, 3D integration, and compatibility with CMOS technology [5]. HfO_2, in particular, is a promising dielectric material for RRAM, with excellent resistive switching properties, including a large resistive window, a low set voltage, and good durability [6]. Previously, the authors studied percolation arrays of pure silver and gold nanoparticles and proposed the phase-field model qualitatively reproduce the memristive dynamics in such systems [7, 8]. In this study, we present the results of an investigation into the memristive properties of a percolative network consisting of silver nanoparticles coated with a dielectric matrix of HfO_x.

Materials and Methods

To study the electrical properties of Ag nanoparticle ensembles covered by HfO_x layer, planar structures of thermally oxidized silicon substrates (SiO_2 – 100 nm) were used. These structures featured two opposing gold electrodes arranged in an interdigital pattern, with pins measuring 12 μm in length and 10 μm in width, separated by a 2 μm gap (Fig. 1, *a*). Within this gap, an array of silver NPs was positioned using the vacuum thermal evaporation method. The size and density of these NPs were finely tuned by controlling the amount of material evaporated (Ag ~ 4.7 mg). After Ag deposition, a few samples were subjected to further vacuum annealing (230 °C). Next, a layer of hafnium oxide (layer thickness – 15 nm) was deposited using the atomic layer deposition method (process temperature 290 °C). As a source of Hf the organometallic precursor, TDMAH($Hf(N(CH_3)_2)_4$), was used. The morphology of the experimental samples was studied using an FEI Helios NanoLab 650i DualBeam electron-ion scanning microscope. The results of cyclic voltammetry were obtained on a Cascade Summit 2000 semi-automatic probe station at room temperature in air.

Results and Discussion

The main difference between samples (Fig. 1, *b*, *c*) lies in the main size of the particles in the array and the nature of particle size distribution. When the array is additionally annealed in a vacuum, the distribution of Ag particle sizes becomes more uniform, indicating that the nanoparticles have less variation in size around the average one. Also annealing makes the nanoparticles more spherical.

The memristive behavior is demonstrated using cyclic voltammetry (Fig. 2). The I-V curves show a reversible change in resistance between high and low states, accompanied by a notable increase in system conductance. When a sufficient potential difference is applied to the system (4–6 V for non-annealed Ag array, and 12–15 V for annealed), Ag atom electromigration is induced, that causes the formation of multiple local contacts between nanoparticles.

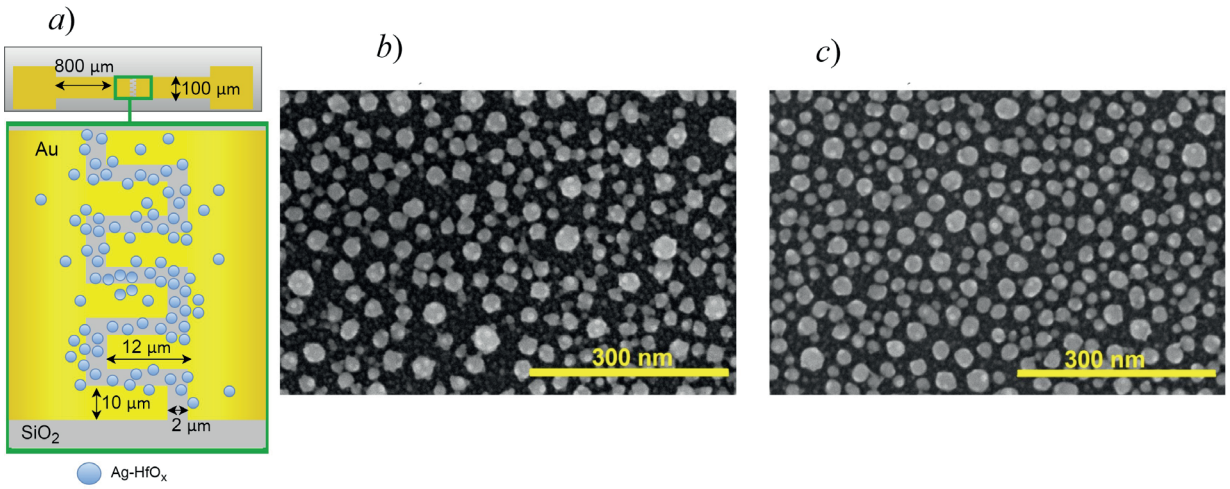

Fig. 1. Schematic view of experimental structure (*a*) with enlarged insert of gap between electrodes, and SEM images of the non-annealed (*b*) and annealed (*c*) array of Ag nanoparticles coated by HfO_x

Over time, this process forms a percolation cluster between the electrodes. This cluster, however, is apparently unstable and can dynamically rearrange with voltage variations. When the voltage is removed, the system gradually reverts back to its original state that is related to filament dissolution [7]. Comparing the authors' previous findings for pure nanoparticles (Fig. 3), we found that the switching dynamics persisted after the addition of an insulating matrix.

