Semiconductor Physics, Quantum Electronics & Optoelectronics, 2017. V. 20, N 1. P. 48-54.
doi: https://doi.org/10.15407/spqeo20.01.048

PACS 81.16.Dn, 81.16.Rf

Micro- and nanostructuring of metal surfaces with polarized femtosecond laser pulses

N.G. Zubrilin[1], I.V. Blonskiy[1], I.M. Dmitruk[1,2], O.E. Dombrovskiy[1], N.I. Berezovska[2], V.I. Stiopkin[1]
[1]*Institute of Physics, NAS of Ukraine, 46, prospect Nauky, 03680 Kyiv, Ukraine*
[2]*Taras Shevchenko National University of Kyiv, 64/13, Volodymyrska str., 01601 Kyiv, Ukraine*
Corresponding author: phone +38(044)-526-45-87; e-mail: n_berezovska@univ.kiev.ua

Abstract. Under irradiation of the surface of metals with femtosecond laser pulses, periodic surface micro- and nanostructures have been obtained. The dependence of orientation inherent to formed structures on direction of the electric field related with the incident electromagnetic wave and type of polarization of this wave has been studied. Typically these laser-induced structures are perpendicular to the electric field of incident light and have period shorter than the laser wavelength. The structures oriented in parallel to the polarization vector with a longer period have been also revealed. The dependence of surface structure formation on the initial surface defects in metal has been found.

Keywords: femtosecond laser pulses, quasi-periodic surface structures, surface plasmons, circular polarization.

Manuscript received 11.11.16; revised version received 09.02.17; accepted for publication 01.03.17; published online 05.04.17.

1. Introduction

One of the effects of high-power femtosecond laser pulses on metal surface is formation of quasi-periodic surface structures [1-4]. Modification of surface topology under the influence of laser irradiation leads to changes in physical properties of matter, including the mechanical and optical ones, and therefore surface structuring becomes widely used, for example for creation of “black” and “color” films [5], super-hydrophobic surfaces [6, 7], *etc*. Good biostability and biocompatibility of some refractory metals make them promising for biomedical applications. For instance, the performed study of femtosecond laser surface treatment of titanium [8] has shown that laser processing the implant surfaces provides suitable surface topography, smoothing the surface with smooth micro-inhomogeneities and less surface contamination as compared with other treatment methods. We propose to use laser-induced periodic surface structures for application as SERS substrates [9].

Naturally, there is reasonable necessity to study physical principles corresponding to formation of surface periodic structures. In some studies, explanation of the effect is based on the conception of interference of the incident electromagnetic waves and those scattered along the surface by surface inhomogeneities, including those induced by incident radiation. In literature, it is also considered the defect-deformation mechanism responsible for formation of surface periodic structures based on creation of generated diffusion-deformation instabilities under the influence of laser irradiation [10].

However, the most appropriate mechanism providing formation of periodic surface structures on metals is related with surface electromagnetic waves (SEW) or surface polaritons that are excited at the surface of metals by laser radiation [11]. Interference of the incident wave and SEW leads to periodic energy distribution on the sample surface, and due to the structural and phase transformations occurring in the treated material a periodic surface structure (PSS) begins to form. According to the plasmon-polariton mechanism responsible for formation of periodic structures, the grooves with a period close to the wavelength of the laser are oriented along the perpendicular to the polarization plane of the incident light beam [12, 13].

In this paper, we describe PSS formed due to direct structuring the metal surfaces by femtosecond laser pulses, study of PSS orientation depending on the direction of the electric field in the incident wave, and on the type of polarization of the incident electromagnetic wave.

2. Experimental setup

In our experiments, the Coherent Ti-sapphire laser system consisting of a femtosecond oscillator Mira-900F and chirped pulse amplifier Legend-HE was used. The output beam had the following characteristics: wavelength close to 800 nm, pulse duration 140 fs with the pulse energy about 0.8…1 mJ. The laser beam was focused on the sample surface by the lens with the focal length equal to 200 mm. The average power density at the surface of metal was of the order of 10^{12} W/cm^2. The power density of irradiation was adjusted by changing the distance from the lens focus to the sample surface, the focus was beyond the sample. Horizontally polarized laser beam was incident normally on the surface of the sample. This polarization was changed using the plates λ/2 and λ/4.

