Surface nanogratings of abnormal orientation in universal polariton model of laser-induced damage of condensed media

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Abstract. An experimental results about formation of small-scale gratings of anomalous orientation under the interaction of polarized laser radiation with condensed media were analyzed. The model based on surface polaritons participation in interference process was put forward to explain observed results.

Sufficient number of experimental publications during last decade have been devoted to the formation of ordered micro- and nanostructures on boundaries of media and inside transparent materials under one beam laser radiation interaction with condensed media. Most frequently just the resonant structures the period of which is proportional to the wavelength of incident radiation ($\lambda$) were the subject. For long pulse durations radiation the model has been developed and verified based on surface polaritons and incident radiation interference [1]. Recently the universal polariton model [2] has been extended together with nonlinear mathematical model of the formation of spatial structures period's multiple to the laser radiation wavelength ($\lambda$) [3] to explain experimental results in wide range of durations (down to ultrashort one [4]), energy density and physical properties of considered media. The universal polariton model accounts for the grating ($g$) formation with orientation $g \parallel E$ and periods $d \sim \lambda$, where $E$ is the electric field strength of incident laser radiation. The explanation was based on the accounting the interference phenomenon with surface plasmon polariton participation excited by polarized laser radiation. Bellow such structures will be named as normal one.

At the same time, in experiments at later stages of normal resonant structures evolution the formation of additional new structures were frequently observed of orthogonal orientation $g \perp E$, the period of which usually was $d \ll \lambda$ [4-14]. Below this structures will be called as anomalous one. Important to note that the anomalous structures are not the peculiarity of ultrashort regime of laser-matter interaction and were observable also for regimes with long pulse durations.

To explain the origin of anomalous structures formation which were observed at the boundaries with materials of different physical properties the set of model was proposed among which we select following. The first one included the formation of a near-surface waveguide in silicon in the process of its electron depletion due to emission under the action of ultrashort pulse (USP) radiation [4]. The second model is based on the phenomenon of metal spallation [5]. The third model proposed for titanium [6] was based on generating the third harmonic of laser radiation in a TiO$_2$ layer with an
optimum thickness. The first model is applicable only for some semiconductors. In addition, according to estimates, there exist difficulties in reaching the threshold thickness of the depleted semiconductor layer for the existence of the lower waveguide mode. As for the second model, the creators of the metal spallation model specifically stipulated that it does not include phenomena caused by excitation and interference of surface polaritons [15]. The third model was proposed only for titanium. However, the formation of saturated titanium oxide (TiO$_2$) with an optimal thickness is very problematic for USP irradiation regimes (in the air). We have proposed a model [16, 17] based on excitation and mutual interference of wedge (channel) surface plasmon polaritons [18, 19]. The optical scheme in which the model is usually implemented in experiments is presented in Fig. 1. Under the effect of linearly polarized laser radiation on the metal surface, resonance linear relief (or dielectric permittivity) gratings shown in Fig. 1 can be formed in the framework of the universal polariton model [2]. The ridges and valleys of this relief are, respectively, waveguiding structures for wedge (channel) surface plasmon polaritons (WSPPs): counterpropagating WSPPs interfere with the formation of a periodic grating with the direction $g \perp E$. The WSPPs are most efficiently excited by a wave the electric field of which is parallel to the direction of the ridge (valley) of the main resonance relief. There exists an opinion [20] that the phenomenon of the formation of small-scale ($d \ll \lambda$) gratings with anomalous orientation is typical only for the interaction between the USP radiation and condensed media. In experiments on the interaction between linearly polarized radiation ($\lambda = 1.064 \mu m$, $\tau = 10$ ns, $f = 17$ Hz) and surface of VT1-0 titanium, we observed structurization of ridges of the formed main resonance relief ($d_0 = 1.02 \mu m$) with a period $d = 0.21 \mu m$ [21]. Gratings, in particular, anomalous ones, are observed in condensed media with significantly different physical properties: metals, semiconductors, and dielectrics. This is related to metallization of semiconductors and dielectrics during the generation of nonequilibrium electrons in them due to multiphoton (or tunnel) ionization.

