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Nanostructure Formation on the Solid Surface under the Action of Intense Laser Radiation

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Model of Nanostructure Formation

Abstract

The paper describes the mechanism for formation of periodic nanostructures on the surface of solids under the action of intense laser radiation. The model based on a nonlinear relaxation of temperature-induced stresses. The solid deformed by laser radiation is considered in a form of three simultaneously coexisting phases. The system of equations, which describes these phases, is reduced to the generalized Ginzburg–Landau equation that has a periodic solution. For estimation the calculation of the step of the periodic structure arising on the silicon surface under the action of a laser pulse is done.

Introduction

In recent years formation of periodic nanostructures in solids by phase transitions begin to receive more attention from researchers. For that matter developing the physical foundations of new effective methods for the formation of two- and three-dimensional structures with characteristic sizes less than 100 nm both at the surface and in the bulk of solids is of great interest.

One possible approach to the creation of these structures is based on the laser processing of solid surfaces. The laser-induced thermal stresses [1] and/or melting [2, 3] can lead to significant changes in the physical properties of the target material. Some progress has been achieved in understanding the general laws governing the formation of real structures during transformations in solids under the action of laser radiation. In the present work it is offered the mechanism for formation of periodic nanostructures on the solid surface under the action of power laser radiation, which is based on the nonlinear relaxation of temperature-induced stresses.

The process of deformation of a solid under sufficiently high stresses is accompanied by residual strain whose appearance is associated with both inelastic effects and the transformation of the defect structure of a crystal. The stress relaxation can be of a heterogeneous character due to the formation of novel-structure domains (relaxation domains) within the old excited structure [4]. This is associated with the collective behavior of excited atoms interacting with each other, which transforms the relaxation process into a nonlinear one. The character of dislocation domains depends on the state of the system under consideration, on conditions of the external action, and on the degree of the development of the deformation process. These domains can be centers of the new phase, groups of dislocations or disclination groups, microcracks, as well as atomic groups or vacancies forming clusters, micropores, dislocation loops, etc.

The nonequilibrium state of an elastic deformed solid is determined by its temperature T , by the strain tensor ε_{ij} or by the stress tensor σ_{ij} , and by the totality of additional internal parameters of state $\psi_{ik}^{(1)}, \psi_{ik}^{(2)}, \dots, \psi_{ik}^{(N)}$, that characterize the degree of the system deviation from the equilibrium state for the given T and ε_{ik} . In this case, we deal with a number of parameters of state $\psi_{ik}^{(\alpha)}$ that together with T and ε_{ik} entirely determine the state of the system. The quantities $\psi_{ik}^{(\alpha)}$ are second-rank tensors. Let's call them order parameters.

The rate of variation of the order parameter $\psi_{ik}^{(\alpha)}$ can be determined from the equation according to which the process rate is a linear function of the thermodynamic force:

$$\frac{\partial F}{\partial \psi_{ik}^{(\alpha)}} = \sum_{\beta} h_{iklm}^{(\alpha,\beta)} \psi_{lm}^{(\beta)} \quad (1)$$

where F is the thermodynamic potential per unit volume of the deformed body and $h_{iklm}^{(\alpha,\beta)}$ are the material constants.

For analysis of the behavior of the deformed solid it is necessary to find an expression for the thermodynamic potential F as an explicit function of the variables T , ε_{ik} and $\psi_{ik}^{(\alpha)}$:

$$F = \int_V [f_1(T) + f_2(\varepsilon_{ik}, T) + f_3(\psi_{ik}^\alpha)] dV,$$

where $f_1(T)$ is the free-energy density as a function of the temperature of a solid occurring in the equilibrium state in the absence of deformation, $f_2(\varepsilon_{ik}, T)$ is the free-energy density obtained upon the expansion of F over invariants ε_{ik} and $T-T_0$, and $f_3(\psi_{ik}^\alpha)$ is the free-energy density obtained upon the expansion of F over invariant $\psi_{ik}^{(\alpha)}$.