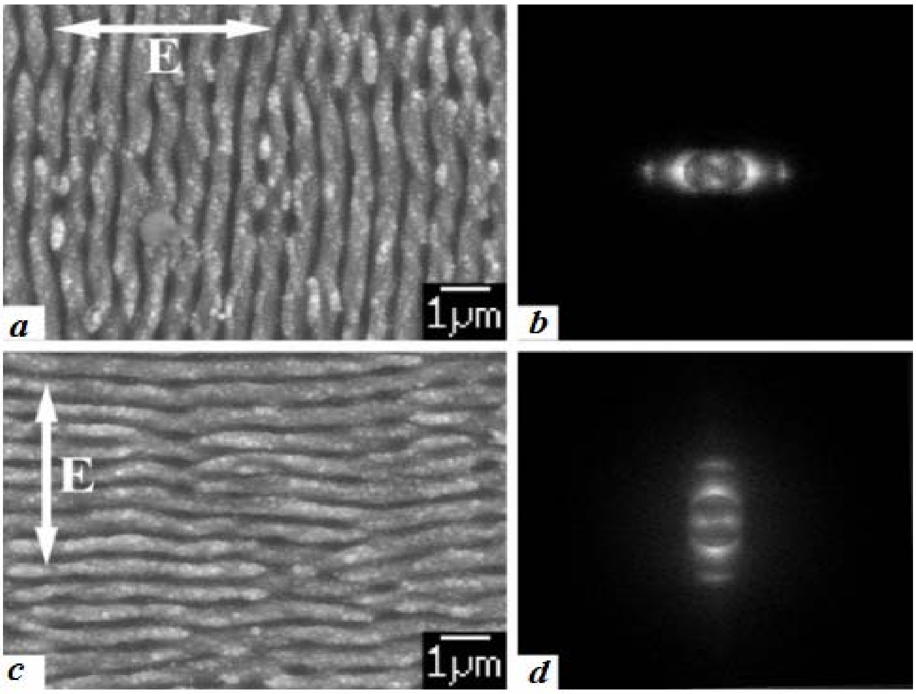

Fig. 1. SEM image of the surface structures on stainless steel formed under the influence of laser radiation with linear polarization (a, c) and their two-dimensional Fourier transform (b, d).

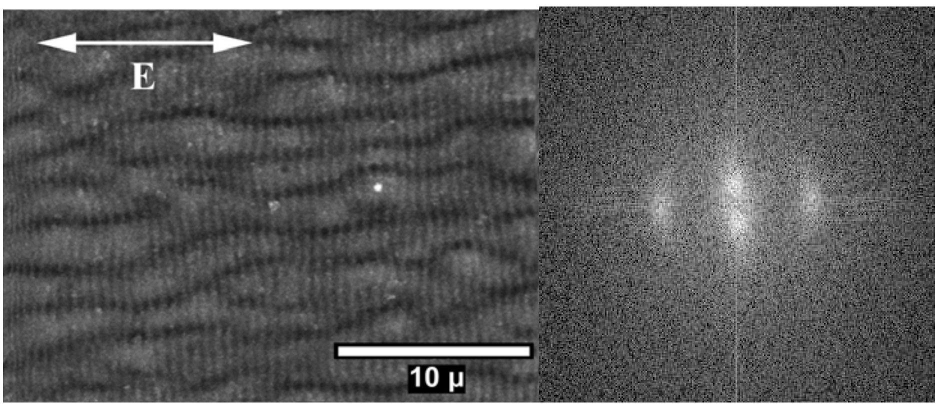

Fig. 2. SEM image of the copper surface irradiated with femtosecond laser pulses, and two-dimensional Fourier transform of the SEM image.

