Formation of various types of nanostructures on germanium surface by nanosecond laser pulses

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Abstract. The paper describes the formation of micro- and nanostructures in different parts of irradiation zone on germanium surface by multiple action of nanosecond pulses of ArF-laser. It proposes a simple method using only one laser beam without any optional devices and masks for surface treatment. Hexa- and pentagonal cells with submicron dimensions along the surface were observed in peripheral zone of irradiation spot by atomic-force microscopy. Nanostructures in the form of bulbs with rounded peaks with lateral sizes of 40-120 nm were obtained in peripheral low-intensity region of the laser spot. Considering experimental data on material processing by nanosecond laser pulses, a classification of five main types of surface reliefs formed by nanosecond laser pulses with energy density near or slightly above ablation threshold was proposed.

1. Introduction
Nanostructures in solids are important object of studies because of their manifold possibilities for applications in science and technology. Surface nanostructuring gives rise to an improvement of thermal, tribological and electrical material properties [1-3]. It increases biocompatibility with living tissues of implants and prostheses used in orthopedics and stomatology [4]. Nanostructures on semiconductor surfaces applied in microelectronics, super-high density storing of information, nanophotonics for development of light-emitting devices and for spectroscopy [5, 6]. Therefore it is of a great interest to develop new effective methods for obtaining surface structures with characteristic sizes less than 100 nm.

Previously various techniques have been used for nanostructuring with laser radiation. These are the masks projected with a demagnification on the treated surface [7], surface screening from incident radiation by micro-, and nanoparticles [8], and interference of two or more laser beams on the surface or in a volume of the material [9]. The combination of laser beam with a tip of an atomic force or scanning tunneling microscope has also been used, and that has allowed induce the change of material surface profile in a number of consequent superficial nanoscale regions [10].

In the given paper for creation of surface nanoreliefs we use only one laser focused beam without any masks and without any auxiliary atomic force microscope tip. It is a so-called “direct” surface nanostructuring. We report the results of experiments, where the formation of micro- and nanostructures was observed on germanium surface under the multiple action of nanosecond pulses of ArF-laser with radiation wavelength of 193 nm.
2. Materials and methods
A scheme of experimental setup is shown on figure 1. The main source of coherent radiation is an excimer ArF-laser marked by 1. Its radiation having a wavelength of 193 nm is strongly absorbed by a large number of materials. The laser radiation passes through the reflector 2, which directs a small part of the energy to NOVA II marked by 3. The other part of the laser energy is directed to the optical forming system consisting of a condenser 4, a forming diaphragm 5 and projection lens 6. The system creates a laser spot with a diameter of several hundred micrometers on the sample surface.

The sample 8 is placed in a gas chamber 9 with fluorite glasses 7, 7’. The gas chamber is connected to a vacuum pump 13 and a gas balloon 15 through the system of gas valves and pressure regulators. If it is necessary the gas chamber allows sample processing at pressures from 50 to 2000 mbar. Also for laser beam scanning it is possible to use a three-dimensional moving platform 10 [11]. In this work the samples were irradiated at atmospheric air in a stationery laser beam.

Figure 1. Experimental setup for surface nanostructuring. 1 - ArF-laser; 2 – reflector; 3 – NOVA II; 4 – condenser; 5 – forming diaphragm; 6 – projection lens; 7,7’ – fluorite glasses; 8 – sample; 9 – gas chamber; 10 – three-dimensional moving platform; 11,12 – gas valves; 13 – vacuum air-pump; 14 – filter; 15 – gas balloon.

In the experiment on direct laser nanostructuring we used germanium samples with transverse dimensions of 8x8 mm and a thickness of 2 mm. After necessary preparatory procedures the samples were placed in the chamber of experimental setup and irradiated by 20 nanosecond laser pulses at rate frequency of 2 Hz. The duration of laser pulses was about 20 ns. The energy density in the center of laser spot was varied from 0.5 to 5 J/cm² with a step of 0.5 J/cm² for each laser spot. All five types of surface reliefs were observed at energy density of about 3 J/cm² on each germanium sample used in experiment. An analysis of irradiated germanium surfaces is carried out by an atomic-force microscope (AFM). Typical AFM views of main reliefs obtained at energy density of 3 J/cm² are represented in this work.

3. Results and discussions
The intensity of the laser radiation takes the maximum value in the center of the spot and falls to its periphery (figure 2a). As a consequence, the crater appears in the center of the spot at the multipulse irradiation of the same surface plot. There is a removal of the material from this crater (figure 2b). As we move from the center of the irradiation spot to its periphery, the AFM analysis showed the presence of various types of micro- and nanostructures on germanium surface.

