Femtosecond Laser Writing of Subwave One-Dimensional Quasiperiodic Nanostructures on a Titanium Surface

E. V. Golosov[a], V. I. Emel'yanov[b], A. A. Ionin[c], Yu. R. Kolobov[a], S. I. Kudryashov[c,*], A. E. Ligachev[d], Yu. N. Novoselov[c], L. V. Seleznev[c], and D. V. Sinitsyn[c]

[a] *Belgorod State University, Belgorod, 308015 Russia*
[b] *Moscow State University, Moscow, 119992 Russia*
[c] *Lebedev Physical Institute, Russian Academy of Sciences, Leninskii pr. 53, Moscow, 119991 Russia*
[d] *Prokhorov General Physics Institute, Russian Academy of Sciences, ul. Vavilova 38, Moscow, 117942 Russia*
* *e-mail: sikudr@sci.lebedev.ru*

One-dimensional quasiperiodic structures whose period is much smaller than the wavelength of exciting radiation have been obtained on a titanium surface under the multipulse action of linearly polarized femtosecond laser radiation with various surface energy densities. As the radiation energy density increases, the one-dimensional surface nanorelief oriented perpendicularly to the radiation polarization evolves from quasiperiodic ablation nanogrooves to regular lattices with subwave periods (100–400 nm). In contrast to the preceding works for various metals, the period of lattices for titanium decreases with increasing energy density. The formation of the indicated surface nanostructures is explained by the interference of the electric fields of incident laser radiation and a surface electromagnetic wave excited by this radiation, because the length of the surface electromagnetic wave for titanium with significant interband absorption decreases with an increase in the electron excitation of the material.

1. It was recently found that the multipulse action of femtosecond laser radiation of the visible and near-infrared ranges on the surface of solids makes it possible to reproducibly obtain subwave (period $\Lambda = 70$–$900\ \text{nm} \leq \lambda$, where λ is the wavelength of exciting laser radiation) one-dimensional quasiperiodic nanostructures (nanolattices) [1–8]. Such nanolattices on the surfaces of various materials are interesting both because nanoscale periodicity leads to unusual physical or physicochemical properties of a surface continuously varying with Λ [4] and as sources of nanoparticles [1, 3, 4–6]. The necessity of the variation of the nanolattice period in a wide range by varying the parameters of laser radiation and choosing materials for writing initiates a number of investigations of the effect of the laser polarization (vector **e**), the wavelength λ and duration of a pulse, the surface energy density F, and the number of acting pulses N on the Λ value [1–8]. In particular, it was found that the wave vector of nanolattices **q** is always collinear to **e** and the lattice period Λ increases linearly with λ for femtosecond and short picosecond laser pulses in a limited interval covering the visible and near-infrared ranges [6, 7]. At first glance, variations in the parameters F (within several orders of magnitude) [8] and N (within several orders of magnitude) [7] provide wider possibilities of varying Λ. However, the preceding works showed that Λ remains almost unchanged [3, 4] or monotonically increases with the surface energy density [5, 8], whereas the duration of the irradiation of the surface usually makes it possible only to develop a nanostructure that initially appears on this surface [2, 6, 7]. The indicated relation between Λ and F hinders the formation of developed one-dimensional nanolattices with minimum possible periods interesting for modern nanotechnologies, because the nanotransport of matter decreases sharply at lower energy densities. In view of this circumstance, it is necessary to seek new regimes and materials for the femtosecond laser writing of subwave one-dimensional nanolattices that would allow for the efficient creation of one-dimensional surface nanolattices of minimum and maximum sizes.

In this work, subwave one-dimensional quasiperiodic nanostructures written under the action of femtosecond laser pulses with different surface energy densities on a polished surface of chemically pure titanium, which is one of the basic materials of the aerospace industry and implant medicine, are investigated using a scanning electron microscope with a magnification of 100 000.