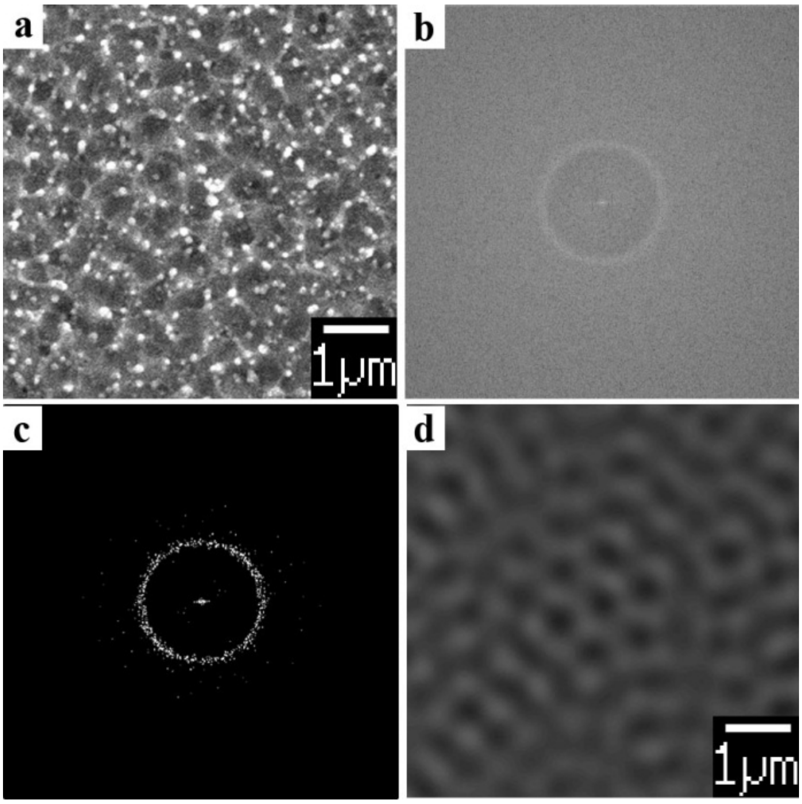

Fig. 3. (a) SEM image of the surface of stainless steel irradiated with laser radiation with circular polarization, (b) Fourier transform of SEM image (a), (c) Fourier image after editing; (d) the result of inverse transform of Fourier image (c).

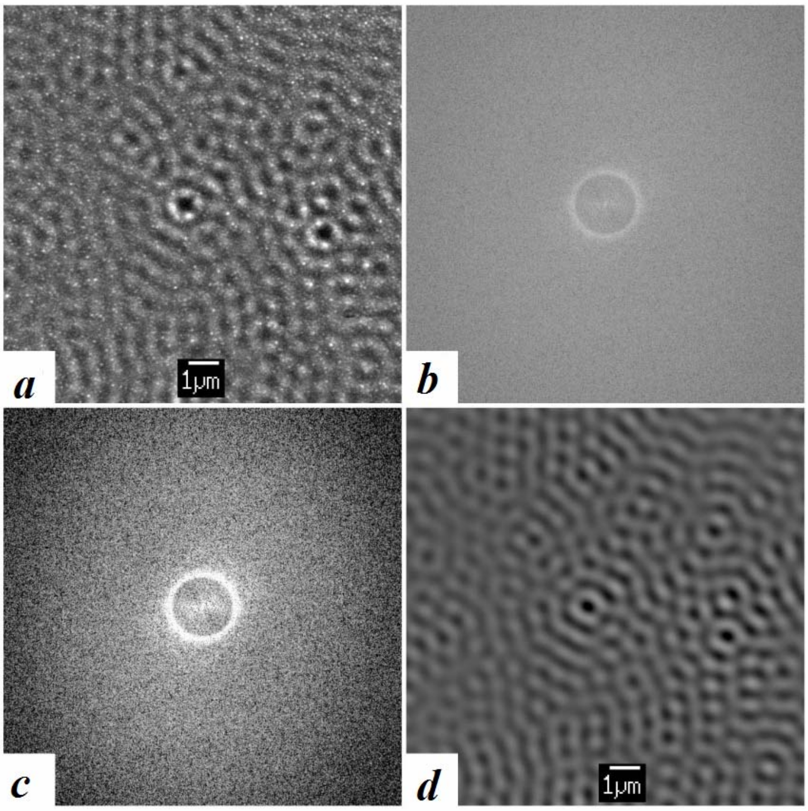

Fig. 4. (a) SEM image of the surface of molybdenum irradiated with laser radiation possessing circular polarization, (b) Fourier transform of SEM image (a), (c) Fourier transform after editing; (d) the result of inverse transform of Fourier image (c).

