INTERACTION OF LASER RADIATION WITH MATTER

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Theory of formation of an ensemble of nanoclusters on the surface of CdTe crystals irradiated by a laser pulse

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***Abstract*. The plasma-deformation theory of formation of an ensemble of nanoclusters on the surface of a CdTe semiconductor irradiated by a laser pulse is proposed. The theory well describes experimental data.**

Keywords: *semiconductor surface, laser radiation, self-organisation of an electron – hole plasma, formation of an ensemble of nanoclusters.*

1. Introduction

The formation of nanostructures on crystal surfaces irradiated by lasers is the topical problem in the physics and technology of semiconductors. In [1], the formation of an ensemble of nanoclusters on the surface of a CdTe semiconductor irradiated by a nanosecond laser pulse was found and the dependence of the longitudinal size of nanoclusters on the radiation intensity having a distinct maximum was established (Fig. 1). The authors of paper [2] proposed the plasma-deformation (PD) mechanism of formation of an ensemble of nanoclusters on the surface of CdTe crystals subjected to such irradiation. In this paper, we developed the PD theory describing consistently the laser-induced formation of an ensemble of nanoclusters on the CdTe surface.

The melting mechanism of CdTe (the melting point is 1365 K [3]) under experimental conditions [1] plays a key role in the development of the theory. The threshold melting energy densities reported in the literature for CdTe irradiated by $\sim 10 - 20$-ns pulses from a 0.69-μm ruby laser (the absorption length was $\alpha^{-1} = 10^{-5}$ cm) are different. The authors of paper [4] interpret their experimental data (the increase in the reflectance and the threshold decrease in the second-harmonic intensity with increasing the incident radiation intensity) by using the threshold value of 40 mJ cm^{-2}. In [5], the pulse laser-induced melting of CdTe was investigated taking into account the surface

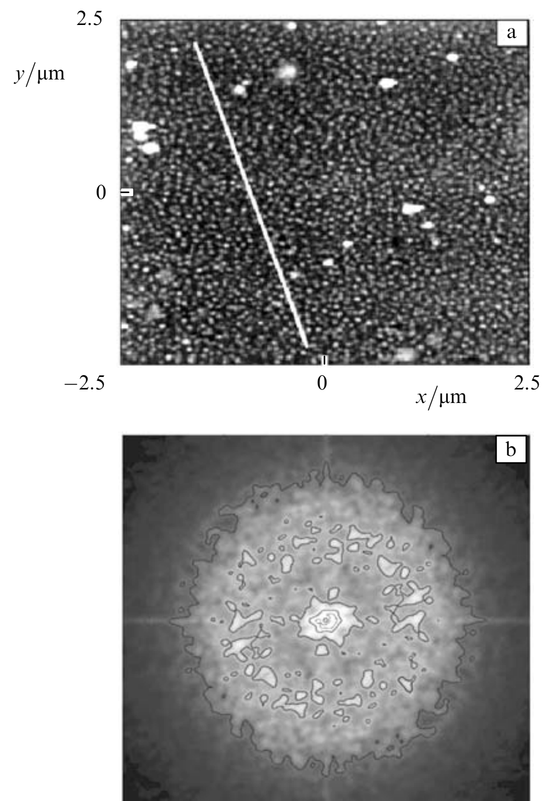

Figure 1. Atomic-force-microscope image of the CdTe surface after irradiation by a 12-MW cm^{-2} single laser pulse (a) and the corresponding Fourier spectrum (b).

evaporation of atoms and it was shown that, due to this effect, the maximum of temperature is achieved at some distance from the surface at a depth of ~ 20 nm. In this case, two melting fronts are formed, one of them moving to the surface and the other – inside the medium. The melting threshold of CdTe irradiated by 20-ns pulses calculated in [5] was 60 mJ cm^{-2}. Because the evaporation rate of Cd greatly exceeds that of Te, a layer enriched by Te should form on the crystal surface. This layer partially attenuates the transmission of exciting radiation through CdTe, which can explain the threshold decrease in the SHG efficiency observed at the energy density 40 mJ cm^{-2} in [4]. Note that, upon irradiation of CdTe by 15-ns pulses from a KrF laser, a Te film was formed on the crystal surface when the energy density of the exciting pulse exceeded precisely this value [6].

