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HYSTERESIS OF CONDUCTIVITY IN THE GRANULAR SILVER FILMS

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The electrical properties of the granular silver films located on a surface of sapphire substrates are experimentally investigated during deposition and thermal annealing. The strong influence of surface-based silver atom diffusion on film formation is revealed, both during and after deposition. The effect of resistance switching in the films of the various thicknesses close to the percolation threshold, depending on the applied voltage is found and investigated. These sharp changes of resistance of 5–7 orders can be reversible or irreversible, depending on film thickness.

Keywords: granular metal films, metal nanoparticles, resistance switching.

1. Introduction

Thin metal films are widely used in various applications as electric current conductor, chemical sensors, optical filters, etc. Their electrical properties depend on the nature of the metal and, to an even greater extent, on their morphology. Continuous films have metallic conductivities, characterized by low resistance and positive temperature coefficients. The resistance of metal films consisting of separate granules is much greater than the resistance of the bulk metal and depends on the substrate material and the distance between the granules. The conductivity of such a system is characterized by a negative temperature coefficient of resistance. The energy of activation is estimated to be about several tenths of an eV. The charge transfer can be carried out either by the hopping mechanism via traps in the subsurface layer of the substrate, or by a process of thermally activated tunneling [1–4].

The granular film that is formed on a dielectric substrate at the beginning of the vacuum deposition process transforms into a continuous film during material accumulation. The appearance of a continuous metal path between the electrodes, spaced from each other on a macroscopic distance, occurs long before the formation of a continuous film, and is called the percolation transition. After the percolation threshold, the electrical properties of the film become similar to properties of the bulk metal.

The electrical properties of metal films at the percolation threshold are most interesting, because when the distance between granules is very small, then small changes in the amount and distribution of the metal cause relatively large changes in the conductivities of the films. Such structure can be obtained by heating of the films having low resistances. Indeed, due to the diffusion of the metal allows, the separated granules are formed [5, 6].

2. Experimental

In this study we investigated granular silver films on the surface of sapphire substrates at the percolation threshold. The granular films were produced by the thermal evaporation of silver onto the surface of the sapphire substrate in the gap (3 mm × 2 cm) between the silver electrodes inside the vacuum chamber PVD 75 (Kurt J. Lesker) at a residual gas pressure less than 5×10-7 Torr. During the deposition, the electrical properties of the films were controlled by a picoammeter (Keithley – 6487). We investigated films with thicknesses from 50 to 150 Å, deposited at the rates of 0.1–1 Å/sec.

During deposition, the film resistance decreases exponentially (Fig. 1a). For the films of the same thickness the resistance was lower provided they were obtained at a larger rate of deposition. Immediately after the deposition, the film resistance continues to change rapidly (Fig. 1b) and after an hour, the resistance can vary by 3–4 orders of magnitude. A day after the deposition, the resistance of the films obtained at the low deposition rate (0.1 Å/sec) was $1.3{\cdot}10^{12}$ ohms, while the resistance of the films obtained at the deposition rate of 0.6 Å/sec was 1 kohm.

