Conductivity switching of labyrinth metal films at the percolation threshold

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Abstract. Electrical properties of silver, gold and copper films at the percolation threshold were investigated experimentally. A convenient method to obtain films at the percolation threshold that consists of two phases: deposition of metal in vacuum on a dielectric substrate and subsequent thermal annealing has been developed. The metallic films produced in this way exist in two different states: a low-conductivity state and a high-conductivity state. The films can be switched between these states by the applied voltage with hysteresis of current-voltage characteristic curves. The conductivity difference between the states reaches seven orders of magnitude. The switching threshold voltage depends on the annealing time. The switching times differ considerably for different metals. They were 200 ns for silver, 2 µs for gold, and 60 µs for copper. A plausible explanation of the switching mechanism based on the voltage induced fine mechanical deformations is suggested and discussed.

1. Introduction

The thin metallic labyrinth films at the percolation threshold attract interest by virtue of their unique characteristic. The labyrinth film at the percolation threshold consists of separate nanoparticles that are at the edge to merge, i.e. to form an unbroken structure. These films conductivity depends on the applied voltage and the previous states in the recent past, i.e. the current-voltage (I-V) characteristic has hysteresis and the structure exists in two different states: a low-conductivity state and a high-conductivity state. The reason for this unusual behavior is an extremely small distance between nanoparticles in the film [1,2]. The threshold voltage depends on the distance between nanoparticles. The results of this study can be used in the future development of novel memory devices [3,4].

The conductivity switching behavior of silver films at the percolation threshold was observed and explained by the electric field induced film structure changes in [5]. According to this explanation at the voltages that exceed the threshold value the bridges between nanoparticles are formed. Thus a continuous metallic path between electrodes establishes and conductivity increases.

Because it is hard to control the structure of the film during the physical vapor deposition in high vacuum and it is almost impossible to catch the percolation transition while monitoring the film conductivity [6,7] another technique for obtaining the films at the percolation threshold has to be employed. Previously it was demonstrated that thermal annealing of conductive films is a convenient way to obtain silver nanostructure at the percolation threshold [8]. Thermal annealing foster the formation of island film with separated spheroidal nanoparticles [9-11]. In this process the height of
nanoparticles and distance between them are rising and that leads to the formation of the film at the percolation threshold. It was also shown that the process of thermal annealing is well controlled.

2. Preparation
The preparation of the structure at the percolation threshold occurs in two phases. The first phase is the physical vapor deposition of metals on an isolating support. It was performed in the vacuum chamber PVD-75 (Kurt J. Lesker) at the residual pressure of ~10^{-7} Torr. The substrate was kept at the room temperature. Three types of metal (silver, gold and copper) were deposited on the sapphire substrates with pre-applied metallic electrodes. The size of electrodes was 5 mm, the distance between electrodes was 3 mm. The deposition rate was monitored by using a quartz microbalance. The average deposition rate was 0.5 Å/s for all metals. The films growth occurs via the of Volmer-Weber growth mode. The deposition process starts with the formation of separate nanoparticles. Discontinuous films have a very high resistance. Its conductivity is due to tunneling of electrons between particles or through electronic levels of the substrate (traps, impurity levels, etc.) depending on the distance between the particles [5]. With the material accumulation the particles start to coalescence (merge) and finally create a continuous highly conductive structure.

![Figure 1](image1.png)  
**Figure 1.** Evolution of the metal film resistances in the course of the deposition process as measured in situ by quartz crystal microbalance. The amount of the deposited material is expressed in terms of the equivalent thickness of a homogeneous film.

![Figure 2](image2.png)  
**Figure 2.** Evolution of the silver film resistance in the course of the thermal annealing. Annealing was immediately terminated as soon as the percolation threshold manifested by the steep rise of the resistivity was reached.

We controlled the deposited film conductivity by the picoammeter Keithley 6487. The deposition was stopped at the moment when the film resistance drops to 100 kΩ. The film resistance continued decreasing for some time after the flap closing.

The dependence of the film resistance on the film mass thickness is presented in figure 1. With the increasing amount of the deposited material expressed in the figure 1 in terms of the films mass thickness resistance is reducing. At the moment when the deposition process was stopped the films of different materials reached different mass thicknesses: 10 nm for silver and 6 nm for gold and copper. With these parameters, we obtained conductive films with the labyrinth structure.

