The melting regimes induced controllable by laser radiation on the surface of solids with the diagnostics of arising micro-nanostructures and hydrodynamic instabilities

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Abstract. We applied a controlled method for producing nanostructures on glass substrates. We made detailed measurements to control the resulting micro- and nanostructures using as the principal example of surface modification of glassy carbon compositions under laser irradiation. The properties of the samples after laser irradiation were studied using atomic force microscopy (AFM) with an accuracy of about 10 nm in the scanning plane. The results of probing the material modification by the AFM images of its surface have been considered in frame of the nonlinear hydrodynamic mathematical approach and computer simulation.

Introduction

Today, new unique materials, structured by nanoparticles into the main matrix of the substance and / or onto the surface, form the basis for the development of promising materials with predetermined properties that can be widely used in various fields of nanoelectronics and photonics as a new element base, for example, information storage elements and energy, thermoelectric sensors, detectors, radiation sources, solar panels, etc [1,2]. The physicochemical properties of such materials substantially depend on the location of structural features on the surface, which makes it possible to control their properties. In this regard, the development of methods for controlling the placement of nanoscale elements on a solid substrate becomes a very important task. Existing methods of substance transfer are technologically complex and expensive, and so impose significant restrictions on the choice of the working material used.

For these reasons, laser-controlled synthesis of nanostructured surfaces is one of the fastest growing tools of modern micro-nanoelectronics and photonics, 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, 4].
Results of experiments
Let us consider the methods of forming nanostructures on substrates using the example of island nanofilms [5]. In our experimental studies, we examined the surfaces of graphite samples, glassy carbon / metal-carbon compositions exposed to laser radiation. The methods used for the above materials can be extended to other materials, but studies knitted with carbon are the most promising for the future development of new generation technologies [6].

The formation of an island nanofilm on a substrate occurs within the framework of self-assembly from the bottom-up mechanism, therefore, the proposed method of direct laser deposition [7] on a transparent substrate allows this process to be controlled by changing the basic parameters of laser radiation, such as, for example, wavelength, power, laser pulse repetition rate, scanning speed, etc. It was shown in [7-8] that a change in the geometry and experimental conditions can lead to a change in the morphology of the deposited layer.

The experimental design for the formation of island aggregates of carbon nanofilms by direct laser deposition is shown in Fig. 1. A YAG: Nd3+ cw laser source with a wavelength of 1.06 μm was used. The radiation power ranged from 5 to 50 W, the diameter of the laser beam on the surface of the carbon target (spectrally pure graphite, h ~ 25 μm, d ~ 400 μm, H = 500 μm) was 100 μm, the distance from the target surface to the substrate plane on which the formation of nanostructures occurred, varied from 0.1 mm to 1 mm, the time of irradiation with a laser beam was 20 seconds.

![Figure 1](image)

Figure 1. Scheme of the experimental setup: 1 — laser radiation; 2 - a substrate transparent to laser radiation, on which a deposited layer is formed; 3 - gas-dynamic channel through which the transportation of the evaporated substance; 4– input channel (diameter - d), limited by side walls (5); 6 - region of interaction of laser radiation with the target; H is the height of the side walls; h is the height of the channel; 7 - periodic relief (has a depression depth h_c and pitch d_c) of the gas-dynamic channel.

After laser irradiation, the surface of the cold substrate was studied using an atomic force microscope with an accuracy of about 10 nm in the scanning plane (figure 2). It was found that in the region of the substrate, the center of which coincides with the region of passage of the laser beam through it, the deposited layer is not formed. The size of this region varies from 50 to 200 microns, and decreases with increasing power. Further, at a distance approximately equal to the distance to the inner edge (200-500 μm) of the technical equipment, a uniformly deposited layer is formed. The deposition structure inside the formed channel and beyond it changes significantly.

A complex profile with an average height of 150 nm is formed inside the channel formed by the plane of the substrate and the surface of the snap. Beyond it, in the region of free expansion of the vapor-gas cloud, self-organization of the deposited layer occurs, and island structures are observed to be formed with a diameter of 100-200 μm and an average height of 30 nm.
Figure 2. Changing the structure of the deposited layer: a) inside the field of technological equipment; b) abroad the field of technological equipment.

Figure 3. Images of the surface of the layer deposited on the substrate (b); obtained at the AFM during exposure using a gas-dynamic channel with a step of periodic relief $d_c = 5 \, \mu m$, $h_c = 3 \, \mu m$ (a).

It can be seen from the figure 3 that the use of a gas-dynamic channel with a periodic system of depressions allows one to order deposition on the substrate surface.

**Laser Deposition Product Propagation Model**

To control the topology of the synthesized island nanolayer, it is necessary to be able to predict the structure of the deposition region, for which a mathematical modeling apparatus is applicable. The distribution of precipitation products is conveniently presented in the hydrodynamic approximation [8].