Sample was fixed to the holder attached to a translation stage, which allowed to change the angle of incidence for laser radiation on the sample and allowed to move the sample relatively to the laser beam during irradiation (scanning beam mode) at a speed of 0.1…30 mm/s.

Morphology of irradiated surface has been studied using the electron microscopes JSM-35, JEOL-8200 and optical microscope Axioskop-2.

3. Results and discussion

Under irradiation of the sample of stainless steel with a laser beam at the speed 0.2 mm/s, energy per pulse of about 0.85 mJ and repetition rate 20 Hz, the comb periodic structures oriented along the perpendicular to the electric field of laser radiation have been observed (Fig. 1a). When the polarization is turned by the angle 90° using the half-wave plate, the quasi-periodic

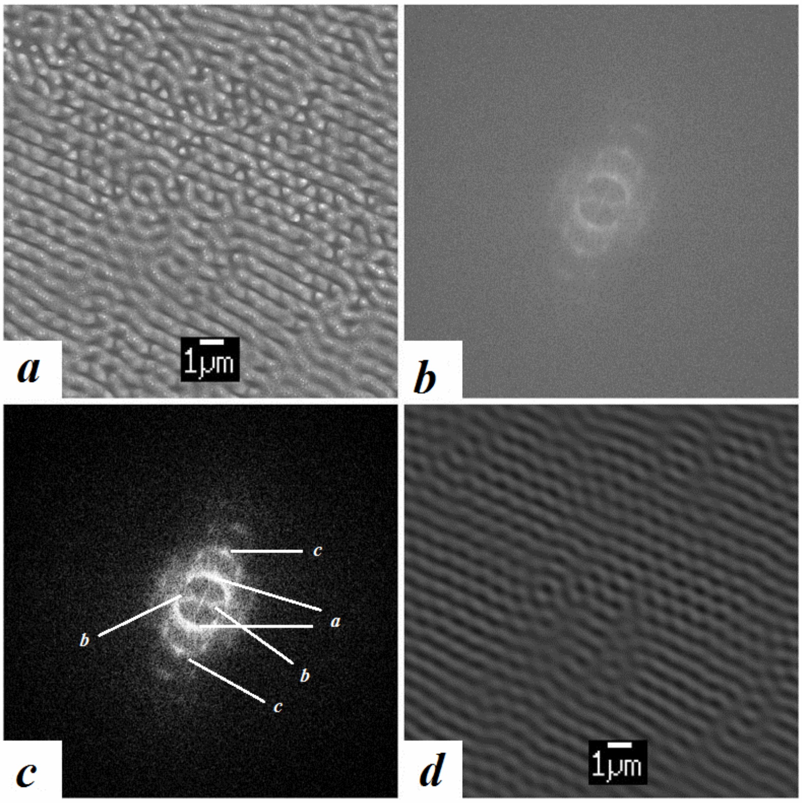

Fig. 5. (a) SEM image of the surface of molybdenum irradiated with femtosecond laser pulses with elliptical polarization, (b) two-dimensional Fourier transform of SEM image (a), (c) the result of Fourier filtering, (d) inverse transform of Fourier image (c). The period of structures is about 650 nm.

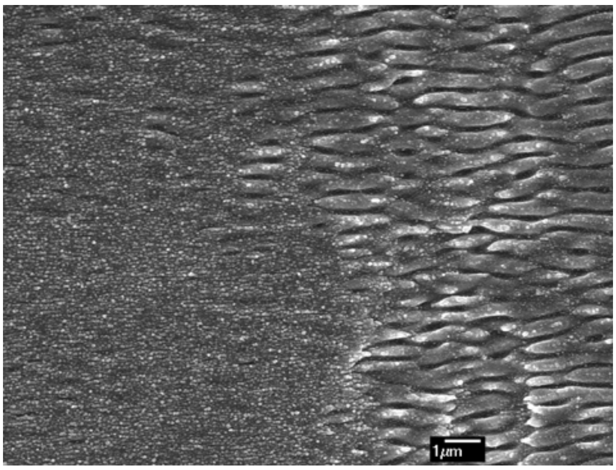

Fig. 6. SEM image of the surface of molybdenum irradiated with femtosecond laser pulses possessing linear polarization.

structures also turn to the angle 90° (Fig. 1c). The period of these structures is about 530 nm in the case of stainless steel, which is smaller than the wavelength of laser radiation. These results are fully consistent with the model of formation of surface structures under the influence of femtosecond laser pulses due to interference of the incident electromagnetic wave and excited plasmon-polariton surface wave.

