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The crossover between tunnel and hopping conductivity in granulated films of noble metals

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ABSTRACT

The conductivity of thin films composed by clusters of gold and silver nanoparticles has been studies in a wide range of temperatures. The switch from a temperature independence to an exponential thermal dependence of the conductivity manifests the crossover between the tunnel and thermally activated hopping regimes of the electronic transport at the temperature of 60 °C. The characteristic thermal activation energy that governs hopping of electrons between nanoparticles is estimated as 1.3 eV. We have achieved a good control of the composition and thicknesses of nano-cluster films by use of the laser ablation method in colloidal solutions.

1. Introduction

Granulated metallic films are considered as promising building blocks for various nano- and micro-electronic applications. These applications take advantage of the unusual electronic and optical properties of the granulated films. In particular, the hysteresis in resistivity of granulated silver films deposited on a GaAs surface has been reported in Ref. [1]. Similar films deposited on sapphire surfaces may serve as resistive memory elements. The characteristic current-voltage characteristics of granulated golden films deposited on dielectric substrates have been studied in Refs. [2–5]. Clusterized metallic structures exhibit the broadening of electronic level due to tunnelling Ref. [6]. Ref. [7] reports on the photoemission in a clusterized film of palladium illuminated by low frequency light. Ref. [8] reports on the formation of superconducting clusters that demonstrate the unconventional Josephson tunnelling through dielectric layers whose widths exceed the coherence length of the corresponding bulk superconductor.

Nano-thermometers and gas sensors may also be based on these granulated metallic films [9,10]. Electronic properties of such films strongly depend on the sizes and on the density of the constituent metallic nanoparticles. In particular, the mechanism of electronic conductivity is governed by the mean distance between nanoparticles: if the mean distance is less than the size of the particles, one can expect the tunnel mechanism to dominate, in general. The tunnelling probability

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depends on the size of nanoparticles, distances between them and the shape of tunnel barriers [11] The variation of the thickness of the film as well as the transition from amorphous to crystalline structure of the film dramatically affect the conductivity [12]. For these reasons, it is important to be able to achieve a precise control on the thickness and the morphology of the film when depositing metallic nanoparticles on surfaces [13]. In this study, we use the laser ablation method for the synthesis of metallic nanoparticles in colloidal solutions and the laser-assisted deposition technique in order to form bi-metallic films of controllable morphology. We study the surface resistivity of the resulting films as a function of the thickness of the film, of the density of metallic nanocrystals and of temperature. We observe the crossover from tunnel to thermally activated hopping conductivity and extract the activation energy of metallic nanoparticles of ~1.3 ± 0.1 eV. These studies show the potentiality of our laser deposition method for tailoring of the electronic properties of bi-metallic thin films.

2. Deposition of cluster films

The colloidal solutions of metallic nanoparticles have been prepared using the laser ablation method [14]. The formation of nanoparticles resulted from the cw laser effect on silver and gold targets immersed in the de-ionised water [15]. The mean size of nanoparticles has been controlled by the dynamical light scattering method. At the concentration of nanoparticles of 1 μg/ml the measured mean size of nanoparticles is 10 nm. We have taken advantage of the laser deposition technique developed in Ref. [16] for deposition of the bi-metallic films. Equal volumes of colloidal solutions of gold and silver nanoparticles (5 ml each) have been carefully mixed. A KB8 glass substrate immersed in the cuvette containing the colloid has been illuminated by a laser beam of the wavelength of 1.06 μm. We have used an Yb fiber laser emitting 100 ns pulses of power 1 mJ per pulse with a 20 kHz frequency. In the focal plane, the diameter of the laser beam was 5 μm. The formation of a nanoparticle array on the surface of the substrate has been achieved by repeatedly scanning the laser beam along the fixed trajectory (from 5 to 25 scans) at the scanning speed from 03 mm/s to 1.2 mm/s. The deposition of films has been realised layer by layer, that is characteristic for island-like structures [17]. The films of thickness ranging from 10 to 50 nm have been formed in this way.

