



5th International Conference on

Industrial Lasers and Laser Applications '95

**Vladislav Ya. Panchenko
Vladimir S. Golubev**
Chairs/Editors

**24–26 June 1995
Shatura, Moscow Region, Russia**

Organized by
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Volume 2713

Mathematical modeling of nonequilibrium heating and melting of Si by Nd-YAG laser radiation at radiation wavelength 1.06 μm

V.I.Mazhukin, V.V.Nosov

Institute for Mathematical Modelling, Russia Academy of Sciences, Moscow, Russia

ABSTRACT

The mathematical model of the nonequilibrium heating and the phase transformations in Si is considered induced by the nanosecond pulse laser irradiation at 1.06 μm . Taken into account are the complex dynamics of the radiation absorption, the electron-hole plasma development, the heat diffusion and the radiation transfer. The simulation results show the self-regenerative nature of the radiation absorption process as well as significant overheating of plasma and formation of overheated metastable region in solid phase.

INTRODUCTION

Investigations of fundamental properties of semiconductor materials irradiated by high-power short and ultrashort laser pulses are of interest for several fields of science. In particular, these investigations are of importance for development of new materials especially with new properties.

Main part of researches devoted to laser induced processes in condensed media is performed under assumption of full thermodynamic equilibrium [1-4]. This approach is justified for modeling of laser influence on highly absorbed media in technological range of radiation intensity. Results predicted are in good agreement with experimental data. However it is the nonequilibrium that essentially influences on peculiarities of processes while considering laser irradiation of semiconductors with energy quantum $h\omega$, which is slightly in excess of the band gap E_g [5-10]. Interband absorption of photon leads to generation of the two carriers - electron in conduction band and hole in valence band. The generated electron-hole pair stores energy E_g until recombination event. Excited carriers (electron-hole plasma) of intrinsic semiconductors with low dopant concentration can be described by concentration N , which exceeds the equilibrium value N_0 . The laser energy deposition for short laser pulses is very fast and therefore equilibrium temperature for the whole system can not be introduced. It can be introduced only for separate subsystems, which have Maxwell-Boltzmann energy distribution. Nonequilibrium of the system appears in $T_e > T_g$, where T_e is the temperature of the excited carriers and T_g is the lattice temperature.

Investigations of laser melting and crystallization processes in semiconductors were initially connected with the problem of laser annealing. They confirmed the highly nonequilibrium nature of these phenomena [11-16]. Formation of overheated region was experimentally observed with its temperature been above the equilibrium temperature of phase transformation T_m [15-16]. The overheating value varied from tens to one thousand degree depending on irradiation regimes. Usually applied for description of melting in pure materials under fast laser action is the surface melting model [1-3]. It is assumed in the frame of this model that liquid phase consisting from several atomic layers appears on the irradiated surface immediately after its temperature achieves T_m . The overheated region appears in the solid phase behind the melting front due to simultaneous influence of phase front velocity and volumetric energy absorption. Emergency of undercooling metastable regions of liquid phase was considered in connection with the problems of amorphous films formation on semiconductor surface during melt crystallization [13, 14].

In this paper we will present the mathematical model which describes heating, melting, crystallization and evaporation of single-crystal Si by Nd-YAG laser pulses at $\lambda_v = 1.06 \mu\text{m}$. The results of numerical simulation primarily illustrate nonequilibrium phenomena under heating and melting of silicon.

1. MATHEMATICAL MODEL AND SOLUTION METHOD

1.1. Main assumptions.

The suggested mathematical model [5] is based on the following assumptions:

1. Electrons and holes concentrations are equal. Dopant carriers concentration is negligible and is not considered.

2. Excited carriers instantaneously establish an equilibrium Maxwell-Boltzmann distribution characterized by a carrier temperature T_e , which is equal for electrons and holes.
3. Liquid Si is characterized by the same assumptions 1-2, as solid Si.
4. Phase transformations (melting, crystallization, and evaporation) depends on lattice temperature T_g and can be described in frame of combined version of Stefan problem [1, 17].
5. The problem is considered in one-dimensional approximation.

