Laser technology for low dimensional nanocluster physics

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Abstract. We studied laser-induced nanocluster structures of different types both in theory and experimentally (in topology and the element noble metal/carbon compositions) taking into account the correlations in nanoparticle ensemble by quantum states. The quantum size effects in both electrophysics and optics are discussed. The problem of high temperature superconductivity, due to topological surface structures with correlated states, is under our consideration in frame of both nonlinear dynamic modeling and the path integral-theory approach for an electronic Cooper pair appearance. The computer simulation of electrophysical and optical properties in such inhomogeneous cluster structures of thin films has been carried out. Good agreement with our experimental results is obtained.

1. Introduction

The physical properties of nanocluster systems are very sensitive to the form, size and distance/spatial distribution between their components. The fact is well known for any material in general, but to change these parameters and to carry out the stable conditions for the ordinary solid state objects we need to put the objects under extremal conditions (cf. [1]). In contrast, nanocluster structures can be easily modified in necessary way in the femto - nanophotonics laser experiments (cf. [2]). They may be presented as a grid ensemble of a single-electron objects (with a certain effective mass \( m_{\text{eff}} \)) demonstrating a nonlinear quantum dynamic behavior around the forbidden gap. In superconductor problem the question is how to fabricate the coupling states for charged particles being responsible for electroconductivity, and we discuss some alternative mechanisms of electronic coupling (in equilibrium states), but not via standard a Cooper phonon coupling [1]).

In optics we obtained some new effects: strong resonant optical response in both the visible spectral and the near-IR ranges for silicon nanoparticles (NPs); broadening of the near-field photoluminescence spectra in hybrid NPs (Si+Au) compared to pure Si-NPs; a remarkable nanoantenna effect for the near field emission of Si-NPs by covering them by small size NPs (golden shells trigger); creation of metasurfaces suitable for controllable manipulation of the transmission and reflectivity of light (important for optical integrated circuits).

The computer simulation of several obtained in experiment results showed a reasonable coincidence both for electroconductivity and optical spectra.
2. Physical basis

We completed several laser procedures for obtaining nanostructures and thin films with controllable topology [2]. They occur under development of different dynamic processes in the system (thermodiffusion, gas-dynamic evaporation in pore-like structures with bubbles, ablation products, ballistic movement of the particles in liquid), being depended on the laser pulses duration. The interaction effects of solid targets with laser pulses of different durations for obtaining various nanocluster structures can be viewed as the possibility of synthesizing the 4D objects, when the result depends not only on the stationary topological/geometric parameters of the system, but also on the dynamic interactions in the system leading to different final stable structures. This is due to the fact that for different durations of laser pulses the specific mechanisms of nanostructuring are activated. Therefore, time plays the role of a control parameter responsible for phase transitions, as well as the spatial parameters do when nanostructures of various dimensions arise – from quantum dots (0D) to 3D nanostructures. In addition, for short laser pulses we have non-equilibrium/transient phase transitions over the steady-state pressure-temperature (PT) phase-diagram according to the laser trajectory of heating. Although the conventionality of this consideration is obvious (the equilibrium phase diagram cannot be used for non-stationary processes), but it allows to discuss the current trends and clarifying the basic physical picture.

The cluster, as a system of many interacting nanoparticles, may be described in frame of different models of collective behavior in dynamics of the composed components (both in stable state and unstable/high excited states). We consider briefly two models (cf. [1,3]).

2.1. Localization-model (Fig.1).

The simple model based on insulator matrix with metallic islands and the quantum well barriers with principal parameters: sizes r; distance R; shape (spherical and/or ellipsoidal); density of distribution over surface (both regular and random); thickness d of the film; amorphous phase and/or crystalline structures and/or also incommensurate phase exhibit.

![Figure 1](image_url)

*Figure 1*: A localized metallic quantum well model in insulator master matrix for the nanocluster (NC) ensemble (a) and the energetic levels scheme (b): $E_{potential} = \hbar^2 r^2/8mr^2$; $m$ – effective mass; $\Delta E(n) \sim n$; $\Delta E(r) \sim 1/r^3$. The designations are shown on the images.

In optics such objects result in modification of the energy spectra: both broadening of electronic level due to tunneling electricity (by analogy with overlapping of energy levels), and photoemission occurred as well by low frequency light (i.e. a low work function takes place for the object) for nanocluster system in comparison with monolith sample.

In superconducting problem the Josephson tunneling happens through dielectric layers (like delocalized metallic conductivity and, in addition, hysteresis in resistivity may arise on semiconductor surface when R>r (due to delayed modification of localized states).

