Granular dynamic structures of different topologies on the surface of solid materials; control of their distribution by laser treatment

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Abstract. The topic is focused on the technological features of the laser radiation action on the surface of metals to study various modes of formation of granular structures, which ultimately determine the functional and structural properties of products being under laser treatment. It is presented the results and algorithms being useful to predict the development of new technological processes on the material surface induced by laser radiation with an appropriate choice of key control parameters for the corresponding phenomena.

Introduction
New unique materials based on granular dynamic nanostructures on a solid surface form the basis for the development of promising materials with predetermined properties that can be used in various fields of nanoelectronics and photonics as a new element base. The controlled physicochemical properties of such materials substantially depend on the location of structural features on the surface. In this regard, the development of methods for controlling the placement of nanosized elements on a solid substrate becomes a very urgent task [1-2].

One such method is controlled laser synthesis, which allows one to obtain a wide class of nanostructured materials with the required surface topology due to the controlled motion of the laser beam [3-5].

The controlled production of granular structures on the surface of various topologies and the study of their features
Granular metal (Ag, Au, their complexes) structures were obtained by the original method of laser deposition of metals from colloidal solutions of noble metal nanoparticles (Ag, Au, Ag / Au sweep) (with an average radius of 100 nm) in glycerol [6-8] on Al the substrate placed in them. The proposed method allows one to obtain films with controlled topology by controlling the deposition process by changing the basic parameters of laser radiation, such as, for example, wavelength, power, repetition rate of laser pulses, scanning speed [9], etc.

The experimental design is shown in Fig. 1.
Figure 1. Schematic diagram of the experiment on laser deposition of metal nanoparticles from a colloidal system: 1 - laser radiation, 2 - cuvette with a colloidal solution, 3 - substrate, 4 - track deposition of a nanostructured surface when the laser beam is displaced.

The laser irradiation process was implemented using a YAG: Nd3+ laser ($\lambda = 1.06$ $\mu$m) with Q switching. The laser pulse duration was 100 ns, the average radiation power was 2.5 W, the pulse repetition rate was 20 kHz, and the diameter of the laser beam on the surface of the glass substrate on which the nanostructures were formed was 50 $\mu$m. The laser beam moved along the surface of the substrate at a speed of 0.4 mm/s to 5 mm/s.

As a result of local laser exposure to a colloidal solution on the surface of the substrate placed in this solution, sintered noble metal nanoparticles (Ag, Au, Ag / Au sweep) were deposited along the beam path with the formation of granules, the character of which depended on the number of passes in the deposition region (fig. 2). The obtained nanostructures were investigated using a Quanta 200 3D scanning electron microscope and an Integra-Aura probe nanolaboratory. So after 5 scans, a granular film is formed (Fig. 2.2 a), with an average relief height of 14 nm, and after 10 (Fig. 2.2 b), the granule area increases significantly, and the average relief height becomes 18 nm.

Figure 2. AFM images of bimetallic Ag / Au nanostructures. Laser radiation power 2.5 W, scanning speed 1.2 mm/s. Image: a) 5 passes, b) 10 passes.

Images were studied and processed in more detail using the Image Processing Toolbox of the MATLAB scientific environment by using the Sobel operator to estimate the gradient [10]. Using the capabilities of the aforementioned tools and assessment, taking into account the connected components with a value of connectivity equal to 8 [11], allowed the selection and grouping of granules by height and area (Fig. 3a, b).
Figure 3. Results of processing AFM images a) image of the film from Fig 2. b with selected granules b) grouping of granules by size.

The studies of the obtained structures (Fig. 3) showed their dendritic character, which was confirmed by the values of their fractal dimensions calculated by the box-counting method [12].

Description of the surface models of the obtained granular structures

To describe the features of the obtained dendritic granules, a diffusion limited aggregation (DLA) model was chosen [13-14] in the vicinity of von Neumann of order 1 [15] (Fig. 4b), with differentiation by the type of particles, the number of which was selected in accordance with the concentration in the colloidal solution. In the framework of the indicated approximation, a particle was generated in the nucleation region, made random walks [16], until it stuck with a given probability of adhesion or destroyed when it fell into the region of destruction (Fig. 4a).