1.2. Equation system.

We write the following equation system for description of laser induced heating and phase transformations in silicon:

$$\left[\frac{\partial E}{\partial t} = \frac{\partial}{\partial x} \left(D_a \frac{\partial E}{\partial x} \right) + \left(\frac{E_{\pi\eta\sigma} - E_g}{E_{\pi\eta\sigma}} \alpha_L + \alpha_{\phi\chi\Lambda} \right) G + E_g \frac{N - N_0}{\tau_n} - \frac{E - 2N(3/2)k_B T_g}{\tau_e} \right]_k, \quad E = 2N(3/2)k_B T_e, \quad (1)$$

$$\left[\frac{\partial N}{\partial t} = \frac{\partial}{\partial x} \left(D_a \frac{\partial N}{\partial x} \right) + \frac{\partial}{\partial x} \left(\mu N \frac{\partial (E_g/2)}{\partial x} \right) + \alpha_L \frac{G}{E_{\pi\eta\sigma}} - \frac{N - N_0}{\tau_n} \right]_k, \quad (2)$$

$$\left[\frac{\partial}{\partial t} (\rho H) = \frac{\partial}{\partial x} \left(\lambda(T_g) \frac{\partial T_g}{\partial x} \right) + \frac{E - 2N(3/2)k_B T_g}{\tau_e} \right]_k, \quad H = c_p T_g, \quad (3)$$

$$\left[\frac{\partial G}{\partial x} = -[\alpha_{\phi\chi\Lambda} + \alpha_L] G \right]_k, \quad (4)$$

$$x \in [\Gamma_{kv}, \Gamma_{sl}] \vee [\Gamma_{sl}, x_s], \quad t \in [t_0, t_1],$$

$$k = \begin{cases} 1, & x \in [\Gamma_{kv}, \Gamma_{sl}] \\ s, & x \in [\Gamma_{sl}, x_s] \end{cases}$$

The k index denotes that all the equations are written in both solid and liquid phases. We use the following notations for the description of the model: T_g [K] is lattice temperature, N [$1/\text{cm}^3$] is carrier concentration, E [J/cm^3] is volumetric density of kinetic energy of carriers and G [W/cm^2] is intensity of laser radiation. ρ [g/cm^3] denotes density, H [J/g] is enthalpy, λ [$\text{W}/\text{cm K}$] is thermal conductivity of lattice, E_{phot} and E_g [eV] are photon energy and band gap width, τ_n and τ_e [s] are Auger recombination time and energy relaxation time, D_a [cm^2/s] and μ [$\text{cm}^2/\text{V} \cdot \text{s}$] are ambipolar diffusivity and carriers mobility, α_L and $\alpha_{\phi\chi\Lambda}$ [cm^{-1}] are lattice absorption and free carrier absorption, N_0 [$1/\text{cm}^3$] is equilibrium concentration of carriers, k_B [J/K] is Boltzmann constant, q [K] is charge of electron, c_p, c_v [$\text{J}/\text{g K}$] are specific heat at constant pressure and at constant volume. s, l, v indexes refer to solid, liquid phases, and evaporated substance, and double indexes sl and kv denote solid-liquid and evaporation boundaries. Γ_{sl} and Γ_{kv} denote boundary locations; V_{sl}, V_{kv} [cm/s] are velocities of melting and evaporation fronts; R_{sr} and A_{sr} are reflectivity and absorptivity of the surface; G_0 [W/cm^2] denotes maximum intensity of laser radiation, τ_v [s] is laser pulse duration (FWHM); L_m, L_v [J/g] are latent heat of melting and evaporation; T_m and T_b are equilibrium temperatures of melting and evaporation; u_v, u_c [cm/s] are velocity of vapor and sound velocity; p [bar] is pressure; R [$\text{J}/\text{g K}$] is gaseous constant of the matter; M is Mach number; T_0 is room temperature.