Assuming the temperature T to be a constant value and the quantities ε_{ik} and $\psi_{ik}^{(\alpha)}$ to be small, let us expand F into a series and restrict the expansion to terms of the fourth order. Since the thermodynamic potential is a scalar quantity, every term in the expansion must also be a scalar:

$$F(T, \varepsilon_{ik}, \psi_{ik}^{(\alpha)}) = F_0(T) + A_{iklm} \varepsilon_{ik} \varepsilon_{lm} + \sum_{\alpha} B_{iklm}^{(\alpha)} \varepsilon_{ik} \psi_{lm}^{(\alpha)} + \sum_{\alpha, \beta} C_{iklm}^{(\alpha, \beta)} \psi_{ik}^{(\alpha)} \psi_{lm}^{(\beta)} + \frac{1}{24} \left\{ \begin{aligned} & A'_{(i\dots s)} \varepsilon_{ik} \varepsilon_{lm} \varepsilon_{np} \varepsilon_{rs} \\ & + 4 \sum_{\alpha} B'_{(i\dots s)}^{(\alpha)} \varepsilon_{ik} \varepsilon_{lm} \varepsilon_{np} \psi_{rs}^{(\alpha)} \\ & + 6 \sum_{\alpha, \beta} C'_{(i\dots s)}^{(\alpha, \beta)} \varepsilon_{ik} \varepsilon_{lm} \psi_{np}^{(\alpha)} \psi_{rs}^{(\beta)} \\ & + 4 \sum_{\alpha, \beta, \gamma} D'_{(i\dots s)}^{(\alpha, \beta, \gamma)} \varepsilon_{ik} \psi_{lm}^{(\alpha)} \psi_{np}^{(\beta)} \psi_{rs}^{(\gamma)} \\ & + \sum_{\alpha, \beta, \gamma, \sigma} E'_{(i\dots s)}^{(\alpha, \beta, \gamma, \sigma)} \psi_{ik}^{(\alpha)} \psi_{lm}^{(\beta)} \psi_{np}^{(\gamma)} \psi_{rs}^{(\sigma)} \end{aligned} \right\} \quad (2)$$

where $F_0(T)$ is the free-energy density as a function of the temperature of a solid occurring in the state of thermodynamic equilibrium in the absence of deformation and A_{iklm} , B_{iklm} , C_{iklm} , ... are material constants. Henceforth, the sign of summation over identical subscripts or superscripts is, respectively, omitted or conserved.

Equations (1) and (2) can be simplified by introducing "normal" coordinates similar to those used in the description of oscillations in complex systems. In other words we have to introduce new variables defined as linear combinations of the old ones ($\psi_{ik}^{(\alpha)}$) so that each of equations (1) and (2) would contain only one variable $\psi_{ik}^{(\alpha)}$. For this

purpose let us use a linear transformation [5] of variables $\psi_{ik}^{(\alpha)}$ to define new $\psi_{ik}^{(\beta)}$ values such that positive quadratic forms in (1) and (2) would take the following form:

$$F = F_0(T) + \frac{1}{2} k \varepsilon_{ik}^2 + \sum_{\alpha} D_{iklm}^{(\alpha)} \psi_{ik}^{(\alpha)} \psi_{lm}^{(\alpha)} + \sum_{\alpha} F_{iklmnp rs}^{(\alpha)} \psi_{ik}^{(\alpha)} \psi_{lm}^{(\alpha)} \psi_{np}^{(\alpha)} \psi_{rs}^{(\alpha)} \quad (3)$$

For an isotropic solid this equation can be rewritten as

$$F = F_0(T) + \frac{1}{2} k \varepsilon_{ik}^2 + \sum_{\alpha} D^{(\alpha)} (\psi_{ik}^{(\alpha)})^2 + \sum_{\alpha} F^{(\alpha)} (\psi_{ik}^{(\alpha)})^4 \quad (4)$$