Let us consider the formation of anomalous structures on metal surfaces. Figure 2a presents the image of a niobium surface destructed with the formation of anomalous gratings [7]. The structures with normal orientation of the grating and periods $d = \lambda/\xi \approx 600$ nm and $d = \lambda/2\xi \approx 300$ nm forming under the action of a linearly polarized radiation ($\lambda = 800$ nm, $\tau = 100$ fs, $f = 1$ kHz) at $Q \approx 0.5 J/cm^2$ and $N \approx (1–2) \times 10^3$ are caused by the interference of the incident radiation and WSPP and mutual interference of the WSPPs with opposite propagation directions, respectively. Here, $\xi$ is the real part of the refractive index of the medium interface for surface plasmon polaritons. At low energy densities ($Q \approx 0.29 J/cm^2$), $N \approx 1100$, and $N \approx 1900$, anomalous nanostructures appear on the niobium surface. Their period can be described by the formula:

$$d = \frac{\lambda}{2k\eta},$$

where $k = 1, 2, 4, 8, \ldots$, $\eta$ is the real part of the refractive index of the medium interface for the WSPPs.

First, there appear structures with period $d = \lambda/(2k\eta) \approx 65$ nm ($k = 4$, $\eta \approx 1.53$); then, with a larger period $d = \lambda/(2k\eta) \approx 145$ nm ($k = 2$, $\eta \approx 1.38$). Larger values of the period correspond to a larger value of $N$. 
Figure 1. Optical scheme illustrating the mechanism of formation and orientation of anomalous gratings. The incident laser radiation excites counterpropagating WSPPs along the extended ridge (valley) of the main resonance relief formed in the process of laser radiation interference with WSPPs. The direction of laser radiation polarization is shown by the double arrow. The direction of the forming nanograting $g$ is perpendicular to the tangential projection of the strength vector of the laser radiation electric field.

Anomalous structures are localized mostly on ridges of the main resonance relief, in particular, at initial stages of its formation (see peripheral zones of the scanning region), which corresponds to the interference with the participation of wedge SPPs. Values of quantity $\eta$ turned out to be rather large, which may be related to the influence of the gas solved in the nearsurface metal layer, as well as of the oxide layer, both formed under the action of the radiation. With an increase in $N$, nanorelief ridges were transformed into rounded nanodroplets. At larger energy densities, about $47 \, J/cm^2$, and $N \approx 300$, anomalous structures were localized only in valleys of the main relief (see the insert in Fig. 2a) and their period was $d = \lambda/(2k\eta) \approx 300 \, nm \, (k = 1, \, \eta \approx 1.3)$, which corresponds to the interference with the participation of WSPPs. The next example is tungsten subjected to a series of femtosecond pulses of a linearly polarized radiation ($\lambda = 800 \, nm$, $\tau = 180 \, fs$, $f = 1 \, kHz$) with energy density $Q = 0.4 \, J/cm^2$ at $N = 1000$ pulses. In Fig. 2b, one can clearly see the formation of the main resonance relief with a period of about $d_0 = \lambda / \xi \approx 600 \, nm$ (and normal orientation of the grating $g \parallel E$) and orthogonal gratings superposed on it with a characteristic period $d = \lambda/(2k\eta) \approx 70 \, nm \, (k = 4, \, \eta \approx 1.4)$. Here, the experimental results were interpreted using conclusions of the nonlinear mathematical model for the formation of spatial periods of structures [3] in the framework of the universal polariton model.
Figure 2. Illustration of anomalous nanostructure formation by a femtosecond linearly polarized radiation under the following conditions: (a) scanning with velocity $v = 0.1$ mm/s in the direction of the laser radiation electric field vector ($Q = 32$ mJ/cm$^2$, $\lambda = 800$ nm, $\tau = 100$ fs, and $f = 1$ kHz) with periods of 145 and 65 nm, respectively, in the peripheral and central (see insert) irradiated regions on the surface of niobium [7] and (b) with a period of $\approx 60$ nm on the surface of mechanically polished tungsten by a series of pulses ($Q = 0.2$ J/cm$^2$, $\lambda = 800$ nm, $\tau = 160$ fs, $f = 1$ kHz, $N = 700$).