2. The experiments were performed on an experimental setup including a Ti:sapphire laser (Avesta Proekt) with fundamental radiation pulses (central

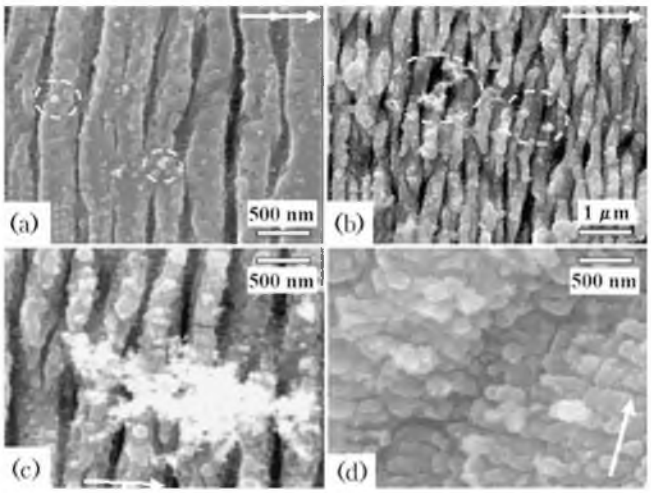

Fig. 1. Scanning electron microscope images of nanostructures written on the dry titanium surface for the energy densities F = (a) 17, (b) 25, (c) 33, and (d) 250 mJ/cm^2. The arrows indicate the coinciding directions of the polarization vector of the laser field **e**, the wave vector of the nanostructures **q**, and the target velocity **v**. The dashed circles show the features of the nanorelief, which are ablation fragments, their flaky clusters, and nanoparticles.

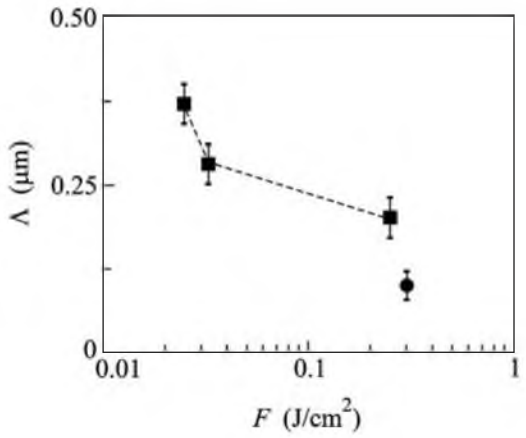

Fig. 2. Nanolattice periods Λ on (squares) dry and (circles) humid titanium surfaces versus the surface energy density F.

wavelength is 744 nm, the FWHM of the generation band is about 15 nm) with a duration of about 80 fs (FWHM) and an energy of up to 8 mJ [9]. The transverse spatial distribution of the laser field corresponded to the TEM_{00} mode. Normally, incident laser radiation was focused on a spot with a diameter of 1.2 mm (at a level of $1/e^2$) on the surface of a target (half-bar, a diameter of 8 mm) made from chemically pure, multiply annealed, mechanically polished (rms ≤ 50 nm) VT1-0 titanium with a mean grain size of 0.25 μm (Center for Nanostructure Materials and Technologies, Belgorod State University). The target was placed on a three-dimensional motorized plate with a computer control. The energy of laser pulses was varied and controlled by, respectively, a reflecting polarization attenuator (Avesta Proekt) and a DET-210 calibrated photodiode (Thorlab) illuminated by a weak laser glare through a rotary dielectric mirror. The writing of nanostructures was performed by scanning of the titanium target surface with a speed of 20 μm/s at low laser radiation energies (<0.5 mJ, peak power $W < 4$ GW) in order to avoid a noticeable degradation of the energy density distribution on the target surface associated with self-focusing in air (the critical self-focusing power is $W_{cr} \approx 3$ GW [10]) and the accompanying effects of chromatic emission, filamentation, and scattering on a plasma [10, 11].