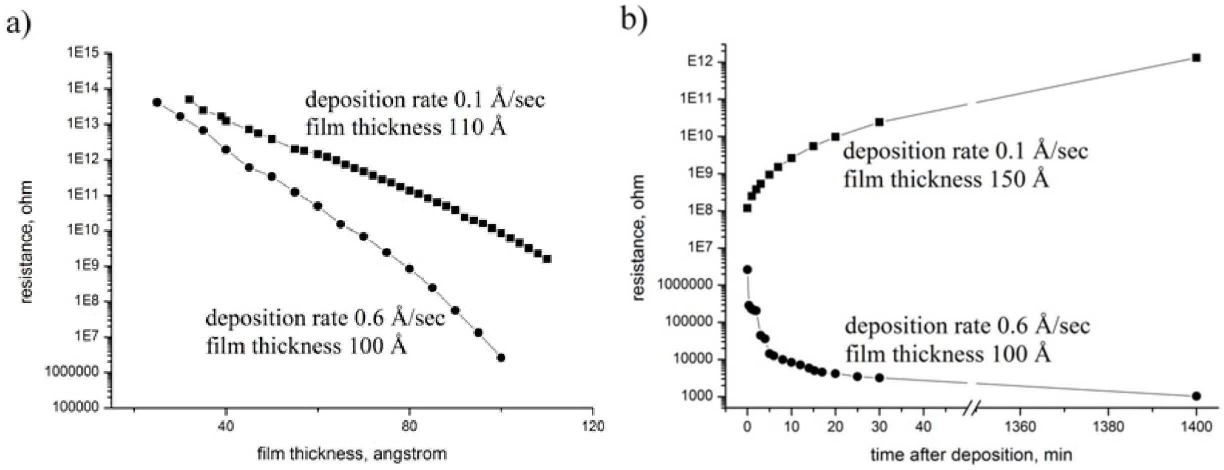

FIG. 1. a) The dependence of the resistance of the films on their thicknesses and rates of deposition; b) the change of resistance of the films during the time after deposition (resistance was measured at a voltage of 5 V)

These results indicate the strong influence that silver atom diffusion has on film formation both during and after deposition. At the low deposition rate separate large particles with irregular shapes and sizes of about 200–300 nm are formed (Fig. 2a). After deposition, small particles and adsorbed atoms diffuse over the surface and stick to the larger particles. Thus, the distance between particles increases and, as a result, the conductivity of the film diminishes. At deposition rates of 0.5 Å/sec or more, films with the thickness of more than 50 Å are formed. They represent the endless conductive labyrinth structure consisting of a network of irregularly-shaped particles. These wires have cross sections of about 30 nm at a film thickness of 10 nm. Such films have resistance typical for bulk metals, namely from several tens ohms to several kohms.

So, it is possible to differentiate two typical cases: the film consisting of separate granules, having a complex shape, and the conductive film having a labyrinth structure. Henceforth, we will consider only the second option.

After deposition, the granular silver films were subjected to heating. During annealing, the material is redistributed to form separate particles. In this case, a nonlinear increase of the resistance over time (Fig. 3) and a sharp step of the resistance after 60 minutes of heat treatment were observed. The sharp increase in the resistance points to a breaking of the conductive metal structure between electrodes.

The inset in Fig. 3 shows a SEM image of a 100 Å granular film deposited at a rate of 0.6 Å/sec after heating. Particles became larger in comparison with the just deposited film.

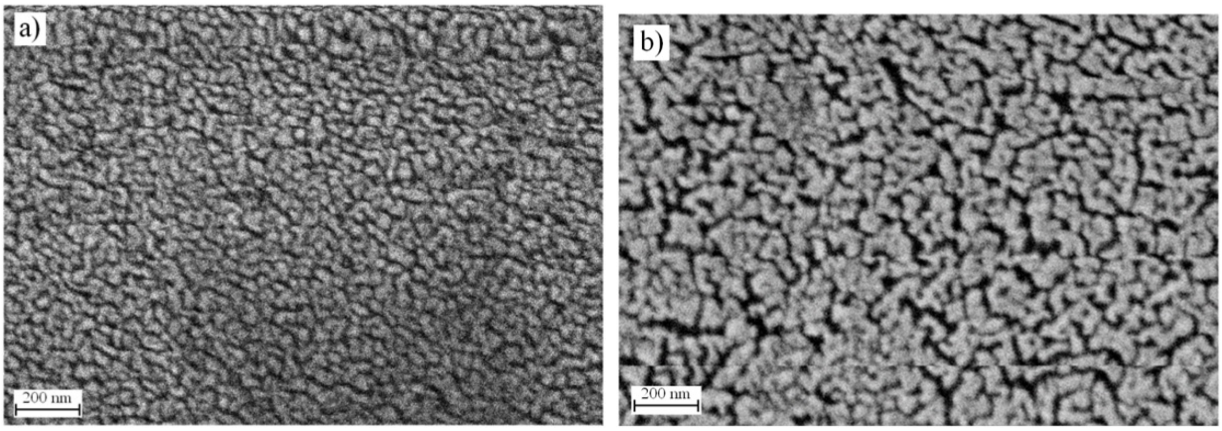

FIG. 2. SEM image of the granular silver films on the surface of the sapphire substrate with thickness of 100 Å deposited at the rate of 0.1 Å /sec (a) and 0.6 Å/sec (b)