Even higher threshold melting energy densities for CdTe were predicted in paper [7], where the heating of CdTe

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produced by 25-ns pulses from a ruby laser was calculated numerically. The calculations show that for the pulse energy density 0.36 J cm^{-2} (the maximum value used in [1]), the thickness $l_{\rm liq}$ of the melted layer should be only ~ 20 nm. Note that losses caused by Cd evaporation, which were neglected in calculations, should lead to even greater decrease in the expected value of $l_{\rm liq}$. It is important to emphasise that CdTe remains a semiconductor in the melted state.

Based on the above discussion, we propose the following mechanism of formation of an ensemble of nanoclusters on the CdTe surface under the action of a single laser pulse. The radiation pulse with the energy density close to the melting threshold produces a near-surface electron – hole plasma. When the pulse intensity exceeds the critical value $I_{\rm c}$, the concentration of the electron – hole plasma on the crystal surface increasing with time exceeds before the pulse termination (and before the onset of melting) the critical concentration required for the development of the PD instability (see below). Due to the rapid development of the latter, surface plasma grating are formed before the onset of melting (in the solid phase). The energy gap in CdTe decreases in plasma clusters and the absorption coefficient increases correspondingly. This situation is preserved after melting during the pulse action because CdTe remains a semiconductor in the melted state. The recombination-induced removal of the material from plasma clusters forms a surface relief grating during the pulse action. The melt rapidly solidifies after the pulse termination, which results in the irreversible formation of the relief grating.

The generation of the electron – hole plasma and heating stimulate the passage of Cd to interstice sites, its diffusion to the surface (see Appendix), and evaporation (recombination-induced processes). As a result, when the pulse energy density exceeds the critical value $W_{\rm Te}$, a Te film begins to form on the CdTe surface. The film strongly absorbs radiation, which reduces the plasma concentration. We show in this paper that the consideration of this factor in the theory of the PD instability of a surface nanorelief allows us to describe quantitatively the experimental dependence of the longitudinal size of a nanocluster on the radiation intensity. The theory uses the model of the defect-deformation instability of the surface layer (film with defects), in which the parameter determining the characteristic scale of the relief modulation is the thickness h of a plasma-enriched layer [8] (see also review [9]). The role of point defects is played by electron – hole pairs, and the longitudinal size of a nanoclusters is proportional to the thickness of the plasma-enriched layer subjected to the PD instability. Although this thickness is proportional to the optical absorption length, it is considerably smaller than the latter.

2. Experimental data

The surface of a p-CdTe crystal semiconductor with the (111) orientation was irradiated at room temperature by a single 20-ns pulse from a multimode ruby laser. The pulse power density was varied from 4 to 18 MW cm^{-2}. It was found that a two-dimensional nanorelief was formed on the surface at pulse intensities exceeding 4 MW cm^{-2}. The typical atomic-force microscope (AFM) image of the surface after irradiation and the Fourier spectrum of this image are shown in Fig. 1. The longitudinal size on nanoclusters (period of the relief structure) first increases and then decreases with increasing the pulse power (Fig. 2).

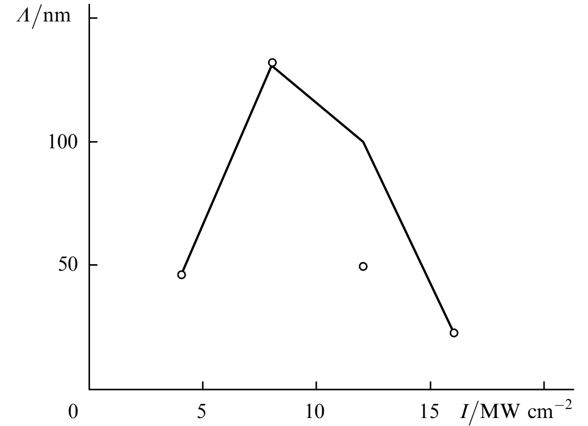

Figure 2. Dependence of the longitudinal size Λ of the radiation intensity I. Circles are experimental data [1], the solid line is calculated by expression (29).