The morphology of deposited films has been studied with use of an atomic force microscope (Fig. 1). The variation of the scanning speed led to the variation of local heating of the colloid under the laser beam. This, in turn, affected the metal deposition regime. In particular, the reduction of the speed of scanning led to the increase of the time of irradiation of each particular local volume of the colloid and acceleration of the laser-induced thermodiffusion of nanoparticles in the solution. As a consequence, the landscape of the deposited film is characterised by multiple lacunas in this regime. On the other hand, at the highest scanning speed of V = 1.2 mm/s the deposited granulated film demonstrated almost no lacunas (see Fig. 1a).

The reduction of the scanning speed to 0.6 mm/s results in a modification of the film surface landscape. One can clearly see the lacunas of the average size of 5 nm separating the granules. The further reduction of the scanning speed leads to the formation of a clusterized film with lacunas of the average size of 30 nm. It also leads to the local increase of the speed of the deposition under the laser beam. Optimizing the number of scans we were able to grow films of the average thickness of 50 nm.

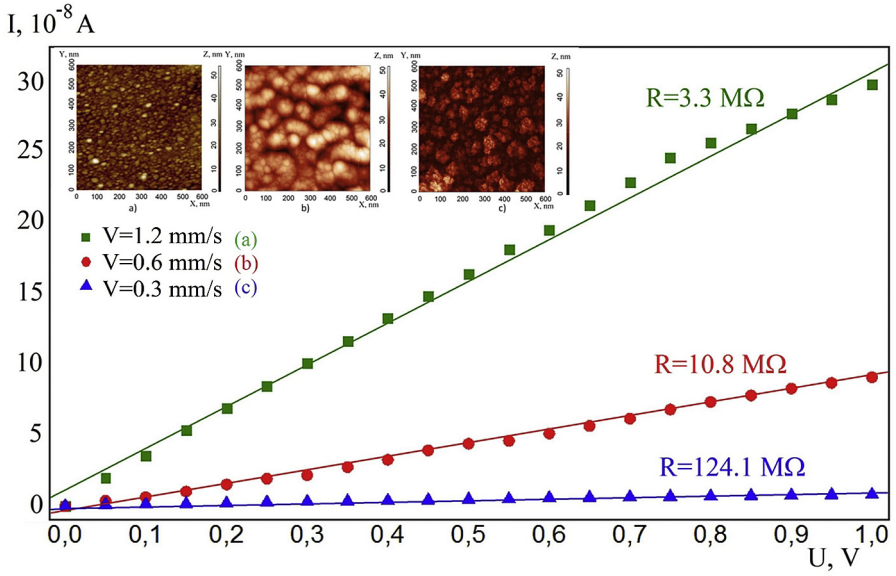

Fig. 1. Upper panels show the atomic force microscopy images of the synthesized bi-metallic films obtained at different scanning speeds V (indicated below the panels a,b,c). Points show the corresponding current-voltage characteristics. Lines are the linear fit. The number of scans was 25(a), 18(b), 14(c).

3. Electronic properties of the synthesized granulated films

We have studied the current-voltage characteristics (CVC) of the synthesized films with use of the four electrode scheme (see Fig. 2) with linearly arranged contacts [18]. The outer electrodes provided the conduction of a constant current I generated with use of the stabilised source. These contacts have been separated by $L_1 = 6$ mm. The inner electrodes represented conducting pins of the atomic force microscope having the curvature radii of 100 nm and separated by $L_2 = 1.5$ mm. A digital electronic voltmeter with high entrance resistivity has been connected to the pins. This set-up has been built in a vacuum chamber allowing for the pressure reduction down to 10^{-3} Torr and heating up to 100°C.