Figure 4. Granule model: DLA scheme (a), von Neumann neighborhood (b).

The main parameter characterizing the dynamics of the thermodiffusion process of dendritic granule formation was the probability of adhesion sc from (0; 1]: sc = 1 - at the maximum colloid temperature at the beginning of the deposition process (t≤1000 * s time steps, s is the value of the side of the computational domain), and sc = 0.01 — at the minimum at the end of the process. At t≥ 1000 * s, it decreased by 0.1 every 1000 time steps, and the minimum value of the probability of adhesion reached 0.01 premature colloid when particles pass a longer distance until adhesion [17].

The results of modeling the surface of granular structures

In the simulation, the initial concentration of aggregation centers and their position were varied, based on the histogram of the size distribution of the granules, as well as the probability of particle adhesion. The computational domain was selected with a side of s = 100 rel. the maximum density of aggregated particles was chosen to be 0.4; the concentration of gold and silver particles in the colloid was chosen to be the same, equal to 0.5.

Figure 5 shows a model image of a granular Ag / Au film (Fig. 3 b) for 7 seed particles (Fig 3a), in the case when the values of the nucleation and destruction regions coincide and are equal to the
calculated value - the particles nucleate at the boundary and do not leave. In Fig. 5 - yellow particles - gold, blue - silver. Numbers 1-7 indicate the seed particles and granules obtained on their basis.

For the simulated structures, the fractal dimension was calculated, which was calculated as $d = \frac{\ln(n)}{\ln(r)}$, where $n$ is the number of particles that make up the fractal structure, $r$ is its radius [18]. So for the structure from fig. 3b, its value was 1.6941. By analyzing various calculation options, one can trace the proportional relationship between the number of seed particles and fractal dimension. So, with an increase in their number, the dimension increases. For example, for the case of 8 seed particles, $d = 1.7298$.

At the initial stages of generation, when the probability of adhesion is high, the structure of the granule is characterized by sufficiently strong branching [19], and the fractal dimension, on the contrary, is low. Over time, the value of the probability of adhesion decreases, and the generated fractal structure of the island becomes almost evenly distributed along the edges, the fractal dimension increases, for example, even to values of 2.06. In the case of aggregate growth from an initially homogeneous system (Fig. 5a), several cluster islands arise simultaneously, and their growth is realized due to the absorption of small particles, as well as the fusion of already formed structures with each other [20]. For example, in Fig. 3b, islands 2, 3, 4, 5 are combined into a single structure. Such conditions make it possible to simulate well-formed granular films obtained at the final stages of experimental studies. The proposed model allows a first approximation to estimate the size of the islands of the nanofilm, moving from relative to absolute units by indicating the characteristic value of the particle.

For example, for island 6, the diameter of the circumference of the coating was 40 rel. units, and the fractal dimension is 1.8286. So for an island with a diameter of 40 rel. By setting the particle size to 10 nm, it is possible to estimate the absolute diameter of the coating circle as 400 nm. This qualitatively coincides with the results of the Integra-Aura probe nanolaboratory.

**Conclusion**

The proposed experimental laser method allows one to obtain granular dynamic structures of noble metals (Ag, Au, Ag / Au) of various topologies on the surface, for example, dendritic ones. The surfaces of the resulting structures were investigated by experimental and theoretical methods, which allowed us to conclude that they had a predetermined relief and properties obtained by controlling the characteristics of the laser radiation, as well as the number of passes of the radiation beam over the treated surface. The proposed model of the formation of the film structure in the DLA approximation, taking into account viscosity variations proportional to the temperature of the system, makes it possible to evaluate the shape, size, and distribution of the resulting granules, and therefore can be a useful description for predicting the properties of structures obtained by the controlled laser method.
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