Let us show that these experimental data can be qualitatively and quantitatively described within the framework of the PD model.

3. Formation of a plasma-enriched layer and a Te film on the CdTe surface exposed to laser radiation

Let the $z = 0$ surface of a semiconductor be irradiated by laser pulse of duration $\tau_{\rm p}$ and the z axis be directed deep in the crystal. Because the laser beam radius on the crystal surface greatly exceeds the absorption length, we can consider the one-dimensional (along the z axis) problem. The absorption of radiation in a direct-gap CdTe semiconductor produces an electron – hole plasma in the surface layer. The change in the plasma concentration $n_{\rm e}$ is described by the one-dimensional diffusion equation

$$\frac{\partial n_{\rm e}}{\partial t} + \frac{n_{\rm e}}{\tau_{\rm e}} = D_{\rm e}\,\frac{\partial^2 n_{\rm e}}{\partial z^2} + \frac{(1-R)\alpha I_0}{\hbar\omega}\exp(-\alpha z), \tag{1}$$

where $\tau_{\rm e}$ is the lifetime of charger carriers; $D_{\rm e}$ is the diffusion coefficient; α is the absorption coefficient; R is the reflection coefficient; ω is the radiation frequency; and I_0 is the radiation intensity on the $z = 0$ surface of the semiconductor. Note that upon laser interband excitation of the semiconductor, the concentrations of holes and electrons are equal. By assuming that $\tau_{\rm p} > \tau_{\rm e}$, we consider the stationary case ($\partial n_{\rm e}/\partial t = 0$). Under the condition that the diffusion length $l_{\rm e}$ of carriers satisfy the relation $l_{\rm e} = (D_{\rm e}\tau_{\rm e})^{1/2} \leqslant \alpha^{-1}$, we neglect the diffusion of carriers from a layer of thickness α^{-1} deep in the medium (this assumption is justified by numerical estimates in section 5). Then, the distribution of the plasma concentration over the depth is described by the expression

$$n_{\rm e}(z) = N_{\rm e}\exp(-\alpha z), \tag{2}$$

having the maximum

$$N_{\rm e} = \tau_{\rm e}\,\frac{(1-R)\alpha I_0}{\hbar\omega} \equiv BI_0 \tag{3}$$

on the surface (the $z = 0$ plane). The initial distribution of the concentration n_e in this plane is uniform.

Let us now take into account in our model that a Te film of thickness h_{Te} ($\sim 10^{-7}$ cm) appears on the crystal surface at laser radiation intensities $I > I_1 = 4$ MW cm^{-2}. This is caused by the predominant removal of more volatile and mobile Cd atoms from surface layers [1, 6]. We assume that an elementary jump of a Cd atom through the potential barrier during diffusion to the surface occurs at the expense of the energy released upon recombination of an electron–hole pair (Auger recombination involving the Cd atom). We show in Appendix that in this case, the thickness h_{Te} is determined by the length of the recombination-stimulated diffusion of Cd atoms from the plasma-enriched surface layer for the time τ_p and

$$h_{Te} = AN_e, \tag{4}$$

where $A = (\Gamma\gamma_k\tau_k a^2\tau_p)^{1/2}$ [see derivation of expression (A6) in Appendix]; Γ is the rate constant of the electron capture by a hole; γ_k is the rate constant of localisation of a free hole near an interstice; τ_k is the lifetime of a localised hole; and a is the crystal lattice. In this case, the plasma concentration N_e on the CdTe surface is specified by (3), where I_0 is the radiation intensity transmitted through the Te film of the CdTe surface: $I_0 = I\exp(-\beta h_{Te})$. Here, β is the absorption coefficient in the Te film and I is the incident radiation intensity. By substituting this expression into (3), we obtain the equation

$$N_e = BI\exp(-\beta AN_e), \tag{5}$$

describing N_e as a function of I.

