Jump electroconductivity in the laser deposited nanoclustered structures

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Abstract. The quantum states verification in cluster semiconductor/metallic structures by jump/tunneling electroconductivity and possible mechanisms for their implementation are considered in experiment and theory. By our laser ablation technique we have nanostructured the films for which the ability to control the change in their electrical properties does exist by variation of the topology for the system. The granular conductivity specificity has been under study. The current-voltage characteristics behavior has been measured for a nanocluster bimetallic film (Au+Ag), and the experiments for multilayer bimetal thin films of the different composition have been carried out. 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.

1. Introduction
The physical properties of nanocluster systems are very sensitive to the form, size and distance between their 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 extremely high pressure ($\gtrsim 10^6$ atm) and to work in a low (liquid He) temperature range ($\lesssim 30$ K) [1].

In contrast, nanocluster structures can be easily modified both in the necessary direction and by the controlled way in femto- nanophotonics experiments. The variation of the above enumerated topology parameters can result in a new type of correlation/quantum states for charge particles [2]. Moreover, electronic energetic bands of the materials can vary dramatically in the case, resulting in a new physical behavior of the system in general.

In the problem of superconductivity the question is, how to fabricate 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$_2$Cu$_3$O$_y$/YBCO – under high intensity IR-laser radiation, and more preferable – by X-ray [3].

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 their density $\sim 10^{12}$ cm$^{-2}$ [4].

In the present paper we give the results of our experiments for the quantum states verification in nanocluster structures due to jump/tunneling electroconductivity. The possible mechanisms of its development are discussed by us in the frame of both tunnel coupled electron system and shell-like model for electron energetic levels in nanoclusters, for which Bohr radius in comparable to the cluster size.
The initial colloidal systems were obtained by continuous laser irradiation of silver and gold targets. The targets were placed in deionized water [5]. The average size of the obtained nanoparticles was about 50 nm and 10 nm, while their concentration was 1 μg/ml. The particle size was controlled by the dynamic light scattering.

For the deposition of the bimetallic structures, the colloidal systems of both metals were mixed in equal proportions. The glass substrate was placed in the mixed solution. The deposition of thin film was made by laser irradiation as described in [6–8]. As a laser source we used Yb-fiber laser (λ=1.06 μm) with pulse duration of 100 ns and with laser repetition rate of 20 kHz. The average power was from 1.5 W up to 4.5 W, the diameter of the laser beam was around 5 μm. The array of nanoparticles was formed on the substrate surface by repeated (up to 10 times) laser beam scanning along one and the same direction. The scanning speed was varied from 0.6 mm/s up to 1.5 mm/s. The obtained in this way array of nanoparticles has the length of about 100 μm, the average transverse dimension was about 5 μm and the average height was about 55 nm.

2. Electroconductivity in nanostructures: experiments and brief interpretation

We will consider below 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.

Experimental results for voltage (U) and ampere (I) behavior and electroresistance (R) for bimetallic system (Au+Ag) are shown in figure 1. They demonstrate the data for different thickness of the bimetallic (Au+Ag) film (figure 1a) and concentration of Ag-substance in (Ag+Ni) system (figure 1c), consequently. 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 (figure 1b). A more detailed behavior of the dependences for electroresistance R vs nanoparticle size near the initial part of the displayed dependences is presented in insert sections in the right part of figure 1a.

It is interesting that the dependence in figure 1a 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 (figure 1b) will be presented in the next division.

Computer simulation results are shown in figure 2. We carried out the computer simulation when a single electron conductivity was modelled for the metallic granular film electroconductivity due to tunneling effect.

We used the algorithm procedures taking into account: granular film growth; neighborhood definition; scaling/transition from computer data to physical parameters; tunneling processes for electron transport; current magnitude/volt-ampere characteristics. The results are shown in figure 2. The control parameters for calculation: F – deposition rate (by speed) being equivalent to T – arbitrary unit (a.u.) time, R – particle radius, S – distance between neighboring particles and/or the different order distance for the particle location/subsequent localization of the particles over the spatial distribution, H – average thickness of the surface layer/film, W – standard deviation for the thickness value.

To have the reasonable results in comparison with our experiments we can manipulate few adjustable parameters (see figure 2a): monolayer F=0.4; R=2.5 nm; S=10 nm; T=2 a.u., H=12 nm and fixed W=7.5556; T=4 a.u., H=24 nm and fixed W=11.9458. The variation of dependences vs different W, can also be shown in figure 2b: H=24 nm, R=2.5 nm, S=10 nm; T=2 a.u., monolayer F=0.8, W=6.9702 nm; T=4 a.u., monolayer F=0.4, W=11.8588 nm; T=8 a.u., monolayer F=0.2, W=13.6342 nm.

