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# Tunnel/jump electroconductivity in the laser-induced nanocluster structures with controlled topology

**S. Arakelian**[1] · **A. Kucherik**[1] · **S. Kutrovskaya**[1] · **A. Osipov**[1]

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**Abstract** By method of laser-induced thermal deposition of colloidal particles laser we have produced the metallic granular films for which the ability to control the change in its electrical properties does exist by variation of the topology for the system. The quantum states verification in cluster metallic structures by jump/tunneling electroconductivity and possible mechanisms for its implementation are considered in experiment and theory. The granular conductivity specificity has been under study. The current–voltage characteristics behavior has been measured for a gold (Au) and Au-carbyne clustered film. Two associated mechanisms for electroconductivity occur in the case, i.e. tunnel transition for electrons and electron activation in the frames of the shell model for a cluster system, in dependence on the nanostructure topology.

**Keywords** Electroconductivity · Tunneling · Nanocluster structures · Jump electroconductivity · Topology control

## 1 Introduction

The physical properties of nanocluster systems are very sensitive to the form, size and distance between its composing elements. The fact is well known for any material in general, but to change these fixed lattice parameters and to carry out the stable conditions for the ordinary solid state object/crystal structure we need both to put the object under

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✉ S. Arakelian
arak@vlsu.ru

[1] Stoletovs Vladimir State University, 87 Gorky Street, Vladimir 600000, Russia

extremely high pressure ($\gtrsim 10^6$ atm) and to work in a low (liquid *He*) temperature range ($\lesssim 30$ *K*) (Drozdov et al. 2015).

In contrast, nanocluster structures can be easily modified in the necessary direction and by the controlled way in femto- nanophotonics experiments both. The variation of the above enumerated topology parameters can result in a new type of correlation/quantum states for charge particles (Arakelian et al. 2015). Moreover, electronic energetic bands of the materials can vary dramatically, resulting in a new physical behavior of the system in general.

The main problem of superconductivity is the fabrication of the coupling states (around the forbidden band) at high (nitrogen) temperature ($\gtrsim 140$ *K*) for charge particles being responsible for electroconductivity. In fact, the superconductivity enhancement temperature may be the result of the mechanism reducing to a temporary change of atom positions, e.g. for $YBa_2Cu_3O_6$/YBCO—under high intensity IR-laser radiation, and more preferable—by X-ray (Cavalleri et al. 2014).

Thus, the topology mechanisms may play a principal role in the physical electrical property of nanostructures. The fact is true for nanoclusters size $\sim 10$ *nm* and its density $\sim 10^{12}$ cm$^{-2}$ (Dragunov et al. 2006).

In the paper we give the results of our experiments for the quantum states verification in Au nanocluster structures due to jump/tunneling electroconductivity. The possible mechanisms of its development are discussed by us from the both points of view, such as tunnel coupled electron system and shell-like model for electron energetic levels in nanoclusters (Bohr radius is comparable to the cluster size).

### 1.1 Laser-induced nanostructures of different types to control the topology-image: experiments

For our experiments we have used different laser techniques to fabricate surface nanostructures and thin films of several types in some materials. The procedures for direct laser modification of solid state surface and laser ablation of target in liquid to produce the colloidal systems are described, e.g. in the monograph (Arakelian et al. 2015). Previously in our original paper (Arakelian et al. 2016) we have partly discussed different obtained nanocluster systems. And now we focus on the jump-conductivity for structured-sensitive transport characteristics, in theory and experiment both.

There are some special cases of the nanostructures, induced by us. Such cases are principal for the application in nanophotonics in the aspect of hybrid electrooptical schemes design.

For the realization of the experimental deposition of metallic structures on the glass substrate (KV8) from colloidal system the laser deposition method was applied (Arakelyan et al. 2016).

For the deposition, we have used ytterbium fiber laser ($\lambda = 1.06$ μ) with a pulse duration of 100 ns, pulse repetition rate of 20 kHz, and a pulse energy up to 1 mJ. The diameter of the laser beam in the focal plane was 50 microns. Nanoparticle array formation on the substrate surface was performed by the scanning laser beam along the same direction (from five to twenty-five times) at a speed of 0.6 up to 1.5 mm/s.

In the proposed method particle deposition occurs due to the local particle heating, so that the energy absorbed by the particles can be determined from the relation:

$$E_{abs} = \pi r_0^2 Q_{abs} \int I(t)dt, \tag{1}$$

where $I(t)$. is laser intensity distribution; $r_0$ is particle radius; and $Q_{abs}$ is the effective parameter.