Let us determine the thickness h of a near-surface plasma-enriched layer subjected to the PD instability from the condition $n_e(h) = N_{ec}$, where N_{ec} is the critical concentration at which the surface PD instability appears (see below). Then, we obtained from (2),

$$h = \alpha^{-1}\left(\ln\frac{BI}{N_{ec}} - \beta AN_e\right),$$

where N_e is specified by expression (5). By using the solution $N_e \approx \beta I$ of equation (5) in the zero-order approximation in the parameter βh_{Te} ($\beta h_{Te} < 1$), we find finally the expression for h in the form

$$h = \alpha^{-1}\left(\ln\frac{BI}{N_{ec}} - \beta ABI\right). \tag{6}$$

Because excited electron–hole pairs have the deformation potential θ_e, the crystal cell size changes in the plasma-enriched layer. Therefore, this layer can be treated as a near-surface film of thickness h with elastic properties different from those of the substrate (the crystal region located below). The Te film thickness can be neglected in this case ($h_{Te} \ll h$).

4. Instability of the uniform plasma distribution on the crystal surface and formation of quasi-periodic plasma-deformation gratings

Consider the one-dimensional problem on a surface, assuming that $n_e = n_e(x, z, t)$. To calculate the symmetry, period, and formation time of the PD structure, it is sufficient to analyse only the initial (linear) stage of the development of the PD instability. Therefore, we represent the plasma concentration in the form $n_e = n_{e0}(z, t) + n_{e1}(x, z, t)$, where $n_{e0}(z, t)$ and $n_{e1}(x, z, t)$ are the spatially uniform and nonuniform over x components of n_e, respectively. Taking into account the redistribution of the plasma only along the surface at small development times of the surface PD, we write the relation

$$n_{e0}(x, z, t) \equiv N_{e0}(x, t)\exp(-\alpha z) \tag{7}$$

for the spatially uniform component n_e, where $N_{e0}(x, t)$ is the plasma concentration on the surface.

The longitudinal diffusion equation for $n_e = n_{e0}(x, z, t)$ has the form

$$\frac{\partial n_e}{\partial t} = D_e\frac{\partial^2 n_e}{\partial x^2} - \frac{n_e}{\tau_e} - \frac{D_e n_e \theta_e}{k_B T}\frac{\partial}{\partial x}\operatorname{div}\boldsymbol{u}, \tag{8}$$

where T is temperature and k_B is the Boltzmann constant. The last term in (8) describes the deformation-induced plasma drift along the surface. For the bending deformation of the film, we have

$$\operatorname{div}\boldsymbol{u} = \nu\left(\frac{h}{2} - z\right)\frac{\partial^2\zeta}{\partial x^2}, \tag{9}$$

where $\zeta = \zeta(x)$ is the displacement of the points on the surface with the initial coordinate $z = h/2$; $\nu = (1 - 2\sigma)\times(1 - \sigma)$ along the z axis; and σ is Poisson's ratio.

We write the equation for ζ taking into account that a bending force acts on the film from the side of the plasma subsystem [9]:

$$\frac{\partial^2\zeta}{\partial t^2} + \frac{c^2h^2}{12}\frac{\partial^4\zeta}{\partial x^4} - \frac{\sigma_\parallel}{\rho}\frac{\partial^2\zeta}{\partial x^2} = \frac{\theta_e}{\rho h}\int_0^h\frac{\partial n_e}{\partial z}\,\mathrm{d}z, \tag{10}$$

where $c^2 = E/(1 - \sigma^2)\rho$ is the modulus of rigidity of the film; E is the Young modulus; and ρ is the density of the medium. It is assumed in (10) that the longitudinal stress $\sigma_\parallel$ stretching the film, which appears due to laser-induced generation of defects in the surface layer [4], is positive and isotropic, so that the x axis is directed arbitrarily on the surface.

Equations (8)–(10) form a closed system describing the formation of the PD grating in the 'defect film-on-substrate' model.

