
**SEMICONDUCTOR STRUCTURES,
INTERFACES, AND SURFACES**

Low-Threshold Defect Formation and Modification of Ge Surface Layer under Elastic and Elastoplastic Pulsed Laser Effects

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Abstract—Changes in the spectra of fluorescence of dye (rhodamine B) molecules adsorbed on a Ge surface and modification of the parameters of Raman and diffuse scattering of light by a semiconductor surface subjected to elastic and elastoplastic effects of pulsed laser radiation are studied. Using contactless photoacoustic measurements based on the laser beam deflection technique, the amplitude of the threshold surface strain is estimated at $\sim 5 \times 10^{-5}$. An appreciable quenching of the fluorescence of the adsorbed probe molecules, an abrupt broadening of the molecular spectra, and an above-threshold increase in the intensity of the diffusively scattered light are observed upon the transition to the range of energy densities corresponding to the inelastic strain formation. The larger the laser-induced strain, the smaller the frequency and the width of the Raman lines, and the higher their intensities. The physical nature of these effects is discussed. © 2002 MAIK “Nauka/Interperiodica”.

INTRODUCTION

Previously, the final stages of the controllable damage of semiconductors and metals exposed to multiple laser pulses were observed at relatively low threshold energy densities $W_0 \lesssim 0.1 \text{ J/cm}^2$ [1–4], which, in the conditions of local (Gaussian beam radius $\omega \approx 10\text{--}100 \mu\text{m}$) short-term heat release, are characterized by the so-called size effect: $W_0 \propto \omega$ [2, 5–8]. Most of the experiments were based on the techniques that are sensitive only to the macrodamage of semiconductors (see, e. g., [2, 3] and the references therein). It was not until recently that the initial stages of microscopic changes, whose accumulation within small regions ($10\text{--}100 \mu\text{m}$) may cause macrodamage, have received the attention they deserve [9–11].

It has been shown already that, under the local effect of a relatively small number of laser pulses ($N \lesssim 10^3$), the thermal stress produced in the surface layer of a semiconductor results in plastic microstrains, which cause (at the energy density $W \approx W_0$) a significant threshold change in the parameters of the insulator slow states (ISS) localized in the oxide layer on the germanium surface [10]. However, in the conditions specified, the microscopic defect formation in the oxide film is not the only result of the photoinduced deformation; a considerable change in the microstructure of the semiconductor surface layer, a radical restructuring of the deeper layers [7, 8, 10], and the formation of superstructures on the surface [3, 12] are also possible.

For a complex investigation of the early stages of microplastic changes produced near the actual (i.e., covered with a thin oxide film) germanium surface, we combined several optical nondestructive techniques; namely, molecular luminescence probing, diffuse and Raman scattering, and photothermal deformation of the surface were used.

EXPERIMENTAL

Similar to [10], we studied the (111) surfaces of high-resistivity (resistivity $\rho = 25\text{--}30 \Omega \text{ cm}$) *n*-Ge single crystals doped with Sb and etched in H_2O_2 at room temperature. After the etching, the germanium samples were kept in air for more than a day, during which a 20- to 30-Å-thick GeO_2 layer of hexagonal structure was formed on the Ge surface. Then, the “real” surfaces thus obtained were subjected to pulsed laser radiation in air. A laser beam of micrometer size, similar to that described in [10], was used in the scanning mode; for the experimental techniques implying nonlocal action, five-to-six regions of $\sim 3 \times 5 \text{ mm}^2$ area were formed by scanning the sample surface (we used the samples of size $20 \times 5 \times 0.3 \text{ mm}^3$). Each of the regions was characterized by its specific energy density W of the laser radiation with $\lambda = 0.53 \mu\text{m}$, the Gaussian spot of the size $2\omega \approx 70 \mu\text{m}$, the pulse duration $\tau_0 \geq 350 \text{ ns}$, and the number of pulses $N \lesssim 10^3$. The range of W variation was chosen between 10 and 250 mJ/cm^2 , which is much

