New challenges of femto- nanophotonics: basic principles and possible applications

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Abstract. The possibility of controlling the functional properties of nanostructured thin films of different topology and elemental composition deposited on solid substrates by laser radiation is under our study. Quantum-correlated states that emerge in the deposited granular nanocluster semiconductor/metal structures lead to both hopping/tunneling electroconductivity and specific optical properties. An increase in electrical conductivity (by several orders of magnitude) is observed in experiments depending on the surface and boundary conditions in various topologically organized cluster systems. The high-temperature superconductivity tendency in such nanocluster structures that are both stable and can give rise to different (non-phonon) electron pairing mechanisms is discussed. New optical effects were observed in such topological structures as well.

1. Introduction

The physical properties of nanocluster/granular systems are very sensitive to the shapes, sizes, and distances between their constituent elements, and also to their different chemical compositions. These phenomena are well known for any material, but changing these parameters and obtaining stable conditions for a monolithic solid object (e.g. in a crystal) requires extremely high pressures (≳10⁶ atm) and low (≲30 K) temperatures [1]. In contrast, a nanocluster structure can be easily modified in a controlled manner in any desired direction by means of femtonanophotonics (see e.g. [2]).

Modification of the above mentioned topological parameters in nanostructures could lead to a new type of quantum correlated states, especially for charged particles. In addition, the electric energy bands/gaps in such systems display considerable variations that determines the unique physical behavior of a system.

The problem of superconductivity faces the question of creating coupled/correlated states (near forbidden gaps) for the charged particles responsible for conductivity at high temperature. It is of fundamental importance that electric current in a superconductor is a surface current [1]. This means that the Meissner effect, which is traditionally used as a verification of superconductivity in monolithic cylindrical samples, is not occured for a thin film of nanocluster structures (thickness <100 nm). In the
case the complex shape of the nanoclusters leads to topologically different superconducting 2D-layers and/or one-dimensional wires that exist in a stationary state.

In this work, we consider the effects based on three fundamental factors: the dependence on size, including quantum size effects, for nanostructures with characteristic spatial scales of ~10 nm (number of atoms, ≲103); surface nanostructures with different defects, including boundary conditions that determines the phase transitions in inhomogeneous layers (1–100 nm); nearfield effects with local extreme values of key physicochemical parameters for low-dimensional inhomogeneous structures.

These factors must be considered to study the functional/physical properties of laser-induced micro-nanostructured composite materials, and are under our discussion for both electrophysical and optical properties.

We applied several laser procedures with different pulse duration (from cw to fs) to obtain the nanostructures and thin films with controllable topology. Namely, in addition to the direct laser modification of solid surfaces, we used, first, the laser ablation of targets in liquid to obtain colloidal systems and, second, to deposit the nanoparticles from the colloid on a solid surface for formation of nanostructures in necessary way by two technique: the laser radiation action and the droplet falling from the nozzle.

2.  Experimental results in electrophysics and discussion

In our experiments, the current-voltage characteristics (CVCs) of thin films were measured using the four probe technique. Two external contacts were used to supply the power voltage; the distance between them was L = 1 mm. Two middle (for measuring) microcontacts were conductive probes of an atom force microscope (AFM) used for diagnostics. During measurements they were scanned across a sample surface; the maximum distance between these contacts was no more than 100 μm. External voltage was applied in both longitudinal and transverse directions relatively to the length of the substrate, and was ranged from 0.1 to 1 V with an increment of 0.05 V. Thus, the magnitude of the external electric field was ranged from 102 to 103 V m⁻¹.

In nanocluster systems is exhibited competition between an increase in the conductivity due to the opening of new channels for charged carriers in a spatially inhomogeneous lateral nanostructure and, on the other hand, a drop in conductivity due to growth of the spatial intervals between localized granules. For a special configuration of the clusters on surface we observed a significant abrupt increase in electrical conductivity.

Several experimental results for thin films composed of silver and/or gold are shown in Fig.1. Measured current (I) – voltage (U) characteristics I(U) for the films with different thickness/heights display the jumps. The insert at the top of Fig. 1b shows in details the initial (left) part of the dependence of electrical resistance R on the size of the nanoparticles. Interestingly, this fragment of the curve can be represented as an analog of the Condo dependence for R on temperature T (i.e. R(T)) [1] but in our case this corresponds to dimensional dependence R(h) on the height h (see [2]).