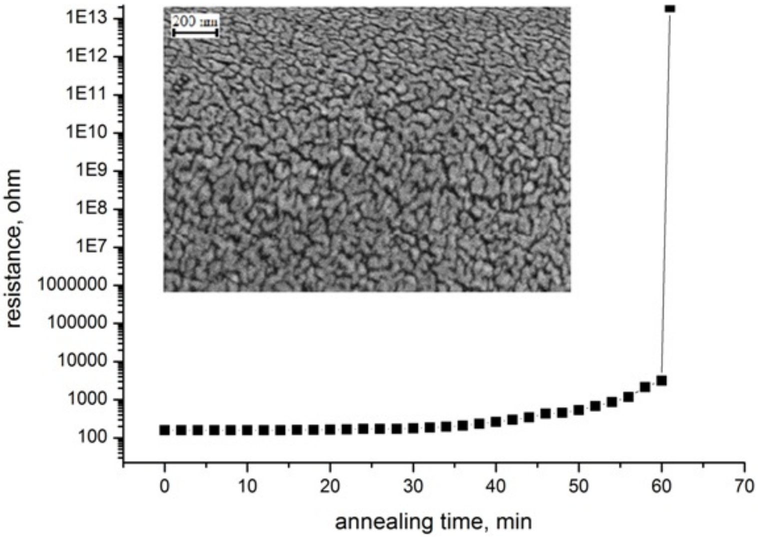

FIG. 3. Resistance of the granular silver film with thickness of 100 Å annealed at 120°C as a function of annealing time. On the insert the SEM image of the silver film after heating is presented

Distances between the particles are still very small, nevertheless, this film consists of individual separated particles as confirmed by its very high resistance. After the jump of the resistance, heating of the film was stopped.

3. Results and Discussion

After heating, the morphology of the films and their optical properties did not change appreciably, however, the resistance of the films increased by 10–12 orders and the films acquired the ability to switch their resistance under the influence of applied voltage. Fig. 4a shows the current-voltage characteristics of the silver film after heating. The 50 Å thick film was deposited at a rate of 1 Å/sec. As can be seen, at an applied voltage of less than 7 V (region I), the film has low conductivity with resistance of $1.5 \cdot 10^{12}$ ohms. In this region the current increases almost linearly with the applied voltage. The film switches to the high conductivity state at the threshold field strength of 7 volts (II). Further increase of the voltage reduces the

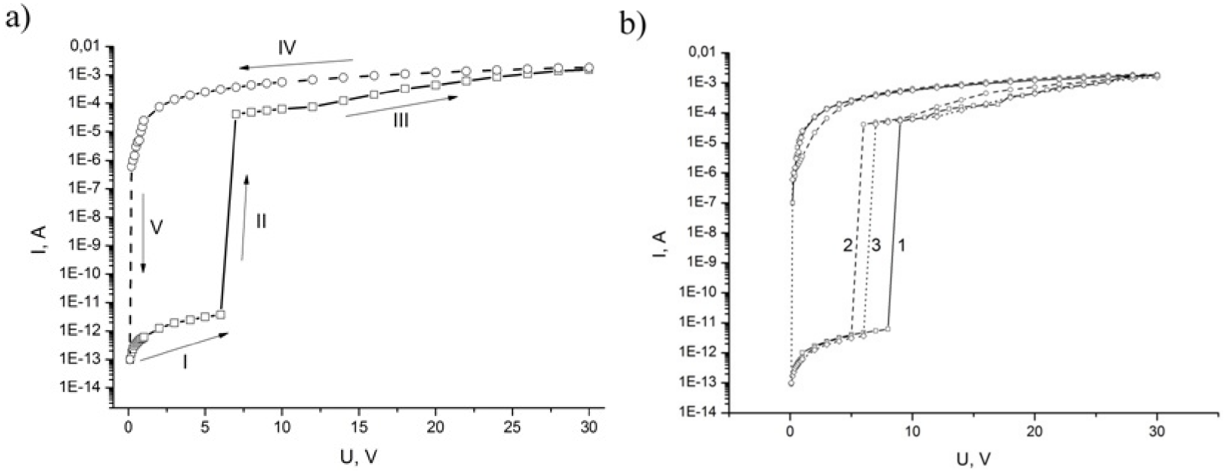

FIG. 4. a) I–V characteristics of the granular silver film on the surface of the sapphire substrate with the thickness of 50 Å after heat treatment at 90 °C for 60 minutes with increasing (solid line) and decreasing (dashed line) voltage; b) series of cycles of I–V characteristics measured with an interval of 3 minutes