In Eq (1), the first term on the right side describes energy transfer results from carriers diffusion, the second one characterizes absorption of laser radiation energy, the third term is equal to energy been transferred to the carriers during recombination event, the fourth is equal to energy exchange rate between the carriers and the lattice. The first term on the right of the carriers balance equation (2) describes ambipolar diffusion, the second term accounts for carriers transfer due to band gap narrowing results from increase of the lattice temperature, the third is rate of particles generation due to lattice absorption and the last term describes processes of Auger recombination and electron impact ionization. The Eq. (3) expresses energy balance in lattice subsystem and takes into account diffusive heat transfer and energy exchange between two subsystems. The carrier energy E does not include the band gap energy that is passed to carriers during interband

transition. The carrier concentration is multiplied by 2 in the energy exchange term $(E - 2N(3/2)k_B T_g) / \tau_e$, since electrons and holes are assumed to behave identically [9].

1.3. Boundary and initial conditions.

The equation system (1)-(4) is supplemented by boundary and initial conditions.

We write the following relations on the left boundary irradiated by laser:

$$x = \Gamma_{kv}: \quad \rho_k V_{kv} = \rho_v (V_{kv} - u_v) \quad (5)$$

$$p_k + \rho_k V_{kv}^2 = p_v + \rho_v (V_{kv} - u_v)^2 \quad (6)$$

$$\lambda_k \frac{\partial T_{g,sur}}{\partial x} = \rho_k L_v V_{kv} \quad (7)$$

$$D_{a,k} \frac{\partial E_k}{\partial x} = 0, \quad (8)$$

$$D_{a,k} \frac{\partial N_k}{\partial x} + \mu_k N_k \frac{\partial (E_{g,k} / 2)}{\partial x} = 0, \quad (9)$$

$$G_k = A_{sur} G_0 \exp\left(-\left(\frac{t}{\tau_v}\right)^2\right), \quad k = s, l. \quad (10)$$

We apply conditions (5)-(7) for description of the surface evaporation in frame of one-phase version of Stefan problem [1, 18]. Relations (8),(9) express the front impermeability for carriers and carriers energy. Surface recombination of the carriers and electron thermoemission are neglected. The equation system (5)-(10) is supplemented by the two relations derived from the Knudsen layer approximation [19]:

$$T_v = T_{g,sur} \left\{ \left[1 + f^2 \left(\frac{\gamma - 1}{\gamma + 1} \right)^2 M^2 \right]^{1/2} - f \left(\frac{\gamma - 1}{\gamma + 1} \right) M \right\}^2,$$

$$\rho_v = \frac{1}{2} \rho_H \left\{ \left(\frac{T_{g,sur}}{T_v} \right)^{1/2} \left[(\gamma M^2 + 1) \exp(b^2 M^2) \operatorname{erfc}(bM) - \frac{4f}{\pi} M \right] + \right.$$

$$\left. + \frac{T_{g,sur}}{T_v} \left[1 - 2fM \exp(b^2 M^2) \operatorname{erfc}(bM) \right] \right\}, \quad (11)$$

$$p_H = R \rho_H T_{g,sur}, \quad p_H = p_B \exp\left(\frac{L_v}{RT_b} \left(1 - \frac{T_b}{T_{g,sur}}\right)\right),$$

$$b = \left(\frac{\gamma}{2}\right)^{1/2}, \quad f = \left(\frac{\pi\gamma}{8}\right)^{1/2}, \quad M = \frac{u_v}{u_c} = 1, \quad \gamma = \frac{c_p}{c_v} = \frac{5}{3}.$$

We consider the back side of the sample to be impenetrability for heat and carriers:

$$x = x_s: \quad \lambda_s \frac{\partial T_{g,s}}{\partial x} = 0 \quad (12)$$

$$D_{a,s} \frac{\partial E_s}{\partial x} = 0, \quad (13)$$

$$D_{a,s} \frac{\partial N_s}{\partial x} + \mu_s N_s \frac{\partial (E_{g,s} / 2)}{\partial x} = 0, \quad (14)$$