Two-dimensional Fourier transform demonstrates a well-defined periodic structure perpendicular to the electric field of the laser radiation. However, in addition to these structures, in the pattern of two-dimensional transform, another periodicity in the vertical direction in the case of horizontal polarization (Fig. 1b) and in horizontal direction according to vertical polarization has been observed (Fig. 1d). This periodicity has several times larger period because of the Fourier decomposition maxima are closer to the center of symmetry of the image.

The structures with this kind of periodicity are also found on the irradiated copper surface (Fig. 2). In addition to the quasi-periodic structures perpendicular to the polarization of laser radiation with a period of the order of the light wavelength, there are structures parallel to the vector of polarization. The period of these structures is about 1.5…2 μm, whereas the period of structures perpendicular to the polarization vector is approximately 600 nm. The same effect has been observed for titanium under laser irradiation with the pulse duration of 10 and 100 ns [14].

The stainless steel sample was also irradiated with femtosecond laser pulses with the same parameters as in the above mentioned case (0.2 mm/s, pulse energy 0.85 mJ and repetition rate 20 Hz), but with circular polarization. SEM image processing using two-dimensional Fourier transform indicates that the obtained structure is periodic in all directions, as evidenced by the ring inside Fourier transform of SEM image (Fig. 3).

If to filter out the other components of two-dimensional Fourier transform and leave only the ring that we are interested in, the inverse Fourier transform will show the ring character of initial surface structures. The calculations indicate that the typical distance between elements of the structure is the same in all directions and is about 630 nm, which is smaller than the laser wavelength and close to the value of the period of comb structures formed under irradiation with the laser beam possessing linear polarization (either horizontal, or vertical).

The quasi-periodic surface structures of this kind are common. The same type of structures was obtained on the surface of molybdenum. The sample was irradiated using the femtosecond laser pulses with the wavelength 820 nm (Fig. 4).

The ring character of the formed structures can be seen at SEM images even without Fourier filtering. The period of these structures in all directions is about 690 nm, which is close to the wavelength of the laser radiation.

Thus, from the above mentioned one can make an unambiguous conclusion on the characteristic difference of surface structures obtained under irradiation with linearly polarized laser radiation and pulses with circular polarization. However, we also received surface structures that occupy intermediate position between the above-mentioned structures, namely, their properties are characteristic partially for circular and partially for parallel quasi-periodic structures.

Fig. 5a represents the SEM image of the surface of molybdenum irradiated with femtosecond laser pulses with elliptical (nearly circular) polarization, while scanning the laser beam along the sample surface at the speed 4 mm/s (in the picture – horizontal direction) at pulse repetition rate 1 kHz, wavelength – 820 nm. Two-dimensional Fourier transform reveals the periodicity of the formed structures in all directions. In addition, there is a pronounced periodicity (Fig. 5c, arrow *a*) in a certain direction, and evidenced for the higher orders of Fourier image (Fig. 5c, arrow *c*). Their presence indicates non-sinusoidal profile of grooves. The direction of parallel quasi-periodic grooves does not coincide with the direction of the laser beam scanning of the sample surface, the angle between them is about 30°. Periods of rings and grooves of surface structures are equal and are ~ 650 nm. And patterns with large period (arrow *b*) are seen in perpendicular direction.

It should be noted that along with the quasi-periodic structures on the irradiated surface the features of nanosized scale have been observed (see Fig. 6). Fig. 7 shows enlarged view of these nanosized features from the left part of the SEM image in Fig. 6.

Fig. 8 shows the SEM image of the surface of an alloy of platinum Pt and 3% of zirconium Zr.

Another important factor that affects both the shape of laser-induced surface structures and their orientation is the quality of the initial surface of the irradiated material.