To calculate the $Q_{abs}$ for spherical particles of 10-100 nm diameter as follows

$$Q_{abs} = \frac{8\pi r_0}{\lambda} Im\left(\frac{\varepsilon^2 - 1}{\varepsilon^2 + 2}\right), \tag{2}$$

where $\varepsilon = n + ik$ and the calculation parameters of gold at the laser wavelength $\lambda = 1064$ nm are given in (SCHOTT refractive Index Database). Depending on the conditions of laser exposure for a single pulse, the value of the absorbed energy is $10^{-6}$ to $10^{-9}$ J.

During laser irradiation of a colloidal system, it is necessary consider the amount of heat transferred to nanoparticles from the laser field.

Under conditions of multi-pulse exposure the local heating may occur, resulting in the the stability loss of the colloidal system (Arakelyan et al. 2016). In addition, agglomerates can be formed due to particles heating, that will absorb a larger fraction of laser energy and will be able to move thermally in the colloid. The local heating of the liquid results in the formation of convective currents also ensuring particle motion of to the substrate surface.

The proposed deposition method allows to change the morphology of the deposited structures depending on the laser exposure conditions and initial size of colloidal particles (Fig. 1).

## 1.2 Electroconductivity in nanostructures: experiments and brief interpretation

Below we consider the quantum mechanism of electroconductivity for two models: tunneling electron transport and/or shell-like structure with transition from coupled electron state to free one, being associated with valence/conductivity bands.

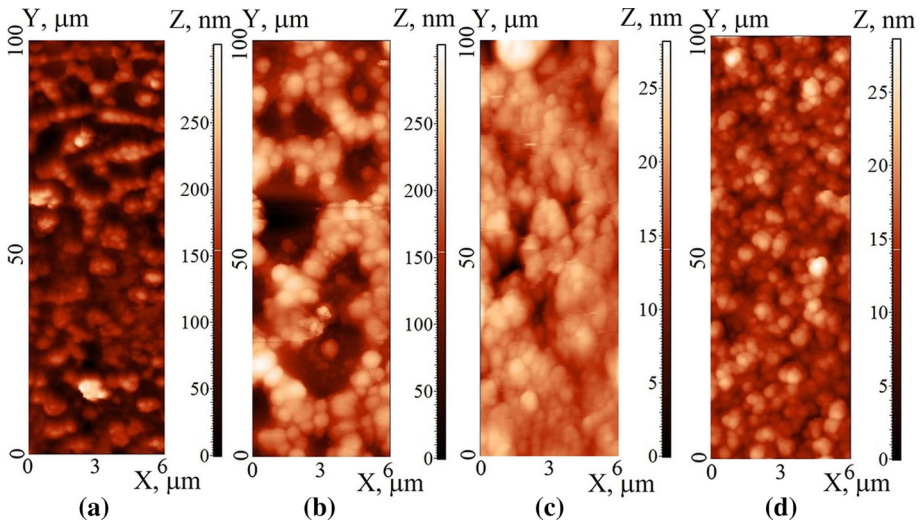


**Fig. 1** AFM-images of deposited Au cluster with different diameter 100 nm (**a**, **b**) and 10 nm (**c**, **d**) of initial colloidal particles

The appearance of some rather unusual size effects in granular thin films prepared by the pulsed laser deposition technique (when an average grain size becomes comparable with the thermal de Broglie wavelength) was discussed in the paper (Sergeenkov et al. 2016).

For the cluster structures the tendency to superconductivity can be obtained due to the boundary topology of the ordered clusters. In our previous experiments we have observed the decrease of the resistance by several times (at the level of several units of Ohms) for Ni-nanostructure by the same reason (Arakelian et al. 2016) when nanocluster size decreased from 100 nm to 10 nm. Some explanations were given in the frame of surface fractal structures with dominant contribution of topological factors.

### *1.2.1 Tunnel coupled electroconductivity*

According to the equations of elementary quantum mechanics textbook (Abrikosov 2009) the quantum effects in nanoparticles are determined by the band gap value ($E_g$) versus dimension (size $R$ for the particles):

$$E_g(R) = E_g(\infty) + \frac{\hbar^2\pi^2}{2R^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) - \frac{1.8e^2}{\varepsilon R} \tag{3}$$

where $m_e$ and $m_h$—effective mass of electron and hole, $\varepsilon$—optical dielectric constant of solid state, $E_g(\infty)$—band gap of bulk sample, second term—dimension contribution, last one—Coulomb forces.

The current density $j$ for electron transport by tunneling mechanism in cluster system can be presented as an equation (Kozhevin et al. 2003):

$$j \propto U\sqrt{\frac{E}{k_BT + 2eUd/L}}exp\left(\frac{eUd/L - E}{k_BT}\right). \tag{4}$$

where $U$—potential difference between macrocontacts, $E$—energy for particles transfer from infinity/ionization energy, $e$—electron charge, $d$—average distance between neighboring clusters, $L$—length of conductive layer between macrocontacts, $k_B$—Boltzmann constant, $T$—temperature.