Thus, there is a qualitative agreement between the computer simulation approach and experimental data (cf. figures 2, 3). Because of flexible experimental conditions, the adjustable parameters can be introduced both in experiment and computer simulation consistently; so, the coincidence of the results (at least qualitative) is not artificial.

Tunnel coupled electroconductivity. According to the formulas of elementary quantum mechanics textbook (see e.g. Abrikosov, 2009) the quantum effects in nanoparticles are determined by the band
gap value \( (E_g) \) vs dimension (size/distance \( R \) for the particles):

\[
E_g(R) = E_g(\infty) + \frac{\hbar^2 \pi^2}{2R^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{eR}
\]

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 monolith sample, second term – dimension contribution, last one – Coulomb forces.

Then, the current density \( j \) for electron transport by tunneling mechanism in cluster system can be presented as a formula \([9]\):

\[
j \propto U \sqrt{\frac{E}{k_B T + 2e Ud/L}} \exp \left( \frac{e Ud/L - E}{k_B T} \right)
\]

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 counted the resistivity \( (R_{\text{cal}}) \), and compared it with our experimental results \( (R_{\text{meas}}) \) in a large range of values for Au as an example.

**Figure 1.** Experimental data for current-voltage characteristics of the deposited layer \( (h \) – the film thickness): (a) experiments for different film thickness for multilayer bimetallic film Au+Ag; (b) AFM-images for the structures: \( h=14 \) nm (1); \( h=52 \) nm (2); \( h=112 \) nm (3) and obtained dependences; 1 – composition in bimetallic film Au:Ag (1:1), the particle diameter 50 nm, a single layer densely packed particles; 2 – Au:Ag (1:1), particle diameter 10 nm, five layers, the distance between the particles 4 nm; 3 – Au:Ag (1:1), particle diameter 10 nm, five layers, the distance between the particles 2 nm; (c) electroresistivity \( R \) of the array of nanoparticles (Ni+Ag) vs mass concentration of Ag nanoparticles.
Figure 2. Computer simulation of voltage-ampere dependences for multilayer bimetal thin films of different parameters.

The results are shown in figure 3 for different topology of nanostructures. In general there is a good coincidence meanwhile we take into account both different types of nanostructures and a large range of values. Moreover, the best coincidence is the for the last case: $R_{\text{calc}} = 5.5 \times 10^7$ Ohm and $R_{\text{meas}} = 3.6 \times 10^7$ Ohm.

Thus, we can nanostructurize the film for which the ability to control the change of its electrical resistance is realized by the topology variation of the system [10]. The problem is to find the optimal relationship between some spatial parameters.

In fact, earlier we obtained in experiment that the tunnel transition for electrons is effective for $a_{\text{cluster}} = 120$ nm and $\Lambda = 8$ nm for the semiconductor PbTe surface nanostructurized sample [11]. On the other hand, the manifestation 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 [10]. This gives us, in fact, the opportunities to make functionally variable electronic devices being modified in the right direction. The experiments carried out under different conditions (figure 1) by using a few experimental adjustable parameters in correspondence with the computer simulation procedure (figure 2), are necessary for that as it was mentioned above.

For the cluster structures considered by us the tendency to superconductivity can be obtained due to the boundary topology of the ordered clusters. In our previous experiments we observed the decrease
of the resistance by several times (at the level of several units of Ohms) for Ni-nanostructure by the same reason [11] 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.

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. We are going now to discuss the effect of electron conductivity in a shell-like structure of the cluster.

The reasonable model for jump conductivity (see figure 1b) in such granular film structure may be associated with the mixture of metal and insulator [12]. This is equivalent to our case due to the existence of the distance between clusters which for a large value results in high electroresistance. In fact, we have a localization of charges in space ~ cluster size $a$, and electrons locked inside a nanoscale cluster (with multi-electron states in the shell model of energetic levels).

Now we mention an activated contribution to the jump conductivity associated with the electron transition mechanism, i.e. activation of electrons in up (delocalized) Habbard band from both down Habbard band in «insulator» and metallic band (energy interval $E_a$). Such electron jumps occur due to different transitions of electrons between discrete energetic states within each localized zone (cf. [12, 13]).

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 levels for electrons.
4. 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 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 [14].

Thus, relying on the fundamental physical effects which demonstrate the dimension like behavior in nanostructures we can hope to create (under laser induced modification of the material surface and thin films) the next generation of hybrid schemes of photonics and optoelectronics on new physical principles.

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