Competition between two mechanisms of the conductivity ($\sigma$), first, the tunnel ($\sigma_0$) and, second, thermally activated/hopping ($\sigma_1$) occurs according to formula: $\sigma = \sigma_0 + \sigma_1 \exp (-E/kBT)$, where $\sigma_0$ is
dominated for $R<r$ (the temperature $T$ independent mechanism), but $\sigma_1$ is dominated for electronic transport at the adjustable temperature vs topology structure ($R>r$), where $E$ – the electron activation energy; $k_B$ – Boltzmann constant.

2.2. Delocalization-model (Fig.2).

In the case a transparency coefficient $D$ for charged particle via potential barriers $U$ is ($U>E$):

$$D = D_0 e^{-\frac{2\alpha R}{\hbar}} = D_0 \exp\left[-\frac{(2R/\hbar)^2}{2m(U-E)}\right].$$

For $U_I=U_{II}$ we have the same kinetic energy $E_{\text{kinetic}}^I = E_{\text{kinetic}}^I$ from both sides of the barrier.

In this representation with many-body barriers, we can tell about the electron propagation in inhomogeneous structure. The multiplicity of spatial distribution of the objects in laser synthesized ensembles of nanoclusters can also lead to the formation of macroscopic quasi-periodic localized structures with fundamentally new effects, including the Anderson localization, etc. In contrast, incommensurate phase structures/superlattices arise in the structures due to laser-induced quasi-particles/phasons. In the case we have the long-wavelength periodic inhomogeneities with respect to one/several parameters with a period that is incommensurate with the underlying solid state/crystalline structure of the material. In general, there are three types of planar inhomogeneous surface structures with nanoparticles: deterministic nonperiodic, deterministic periodic, and randomly rough (cf. [4]).

Moreover, we can draw an analogy with an ensemble of clusters in which the point defects determine the forbidden areas, in particular for phasons, affecting on the quantum states of the electron subsystem (the probability density of electronic states is determined by their wave functions). For that, it is useful to introduce an optical analogue of this situation when we consider the intensity of light scattering $I_{\text{scat}}$ in such structures. In fact, the intensity of scattering by phasons is $I_{\text{scat}} \sim 1/(1 + q^2 \xi^2)$, where $q = 2k_0 \sin \theta/2$ is the wave vector of scattering, $\xi$ is the length of correlation, $k_0$ is the wave vector of the incident light, $\theta$ is the scattering angle (using the Ornstein–Zernike approach) [4]. Although we do not consider acoustic oscillations (i.e. the phonons) in this case, that change the phase of the waves, and we can talk about the similar problem with Bloch oscillations.

Quantum mobility of electrons over different trajectories in a spatially inhomogeneous structure, i.e. in nanocluster network system, may be presented in accordance with the path integral-theory approach [5]. For the sequence (in time $t$) of spatial position (over x-coordinate) of electrons the conditions are: $x(0) = 0, a_1 < x(t_1) > b_1, ..., a_n < x(t_n) > b_n$, where $(a_i - b_i)$ – the i-section along $x(t)$, $0 < t_1 < t_2 < ..., < t_n$. Typical trajectories for quantum particles can be displayed by the following scheme: $F(x(t)) \rightarrow F(x_n, x_{n+1}, ...)$.

For a small time internal $\Delta t$, where $\Delta t = \varepsilon$, and $t_{i+1} = t_i + \varepsilon$ we can present $x(t) \approx x_i = x(t_i)$ and have an ordinary function with the functional parameter $\langle (x_{i+1} - x_i)/\varepsilon \rangle^2 \sim 1/\varepsilon$. But though the quantum trajectories are of chaotic and fractal type (and for $\varepsilon \rightarrow 0$ are infinite) we can, nevertheless, have for electrons a finite drift velocity controlled by topology due to averaging over some
reasonable on practice both time interval and spatial areas. Thus, we can use a traditionally nonlinear/quantum mechanics procedure for the charged particle moving.

In fact, in frame of the Brownian particle movement for \(x=x(t)\)-trajectories in the Einstein-Smolukhovskii approach the problem can be formulated by following way.

We have for the probability \(W(x_t)\) describing the particle travelling along \(x(t)\):

\[
W(x_t) = \int \cdots \int P(0\mid x_1 b_{n-1} a_n b_1 a_1; t_1) P(x_1 \mid x_2, t_2 - t_1) \cdots P((x_{n-1} \mid x_n, t_n - t_{n-1})
\]

where \(P(x \mid y; t) = \frac{1}{2\sqrt{\pi D t}} e^{-\frac{(y-x)^2}{4Dt}}\), \(D\) – diffusion coefficient, \(t\) – time. In the limit \((t_k - t_{k-1}) \to 0\) we have \(W(x_t) \to \) the infinity dimension path integral.