By assuming that deformation adiabatically follows the defect subsystem ($\partial^2\zeta/\partial^2 t^2 = 0$), we obtain from (10) after integration

$$\frac{\partial^4\zeta}{\partial x^4} - \frac{1}{l_\parallel^2}\frac{\partial^2\zeta}{\partial x^2} = -\frac{A_1}{2}[n_{e1}(z = 0) - n_{e1}(z = h)], \tag{11}$$

where $A_1 = 2\theta_e/(hl_0^2\rho c^2)$ and the characteristic scale parameter $l_\parallel$ of the defect-deformation grating is determined by the expression

$$l_\parallel = h\left(\frac{\rho c^2}{12\sigma_\parallel}\right)^{1/2}. \tag{12}$$

By linearising (8) taking (7) into account, we obtain the equation

$$\frac{\partial n_{e1}(x,z,t)}{\partial t} = D_e \frac{\partial^2}{\partial x^2} n_{e1} - \frac{n_{e1}}{\tau_e} - D_e B_1 N_{e0} \frac{2}{h}\left(\frac{h}{2} - z\right)\exp(-\alpha z)\frac{\partial^4 \zeta}{\partial x^4}, \tag{13}$$

where $B_1 = v\theta_e h/(2k_B T)$. Equation (13) describes the plasma redistribution over x at the depth z caused by the action of the self-consistent deformation field.

We seek the solution of (13) in the form

$$n_{e1}(x,z,t) = \frac{2}{h}\left(\frac{h}{2} - z\right)\exp(-\alpha z) N_{e1}(x,y,t). \tag{14}$$

In the case under study, the condition $\alpha h \ll 1$ is fulfilled (see below) and expression (14) is simplified,

$$n_{e1}(x,y,z,t) = \frac{2}{h}\left(\frac{h}{2} - z\right) N_{e1}(x,y,t). \tag{15}$$

It follows from (15) that

$$n_{e1}(z=0) = -n_{e1}(z=h) = N_{e1}. \tag{16}$$

Then, equation (11) takes the form

$$\frac{\partial^4 \zeta}{\partial x^4} - \frac{1}{l_\parallel^2}\frac{\partial^2 \zeta}{\partial x^2} = -A_1 N_{e1}, \tag{17}$$

and equation (13), after the substitution of expression (15) into it, is reduced to the equation

$$\frac{\partial N_{e1}}{\partial t} = D_e \frac{\partial^2 N_{e1}}{\partial x^2} - \frac{N_{e1}}{\tau_e} - D_e B_1 N_{e0}\frac{\partial^4 \zeta}{\partial x^4}. \tag{18}$$

Equations (17) and (18) form a closed system

Let us represent N_{e1} and ζ as a sum of spatial harmonics with the vectors $\boldsymbol{q}$ of the PD grating, growth rates λ_q, and amplitudes N_q and ζ_q, respectively,

$$N_{e1} = \sum_q N_q \exp(\lambda_q t + iqx) + \text{c.c.}, \tag{19}$$

$$\zeta = \sum_q \zeta_q \exp(\lambda_q t + iqx) + \text{c.c.} \tag{20}$$

By substituting (19) and (20) into equations (17) and (18), we obtain that, with the condition $\lambda_q^2 \ll q^4 c^4 h^4/12$, the dispersion relation for the increment has the form

$$\lambda_q = D_e Q_e^2 \frac{l_\parallel^2 q^2}{1 + l_\parallel^2 q^2} - D_e q^2 - \tau_e^{-1}, \tag{21}$$

where

$$Q_e^2 = \frac{1}{h^2}\frac{12 v\theta_e^2 N_{e0}}{\rho c^2 k_B T} \tag{22}$$

is the parameter governing the PD instability (plasma pump parameter).