Some variation in the presented dependences can be explained by the presence of the different electrical conductivity (σ) mechanisms in the cluster system: ballistic, diffusive, hopping, and thermo-activation. They correspond to different experimental conditions: the topological feature of the film structure leads to realization of the optimum modes (with minimum electroresistivity) for a given type of conductivity. The shape of the curves is generally the same for the lengthwise or crosswise directions of the voltage applied to a sample in the lateral plane using the microcontacts, i.e. it is indeed due to structural features of the film. Another distinctive feature is that when multiple trajectories for charged carriers are simultaneously available, we can speak about an effective integrated cross section of such structure determined by the surface area of the microcontacts/electrodes.

Indeed, the topology of cluster structures (the variation of parameters of the islands, including their overlap in some areas) leads to different mechanisms of a charged carrier propagation, and any of this can be observed in practice.
Figure 1: (a) Experimental CVCs curves for deposited layers of cluster Au films with different heights h. (b) Dependence of electrical resistance R on h. The insert shows a more detailed image for the initial part of the dependence. (c) Scheme of the experimental setup for measuring the electrical conductivity of granular samples (two ways of applying the external electric voltage are shown).

For tunneling conductivity between different zones separated by a potential barrier it should be a delocalized/metallic conductivity on both sides of the barrier boundaries. The hopping conductivity between neighboring/closed clusters, caused by charge transfer from one cluster to another (being the separated localized centers), is the effect of a quantum conductivity from corresponding discrete Hubbard levels with different hopping lengths.

Such hopping conductivity $\sigma$ in metallic structures is shown in Fig. 2a for certain experimental conditions. The behavior corresponds to the characteristic dependence for the Vannie–Stark effect observed in a superlattice [1]. The mechanism can be associated with cascade transition of charged carriers in a super-lattice ladder like it is happened in multiple quantum structure with discrete energetic levels. Obtained results demonstrate the absolutely reproducible negative slope (N-like differential electroresistance) due to concrete topology of the nanostructure resulting in transition from localized states of electrons to delocalized processes in whole.
Figure 2. (a) Experimental CVCs for a deposited layer of bimetallic film with equivalent concentrations of Au and Ag (1/1): (1) size of the nanoparticles $\sim 50$ nm, a single layer of close-packed particles; (2) size of the nanoparticles $\sim 10$ nm, five layers; distance between particles 4 nm; (3) size of the nanoparticles $\sim 10$ nm, five layers; distance between particles 2 nm. (b) Temperature dependence of resistance R for the samples with bimetallic film (Au + Ag). The films with heights of $\sim 50$ nm were deposited in laser experiments at different scanning rates of the laser beam: slow ($R_{slow} \sim 0.6$ mm s$^{-1}$) and fast ($R_{fast} \sim 1.5$ mm s$^{-1}$).

At the same time, the effect of thermoactivation also affects the magnitude of the current in the resulting island structure. We obtained that the temperature effect in the 20–100°C range for the charged carrier propagation depends on different rates of laser deposition of the substance on the substrate (slow and fast scanning of the laser beam) for two samples with the same average thickness of 50 nm. As can be seen from the dependences in Fig. 2b the resistance of both samples is virtually constant at the initial stage of heating due to the prevalence of tunneling transitions of electrons in the gold and silver films. Starting at $T=60^\circ$C the resistance falls vs temperature. This is reasonably due to the thermoactivation of electrons. The activation energy determined from the slope of the Arrhenius-type curves ($\ln \sigma \sim 1/T$) is in the 0.98–1.1 eV range being a small value in comparison with much more magnitude for bulk samples ($\sim 4$ eV). The effect is due to surface conditions on the substrate (see e.g. [3]).

Another principal factor for the thermoactivation mechanism is the strength of the local field acting on the charged carriers in a potential quantum well. If its strength is sufficient (which is determined by the specific topology of the sample surface), the conductivity can increase dramatically due to the charge exiting from the potential well according to the energy parameters, regardless of the fixed value of temperature (cf. [4]). This effect of the amplification of the electrical conductivity (similar to the mechanism of the SERS effect in spectroscopy) was also observed in our experiment.

Fig. 3 shows the variation of the R-value (in 4 orders of magnitude) on the dependence of the electrical resistivity R on the topology of a cluster structure deposited on a substrate. Fractal dimension D is a quantitative characteristics of topological features. Its value for different granular structures was estimated according to the procedure described in [2]. The measured ($R_{meas}$) and estimated ($R_{calc}$) values of the electroresistance are in good agreement. The latter value ($R_{calc}$) was estimated for the tunneling mechanism using standard percolation model.