Fig. 1 shows CVCs of the studied granulated films. One can see that on the scale of the figure they can be approximated by linear functions with a good accuracy. On the other hand, it is well known [19] that the conductivity of a clusterized metallic field shows a rapid, nearly exponential increase with the increase of the thickness of the film for thin films. Such a behaviour is caused by a sharp increase of the electronic hopping probability with the decrease of the average spacing between metallic islands. Fig. 2 (2) shows the measured dependence of the conductivity of our films on their thickness in the limit of relatively thick films. One can see that in this limit the conductivity depends linearly on the mean thickness of the film. In order to account for the probes geometry (Fig. 2(1)) the following expression for the film conductivity Σ was employed:

$$\sum = \frac{I}{V\pi}\ln\left(\frac{L_1 + L_2}{L_1 - L_2}\right) \tag{1}$$

Eq. (1) is similar to the well-known expression for the normalised conductivity [18], while in our case Σ is not normalised by the thickness of the film d. The monotonous dependence of the conductivity on the thickness of the film shown in Fig. 2(2) is characteristic for granulated films. In the limit of an ultrathin film, the distances between granules are so large that the conductivity vanishes. The granules get closer to each other as the mean thickness of the film increases that leads to the increase of the hopping conductivity.

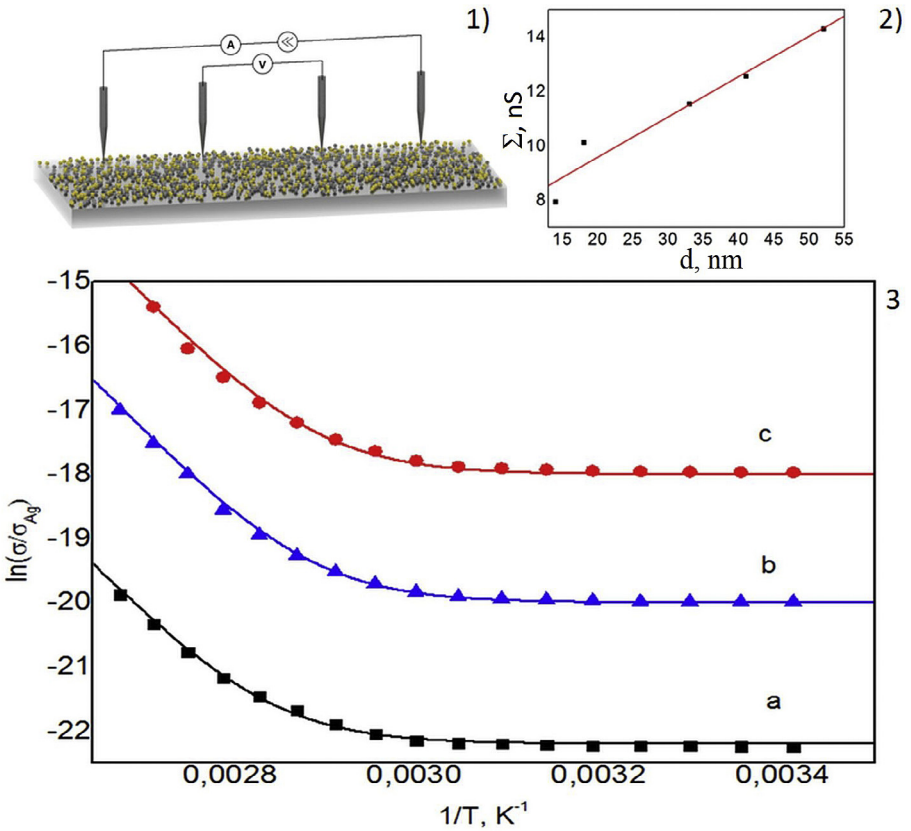

Fig. 2. The schematic of a four-electrode measurement scheme (1). The dependences of the conductivity of the bi-metallic film Σ on its thickness d (2). The temperature dependence of the logarithmic conductivity of the firms synthesized with use of different deposition regimes (3). Dots show the experimental data. The solid lines show the fitting results obtained using Eq. (2). In all cases the activation energy has been taken equal 1.3 eV. The values of other fitting parameters have been (a) $\sigma_0 = 0{,}95$ S/m, $\sigma_1 = 6{,}1{*}10^{18}$ S/m (b) $\sigma_0 = 0{,}13$ S/m, $\sigma_1 = 0{,}75{*}10^{18}$ S/m (c) $\sigma_0 = 0{,}014$ S/m, $\sigma_1 = 4{,}1{*}10^{16}$ S/m. The data shown here correspond to the films shown in Fig. 1.

We note that in the investigated range of thicknesses of the films the percolation threshold is not achieved, so that the electrons need to transfer through lacunas separating the metallic granules in order to contribute to the conductivity. This is confirmed by low absolute values of the measured conductivities. For the sake of comparison with uniform metallic films we normalise the measured conductivities Σ by the corresponding film thicknesses d. The resulting effective normalised conductivities range from 0.04 S/m to 0.5 S/m that is by many orders of magnitude lower than normalised conductivities of uniform gold and silver films being $\sigma_{Au} = 4.55 \times 10^7$ S/m and $\sigma_{Ag} = 6.25 \times 10^7$ S/m, respectively.