Note that detailed experimental data on the formation of anomalous nanostructures on the titanium surface were published in [5, 6, 10, 22, 23]. Figure 3a illustrates the formation of anomalous gratings on a SiC semiconductor under the action of a linearly polarized femtosecond radiation and beam scanning in the direction of electric field strength vector $E$ [12]. One can see the formation of main resonance structures with a period $d_0 = 500$ nm, as well as the formation of nanochannels (nanocracks). Each nanocrack turns out to be spatially modulated by a grating in the form of nanoholes with period $d = 60$ nm, which corresponds to $k = 4$ and $\eta = 1.25n$ of formula (1), where $n = 1.33$ is the refractive index of water. The formation of a grating in the form of nanoholes is related to the specificity of the SiC surface destruction: in regions of intensity maximums, destruction of the material occurs with the removal of decomposition products from the affected area. Anomalous gratings of nanostructures were experimentally found for the first time on the surface of silicon in the region of its transparency ($\lambda = 1.25$ $\mu$m, $\tau = 10$ fs) [4]. However, they were studied experimentally in most detail in [11] using irradiation of silicon immersed in water ($\lambda = 800$ nm, $\tau = 150$ fs, and $f = 1$ kHz). The irradiation process consisted of two stages: after the formation of main resonance structures ($d_0 = \lambda/(n\xi)$), the direction of linear polarization was changed by $90^\circ$ and the irradiation continued with a somewhat decreased power density. As a result, ridges of the main resonance relief turned out
to be modulated with \( d = \frac{\lambda}{(kn\eta)} = \frac{800}{(1.33 \times 4 \times \eta)} \approx 90 \text{ nm for } \eta \approx 1.3 \) due to WSPP interference. The polarization change provided effective WSPP excitation and comparatively deep modulation of the relief ridge. The gratings at adjacent ridges were not phased, which is related to strong transverse (along the surface) localization of WSPP fields. Note that the small component of vector \( E \) in the direction of WSPP propagation in the scheme of Fig. 1 appeared due to radiation focusing. The contact with water ensured effective cooling of the irradiation zone. With a further increase in the number of radiation pulses, regions of local nanoridges were transformed into nanocolumns with a high (1 : 8) aspect ratio.

![Figure 3](image)

**Figure 3.** Illustration of the formation of anomalous nanostructure gratings in valleys (nanocracks) of the main resonance microrelief after the action of a series of femtosecond linearly polarized radiation pulses on surfaces of condensed media: (a) SiC \((P = 15 \text{ mW}, \lambda = 800 \text{ nm}, \tau = 150 \text{ fs}, \text{ and } f = 1 \text{ kHz})\) and scanning in the direction of strength vector \( E \) of the laser radiation electric field with velocity \( v = 1500 \text{ μm/s} \) [12] and (b) silicate glass \((E = 0.5 \text{ mJ}, \lambda = 1030 \text{ nm}, \tau = 300 \text{ fs}, f = 200 \text{ kHz}, v = 200 \text{ μm/s})\), laser radiation polarization is perpendicular to the direction of scanning [14]. Vectors \( g \) of the forming nanostructure gratings in the form of nanoholes are perpendicular to the direction of laser radiation polarization.