It follows from (21) that the dependence $\lambda_q = \lambda(q)$ has the maximum $\lambda_q = \lambda_m$ at $q = q_m$:

$$\lambda_m = \frac{D_e}{l_\parallel^2}(Q_e l_\parallel - 1)^2 - \frac{1}{\tau_e}, \quad q_m = \frac{1}{l_\parallel}(Q_e l_\parallel - 1)^{1/2}. \tag{23}$$

One can see from (23) that for the condition $\lambda_m > 0$ to be fulfilled, the pump parameter should exceed the critical value Q_{ec}:

$$Q_e > Q_{ec} = \frac{1}{l_\parallel}\left[1 + \frac{l_\parallel}{(D_e \tau_e)^{1/2}}\right]. \tag{24}$$

At the same time, q_m becomes real for $Q_e < 1/l_\parallel$. Thus, if $Q_e > Q_{ec}$ (i.e. if the plasma concentration exceeds the critical concentration N_{ec}), the Fourier amplitudes of the coupled gratings of bending deformation (20) and plasma concentration (19) begin to increase exponentially in time, the Fourier harmonic with $q = q_m$ having the maximum increment $\lambda_q = \lambda_m$ and dominating in the excitation spectrum. Below, we restrict our consideration to a grating with $\lambda_q = \lambda_m$ and $q = q_m$.

Le us find the critical plasma concentration from the condition $Q_e \geqslant Q_{ec}$. We have from (22) and (24) that

$$N_{ec} = \frac{\sigma_\parallel k_B T}{\theta_e^2 v}\left[1 + \frac{l_\parallel}{(D_e \tau_e)^{1/2}}\right]^2. \tag{25}$$

The second term in brackets in (25) becomes smaller than the first one when $h \leqslant [12\sigma_\parallel/(\rho c^2)]^{1/2}(D_e\tau_e)^{1/2}$. For $\sigma_\parallel \approx 10^9$ dyn cm^{-2}, $\rho c^2 \approx 10^{10}$ erg cm^{-3}, $D_e \approx 1$ cm^2 s^{-1}, $\tau_e = 10^{-10}$ s, $v \approx 1$, we obtain that this situation takes place for $h \approx 10^{-5}$ cm. Because we are interested in the case $h \leqslant \alpha^{-1} = 10^{-5}$ cm, the second term in brackets in (25) can be neglected. Then, the expression for N_{ec} takes the form

$$N_{ec} = \frac{\sigma_\parallel k_B T}{\theta_e^2 v}. \tag{26}$$

The critical plasma concentration estimated from (26) for the values of parameters presented above and $T = 1000$ K is $N_{ec} = 10^{18}$ cm^{-3}. By using (26), the expression for q_m (23) can be written in the form

$$q_m = \frac{1}{l_\parallel}\left[\left(\frac{N_e}{N_{ec}}\right)^{1/2} - 1\right]^{1/2} = \frac{1}{h}\left(\frac{12\sigma_\parallel}{\rho c^2}\right)^{1/2} \times \left[\left(\frac{N_e}{N_{ec}}\right)^{1/2} - 1\right]^{1/2}. \tag{27}$$

For $N_e = 10^2 N_{ec} = 10^{20}$ cm^{-3}, we obtain $q_m \approx 3/h$. Thus, when the concentration N_e greatly exceeds the critical plasma concentration, the value of q_m begins to exceed the maximum value $q_c = \pi/h$: $q_m > q_c$. This means that for $N_e > 10^2 N_{ec}$, the growth rate maximum is achieved for $q = q_c$ and its position becomes independent of N_e. Therefore, for $N_e > 10^2 N_{ec}$, the period Λ of the dominating PD grating is independent of N_e:

$$\Lambda = \frac{2\pi}{q_c} = 2h, \tag{28}$$

where the thickness h is described by expression (6).

As shown above, when the concentration of electron–hole pairs in a stressed film exceeds the critical value

($N_e > N_{ec} \sim 10^{18}$ cm^{-3}), the PD instability develops with the increase in the amplitude of the surface relief grating along the x axis: $\zeta(x) = \zeta_q \cos(q_m x)\exp(\lambda_m t)$. Simultaneously, similar PD gratings appear with vectors $\boldsymbol{q}_m$ whose directions are distributed uniformly in the xy plane. The period $\Lambda = 2\pi/q_m$ of these dominating PD gratings (with the maximum growth rate λ_m) is proportional to the film thickness h and is $\sim 2h$ at the high enough plasma concentration. Apart from domination PD gratings with vectors $\boldsymbol{q}_m$ randomly distributed in the xy plane, a continuum of PD gratings is developed with vectors whose moduli are also randomly distributed in region near q_m in the xy plane where $\lambda_q > 0$. The superposition of these gratings leads to the formation of a seed surface PD structure – a two-dimensional chaotic modulation of the surface relief with the characteristic longitudinal scale $2h$.