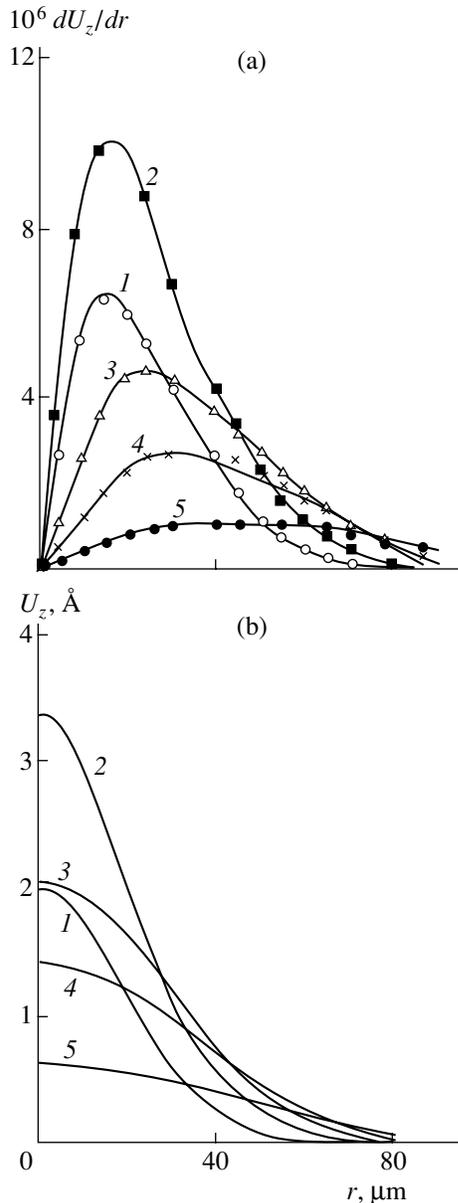


Fig. 1. Kinetics of the spatial profiles of (a) quasi-static strains $dU_z/dr = f(r)$ and (b) the effective normal displacements $U_z(r)$ of the actual Ge surfaces at the elastic stage of the focused laser-beam effect $W \approx 8\text{--}10 \text{ mJ/cm}^2 \ll W_0$. The profiles were measured at the time t counted from the beginning of the laser pulses, which recurred within intervals $\Delta t \approx 100 \mu\text{s}$ and featured the following coordinate r and time t dependence of the intensity [15]: $I(r, t) = W \exp(-r^2/\omega^2)(t/\tau_0^2) \exp(-t/\tau_0)$ with the characteristic time constant $\tau_0 \geq 350 \text{ ns}$. $t = (1)$ 1, (2) 2, (3) 6, (4) 10, and (5) 18 μs .

lower than the melting threshold $W_m \approx 1.2 \text{ J/cm}^2$ [13] calculated at $\tau_0 \approx 350 \text{ ns}$ [13].

The fluorescence spectra were measured using a hyperspectrometer, which is a system with a position-sensitive sensor and ensures a wavelength resolution of

$\sim 0.8 \text{ nm}$ and a spatial resolution along a sample of $\sim 10 \mu\text{m}$. As the position-sensitive device, we used a microchannel plate and a CCD array for detecting the fluorescence spectra and for studying the Rayleigh scattering, respectively. A halogen lamp (1000 W) with an interference filter adjusted to 530 nm excited the fluorescence of the probe molecules.

Probe molecules were those of rhodamine B deposited on the semiconductor surface from an alcoholic solution. The surface concentration of the dye molecules amounted to $2 \times 10^{13} \text{ cm}^{-2}$, which corresponds to a ~ 0.2 monolayer according to the data obtained using a piezo-resonance balance. Special experiments indicated that neither the adsorption of the dye at the surface nor the radiation with intensities used in the experiments changed the degree of homogeneity of the surface or the spectrum of surface electron states (SES).

Additional study of Raman and diffuse scattering spectra of the probing light was carried out using a DFS-52 spectrograph for the germanium samples excited by an argon laser with $\lambda = 0.488 \mu\text{m}$. The resolution of the Raman scattering (RS) spectral measurements was improved by using p polarization of the laser beam incident upon the sample surface at the Brewster angle with an intensity of $\sim 0.5 \text{ W/cm}^2$.

Instantaneous spatial profiles of the quasi-static strains on the germanium surface $dU_z/dr = f(r)$ and the effective normal elastic displacements $U_z(r)$ were detected using an advanced method of photothermal surface strain (PTSS) in accordance with the technique employed in [14, 15].

RESULTS AND DISCUSSION

The results will be outlined by proceeding mainly from the lower to higher densities of laser pulse energy W .