The regime of anomalous grating formation in mode of nano-holes on mono-silicon surface has been realized in standard scheme of experiment (see Fig.1) [24]. The irradiation was made by linear polarized laser radiation \((\lambda=800 \text{ nm}, \tau =130 \text{ fs}, f =1 \text{ kHz})\) and scanning in direction perpendicular to the vector \( E \) direction (in air). The laser energy density was near material ablation threshold. The main resonant structures were the prerequisite for anomalous grating formation as stressed by authors [24]. The period of anomalous grating can be estimated using their images as \( \sim 200 \text{ nm} \) (authors of [24] did not indicate the period value).
The different scheme of experiment have been realized in [25] also on silicon surface. The anomalous gratings were observed in conditions of radiation scanning (v~ 1mm/s) in direction of laser radiation polarization. In such conditions the gratings of normal orientation, if produced, must have orientation perpendicular to the scanning direction. But produced anomalous gratings were oriented along electric field strength vector direction. Their formation were due to channel SPP and incident laser radiation interference (the grating was localized in valleys of relief formed by scanned radiation), and their period \( d = \lambda / 2 \xi \approx 720 \text{ nm} \). The productions of two or more anomalous gratings were observed with increasing laser energy density separated by distance of the order of 2 \( \mu \text{m} \). This residual grating causes the selective absorption of radiation from white light and structured surface coloration.

In one of first works on the formation of gratings with normal orientation in a volume of glass (dielectric) and periods \( \lambda / (n \eta) \), \( \lambda / (2n \eta) \), \( \lambda / (4n \eta) \), ..., traces of the formation of a grating in the form of nanoholes were observed along regions of nanocracks; on the ridges, nanostructure gratings were observed [26]. Figure 3b [14] more explicitly illustrates the formation of an anomalous grating on valleys and ridges of the relief with normal orientation (\( d_1 = \lambda / (2n \xi) \approx 230 \text{ nm} \) and \( d_2 = \lambda / (4n \xi) \)) on the silicate glass with periods \( d = \lambda / (2n \eta) \approx 50 \text{ nm} \) (\( k = 4, \eta \approx 1.34 \)) (wedge SPPs) and in valleys (nanocracks) with \( d \approx 58 \text{ nm} \) (\( k = 4, \eta \approx 1.16 \)). According to the model that we propose, the formation of the last structures is caused by interference of WSPPs localized and propagating along linear nanocracks and explains the physical cause of the formation of nanopores (see the discussion in [14]).

Fluorite (CaF\(_2\)) [13] and TiO\(_2\) [27] serve as additional examples of the formation of anomalous gratings on dielectrics. Structures with anomalous orientation on silica glass were found also in the case of the action of axisymmetrically polarized laser radiation [28].

**Conclusion**

Thus, experimental data on the formation of gratings of structures with anomalous orientation under the action of linearly polarized laser radiation pulses in condensed media have been analyzed. To explain the causes of the formation of anomalous gratings, a model predicting spatial periods and orientation of gratings has been proposed. The model is based on (i) mutual interference of WSPPs propagating in opposite directions and (ii) a nonlinear mathematical model predicting the formation of spatial nanograting periods multiple to the wavelength. The proposed model well describes the available experimental data on anomalous structures on media with different physical properties: metals, semiconductors, and dielectrics. The model is applicable not only to USP radiation, but also to nanosecond radiation. Like periods of gratings with normal orientation, periods of anomalous gratings obey the inverse Feigenbaum universality of doubling the spatial period. The spatial period of anomalous gratings can be considerably less that the diffraction optical limit (e.g., for stainless steel, \( d \approx 30 \text{ nm} \) \( \lambda = 515 \text{ nm} \)) and physically restricted by processes of thermal conductivity “smoothing.” Note that the process of the decrease in the spatial scale of structures can continue due to interference of WSPPs excited on ridges (valleys) of already formed anomalous gratings. Traces of this process are found in a series of irradiated regions. The excitation of WSPPs can be considered as a new channel of transforming the laser radiation into heat under the interaction of powerful USP radiation with condensed media. Anomalous gratings make an additive contribution to the absorptive capacity of the so-called «black metals».

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