We describe the melting and crystallization processes by means of classic version of Stefan problem [1, 20]:

$$x = \Gamma_{sl}: \quad \lambda_s \frac{\partial T_s}{\partial x} - \lambda_l \frac{\partial T_l}{\partial x} = L_m \rho_s V_{sl}, \quad (15)$$

$$T_s = T_l = T_m \quad (16)$$

$$D_{a,s} \frac{\partial E_s}{\partial x} = D_{a,l} \frac{\partial E_l}{\partial x} \quad (17)$$

$$E_s = E_l \quad (18)$$

$$D_{a,s} \frac{\partial N_s}{\partial x} + \mu_s N_s \frac{\partial (E_{g,s} / 2)}{\partial x} = D_{a,l} \frac{\partial N_l}{\partial x} + \mu_l N_l \frac{\partial (E_{g,l} / 2)}{\partial x}, \quad (19)$$

$$N_s = N_l \quad (20)$$

The relations (17)-(20) express continuity conditions for carriers energy, carriers energy flow, carriers concentration and carriers flow .

At the initial point all quantities have uniform spatial distribution. Lattice and carriers temperatures are equal to T_0 , carriers concentration is equal to the equilibrium value N_0 .

$$t = t_0: \quad T_{g,s} = T_{e,s} = T_0, \quad N_s = N_0(T_0). \quad (21)$$

1.4. Parameters of silicon.

Solid silicon properties in high temperature range and ones of liquid silicon are not investigated well. Therefore we use extrapolation in some cases to determine parameters been included into the model. It should also be noted, that the main part of the data correspond to slow heating conditions, when nonequilibrium phenomena do not take place in opposite to fast laser heating.

Phase transformations. The following values are used for temperature and latent heat of melting and evaporation [21, 22]: $T_m=1687$ K, $L_m=1.778$ kJ/g, $T_b=3573$ K, $L_v=13.42$ kJ/g.

Density. We consider density of both phases to be linear dependent on temperature:

$$[\rho = \rho_0(1 - \beta(T - T_0))]_k, k = s, l \quad (22)$$

where β [1/K] is thermal extension coefficient. The density value at the room temperature is $\rho_{0s}=2.33$ g/cm³ and at the melting temperature $\rho_{0l}=2.53$ g/cm³ [5, 23]. The β coefficient values in solid and liquid phases are equal to $\beta_s=4.65 \cdot 10^{-6}$ 1/K [21] , $\beta_l=1.4 \cdot 10^{-4}$ 1/K [23]. Note, that the β value of liquid silicon is approximately 30 times as high as the one of crystalline silicon.

Specific heat. Specific heat values in both phases are assumed to be independent on temperature and equal to $c_{p,s}=0.88$ J/g, $c_{p,l}=0.91$ J/g [5, 23].

Thermal conductivity. We calculate the solid phase conductivity by means of the following expression [5, 24]:

$$\lambda_s = \frac{299}{T_g - 99} \quad [\text{W/cm K}] \quad (23)$$

that approximates experimental data [25] with the accuracy of 5%. We also postulate that thermal conductivity value increases by a factor of 2 on phase transition: $\lambda_l = 2\lambda_s(T_m)$.