Figure 3 shows a three-dimensional AFM image of the relief of the initial non-irradiated germanium surface. One can see a roughness in the form of protuberances with characteristic dimensions along the surface of 40-90 nm and a height of about 40 nm. Also traces of mechanical surface treatment are observed in the form of long linear scratches with a width of 40-80 nm.
Figure 2. Schematic views of (a) laser pulse energy spatial distribution and (b) irradiation spot with five main types of surface reliefs on germanium surface.

Figure 3. AFM image of non-irradiated germanium surface.

Figure 4 represents main types of reliefs obtained by irradiation of germanium surface with nanosecond pulses of ArF-laser. The pulse energy density in the centre of laser spot was about 3 J/cm². Considering that pulse energy had quasi-Gaussian distribution and germanium absorption capacity at wavelength of 193 nm was about 0.35, we can estimate deposited energy density in different places of laser spot.

In the central part (deposited energy density was about 1.1 J/cm²) of the irradiation spot (figure 4a), which is ablation zone, a wavelike relief with periods of 200-400 nm and amplitude of about 150 nm was observed. Figure 4b shows an example of a wavy relief with the periods of about 1500 nm and the amplitude with a value of about 700 nm in the zone of a "deep" melt without significant ablative removal of the material. Estimation for deposited energy was from 0.9 to 1.1 J/cm². This wavy micron relief corresponds to mechanism of capillary waves, that has been studied before [12].

Figure 4c represents relief in the form of hexa- and pentagonal cells with characteristic dimensions along the surface of 300-500 nm and the height of the edges between the cells of 20-25 nm in the region of "shallow" melt (deposited energy density was about 0.4 J/cm²). The formation mechanism of this type of relief on germanium surface under the action of laser pulses is unknown and it is an interesting scientific problem to solve.

Figure 4d shows nanostructures in the form of bulbs with rounded peaks with characteristic dimensions along the surface of 40-120 nm and height of 40-70 nm. They are observed in peripheral low-intensity region of the laser spot and its size makes it possible to use such structures as quantum
dots. Estimation for deposited energy was about 0.1 J/cm². The studies for the structures in the form of microcones are presented in [13], where the mechanism of p-n junction formation by laser radiation and thermogradient effect in the elementary semiconductor is proposed.

![AFM images of irradiated germanium surface in different parts of irradiation spot: (a) central part (ablation zone); (b) zone of a "deep" melt without significant ablative removal of the material; (c) low-intensity peripheral zone of the “shallow” melt; (d) peripheral low-intensity spot zone outside the visible melt area.](image)

**Figure 4.** AFM images of irradiated germanium surface in different parts of irradiation spot: (a) central part (ablation zone); (b) zone of a "deep" melt without significant ablative removal of the material; (c) low-intensity peripheral zone of the “shallow” melt; (d) peripheral low-intensity spot zone outside the visible melt area.

Considering our experimental data for germanium and data from other works [14-17] concerning material processing by nanosecond laser pulses, we propose five main types of surface reliefs formed by nanosecond laser pulses with energy density near or slightly above ablation threshold:

(I) undulating relief with micron/submicron periods in the ablation zone in the central part of spot;
(II) wave-like relief with periods of one or several microns in the "deep" melt zone (melt thickness is about several hundred nanometers) without significant ablative removal of the material, what corresponds well known effect of excitation of capillary waves [18, 19];
(III) submicron relief with periods of several hundred nanometers in the low-intensity peripheral zone of the "shallow" melt (melt thickness is about several tens nanometers), when energy density is near or slightly above the melting threshold;

(IV) a small-scale relief with periods of several tens of nanometers in the peripheral low-intensity spot zone outside the visible melt area;

(V) micron/submicron relief of the original non-irradiated surface.

These types of relief considered may appear in the form of corresponding superpositions ((I) + (II) or (III) + (IV)) in different transition regions between the zones mentioned above. As it was shown above all five types of reliefs were observed on the germanium surface irradiated by nanosecond pulses of ArF-laser.

4. Conclusions

Formation of micro- and nanostructures on germanium surface by the multiple action of nanosecond pulses of ArF-laser has been demonstrated. A simple method of direct laser nanostructuring without any optional devices and masks has been proposed for surface treatment. The analysis of surfaces by an atomic-force microscope has shown various types of surface structures in different parts of irradiation zone. Hexa- and pentagonal cells with characteristic dimensions along the surface of 300-500 nm and the height of the edges between the cells of 20-25 nm were observed in peripheral zone of shallow melt and its formation mechanism requires following studies. Nanostructures in the form of bulbs with rounded peaks with characteristic dimensions along the surface of 40-120 nm and height of 40-70 nm were obtained in peripheral low-intensity region of the laser spot and could be used for quantum surface effects. Considering experimental data on material processing by nanosecond laser pulses, a classification of five main types of surface reliefs formed by nanosecond laser pulses with energy density near or slightly above ablation threshold was proposed.

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