The profiles of $dU_z/dr = f(r)$ and $U_z(r)$ obtained in germanium *in situ* under the nondestructive (elastic) pulsed laser effect at $W \approx 8\text{--}10 \text{ mJ/cm}^2 \ll W_0$ are plotted in Fig. 1. The profiles have the shape of a hump appearing at the semiconductor surface and turned out to be similar to those previously obtained for metals [14, 15]. The kinetics of the displacement profiles makes it clear that the intervals between laser pulses ($\Delta t \approx 100 \mu\text{s}$) is sufficient for the sample surface to cool entirely and return to its unperturbed (unstrained) "horizontal" state. When W increased to $W_0 \approx 70 \text{ mJ/cm}^2$, the displacement profiles retained their smooth shape and no small-size (on the order of micrometers) spatial fluctuations U_z appeared. As in [2], the profiles at W_0 corresponded to the largest (along the beam radius r and for the time t) shear strain $\phi_0 \equiv (dU_z/dr)_{\text{max}} \approx 5 \times 10^{-5}$ (Fig. 2, curve 1). Note that the drop in the photostrain signal at the thresholds W_0 is mostly caused by the development of the final stages of damage in germanium (at $N \geq 10^6$) accompanied by an abrupt decrease in the fraction of mirror-reflected light [2].

The results of studying the fluorescence of the dye on the germanium surface are shown in Fig. 3. It is clearly seen that, at small W ($W < W_0$), both the intensity (I_{PL}) and the half-width of the rhodamine B spectral line ($\lambda_{1/2}$) are nearly constant. This corresponds with the data previously obtained from electrical measurements of the slow states in an insulator [10], which suggest that no dramatic changes are produced under the thermoelastic local laser effect either in the germanium layer (Ge) or in the oxide film (GeO_2). We observed only a slight quenching of the fluorescence from the adsorbed rhodamine B molecules (at $W \approx 50\text{--}70 \text{ mJ/cm}^2$), which was attributed to the prethreshold laser-induced generation of a small number of deep slow states in the oxide layer [10]. Such states may apparently arise from the elastic bending flexure of the thin insulator films during the multiple photostimulated expansion of the surface-layer bulk with the vertical displacement amplitude $U_z \approx 1\text{--}10 \text{ nm}$ [2, 8]. As is known [16], the deep traps in an insulator can act as acceptors of the electron excitation energy transferred from the probe molecules, thus, promoting moderate quenching of the molecular fluorescence observed at $W < W_0$.

The most abrupt changes in the rhodamine B molecular spectra of fluorescence are observed at $W \approx 70\text{--}85 \text{ mJ/cm}^2$, i. e., at the thresholds W_0 [10]. These changes comprise an appreciable (from five to ten times) quenching of the fluorescence intensity (Fig. 3, curve 1) and a simultaneous broadening of the fluorescence spectra of the probe molecules (Fig. 3, curve 2). Let us emphasize that, at $W \approx W_0$, no shift of the fluorescence peak (λ_{max}) was noticed at the threshold. In our opinion, this may be explained by the fact that the irreversible plastic strain induced at the energy densities in the vicinity of W_0 (Fig. 2) results in the additional electronic states in the damaged oxide layer on the germanium surface. Along with an increase in the concentration of the deep electron traps (the ISS), we observed a pronounced increase in the concentration of shallow fluctuation states in GeO_2 in the vicinity of the allowed band edges. The latter circumstance is indicated by an abrupt drop in the ISS charging threshold upon the photoinjection of charge carriers from Ge [10].

Similar to the deep traps in insulators [16], the fluctuation states in GeO_2 are likely to be effective acceptors of the probe-molecule photoexcitation energy that is nonradiatively transferred into the solid medium. In fact, the critical radius of the energy transfer by the Forster–Dexter mechanism in such structures equals $\sim 5 \text{ nm}$, and the most intense generation of the fluctuation states is in the oxide region (with a thickness $\leq 3\text{--}5 \text{ nm}$) that is directly adjacent to the germanium interface; this region is the most disordered [17]. It should be noted that the local electric fields that appear upon the recharging of such defects could produce only a slight effect on the position of the fluorescence peak λ_{max} of the probe molecules, because the Coulomb charged centers affect only the molecules which are located in their vicinity, i. e., within 1 nm [18].