Further, to break down the continuous metal paths that lead from one electrode to another and to obtain separate nanoparticles with small distances between them thermal annealing was used. The silver and gold films are noble metals, so the heating is carried out both in the air and in the vacuum, but for the copper films it could be done only in vacuum, because copper has strong oxidation in the
air. For silver the annealing temperature is 90-120 °C, while for gold it is 160-200 °C and for copper it is 180-220 °C. The process of thermal annealing was controlled by picoammeter Keithley 6487. The measured resistance of the silver film is presented in figure 2. The thermal annealing process was stopped when the conductivity dropped sharply, and the film resistance exceeded 100 GΩ. The time variation of the conductivity during the annealing process was similar for all studied metals. Firstly, the conductivity reduces slowly. The reason for that is further narrowing of the narrowest parts of the labyrinth film. Then, conductivity decreases sharply because the narrowest parts were finally broken. The threshold voltage (the voltage of switching) depends on the time of annealing after this sharp increase of the film resistance.

![Figure 3. SEM images of silver (a) and gold (b) films at the percolation threshold and AFM image of copper film (c).](image)

Figure 3 shows SEM and AFM images of the metal films at the percolation threshold. The structures of films look like labyrinths. In the gold film separated nanoparticles are more elongated, and in the silver and the copper film nanoparticles have more rounded shape.

3. Results
The films at the percolation threshold exist in two different states. The first state is the low-conductivity state which is obtained after the two-step preparation procedure described above. The film is preserved in this state provided the applied voltage is less than a definite threshold value. When
the applied voltage exceeds the threshold value the films pass to a high-conductivity state. After the switching the film stays in the high-conductivity state at lower voltages as well. After the voltage removal the films pass to the low-conductivity state. Hence, the hysteresis of conductivity is observed. Figure 4 plots the corresponding I-V characteristics.

The silver film differs from gold and copper films because switching of silver films is very sharp (figure 4a). The threshold voltage for silver films equals to 8 V. Below this voltage the film remains in the low-conductivity state ($R \sim 10^{12} \Omega$). At the voltage of 8 V the film conductivity rises sharply and the film passes to a high-conductivity state ($R \sim 10^5 \Omega$). The difference of conductivities in two states reaches seven orders of magnitude. The film remains in the high-conductivity state even at the voltages that are less than the threshold voltage and returns to the low-conductivity state only when the voltage drops almost to zero. The voltage cycling leads to the slight reduction of the threshold voltage.

Similar behavior was observed in copper and gold films although the transition between the states in these metals is less sharp. The corresponding I-V characteristics are presented in figure 4 (b) and (c).

![Figure 4. Current-Voltage characteristics of silver(a), gold(b) and copper(c) films at the percolation threshold.](image_url)
The switching times were measured by the oscilloscope Rigol DS4052 that possesses the bandwidth of 500 MHz. Figure 5 shows how fast the films pass to a new state after a voltage in excess of the threshold voltage is applied. The measurements were performed with the series-connected resistor and the voltage source. The characteristic switching times for silver is close to 200 ns, for gold it is about 2 µs, and for copper it is about 60 µs. Figure 5 shows the kinetics of both the voltage and the current for films made of each metal. On the time scale presented in this figure it is evident that in the case of silver switching between the states proceeds in two steps due to the build up of two continuous paths formed at different voltages.

![Figure 5](image1.png)

**Figure 5.** Switching kinetics between the low-conductivity and high-conductivity states of silver (a), gold (b) and copper (c) films brought to the percolation threshold by the procedures described in the text. The inserts show the transition regions on a still finer time scale.

4. **Conclusions**

The two step method consisting of the conductivity controlled physical vapor deposition followed by the conductivity controlled thermal annealing leads to the robust production of the metal films at the percolation threshold. The films obtained in this way exist in two stable states with low and high conductivity. The conductivity difference of these states reaches seven orders of magnitude. The films may be switched between these states by the applied voltage, the threshold value being 8 V for silver and slightly larger for gold and copper. The voltage cycling leads to the slight reduction of the threshold voltage. The switching time for silver is 200 ns, while for gold is 2 µs and copper is 60 µs, it is much longer. A plausible explanation of the switching mechanism may be related to the fine
mechanical deformations of the metal nanoparticles induced by the applied voltage. This deformation may greatly enhance the probability of electron tunneling between almost touching nanoparticles. Despite the applied voltage is rather small the electric field in the nanogaps between the particles can exceed $10^3$ V/cm. This value is large enough to stimulate tiny deformations of nanoparticles and cause the resistance drop. After the voltage switch off the particles restore their original shape and the conductivity reduces as well.

The results of this study can be used in the future development of the resistive memory devices.

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