Calculation of the hydrodynamic model in a first approximation allows us to determine areas with sufficiently high concentrations of precipitation products, from which the formation of well-formed islands is possible.

The hydrodynamic model of the propagation of laser deposition products [9] is described by the stationary Navier-Stokes equations for the plane geometry problem [10]. The computational domain was a channel with one input and two output sections (fig. 4).

The mathematical model in the framework of the Navier-Stokes equations represents a system of dimensionless equations for the stream and vortex functions. The boundary conditions at the inlet and outlet sections are determined in accordance with the Poiseuille flow. On the walls of the channel, the values of the current function are set based on the sticking conditions. The boundary conditions for the vortex were set approximately according to the Woods formula [11]. When constructing the numerical model, a uniform grid was used. Difference equations for determining the solution at the grid nodes are obtained on a five-point pattern [12]. The difference scheme approximates the initial problem with the second order relative to the grid steps. The equations for the vortex were obtained on the basis of the integral method [13], so that the difference scheme is conservative. An important feature of the circuit is its monotonicity, which ensures its stability without special restrictions on the size of the grid steps. The system of equations for the values of the solution at the nodes of the grid is solved by the
relaxation method. The relaxation procedure is applied not only in internal nodes, but also extends to boundary conditions. The accuracy of the calculations was supposed to be about 0.1%.

Figure 4. Calculation area: channel with one input and two output sections.

Figure 5. The trajectory of the deposited atom.

Substrate nanostructure model
To calculate the characteristics of a nanofilm, as a first approximation, one can use a model based on the principles of molecular dynamics [14,15], with plane symmetry, when an atom during deposition moves in the same plane perpendicular to the substrate (Fig. 5). An atom is introduced into the calculation zone at an arbitrary point \((x_0, y_0)\) with predetermined velocity projections on the \(x\) and \(y\) axes: \(u_{0x}=u, u_{0y}=v\), and is deposited on a substrate with atoms uniformly located on it. The model allows you to determine the \(x\) coordinate in which the atom sticks to the substrate. Particle dynamics is described by Newton’s equations of motion, in which the Lennard-Jones potential [16, 17] is used to take into account interactions between deposited atoms and substrate atoms. To solve the system of equations of Newton’s motion, presented in a dimensionless form, an explicit scheme with overstepping [18] with an error of not more than 1% is used.

Simulation results
The hydrodynamic model and the deposition model were used to determine the basic geometric characteristics of the coating obtained by us in experiments on the deposition of molecular carbon \(C_2\) on a glass substrate. In fig. Figure 8 shows the calculated problem domain and the zones from which deposition is possible. The main dimensions of the region in relative units have the following values: \(d_1 = 1, d_2 = 0.1\). The uniform deposited layer has the form of a ring with an inner radius \(r_1 = 0.1\) and an outer radius \(r_2 = 0.5\).

Figure 6. Settlement area with deposition zones.

The uneven deposition of the precipitation products on the substrate is apparently due to the uneven distribution of the molecular carbon concentration at the surface of the substrate. We believe that the formation of a coating in the form of a ring is due to the deposition of particles from zones with a
maximum concentration of ablation products. To construct these zones, we carried out a series of flow calculations for various values of the Reynolds number (Re) [20].

An analysis of the results of the calculation of the hydrodynamic model shows that in the central part of the channel near the substrate there is a region in which the flow velocity is one to two orders of magnitude lower than the input flow velocity (Fig. 7). Since there is practically no movement in this region, the concentration of the precipitation products is insufficient for noticeable deposition and the formation of an island of the film.

As a first approximation, we can assume that the boundary of this region passes through points at which the velocity of the deposited particles is an order of magnitude lower than the velocities of the input stream. In fig.6, this boundary is on line AB. As you move away from it in the direction of the output section, the flow velocity increases, so that its maximum value in the output section in our calculation is 5 times higher than the maximum speed of the input section. We believe that the concentration of precipitation products also decreases in this direction, and therefore, as the second boundary of the region of possible formation of the film island, we can take a line at which the flow velocities are an order of magnitude lower than the flow velocities in the outlet section. Since it is sufficient to know this boundary in the region of the substrate to calculate the deposition process, information can be used to construct it at several nodes of the calculation region. In fig. 8, this boundary corresponds to the straight line FH.

By varying the values of the Reynolds number, we can trace the dynamics of changes in the size of the island depending on the experimental conditions. The results of the calculation of deposition zones for various values of the Reynolds number (Re) are shown in table 1.