3. In the process of the writing of nanostructures at low energy densities $F \approx 17$ mJ/cm^2 and the number of incident pulses $N \approx 500$, pronounced quasiperiodic (mean period $\Lambda \approx 0.4$ μm) narrow ($\Delta \leq 0.1$ μm) grooves with the wave vector **q** ($|\mathbf{q}| = 2\pi/\Lambda$) collinear to the radiation polarization vector **e** and scanning direction **v** are formed on the titanium target surface (see Fig. 1a). The target surface beyond the grooves does not contain any traces of the removal of the material, but is contaminated owing to the reprecipitation of the fragments of ablation products from the grooves. At higher energy densities $F \approx 25$–350 mJ/cm^2 and the same number N, pronounced nanolattices with $\mathbf{q} \parallel \mathbf{e}, \mathbf{v}$ and subwave periods in the range of 0.2–0.4 μm are formed on the surface (see Figs. 1b–1d), although the degradation of the grooves occurs with increasing F and they degrade to linear sets of nanopeaks at $F \geq$ 400 mJ/cm^2. In particular, even at intermediate F values, the lattices contain flaky traces of the reprecipitation of the material (see Fig. 1b). In the entire F range, round (drop) fragments (nanoparticles) are seen on the lattice grooves. This likely indicates that ablation is supercritical thermal rather than subcritical (slabbing) [12]. Indeed, in this case, the condensation of the vapor drop products of ablation in their gas-dynamic scattering expansion from narrow nanovalleys of the surface relief can be expected (see Fig. 1). However, the monotonically decreasing dependence $\Lambda(F)$ (see Fig. 2) is of particular interest; it certainly contradicts the results of preceding investigations for other metals [3, 8]. It is worth noting that the twofold decrease in the period of the nanostructures written on the titanium surface by means of infrared femtosecond laser pulses was previously mentioned in [13], but was referred to two-dimensional recondensation peak structures and, in the latter case, was attributed (in the surface electromagnetic wave model) to the doubling of the period of dissipative surface nanostructures.

In our case, the pronounced orientation of the obtained surface nanostructures perpendicular to the laser radiation polarization, the quasiperiodicity of the

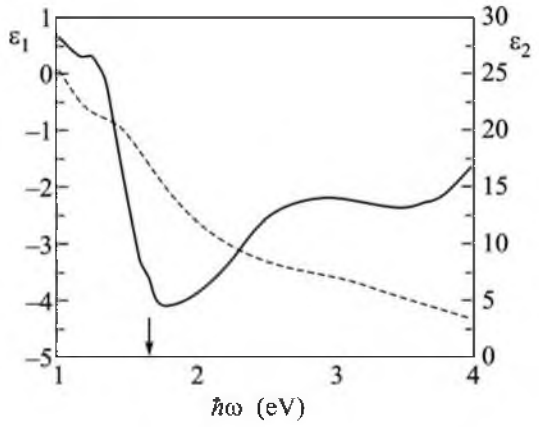

Fig. 3. Spectral dependence of the (solid line) real, ε_1, and (dashed line) imaginary, ε_2, parts of the relative permittivity for unexcited titanium (according to [15]). The arrow marks the energy quantum of a femtosecond laser pulse ($\lambda \approx 744$ nm).

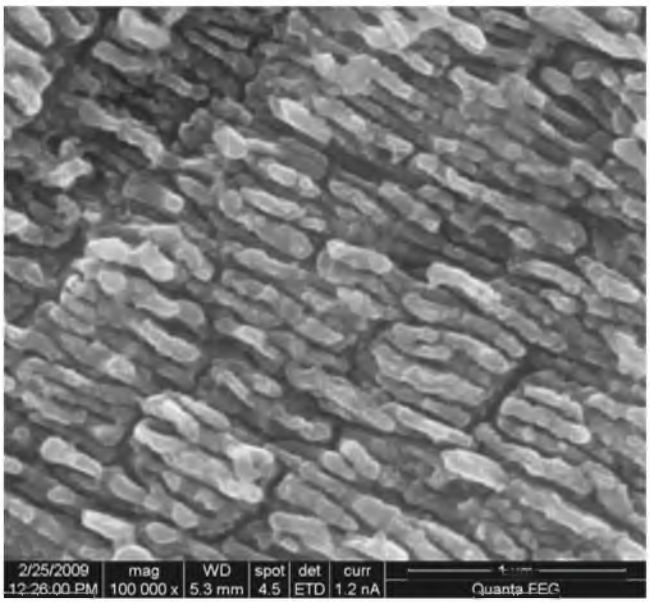

Fig. 4. Scanning electron microscope image of the nanolattice with the period $\Lambda \approx 100$ nm written on the humid titanium surface at $F \approx 300$ mJ/cm^2.

initial nanogrooves (see Fig. 1a), and the high-energy character of local ablation in nanogrooves in the absence of visible ablation of the material surface itself clearly indicate the local enhancement of the electric field of femtosecond laser radiation on the surface, which is most probable in the case of the excitation of the surface electromagnetic wave [1, 3, 5–7, 13, 14]. When the surface electromagnetic wave interfering with the light wave incident on the surface with the wavelength λ is generated, the roughness component with the wave vector $\mathbf{q} \parallel \mathbf{e}$ and period [14]

$$\Lambda = \lambda\left(\sqrt{\frac{|\varepsilon_1|}{|\varepsilon_1| - 1}} \pm \sin\theta_{inc}\right)^{-1} \quad (1)$$

increases. Here, $|\varepsilon_1|$ is the absolute value of the real part of the relative permittivity of the material at the wavelength of laser radiation and θ_{inc} is the angle of incidence of radiation on the surface (in this work, $\theta_{inc} \approx 0°$).