The calculation of the amplitude of the resulting grating written in this way (a nonocluster height) is a separate problem, which is not considered here.

5. Comparison of theoretical and experimental results

One can see from Fig. 2 that the theoretical dependence of the longitudinal size Λ of a nanoclusters on the laser radiation intensity I

$$\Lambda = 2h = 2\alpha^{-1}\left(\ln\frac{I}{I_c} - C\frac{I}{I_c}\right) \tag{29}$$

[where h is specified by expression (9), $C = \beta A N_{ec}$, and $I_c = N_{ec}/B$] qualitatively describes the experimental dependence [1].

Let us show that the values of parameters $C = 0.265$ and $I_c = 2.2$ MW cm^{-2} used to construct the dependence in Fig. 2 correspond to the values calculated from theoretical expressions $C = \beta A N_{ec}$ and $I_c = N_{ec}/B$ for physically reasonable values of quantities entering these expressions. For the absorption coefficient of a tellurium film $\beta = 10^6$ cm^{-1}, $N_{ec} = 10^{18}$ cm^{-3}, and $A \sim 10^{-25}$ cm^4 (see Appendix), we have $C \sim 0.1$. For the parameter $B = \tau_e(1 - R)\alpha/(\hbar\omega)$ for $R = 0.21$ [3], $\alpha = 10^5$ cm^{-1}, $\hbar\omega = 1$ eV, $\tau_e = 10^{-10}$ s, we obtain $B \sim 10^6$ s erg cm^{-1} and $I_c \sim 1$ MW cm^{-2}.

The formation time of the PD grating $(D_e q_m^2)^{-1} = \Lambda^2 \times (4\pi^2 D_e)^{-1} \sim 2$ ps is considerably shorter than the laser pulse duration τ_p (for the diffusion coefficient of carriers $D_e = 1$ cm^2 s^{-1}). The diffusion length l_e for carriers for the time $\tau_e = 10^{-10}$ s is $\sim 10^{-5}$ cm, i.e. is of the order of the absorption length α^{-1}.

The Fourier spectrum of the AFM image of the surface after irradiation (Fig. 1b) consists of a ring of finite thickness with several pairs of local maxima on it. The ring corresponds to the formation of a set of PD gratings with vectors whose moduli lie within a region near q_m, where $\lambda_q > 0$. The presence of maxima on the ring suggests the beginning of the nonlinear angular self-organisation of PD gratings, i.e. the trend to the formation of a hexagonal structure. Note that a similar hexagonal self-organisation was also observed during the laser-induced formation of a surface roughness of micron size [10] and etching of hexagonal ensembles of pores [11, 12].

Thus, the PD theory can describe the formation of an ensemble of nanoclusters on the surface of CdTe crystals irradiated by single laser pulses.

Appendix. Recombination-stimulated diffusion length for Cd atoms and the thickness of a Te film produced upon laser irradiation of CdTe

Upon laser irradiation of CdTe, a near-surface layer enriched with charge carriers is produced. We will assume that due to thermal fluctuations a part of Cd atoms in this layer pass to interstices.

An electron–hole pair can localise near such an interstitial atom. First a hole is localised (whose effective mass is greater) and then an electron is localised in the hole field. The subsequent recombination of the localised electron–hole pair is accompanied by the local release of energy, which is transferred to the interstitial Cd atom. This atom can jump over the atomic potential barrier. Such elementary events of transitions over the atomic barrier lead to the diffusion of interstitial Cd atoms.