In quantum theory a probability amplitude is equivalent to path integral with core 
\[K(b, a) = \int_a^b e^{iS[\pi_x]} Dx(t),\]
where \(D\) – differential operator on all coordinates \(x_1 \ldots x_n\), 
\(S\) – action parameter, the core \(K(b,a)\) for transition \(x_a(t_a) \to x_b(t_b)\) is a sum of contributions of all possible \(i\)-trajectories \((a,b)\) with phases \(\phi_i[x(t)]\) in contrast with a single/averaging trajectory \(\bar{x}(t)\) in classical case. The physical parameters for the problem are the transition amplitudes between different states \(\{a_i\} \to \{b_i\} – \text{Fig.3}.

![Figure 3](image)

**Figure 3.** Transition scheme from initial state (a) to final state (b) by multiple \(i\)-trajectories with phases \(\phi_i[x(t)]\).

### 3. Reasonable models

In our study the physical properties of the nanostructure thin films are based on several principal models. First, the phenomena is strongly depending on the topology of a nanostructured film surface (Fig.4). The original shape of the nanoobject was considered spherical (radius \(R\)); the shape is indignant at the change of key parameters – the azimuthal and zenithal angles.

![Figure 4](image)

**Figure 4.** Model of various topology structure with distortion of the original spherical object. Key parameters: \(R>0\) is a particle radius, and the angles \(\phi, \theta\) are in a spherical coordinate system.
0 ≤ k1 ≤ 1 – value of the azimuthal distortion coefficient (in term of «latitude»); 0 ≤ k2 ≤ 1 – value of the zenithal distortion coefficient (in term of «longitude»); p1 = 0, 1, 2, ... – is the number of azimuthal distortions; p2 = 0, 1, 2, ... – is the number of zenithal distortions.

Calculation formula: 
\[ F(\phi, \theta) = R \cdot \left\{ (1 + k_1 \cdot \cos(\theta)^2 \cdot \sin(p_1\phi)) + k_2 \cdot \left[ (-1)^{\frac{p_2-1}{2}} \cdot \mod(p_2, 2) \cdot \sin(p_2 \neq 0) \cdot \mod(p_2 + 1, 2) \cdot \cos(p_2 \cdot \theta) \right] \right\} \]

For electroconductivity the results of our modeling are shown in Fig. 5A,B. Such electrical transport properties is due to the quantum correlated states resulting in tunnel and hopping electrical conductivity. There is a competition between the bulk and surface electrical conductivity contributions controlled, to a great extent, by a deposited cluster topology. In our modeling for electroconductivity the original shape of the nanoobject was considered spherical, as well, but also being transformed by the key parameters: values and numbers of the azimuthal distortion coefficient (in terms of «latitude»). And the zenithal distortion coefficient (in terms of «longitude»). There is a good correspondence with our experimental results (Fig. 5C) – see [3].

**Figure 5.** Volt-Ampere Characteristics (vertically axis – current I, horizontally axis – voltage U) of thin films when (A) the distance (S) between the conducting islands changes and (B) the radius (R) of the
deposited particles changes. Different values of the parameters are directly indicated in the Figures. C) Experimental results of VAC obtained by us for PbTe-nanostructure.

Moreover, electronic energetic bands of the materials may vary dramatically in the case. Some new physical states of the system, particularly in optical response, consider in [6,7].

In nano-optics, to calculate the spectral reflection and transmission coefficients, we used the Finite Difference Time Domain Method, FDTD. The calculation was performed using the transmitted and scattered fields, (TF/SF)-method, with a simulation of a plane optical wave source. This method is based on the linearity of the Maxwell equations for electric and magnetic fields, and also on the principle of superposition. The calculated transmission spectra are in qualitative agreement with the experimental data (Fig.6).

Figure 6. Transmission spectra $T(\lambda)$ of deposited films: 1 – Au:Ag (weight ratio 1:1), particle diameter (D) – 50 nm, one layer, distance between particles (gap) – 5 nm; 2 – Au:Ag (1:1), D – 10 nm and five layers, gap 4 nm; 3 – Au:Ag (1:1), D – 10 nm and five layers, gap 2 nm; (a) – experiment, (b) – theory.

Second, nonlinear dynamic model may be applied for superconductivity (by different mechanisms) in the frame of nonlinear Verhulst model being initially applied to the genetic processes (development in time t) [8]:

$$\frac{dN}{dt} = (\alpha - N + \gamma N)(1 - N),$$

where $N$ – density number of the Cooper pairs; $\alpha$ – some numerical parameter for concrete physical process, $\gamma$ – parameter of the pair arise which shows the difference between two processes, i.e. appearance and disappearance of the electronic Cooper pairs for $\gamma \neq 0$. Last term $\sim (-\gamma N^2)$ indicates a natural limitation/saturation of the charge concentration being determined by different reasons in each physical system. When $\gamma < 0$ we have not the coupling pairs, and for a steady state solution $N_0 = 0$. But for critical quantity $\gamma = 0$ the state $N_0 = 0$ becomes unstable, and a new branch in the solution arises: we have a bifurcation and transition to the steady state $N_0 = \gamma$ (second order phase transition). If we take into account the fluctuations in the system, such critical quantity is modified, and the condition $\gamma > 0$ occurs in respect of the noise value. In our case it is a question of the topology variation structure. Moreover, there is a critical value of fluctuations in the system $\sigma_c$; when for $\sigma^2 > \sigma_c^2$ the splitting of the thermodynamic free energy density $W(N)$ in two peaks (bimodal state) takes place. This can interpretate as a spontaneous breaking of symmetry being a principal effect for the problem of superconductivity. The case means that noise induces the transition in the system being stable in determinate conditions. In our case the noise means that the variations of topological parameters occur (cf. Fig.5).

Third, the multiple trajectories for charged carriers/electrons in inhomogeneous cluster structure may be presented in general fundamental approach based on statistical/quantum statistical physics, including analogy with the quantum path integral theory. We discuss now the problem shortly.

Two cases may be under consideration (according with [5]).
(1) In one dimensional moving electron transition for x(t) between two fixed points \(x_1 \rightarrow x_2\) during time interval T we can write: \(<x(0)> = x_1 <1>, \) where the initial state is \(<0>, \) and sing \(<…>\) means the average/expected magnitude in consequent state; \(<x(T)> = x_2 <1>. \) For that we have a quantum analogue of the Newton equation in ordinary form \(<m\ddot{x}> = - <V'(x)>, \) where \(V(x)\) - field potential, \(V'(x)\) - its gradient. Thus, \(<x(t)> = [x + \frac{\pi}{T}(x_2 - x_1)] <1>, \) being an universal result for transition matrix element along the classical trajectory \(\tilde{x}(t). \)

(2) In multitrajectories model in two different times \(t, \tau\) for moving electrons:
\[<x(t)x(\tau)> = [x(t)x(\tau) + \hbar \frac{m}{T}(t-\tau)] <1> \] at \(\tau <t\) and \[<x(t)x(\tau)> = [x(t)x(\tau) + \hbar \frac{m}{T}(T-\tau)] <1> \] at \(t <\tau. \)
Thus, we have a quantum addition (second term) due to the different trajectory matrix elements for different closed trajectories.

In addition, taking into account the topology variation, being associated with field potential \(V(x)\) variation in the approximation of harmonic oscillator with \(V(x) = V(x)(e^{\text{iat}} + e^{-\text{iat}})\) for matrix element \(x(t)x(\tau) \equiv f(t,\tau)\) we have:
\[<f(t,\tau)> = [\tilde{x}(t)\tilde{x}(\tau) + g(t,\tau)] <1>, \] where quantum terms \(g(t,\tau) = \hbar \frac{m}{T} \text{sin} \omega \tau \text{sin} \omega (T-\tau)\) at \(\tau <t, \) and \(g(t,\tau) = \hbar \frac{m}{T} \text{sin} \omega t \text{sin} \omega (T-\tau)\) at \(t <\tau. \)

In frame of such approach we can obtain the transition amplitude for both Hamiltonian \(H\) and matrix element \(<\chi|H_k|\Psi>\) between two quantum states \(\chi\) and \(\psi\) (for one dimensional movement of electrons in time \(t_k)): 
\[H_k (t=t_k) = (m/2)x_k + \frac{\hbar}{T} \sin \omega t \text{sin} \omega (T-\tau) \]
\[<\chi|H_k|\Psi> = \int_{-\infty}^{\infty} \chi^* x_k \frac{p^2}{2m} + V(x) |\Psi dx = \int_{-\infty}^{\infty} \chi^* H \Psi dx. \]
Thus, in cluster system it is possible to have quantum picture for electron transitions between initial and final states which can be associated with classical trajectories (cf. [3]).

All these processes may be analyzed in accordance with different nonlinear hydrodynamic regimes. We consider the possible nonlinear mechanisms (cf. [8]) being responsible for both a high electroconductivity and the features of obtaining a hopping conductivity in such inhomogeneous thin film surface structures (with the thickness of up to 100 nm) when the charged particles are propagating along the boundary surface.

The approach is reasonable because there is a fundamental problem of a critical current density drop caused by the coating thickness (more than several microns) for superconductor layers. An important fact is that in a thin film/granular structure the Meissner effect, being traditionally a verification for superconductivity, doesn’t work [1]. Therefore, the fact of abrupt increase of the electrical conductivity (at the room temperature in our experiment) is principal in respect of the superconductivity tendency manifestation in a cluster system (cf. [3]).

4. Conclusions
Obtained results give us an opportunity to establish the basis of new physical principles to create the functional elements for topological photonics in hybrid set-up (optics + electrophysics) being controllable by nonlinear quantum dynamic processes.

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