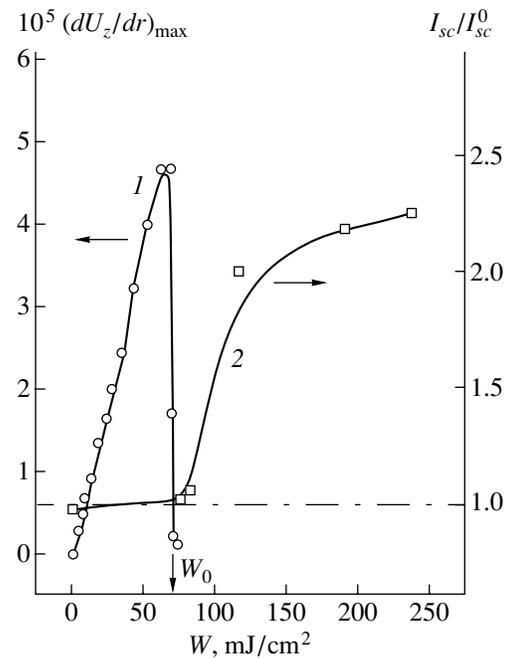


Fig. 2. (1) The increase in the largest (along the radius r and for the time t) elastic strain $(dU_z/dr)_{\text{max}}$ with increasing W and the drop of the PTSS [2] signal at the thresholds W_0 (1); (2) W -dependence of the intensity of light diffusely scattered from the Ge surface I_{sc}/I_{sc}^0 , where I_{sc}^0 is the intensity of light scattered from an unirradiated surface ($W = 0$).

The considerable (from 1.5 to 2 times) broadening exhibited by the fluorescence spectra of probe molecules at the thresholds W_0 , i. e., upon the transition from the elastic to the elastoplastic straining of the semiconductor, may be attributed to the pronounced growth of the geometric heterogeneity of the surface, which presents direct evidence of the initiated irreversible (residual) displacements ΔU_z of the real germanium surface. The amplitude of these displacements is apparently close (within an order of magnitude) to the amplitude of the maximal reversible elastic displacements of the germanium surfaces $U_{z \text{ max}} \sim 1\text{--}10 \text{ nm}$, which were previously studied by the PTSS method [2, 8]. Note that, at the thresholds W_0 , the value $U_{z \text{ max}}$ is comparable to the mean radius of the induction-resonant Forster–Dexter transfer of the electron excitation energy $r_0 \approx 5\text{--}6 \text{ nm}$ [16] and the inhomogeneous broadening of spectra is maximal; therefore, the molecular probe technique turned out to be especially effective in this case.

A distinct increase in the intensity of the diffuse scattering was observed at $W \geq 85\text{--}100 \text{ mJ/cm}^2$ and tended to level off at higher energy densities (Fig. 2, curve 2). In contrast to the short-range testing of the surface by the luminescent molecular probes, the scattered light allows one to probe the germanium surface to a depth that is essentially larger than r_0 and can be as large as $R_0 \sim 100 \text{ nm}$ for the excitation wavelength λ

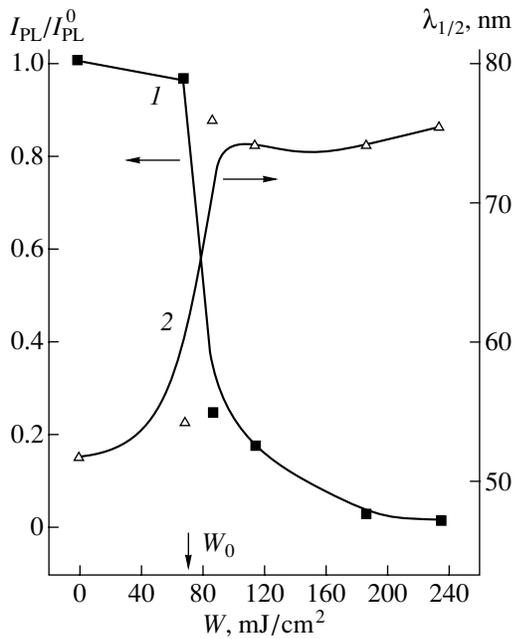


Fig. 3. (1) Threshold quenching of rhodamine B molecular fluorescence and (2) threshold broadening of the fluorescence spectra of the probe molecules on the actual germanium surface that was preliminarily subjected to elastic ($W < W_0$) or elastoplastic ($W > W_0$) strains as a result of pulsed laser irradiation. I_{PL}^0 is the fluorescence intensity of an unirradiated sample.

used in the experiment. In these conditions, the enhancement of the diffuse scattering observed at $W \approx (1.2-1.5)W_0$ most likely reflects the kinetics of the gradual accumulation of the microplastic changes, when the scattering inhomogeneities induced in the surface layer grow with W and become comparable in size with R_0 or λ .