However, it is worth noting that the expected subwave periods of the modulation of the electromagnetic field on the titanium surface in the range of 0.2–0.4 μm under femtosecond laser irradiation correspond to the values $\varepsilon_1 \approx -(1.1-1.5)$, which are strongly different from the value $\varepsilon_1^0 \approx -3.5$ for the unexcited material at $\lambda \approx 744$ nm [15] (see Fig. 3) with the real, $n = 2.65$, and imaginary, $k = 3.24$, parts of the refractive index. Such an inconsistency was previously observed in [3, 7], where it was explained by the inapplicability of tabulated optical constants for the flat surface to the rough (nanostructured) surface and the electron excitation of the material, respectively. Similar to [7], we assume that the nanostructuring of titanium can be accompanied by a change in the component ε_1 of the relative permittivity of the titanium surface excited by femtosecond laser pulses, including the contributions from free and quasibound electrons; this component has the form

$$\varepsilon_1 = \varepsilon_{1,\,inter} - \frac{\omega_p^2\tau_e^2}{1 + \omega^2\tau_e^2}. \quad (2)$$

This change can occur due to, first, a decrease in the relaxation time of the electron momentum $\tau_e \propto 1/T_e^2$ as a result of the heating of the electron subsystem to temperature T_e [16] (in this case, the plasma frequency ω_p can increase due to the thermal ionization of the d bands [17]) and, second, a characteristic decrease in the term $\varepsilon_{1,\,inter}$ determined by transitions between narrow d bands with a high density of states near the Fermi level under the excitation by photons with energies higher than the interband transition energy maximum; this decrease is caused by the thermal spreading of the electron distribution near the Fermi level [18]. However, a detailed simulation of a change in the relative permittivity of titanium during its femtosecond laser excitation is complicated owing to the complex structure of its band spectrum [17]; for this reason, direct experimental investigations of the ultrafast dynamics of its optical constants are expedient.

To illustrate the surface character of the local enhancement of the electromagnetic field in the femtosecond laser writing of subwave lattices on the titanium surface, we carried out similar experiments on its nanostructuring at high energy densities $F \approx 0.3$–0.4 J/cm^2 and the number of incident pulses $N \approx 500$ under a thin (≈1 mm, to avoid self-focusing) layer of

doubly purified distilled water. In this case, nanolattices with a much smaller period of $\Lambda \approx 0.1$ μm were observed (see Figs. 2, 4); this was preliminarily attributed to an additional decrease in the effective n value for titanium in the aqueous medium, which promotes the formation of small-scale nanolattices according to Eq. (1).

The revealed unusual dependence of the period Λ of one-dimensional nanolattices for titanium on the surface energy density F of femtosecond laser radiation implies that not only titanium, but also many transition metals and other metals with a complex electronic structure (lanthanides, actinides) can likely exhibit similar dependences determined by the relation between the laser radiation energy quantum and the interband transition maximum. As a result, a variation of the wavelength, angle of incidence, and energy density of femtosecond laser radiation opens possibilities for the writing of one-dimensional nanolattices with periods varying from the minimally possible subwave ($\Lambda \ll \lambda$) to a superwave ($\Lambda > \lambda$) on the surface of such metals.

4. To summarize, sets of oriented quasiperiodic nanostructures (one-dimensional nanolattices) whose subwave periods lying in the range of 0.1–0.4 μm *decrease* with increasing surface energy density rather than increase as for other metals have been written on dry and humid titanium surfaces by means of femtosecond laser pulses. Such an anomalous behavior is explained by the features of the electron spectrum of this metal (the existence of interband transitions), which are manifested in the writing of nanolattices by femtosecond laser pulses of the visible and near-infrared ranges.

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