In order to reveal the mechanism of conductivity in the synthesized bi-metallic films we have studied the temperature dependence of the conductivity in the range from 20 to 100 °C. Fig. 2 (3) shows the logarithms of the measured conductivities as functions of the reversed temperature. The curves (a), (b) and (c) correspond to the films of the same thickness (50 nm) deposited at the different scanning speeds, being 0.3, 0.6. and 1.2 mm/s, respectively.

One can conclude from these measurements that the mechanism of conductivity in bi-metallic films dramatically changes at the temperature of 60°C. At the temperatures below 60°C the conductivity appears to be temperature independent that is characteristic of a tunnelling mechanism. At the temperatures above 60°C the superlinear increase of the conductivity as a function of temperature is characteristic of the thermal activation mechanism of the conductivity.

The crossover from the tunnel to the thermal activation mechanism of conductivity manifested by its temperature dependence can be phenomenologically described by a simple expression for the normalised conductivity of the film:

$$\sigma = \sigma_0 + \sigma_1 \exp\left(-\frac{E}{kT}\right) \tag{2}$$

The first term in the right part of Eq. (2) describes the tunnelling conductivity that is independent of temperature, while the second term corresponds to the thermal activation mechanism. Here k is the Boltzmann constant, E is the thermal activation energy. One can see from Fig. 2(3) that the temperature dependences of the normalised conductivities corresponding to three different bi-metallic films could have been fitted with the same value of the activation energy: $E = 1.3 \pm 0.1$ eV. We conclude that this is a universal characteristic of the metallic clusters under study that is independent on the morphology of the film.

Interestingly, the thermoactivation energy extracted from our measurements is significantly lower than the work function of gold and silver (~4eV). Similar results have been obtained recently is a series of studies of granulated films deposited on insulating surfaces [20–22]. The most likely reason for the decrease of the hopping barrier in supported granulated films seems to be the influence of the surface.

4. Conclusion

We have developed a laser deposition method of granulated metallic films from colloidal solutions of metallic nanoparticles prepared by laser ablation. The method is relatively simple and reliable. It allows for the controllable synthesis of films characterised by interesting and somewhat unusual electronic properties. It allows for combining of nanoparticles of different metals in a nano-clustered thin film. The measured current-voltage characteristics allowed us to reveal the interplay between tunnel and thermal activation conductivity mechanisms in the synthesized films. From the analysis of the temperature dependence of the conductivity we have deduced the thermal activation energy that is significantly lower than the work functions of constituent metals. These experiments pave way to applications of granulated metallic films as highly resistive nano-thermometers.

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