**Table 1.** Results of the calculation of deposition zones for various values of the Reynolds number.

| Re  | AO | OB | OF | BF |
|-----|----|----|----|----|
| 10  | 0.08 | 0.21 | 0.40 | 0.19 |
| 50  | 0.07 | 0.15 | 0.37 | 0.22 |
| 100 | 0.06 | 0.12 | 0.36 | 0.23 |
| 500 | 0.05 | 0.07 | 0.27 | 0.20 |
| 1000| 0.05 | 0.06 | 0.25 | 0.19 |

It can be seen from the table that, with an increase in the Reynolds number, the deposition zone shifts toward the center of the substrate — this leads to a decrease in the inner radius of the deposited layer. In this case, the width of the zone varies little, but the concentration of ablation products decreases with an increase in the modulus of the flow velocity, which should lead to a decrease in the thickness of the deposition layer. Using the molecular dynamics model, it is possible to estimate the boundary of the CH deposition zone. The deposition of molecular carbon at a certain point in the substrate is the result of the interaction of the atoms of the substrate with carbon molecules. At large distances, these interaction forces are insignificant, therefore, in the calculations, the height of the zone...
from which the deposition is possible varied from 2 to 50 interatomic distances. At large distances from the substrate, the longitudinal component of the velocity of the molecule practically does not change, and therefore the projection of the displacement on the horizontal axis is mainly determined by the time the molecule approaches the substrate. To determine the main characteristic of the deposition model — the time of deposition of the molecule on the substrate, a series of calculations was performed. In this case, the data corresponding to carbon were used for potential interaction [19]. The calculation results are summarized in Table 2.

| y    | $u_0=0$, $v_0=0$ | $u_0=1$, $v_0=0$ |
|------|------------------|------------------|
| 2    | 9,10             | 9,10             |
| 3    | 3,91·10$^1$      | 3,91·10$^1$      |
| 4    | 1,08·10$^2$      | 1,08·10$^2$      |
| 5    | 2,36·10$^2$      | 2,36·10$^2$      |
| 10   | 2,70·10$^3$      | 2,70·10$^3$      |
| 15   | 1,15·10$^4$      | 1,14·10$^4$      |
| 20   | 3,32·10$^4$      | 3,33·10$^4$      |
| 25   | 7,65·10$^4$      | 7,65·10$^4$      |
| 30   | 1,53·10$^5$      | 1,51·10$^5$      |
| 40   | 4,56·10$^5$      | 4,56·10$^5$      |
| 50   | 1,11·10$^6$      | 1,09·10$^6$      |

The first column of Table 2 sets the relative initial distance from the moving molecule to the substrate (y), the second — the relative deposition time at zero initial velocity ($t_0$), the third — the projection of the molecule’s movement on the x axis for $u_0 = 0$, $v_0 = 0$, and the fourth — time deposition at $u_0 = 1$, $v_0 = 0$. An analysis of the data from the table shows that for $y > 2$ and $v = 0$, the movement of a moving molecule along the substrate can be determined using the simple formula $\Delta x = u \cdot t_0$. In the calculations, the maximum value of the vertical component of the velocity of the molecule was also controlled. $y = 1.5 \cdot v_{\text{max}} = 0.28$, for $y = 2$ we have $v_{\text{max}} = 0.34$, for $y = 4 \cdot v_{\text{max}} = 0.35$. For $y$ values from 4 to 50, $v_{\text{max}}$ differs from 3.5 by less than 1%. It follows that the "effective acceleration" of the molecule under the action of the forces in question actually occurs at distances from the substrate to several interatomic distances. To determine the width of the film, it is necessary to have information on the height of the deposition zone ($y_{\text{max}}$) and the velocity distribution of the molecules. Then, based on calculations by the deposition program, it is possible to obtain a sample of $\Delta x$ values, the average value of which allows one to determine the change in the film width due to the motion of molecules during deposition. Since there is currently no information on the velocity distribution, only rough estimates of the film width can be obtained based on simple estimates of the displacement $\Delta x = u \cdot t_0$. If $y_{\text{max}}$ lies in the range 30–40, then for $u = 1$ the displacement of the molecule belongs to the range 40–110 (μm). Taking into account the deposition zone for $Re = 50$ at $y_{\text{max}} = 30$, the following values of the film width parameters $r_1 = 150–40 = 110$ (μm), $r_2 = 370 + 40 = 410$ (μm) are obtained. For $y_{\text{max}} = 40$, the following values $r_1 = 10$ (μm), $r_2 = 510$ (μm) are obtained similarly. In our opinion, these two options best fit the experimental data, for which $r_1\approx100$ (μm), $r_2\approx500$ (μm).

**Conclusion**

We used a controlled laser method to obtain carbon nanostructures on a glass substrate with a predetermined structure. Varying the parameters of laser radiation crawled to generate structures with different reliefs, which were investigated by atomic force microscopy. The proposed models of motion in the hydrodynamic approximation and molecular-dynamic deposition of direct laser exposure...
products make it possible, as a first approximation, to assess the regions where the formation of nanostructures at the “general structural level” is possible.

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