Until this point we have considered isothermal processes. With allowance for temperature variations the state of a solid is determined by the deformation of ε_{ik} , temperature T , and order parameters $\psi_{ik}^{(\alpha)}$. The free energy as a function of the state also depends on ε_{ik} , T , and $\psi_{ik}^{(\alpha)}$. For small variations $T - T_0$ of the temperature and small values of ε_{ik} and $\psi_{ik}^{(\alpha)}$ the free energy can be expanded into series with respect to invariants constructed from the variables ε_{ik} , $\psi_{ik}^{(\alpha)}$, and $T - T_0$:

$$F = F_0(T) + \beta_{ik} \varepsilon_{ik} (T - T_0) + \sum_{\alpha} \lambda_{ik}^{(\alpha)} \psi_{ik}^{(\alpha)} (T - T_0) + \sum_{\alpha} E^{(\alpha)} (\psi_{ik}^{(\alpha)})^2 (T - T_0) + \sum_{\alpha} D^{(\alpha)} (\psi_{ik}^{(\alpha)})^2 + \sum_{\alpha} F^{(\alpha)} (\psi_{ik}^{(\alpha)})^4 \quad (5)$$

where β_{ik} , $\lambda_{ik}^{(\alpha)}$, $D^{(\alpha)}$, $E^{(\alpha)}$, and $F^{(\alpha)}$ are the material constants and T_0 is the initial temperature at which the unstressed solid is considered to be unstrained.

In the isotropic case the kinetic equation (1) can be written as follows:

$$\dot{\psi}_{ik}^{(\alpha)} = 2 \sum_{\alpha} D^{(\alpha)} \psi_{ik}^{(\alpha)} + 4 \sum_{\alpha} F^{(\alpha)} (\psi_{ik}^{(\alpha)})^3. \quad (6)$$

The set of equations (1) and (4)-(6) describes the relaxation kinetics. It determines the behavior of an elastically deformed solid under conditions of stress relaxation at small ε_{ik} , $\psi_{ik}^{(\alpha)}$, provided that kinetic equation is valid. However this set of equations has a general character because it has been derived using almost no model notions. This circumstances accounts for both the advantages and the

disadvantages of any phenomenological theory. Equations of this type determine the stable steady states corresponding to various spatial structures [6], which possess some general features. In particular, (a) transformation of any region in a solid leads to a certain microscopic change in the form of this region that is manifested by the appearance of a characteristic relief on the flat surface of a sample; (b) there is a definite tendency toward an ordered mutual arrangement of transformed regions in the crystal.

In order to determine the constants in (6) let's represent the entire spectrum of order parameters $\psi_{ik}^{(\alpha)}$ by a single quantity of a residual strain $\varepsilon_{ij}^0(r, t)$. Let's also introduce a mesoscopic parameter that describes the field of the relaxation process as

$$\varphi_{ik}(r, t) = \frac{1}{V_0} \int_{V_0} \varepsilon_{ik}^0(r, t) dV,$$

where V_0 is the volume over which the $\varepsilon_{ik}^0(r, t)$ value is averaged. Thus, the system under consideration, namely, the deformed solid, can be represented in a form consisting of three simultaneously coexisting phases. These are the relaxation field determined by the parameter $\varphi_{ij}(r, t)$, the stress field $\sigma_{ij}(r, t)$ corresponding to external loads, and relaxation domains of the concentration n .