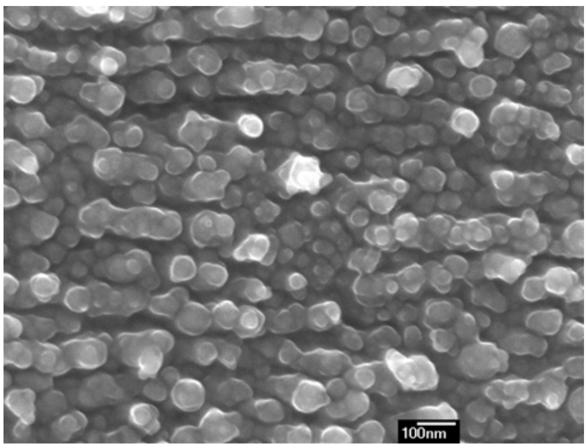

Fig. 7. SEM image of features of nanosized scale on the surface of molybdenum (enlarged Fig. 6).

Semiconductor Physics, Quantum Electronics & Optoelectronics, 2017. V. 20, N 1. P. 48-54.
doi: https://doi.org/10.15407/spqeo20.01.048

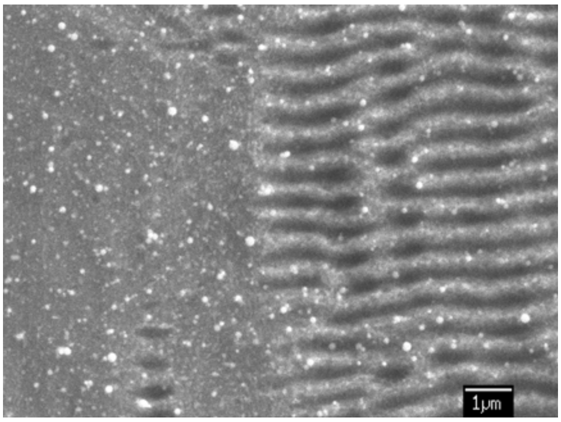

Fig. 8. SEM image of formed periodic surface structure on the surface of Pt-Zr alloy.

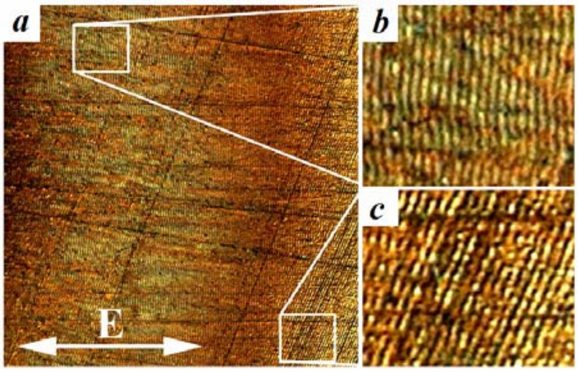

Fig. 9. Optical image of the surface of copper sample irradiated with femtosecond laser pulses with linear polarization: (a) a general view of the sample surface, (b, c) views of different places on the sample.

Fig. 9 shows the copper surface irradiated with femtosecond laser pulses. Inclined dark strokes are initial defects (scratches) that were present on the sample surface before laser irradiation. Fig. 9 also shows the right edge of the spot irradiated by about 600 femto-second laser pulses. At inserts, enlarged regions of the irradiation spot are shown, closer to the center (b) and closer to the edge (c) of irradiation spot. In Fig. 9b, the structures are extended along the perpendicular to the polarization vector, which is consistent with the proposed model of laser-induced formation of structures on the surface of metals. However, in Fig. 9c it could be noticed that grooves are at an angle to the polarization vector and parallel to the initial scratches on the sample surface, indicating their direct influence on the orien-tation of surface structures. This effect is manifested in area away from the center of spot, likely because of surface defects have a greater influence in the case of relatively lower power density of laser irradiation, in other words, when the power density of laser irradiation is near the ablation threshold of this material.

4. Conclusions

In our experimental conditions, quasi-periodic structures are formed on the surface of metals and alloys under the polarized laser pulses always along the perpendicular to the direction of the electric field in the incident wave and have a period within 500…650 nm, which is less than the wavelength of radiation 800…820 nm.