Let us determine the coefficient of recombination-stimulated diffusion of Cd interstitials from the expression $D = a^2/\tau$, where a is the length of an elementary jump (the crystal cell size) and τ is the jump duration. This time is the sum of the hole localisation time τ_h near a defect ($\sim 10^{-11}$ s), the electron capture time by a hole τ_1 ($\sim 10^{-11}$ s), the recombination time τ_{rec} of the localised electron–hole pair ($\sim 10^{-12}$ s), and the time τ_0 ($\sim 10^{-13}$ s) of jump over the potential barrier by a distance a. Because $\tau_0, \tau_{rec} \ll \tau_{eh} \equiv \tau_h + \tau_1$, we can assume that the electron jump time is $\tau = \tau_{eh}$. We will assume for simplicity that $\tau_1 > \tau_h$ (see the estimate below) and, therefore, the duration of an elementary jump is $\tau = \tau_1$.

To find τ_1, we write the expression for the localisation rate of electrons on localised holes with concentration n_k:

$$\frac{\partial n_e}{\partial t} = -\Gamma n_k n_e, \tag{A1}$$

where $\Gamma = \sigma_e v_e = 4 \times 10^{-9}$ cm^3 s^{-1} is the rate constant of the electron capture by the localised hole; $\sigma_e = 4 \times 10^{-17}$ cm^2 is the electron capture cross section; v_e is the electron velocity; and n_e is the concentration of free electrons. The time of electron capture by the hole is $\tau_1 = (\Gamma n_k)^{-1}$. The equation for n_k has the form

$$\frac{\partial n_k}{\partial t} = \gamma_k n_h n_i - \frac{n_k}{\tau_k}, \tag{A2}$$

where γ_k is the rate constant of localisation of a free hole near an interstice; n_h and n_i are concentrations of free holes and interstitial atoms, respectively. The localisation time of the hole is $\tau_h = (\gamma_k n_i)^{-1} \sim 10^{-11}$ s. For $t > \tau_k$, we obtain from (A2) the concentration of localised holes $n_k = \gamma_k \tau_k n_h n_i = \varepsilon n_h n_i$, where $\varepsilon = \gamma_k \tau_k$. Then, according to (A1), the number of electrons captured in a unit volume per unit time is described by the expression

$$\frac{\partial n_e}{\partial t} = -\Gamma \varepsilon n_i n_h n_e. \tag{A3}$$

By dividing both parts of (A3) by n_i, we obtain

$$\frac{1}{n_i}\frac{\partial n_e}{\partial t} = -\Gamma \varepsilon n_h n_e. \tag{A4}$$

The right-hand side of (A4) corresponds to the number of

electrons captured by one interstice per unit time. Thus, the inverse localisation time of an electron on one interstice is $1/\tau_1 = \Gamma \varepsilon n_h n_e = \Gamma \varepsilon n_e^2$. As mentioned above, the concentrations of holes and electrons upon laser interband excitation of a semiconductor are equal. Then, the recombination-stimulated diffusion coefficient for cadmium interstices is $D = \Gamma \gamma_k \tau_k a^2 n_e^2$. The recombination-stimulated diffusion length h_{Te} for Cd along the z axis during the pulse duration τ_p is proportional to the plasma concentration:

$$h_{Te} = (D\tau_p)^{1/2} \equiv A n_e \approx A N_e, \qquad \text{(A5)}$$

where

$$A = (\Gamma \gamma_k \tau_k a^2 \tau_p)^{1/2} = \left(\frac{\Gamma a^2 \tau_p n_k}{n_h n_i} \right)^{1/2}. \qquad \text{(A6)}$$

Due to recombination-stimulated diffusion, the interstitial Cd atoms leave the CdTe volume during the time τ_p from the depth determined by the diffusion length h_{Te} (A5). As a result, a layer enriched with the Te atoms (a Te film) of thickness h_{Te} is formed on the CdTe surface. Expression (A5) is used in section 3. Let us estimate the constant A. For $\Gamma = 4 \times 10^{-9}$ cm^3 s^{-1}, $a = 5 \times 10^{-8}$ cm, $n_k/n_h \sim 10^{-1}$, $\tau_p = 20$ ns, $n_i = 10^{18}$ cm^{-3}, we obtain from (A6) $A = 10^{-25}$ cm^4. This value is used for numerical estimates in section 5.

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