We believe that, at the initial stages of the microplastic changes (i. e., in the vicinity of W_0), the inhomogeneities grow mainly due to pulse-to-pulse accumulation and the subsequent diffusion of point rather than extended defects [3]. This is because the local laser irradiation with an energy density near the threshold W_0 induces the thermal stresses $\sigma_0 \approx 2-3 \text{ MN}/\text{m}^2$ [2, 8], which are far below the minimal stresses that give rise to the heterogeneous nucleation and motion of dislocations at room temperature and the related dislocation-related plasticity of germanium $\sigma > 20-200 \text{ MN}/\text{m}^2$, as determined from the experiments with contact loading of germanium [19]. In fact, in our experimental conditions, the local laser-induced heating does not exceed $\Delta T \approx 100^\circ\text{C}$ [2, 8] at the thresholds W_0 , while the brittle point in germanium is $T \approx 500^\circ\text{C}$. In accordance with the well-known classification of the microplasticity phenomena ([19], p. 243), in the range of a relatively low photoinduced stress, which is the case, the hetero-

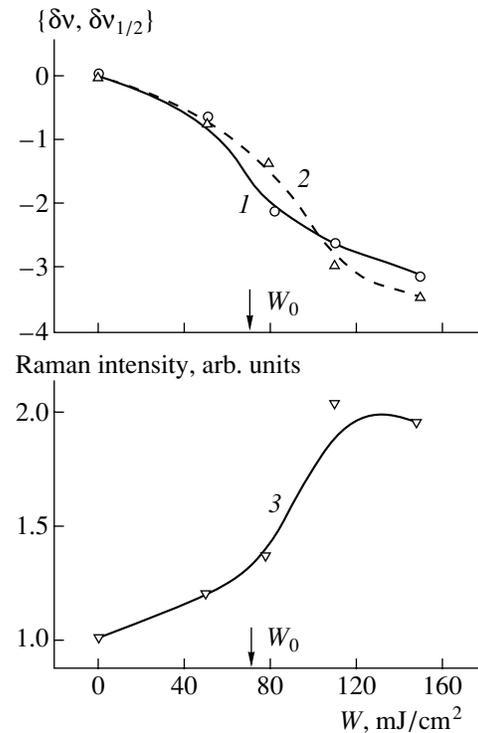


Fig. 4. Changes in the parameter of Raman scattering from actual germanium surfaces subjected to preliminary pulsed laser irradiation versus the energy density at the center of the laser spot W : (1) Raman line frequency shift $\delta\nu$, (2) narrowing of the linewidth $\delta\nu_{1/2}$, and (3) an increase in the intensity of Raman scattering.

geneous-dislocation mechanism of microplastic strain gives way to a defect-diffusion mechanism: both the initial nucleation of the plastic microstrains (dislocation loops) and their further growth are entirely governed by the diffusion processes in the field of the point defects.

The significant role of the kinetics of defects in the observed microplastic processes is also indicated by the somewhat unexpected behavior of the Raman spectra. As W grows, the RS line ($\sim 301 \text{ cm}^{-1}$) shifts to lower frequencies by $\delta\nu$, which is usually observed during amorphization, when the degree of crystallinity decreases and microcrystals appear in the material [20] (Fig. 4, curve 1). Along with this, the full width of the RS line at half maximum decreases with W by $\delta\nu_{1/2}$ (Fig. 4, curve 2), which is typical of a growing degree of order. It should be emphasized that the aforementioned changes in the RS spectra of the germanium samples were observed in both the elastic ($W < W_0$) and the elastoplastic ($W > W_0$) modes of the multiple ($N \leq 10^3$) laser-induced straining and did not feature a pronounced threshold character (Fig. 4).