Figure 3. Comparison of both experimental and theoretical values of electrical resistance R for different topology of Au-nanostructures (AFM-images of surface structures are shown). The results for selected topological conditions: a) $R_{meas} = 6.1 \times 10^{11}$ $\Omega$, $D = 1.39$, $R_{calc} = 2.8 \times 10^{11}$ $\Omega$; b) $R_{meas} = 8.3 \times 10^{10}$ $\Omega$, $D = 1.57$, $R_{calc} = 1.9 \times 10^{10}$ $\Omega$; c) $R_{meas} = 5.4 \times 10^{8}$ $\Omega$, $D = 1.84$, $R_{calc} = 9.3 \times 10^{8}$ $\Omega$; d) $R_{meas} = 3.6 \times 10^{7}$ $\Omega$, $D = 1.93$, $R_{calc} = 5.5 \times 10^{7}$ $\Omega$, where $R_{meas}$ and $R_{calc}$ denote the measured and calculated values, respectively, $D$ is the fractal dimension of the cluster structures. For samples a), b) the size of nanoparticles is $a = 50$ nm; for samples c), d) $a = 5$ nm.
By this result we may discuss the problem of high temperature superconductivity in topological nanostructures. In fact, the experimentally observed abrupt increase in electrical conductivity (depending on the topology of a nanostructured film surface) may be presented as a tendency to high-temperature superconductivity in inhomogeneous system in the context of new principles of the state coupling occurring for systems with reduced dimensionality. When forbidden gap arises we have an opportunity/tendency to room-superconductivity especially for topological defects with electron hybridization. The problem should be discussed separately.

3. The nanoplasmmonic optical measurements

Several obtained by us optical characteristics depending on the topology factors of thin films (Au+Ag) are shown in Figs. 4. Different degrees of modifications for plasmon resonances are demonstrated. The case is reasonable because different ratio between the spatial scale of the inhomogeneities in comparison with the wavelength of local Mie-resonance in the substances occurs.

Figure 4. Experimental results for both optical density D (a) and transmission T (b) spectra of the Au+Ag complex deposited on glass substrate. Different thicknesses are indicated by numbers (in nm). Three types of AFM-images are shown at the right; the numbers (1) –(3) indicate correspondence with spectra-curves. Plasmon resonance wavelength in monolith samples: 390 nm for Ag; 520 nm for Au.

Thus, it is possible to control both the plasmon resonance behavior and propagating plasmon waves due to inhomogeneous structure (being a random manifestation of special schemes for travelling waves). Absence of narrow plasmon resonance is namely due to inhomogeneous nanostructure.

According to general view the results for electroresistance R (see Fig. 3) should be correlated with optical spectra (plasmon resonance for metallic films) vs structure: more electroconductivity in shell like system may be a result of a high density distribution of electronic levels, i.e. due to large spectra. Key parameters for that, first, sharpness of the surface (width and depth of inhomogeneities), second, observable shift and peculiarities of spectra. The comparison of these two factors is shown in Fig. 5. But for a granular structure it is not so easy to have one-way correspondence (like uncertainty in spectrum for photonic crystals with a spatially varied parameters).
Figure 5. The plasmon resonance curves for transmission spectra of Au-nanostructures associated with AFM-images of the thin films (are shown as insert)

4. Conclusions

The electrophysical and optical properties of different types of nanocluster structures (in both topology and composition) were studied. For the nanosystems obtained by laser means, emphasis was placed on considering correlations in an ensemble of nanoparticles with quantum states (localized and delocalized).

The high-temperature superconductivity caused by topological surface/boundary structures with localized states was discussed in the context of new principles of the electron state coupling occurring for systems with reduced dimensionality. Further research in this area should be focused, on the one hand, on a more detailed comparison of experimental results on the increasing electrical conductivity in correlation with topology of laser-induced nanocluster thin-film systems and, on the other hand, on the specific mechanisms of such correlation development for coupled electrons at different (controlled) conditions.

The experimentally observed optical spectra (depending on the topology of a nanostructured film surface) can be considered an indicator of the high-temperature superconductivity tendency arising due to topological features of a synthesized nanocluster system. Separate direction is to control the plasmonic resonance behavior in complex metal-dielectric structures especially for artificial meso-atom nanoobjects of the different element composition with unique optical characteristics.

Achievements in this area should provide direction for possible applications of these phenomena in a new generation of fentronanophotonic devices. Hybrid schemes that combine the electrophysical and optical properties of such structures (exhibiting macroscopic quantum states) would seem to be most promising for modern topological photonics.

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