According to the approach we had counted the resistivity ($R_{cal}$), and compared it with our experimental results ($R_{meas}$) in a large range of values for *Au* as an example.

*Experimental results* for voltage ($U$) and amperage ($I$) behavior and electroresistance ($R$) for Au cluster films are shown in Fig. 2.

We can see the jumps on the obtained $I(U)$ dependences for different thickness. For three cases we show AFM-images for the nanostructures under the measurements (Fig. 1). A more detailed behavior of the dependences for electroresistance $R$ versus nanoparticle size near the initial part of the displayed dependences is presented in insert sections in the right part of Fig. 2.

It is interesting that the dependence in Fig. 2 for $R$ may be presented as the analogue of Kondo dependence on the temperature for $R(T)$ in contrast with our case for the dependence $R(h)$ on $h$.

The theoretical description for jump conductivity (Fig. 2) will be presented in the next part of the article.

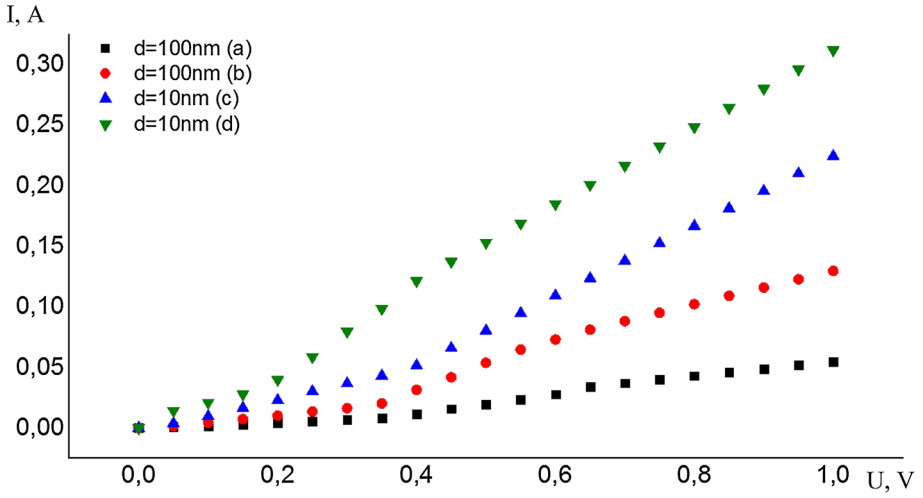


**Fig. 2** The experimental data of the deposited layer for clustered Au films presented on Fig. 1

### 1.3 Quantum activation mechanism for electroconductivity

In experiment, with different topology structures, we observed the competition between: (1) the increase of conductivity while opening new channels and (2) the increase of resistance by expanding the area for the grain/cluster. In addition, (3) the thermal activation and/or variation of the potential barrier value also works due to intrinsic electric field in the structure. The last process can result in the current value enhancement in the formed island films by jump effect. The effect of electron conductivity in a shell-like structure of the cluster will be discussed next.

The reasonable model for jump conductivity (see Fig. 2) in such granular film structure may be associated with the mixture of metal and insulator (Demishev et al. 2002). This is an equivalent to our case due to the existence of the distance between clusters is responsible for the electroresistance, and the changing value of it results in the elecroresistance control. In fact, we have a localization of charges in space $\sim$ cluster size $a$, and electrons locked inside a nanoscale cluster (with multi-electron states in the shell model of energetic levels).

An activated contribution to the jump conductivity associated with the electron transition mechanism, i.e. activation of electrons in up (delocalized) Habbard band from down Habbard band in «insulator» and metallic band (energy interval $E_a$) both. Such electron jumps occur due to different transitions of electrons between discrete energetic states within each localized zone (Demishev et al. 2002; Meilikhov 1999).

We have obtained the current–voltage characteristics for a Au clustered film The *N*-like behavior in the dependence can be explained in the framework of the model based not only on the thermal activation of electrons (resulting in the electron going away from a hole through the barrier) (Meilikhov 1999) but and/or variation of the quantum barrier parameters themselves under the appearance of the intrinsic local electrostatic field $E_i$ inside nanodots.

The dependence of the current density on the external applied field ($E$) has the form of:

$$j(E) = \sigma E, \tag{5}$$

where σ—electroconductivity.

Energy $E_N$ of the upper/filled level ($N$) for particle mass m* in the quantum well of the $2a$ width can be presented as:

$$\varepsilon_N = N^2\pi^2\hbar^2/8m^*a^2. \tag{6}$$

The principal point here is the decrease of the height of the barrier/potential well due to the intrinsic local electric field $E_i$ but not because of the electron kinetic energy variation arising due to the increase of the temperature factor (see Fig. 3).