The RS spectrum narrowing observed in the entire W range may be caused by the existence of an initial (at $W = 0$) inhomogeneous broadening of the RS spectra in the studied samples due to the overlapping of local

stress fields that exist in the vicinity of various growth-related microinclusions and extended defects, e. g., dislocations. As it well known that such local fields of compression and tension of the crystal lattice in the vicinity of defects give rise to a considerable broadening of the RS spectra [21]. In fact, the initial RS linewidth for unirradiated samples was $\nu_{1/2} \approx 7.5 \text{ cm}^{-1}$, whereas the RS line of the reference germanium single crystal with a low concentration of growth dislocations had a width of $\sim 5.5 \text{ cm}^{-1}$. In the conditions of multiple laser irradiation realized in our experiment (in both the elastic and elastoplastic modes), an increase in W resulted in the increase of the concentration of “frozen” vacancies (“vacancy pump” model [19, 22]), whose migration to dislocations or other sinks may effectively reduce the fluctuations of microstresses existing before exposure in the vicinity of defects. To illustrate such a positive influence of defects, we may recall the well-known relaxation of microstresses in the elastic model of interstitial precipitate, where the discrepancy in the size of an inclusion and semiconductor void (for example, the inclusion is larger than the void) is significantly reduced because the “excess” material of the host is removed in the course of the diffusive absorption (emission) of point defects: vacancies, interstitial atoms, etc. ([19], p. 203).

Another argument in favor of the noticeable contribution of vacancies (and other point defects) to the observed defect–diffusion microplasticity [19] is presented by an increase in the intensity of RS (Fig. 4, curve 3). According to the theory of RS for an anharmonic crystal containing vacancies [23], the presence of vacancies should produce an additional polarization of the lattice around the point defect, thus making additional contributions to the dipole moment and renormalizing the spectral width and position of both the fundamental and combination absorption lines. Usually, the defects make only a moderate contribution to these parameters; however, the laser-induced cyclic thermal strains may cause a considerable accumulation of defects (vacancies) [3], which can contribute significantly to both the frequency shifts and the increase in the intensities of the Raman scattering and the fundamental absorption [23].

It should also be noted that, when the concentration of the point defects is high, various types of instabilities might develop and give rise to the formation of a microcrystalline superstructure, which is possibly the case in our experimental conditions [3, 12]. In order to verify the latter statement, one has to perform a direct study of the changes induced in the micromorphology of the surface by the elastoplastic laser effect. This may be done using scanning atomic-force microscopy, which we are planning to perform.

CONCLUSION

(1) We studied the changes in the fluorescence spectra of dye (rhodamine B) molecules adsorbed on a ger-

manium surface and in the parameters of the Raman and diffuse scattering of light, which were the result of elastic ($W < W_0$) and elastoplastic ($W > W_0$) pulsed laser effects with a threshold strain amplitude of $\sim 5 \times 10^{-5}$ [2].

(2) Along with the deep traps in the insulator (GeO_2), the slow fluctuation states appearing in the oxide layer at the thresholds $W_0 \approx 70 \text{ mJ/cm}^2$ [10] effectively absorb the electron photoexcitation energy from the adsorbed probe molecules and cause a pronounced quenching of their fluorescence at $W \geq W_0$. The energy transfer to the fluctuation states near the insulator/semiconductor interface is accompanied by a threshold (with respect to W) broadening of the fluorescence spectra of the dye, which suggests a steep rise in the geometric heterogeneity of the germanium surface due to irreversible (residual) surface displacements $\Delta U_z \sim 1\text{--}10 \text{ nm}$ that arise at the thresholds W_0 .

(3) The observed behavior of the Raman and the diffuse scattering parameters indicates that a gradual accumulation of microplastic changes occurs in the surface layer of the semiconductor (Ge). The initial stage of modifications includes primarily the generation, the accumulation (from pulse to pulse), and the diffusion to sinks of the point defects (presumably, vacancies), which, at $W \geq (1.2\text{--}1.5)W_0$, (i) lead to the growth of scattering irregularities thus enhancing the intensity of the diffuse scattering and (ii) effectively reduce the inhomogeneous broadening of the RS spectra caused by local microstress fields.

(4) High concentrations of point defects in germanium are attainable in the elastoplastic mode of multiple local laser effects; therefore, irradiation in this mode may cause an instability in the point defect field with the subsequent formation of periodic surface superstructures.

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