The time dependences of $\varphi_{ik}(r, t)$, $n(r, t)$ and $\sigma_{ij}(r, t)$ are determined by the following system of nonlinear differential equations

$$\begin{cases} \dot{\varphi}_{ik} = -\kappa\varphi_{ik} + g_1 n, \\ \dot{n} = -\gamma n + \varphi_{ik} \sigma_{ik} / g_2, \\ \dot{\sigma}_{ik} = \nu(\sigma_{ik} - \sigma_0) - g_3 \varphi_{ik} n. \end{cases} \quad (7)$$

The first terms standing on the right-hand side of these equations describe, respectively, the attenuation of the relaxation process, the decay of the relaxation domains formed, and the relaxation of stresses. The description occurs in the linear approximation when mutual influence is absent. The second terms make the relaxation process nonlinear. In the first equation, this is associated with the generation of the relaxation field due to the formation of relaxation domains. The second equation allows for the effect of both the relaxation field $\varphi_{ik}(r, t)$ and the stress field $\sigma_{ij}(r, t)$ on the nucleation of the relaxation domains. In the third equation, the relaxation process is stipulated by the effect of the relaxation field on the stress-relaxation rate. Here $\nu, \gamma, \kappa, g_1, g_2, g_3$ are the material

constants. The quantity σ_0 is determined by the external loads applied and corresponds to residual stresses produced as a result of the relaxation. The relaxation-field variation rate is considerably lower than that of atomic processes described by the constants γ and ν . This makes it possible to employ in (7) the adiabatic exclusion of variables. As a result, relaxation equation takes the form

$$\dot{\varphi}_{ik} = A\varphi_{ik} - B\varphi_{ik}^3,$$

$$\text{where } A = \frac{g_1}{g_2\gamma}(\sigma_0 - \frac{g_2\gamma}{g_1}\kappa); \quad B = \frac{g_1 g_3}{g_2^2} \frac{\sigma_0}{\gamma^2\nu}.$$

The approach described above do not take into account possible spatial fluctuations of the relaxation parameter whose role grows with the elevation of external loads and temperature. Considering these fluctuations we get

$$\dot{\varphi}_{ik} = A\varphi_{ik} - B\varphi_{ik}^3 + D\Delta\varphi_{ik} \quad (8)$$

Here D is coefficient of atom diffusion in heated crystal area. If we allow for the diffusion dispersion, Eq. (8) transforms into the generalized Ginzburg–Landau equation [7].

For $\sigma_0 < \frac{g_2\gamma}{g_1}\kappa$ Eq. (8) has one stable solution

$\varphi(r, t) = 0$. Beyond the critical stress level

$\sigma_0 \geq \sigma_c = \frac{g_2\gamma}{g_1}\kappa$, new coherent system states

exhibiting spatial periodicity are realized. The period of these structures is as follows

$$T = \frac{\sigma_0 - \sigma_c}{2\pi\sigma_0} \sqrt{\frac{3}{8} \frac{D}{\nu}}.$$

We now estimate the step of the periodic structure arising on the silicon surface under the action of a laser pulse. We assume that the residual stresses are $\sigma_0 = 10^9$ N/m², $\kappa \approx \gamma \approx \nu \approx g_1 \approx 10^3$ s⁻¹ (since they determine the frequency of atomic transitions from one equilibrium state into another), $g_2 \approx g_3 \approx 10^{10}$ N/m² are the stresses in the relaxations domains, $D \approx 10^{-8}$ cm²/s is coefficient of atom diffusion in heated crystal area. In this case the period is $T \sim 3$ μ m. With increasing σ_0 , which corresponds to harder laser action, the period of structures formed must be determined by the diffusion coefficient D and by the stress-relaxation rate ν . In this case nanostructures with a period $T \sim 50$ – 100 nm arise.

Conclusion

In conclusion, we should note that the above consideration was performed for the three-dimensional case. We also assumed that the appearance of periodic structures in a thin near-surface layer leads to the appearance of the

corresponding structures on the surface. Thus, on the basis of the approach suggested in this study, we manage to explain the appearance of nanostructures in solids under the action of an intense laser pulse. The mechanism under consideration can be realized along with other mechanisms suggested previously. The realization of this mechanism is associated with the conditions excluding the melting of the surface and its evaporation under the laser action.

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