A few simple equations for that will be introduced below.

Energy difference for the electrons relative to the top of the potential well becomes less due to $E_i$ impact at the fixed temperature:

$$E_i 2a \sim \Delta_N e \geq k_B T \tag{7}$$

where $T$—temperature, $k_B$—Boltzmann constant, $\Delta_N e$—the electron boundary energy difference between level N and the barrier top.

Electrons can jump out from the hole when the barrier height decreases.

The effect is an electrostatic analogue of the resonance enhancement of the amplitude of the optical field near the local surface roughness of precious metals (Emelyanov and Koroteev 1981).

This fact has been confirmed by our demonstration of super-high sensitivity of the substance concentration of *Rhodamine 6G* due to plasmon resonance in nanostructure of (*C, Au, Ag*)-system due to the same reason for the increase of local field $E_i$ (Emelyanov and Koroteev 1981; Kucherik et al. 2016a, b). In a special case, such SERS-effects can be very useful with resonance atoms in nanostructures to create the optical elements for different applications. In hybrid elements with organic substance doped in nanostructure, the subject is under intensive study at the present time (Hu et al. 2016).

Thus, the modification of a potential well due to the topology of nanostructures can result in the effect with additional contribution to jump conductivity for discrete energetic

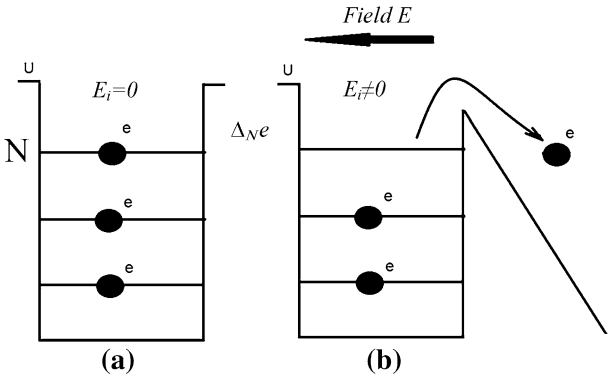


**Fig. 3** Schematic picture of electron activation through the potential barrier. The electrons stay at the levels of dimensional quantization (when $E_i = 0$) in the potential hole with depth U. But under the effective field $E_i \neq 0$ the electrons jump out due to the decrease of the barrier height

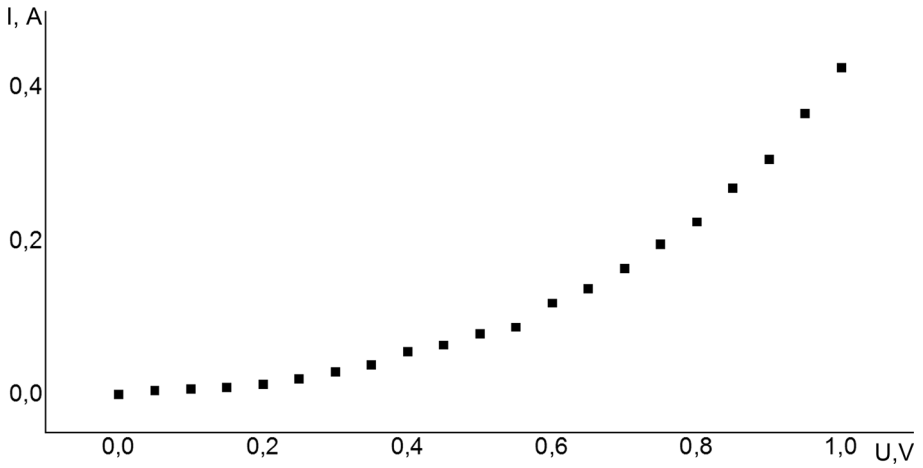


**Fig. 4** VAC Au-carbyne thin films with thickness 30 nm

levels for electrons. We can demonstrate this assumption deposited metal–carbon films based on carbyne (Kucherik et al. 2016a, b) and gold. As can be seen in the case, the VAC is a fundamentally different way, showing (Fig. 4) the deviation from linearity and passing to the exponential increase in current strength.

## 2 Conclusion

In the paper the electroconductivity for the laser-induced surface and cluster/thin films nanostructures with controlled topology have been under study.

The quantum state verification in cluster structures obtained in the experiment, i.e. jump/tunneling electroconductivity, and some possible mechanisms of explanation for nanocluster systems were introduced. Our experiments and theoretical discussions may be reasonable for the design the variable photonic devices in hybrid schemes with light and electrons

Thus, relying on the fundamental physical effects which demonstrate the dimension like behavior in nanostructures we expect the craton (under laser induced modification of the material surface and thin films) of the next generation of photonic and optoelectronic hybrid schemes on new physical principles.

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