The structures parallel to the polarization vector with a period several times larger than the wavelength of the laser radiation have been also revealed on the irradiated surface. The period of these structures is 1.5…2 µm. Availability of these structures indicates possibility of another mechanism of their formation. It could be capillary waves on the surface of molten metal.

Surface structures periodic in all directions have been observed in the case of irradiation of metal surface with circularly polarized pulses.

The dependence of the formation of periodic surface structures on the initial surface defects of the metal has been demonstrated in the case of copper surface.

Acknowledgements

Publication is based on the research provided by the grant support of the State Fund for Fundamental Research (project F64/23-2016), and NATO Science for Peace and Security (SPS) Programme (grant NUKR.SFPP 984617).

References

1. Emmony D.C., Howson R.P., and Willis L.J. Laser mirror damage in germanium at 10.6 µm. *Appl. Phys. Lett*. 1973. **23**, No. 11. P. 598–600.
2. Makin V.S., Makin R.S., Vorobyov A.Y., Guo Ch. Dissipative nanostructures and Feigenbaum's universality in the 'Metal-high-power ultrashort-pulsed polarized radiation' non-equilibrium nonlinear dynamical system. *Tech. Phys. Lett.* 2008. **34**, No. 5. P. 387–390.
3. Golosov E.V., Emel'yanov V.E., Ionin A.A. et al. Femtosecond laser writing of subwave one-dimensional quasi-periodic nanostructures on a titanium surface. *JETP Lett.* 2009. **90**, No. 2. P. 107–110.
4. Korol'kov V.P., Ionin A.A., Kudryashov S.I. et al. Surface nanostructuring of Ni/Cu foils by femtosecond laser pulses. *Quantum Electronics*. 2011. **41**, No. 4. P. 387–392.
5. Vorobyev A.Y., Guo C. Femtosecond laser nano-structuring of metals. *Opt. Exp.* 2006. **14**, No. 6. P. 2164–2169.
6. Vorobyev A.Y., Guo C. Multifunctional surfaces produced by femtosecond laser pulses. *J. Appl. Phys*. 2015. **117**. P. 033103.

7. Groenendijk M. and Meijer J. Microstructuring using femtosecond pulsed laser ablation. *J. Laser Appl*. 2006. **18**. P. 227–235.
8. Vorobyev A.Y., Guo C. Femtosecond laser structuring of titanium implants. *Appl. Surf. Sci*. 2007. **253**. P. 7272–7280.
9. Vovdenko S., Dmitruk I., Berezovska N. et al. Laser-induced quasi-periodic metal structures for efficient excitation of surface plasmons. *Ukr. J. Phys*. 2016. **61**, No. 9. P. 780–783.
10. Emel'yanov V.I., Seval'nev D.M. Three-wave interactions of surface defect-deformation waves and their manifestations in the self-organisation of nano- and microstructures in solids exposed to laser radiation. *Quantum Electronics*. 2009. **39**, No. 7. P. 678–684.
11. Bazhenov V.V., Bonch-Bruevich A.M., Libenson M.N., and Makin V.S. Interference of surface electromagnetic waves in connection with periodic structures formed during intense illumination of a semiconductor surface. *Sov. Tech. Phys. Lett.* 1984. **10**, P. 642–645 (in Russian).
12. Bonch-Bruevich A.M., Libenson M.N., Kochengina M.K., Makin V.S., Pudkov S.D., and Trubaev V.V. Surface electromagnetic and waveguide modes excitation during the intense laser illumination and their influence on the character of condense media breakdown. *Izvestiya Akademii Nauk SSSR*, *Ser. Fiz*. 1982. **46**, No. 6. P. 1186–1195 (in Russian).
13. Öktem B., Pavlov I., Ilday S., Kalaycioglu H., Rybak A., Yavas S., Erdogan M. and Ilday F.Ö. Nonlinear laser lithography for indefinitely large-area nanostructuring with femtosecond pulses. *Nature Photonics*. 2013. **7**, No. 11. P. 897–901.
14. Makin V.S., Pestov Yu.I., and Privalov V.E. Controllable grain-boundary displacement during recrystallization and the microrelief of a titanium surface induced by laser radiation pulses. *J. Opt. Technol.* 2013. **80**, No. 2. P. 91–95.