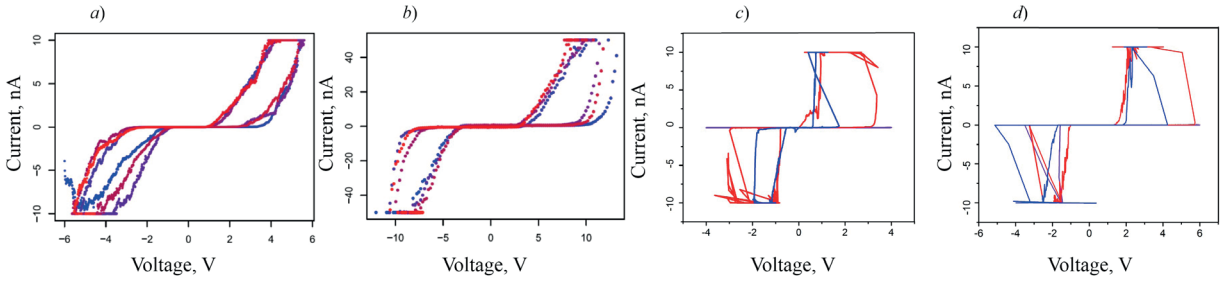

Fig. 2. Cyclic voltammograms for non-annealed (*a*) and annealed (*b*) Ag ensembles with coating, and data for the same structures, respectively, (*c*) and (*d*), measured 1 year later

Results show that in assemblies of non-annealed Ag nanoparticles, switching to the memristive state occurs at lower voltages compared to arrays of annealed ones. It is assumed that this is due to the nanoparticles shape in the gap, since the presence of “tips” on particles without annealing better promotes the growth of filaments due to locally higher field strength.

The temporal stability of the samples coated with hafnium oxide was confirmed a year later by repeating similar measurements of cyclic voltammetry (Fig. 2, *c*, *d*). Resistive switching is observed in the first case at voltages of approximately 4 V, while for annealed sample it occurred around 6 V. Despite the presence of fluctuations in the graphs, the structures replicate the memristive behavior. The results make the use of hafnium oxide coating suitable for increasing the stability of structures, however further development of the model is required to describe the internal dynamics in the Ag-HfO_x system.

To compare the temporal stability, the results for samples with pure Ag NPs array without coating are presented below.

As Figure 3 shows, the operating voltage for the silver NPs array, both without and with annealing, is lower compared to that for the coated samples (3 V and 8 V, respectively). In this case, the dynamics are similar to samples coated with hafnium oxide, however, over time, the operating voltage required for transition to the memristive state increases. It is worth noting that the width of the hysteresis “loop” in the case of pure nanoparticles expands that is associated with

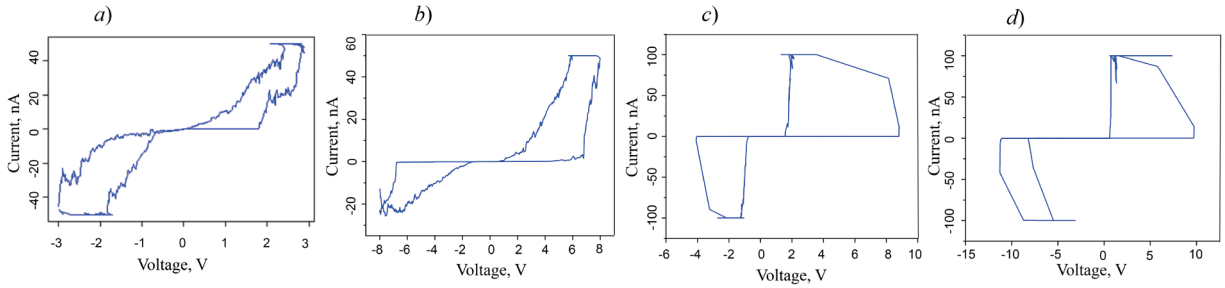

Fig. 3. Voltammograms for non-annealed (*a*) and annealed (*b*) Ag ensembles without coating, and data for the same structures, respectively, (*c*) and (*d*), measured 1 year later

the process in which neighboring NPs partially consolidated into larger clusters with increasing the distances between them. This assumption is based on the SEM results presented in Figure 4.

As can be seen for the sample of pure silver, the nanoparticles are formed into significantly larger "droplets" with sizes up to 100 nm compared to that with HfO_x layer, with higher distances between them; the coated sample is characterized by greater retention of particle morphology. Although such have been widely known [9], the results obtained require further in-depth research, since the effect of nanoparticle coalescence may force the percolation threshold affecting the conditions for a conductive path to form between the two electrodes.

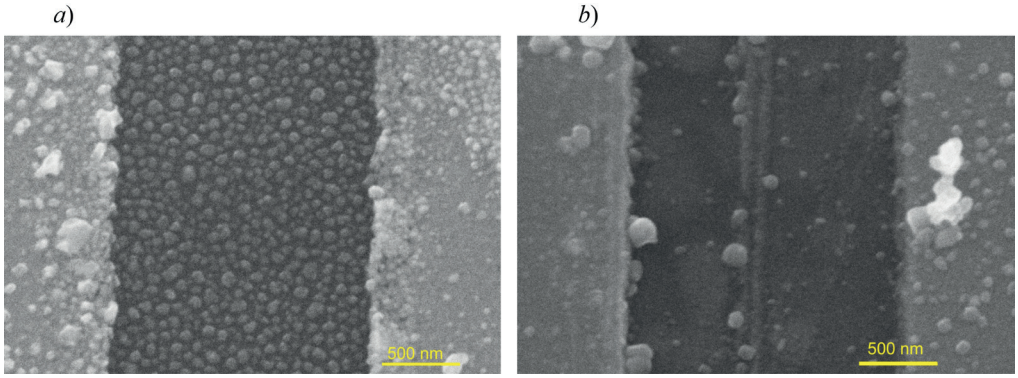

Fig. 4. SEM images of the non-annealed array of Ag nanoparticles in the gap without (*a*) and coated by HfO_x (*b*) measured 1 year later

Conclusion

HfO_x showed no negative effect on the memristive behavior of the nanoparticle ensemble and was used both to isolate the structure from environmental influences and prevent changes in the granulometric parameters of nanoparticles by stabilizing the array with a matrix coating (positive dynamics – decrease in operating voltage by ~1.5 times after a year). Studies of network dynamics in a matrix are essential, as encapsulating the network in an insulating medium is often an unavoidable step in the integration of electronic devices.

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