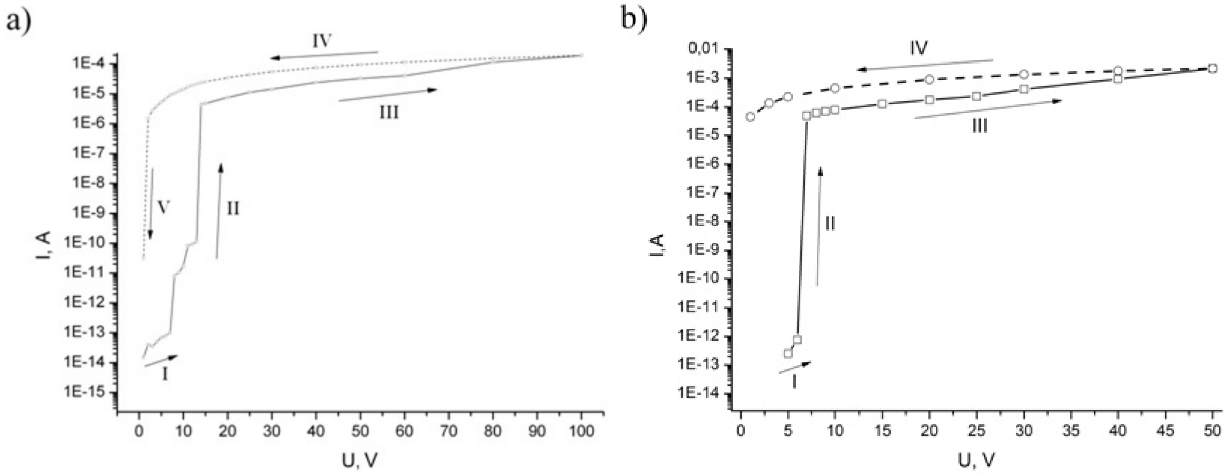

FIG. 5. I–V characteristics of the granular silver films on the surface of the sapphire substrate with the thickness of 85 Å (a) and 115 Å (b) after heat treatment at 120 °C for 60 minutes with increasing (solid line) and decreasing (dashed line) voltage

resistance to 16 ohms (III). The current-voltage characteristic has an ohmic character, then the voltage is reduced (IV), but at a voltage of 0.1 V film passes to the initial high-resistance state (V).

During subsequent voltage increase/decrease cycles the current-voltage characteristics of the film were very stable (Fig. 4b), with slight fluctuations in the voltage required to switch the film into its low-resistance state.

The situation is different for thicker films. Fig. 5 shows the current-voltage characteristics of heated 85 and 115 Å films , deposited at 0.6 Å/s. For these films, a nonlinear increase of the current was observed in region I , wherein, noticeable fluctuations of the resistance were observed. In repeated measurements for the 85 Å film, the switching voltage was greatly decreased, and after the third cycle, the film remained in the low-resistance state after removing the applied voltage. The 115 Å film remained in the low-resistance state after the first switching of the resistance, but it could be switched into the low-conductivity state after short-term heating.

Similar resistance switching has been described in previous literature for different thin-film materials. They can be divided into two general categories: threshold switching, in which electrical power is required to maintain the ON state (state with low resistance) and memory switching, in which both states (ON and OFF) can be maintained without electrical power [7–9]. Changes in conductivity can be either structural, involving nanoparticle deformation or diffusion of the material under an applied voltage, or electronic, i.e. caused by the injection of electrons under the influence of high electric fields arising between nanoparticles at film discontinuities. However, the fact that granular silver films with thickness greater than 85 Å do not switch to low conductivity states indicate that the transfer of material plays an important role in creation of the conducting channels.

4. Conclusion

The paper presents the results of conductivity studies for silver granular films with different thicknesses deposited on the surface of a sapphire substrate. The films were produced by the standard method of thermal deposition of an atomic beam on the cold substrate. The resistance changes during and immediately after deposition were measured. After thermal treatment of the films, a resistance switching effect was observed, while the film structure and its optical properties were not substantially changed. The value of the resistance switching can be up to 10^7 ohms, and the voltage required to switch ON the structure (to the low-resistance state) may vary within a wide range depending on the duration of the annealing.

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