Energy gap. Temperature dependence of the band gap is [5, 24]:

$$E_{g,s}(T_{g,s}) = 1.16 - \frac{7.02 \cdot 10^{-4}}{T_{g,s} + 1108} \quad [\text{eV}]. \quad (24)$$

There is no data available for energy gap in liquid silicon therefore we assume constant value: $E_{g,l}(T_{g,l}) = E_{g,s}(T_m)$

Lattice absorption. Lattice absorption is evaluated by means of the following formula [5, 26, 27]:

$$\alpha_{L,s} = 6000 \left[\frac{(E_{\pi\sigma\tau} - E_g - 0.0575)^2}{1 - \exp(-670/T_g)} + \frac{(E_{\pi\sigma\tau} - E_g + 0.0575)^2}{\exp(-670/T_g) - 1} \right] [1/\text{cm}] \quad (25)$$

which is derived assuming only one phonon 0.0575eV ($\theta=670\text{K}$) been participating in fundamental absorption at the considered wavelength. The lattice absorption of liquid silicon is considered to be temperature independent $\alpha_{L,l} = \alpha_{L,s}(T_m)$.

Carriers mobility and ambipolar diffusivity. We calculate carriers mobilities for solid Si with two scattering mechanisms been taken into account: acoustic phonon scattering and electron-hole scattering. The first process determines electron-lattice μ_{Le} and hole-lattice mobilities μ_{Lh} [5, 28]:

$$\begin{aligned} \mu_{Le,s} &= 1350(T_{g,s}/300)^{2.4} [\text{cm}^2/\text{Vs}] \\ \mu_{Lh,s} &= 480(T_{g,s}/300)^{2.5} [\text{cm}^2/\text{Vs}] \end{aligned} \quad (26)$$

For intrinsic semiconductors electron-hole mobility can be calculated as [5, 28, 29]:

$$\mu_{he,s} = \frac{2^{1/2} 2.45 \cdot 10^{21} (T_{g,s}/300)^{1.5}}{2N_s \ln \left[1 + \left(1.4 \cdot 10^{20} / 2N_s \right) (T_{g,s}/300)^2 \right]} [\text{cm}^2/\text{Vs}] \quad (27)$$

Using ordinary relations [24],

$$\frac{1}{\mu_{e,s}} = \left(\frac{1}{\mu_{Le,s}} + \frac{1}{\mu_{he,s}} \right), \quad \frac{1}{\mu_{h,s}} = \left(\frac{1}{\mu_{Lh,s}} + \frac{1}{\mu_{he,s}} \right), \quad (28)$$

the total mobility is expressed:

$$\frac{1}{\mu_s} = \left(\frac{1}{\mu_{e,s}} + \frac{1}{\mu_{h,s}} \right), \quad (29)$$

These relations are verified for moderate temperatures and concentrations up to $N < 10^{18} \text{cm}^{-3}$ [28]. However the mobilities changes are very slow for temperatures above 1000K and high concentrations. Therefore we use the above relations for the whole range of T and N variations without essential error been introduced. The relations (26)-(29) are also used for the mobility calculation in liquid silicon.

Ambipolar diffusivity can be determined by means of nondegenerate Einstein relation:

$$\left[D_a = \frac{k_B T_g}{q} \mu \right]_k, \quad k = s, l \quad (30)$$

Free carrier absorption. Optical properties of a material are determined by its index of refraction n and extinction coefficient k. The $\omega_\nu(\tau) \gg 1$ relation is true for the considered frequency of radiation ω_ν , so the n and k values are determined as solution of the following equation system [5, 30]:

$$\left[n^2 - k^2 = n_0^2 - \frac{\omega_p^2}{\omega^2} \right]_k, \quad (31)$$

$$\left[2nk = 1.13 \frac{\omega_p^2}{\omega^2} \frac{q}{(\mu m)^*} \right]_k, \quad k = s, l \quad (32)$$

where n_0 denotes intrinsic index of refraction, ω_p is plasma frequency, $(\mu m)^*$ is effective production of mass and mobility.

$$\left[\omega_p = \left\{ \frac{Nq^2}{\epsilon_0} \left(\frac{1}{\mu_e} + \frac{1}{\mu_h} \right) \right\}^2 \right]_k, \quad (33)$$

$$\left[\frac{1}{(\mu m)^*} = \frac{1}{2} \left(\frac{1}{\mu_e m_e} + \frac{1}{\mu_h m_h} \right) \right]_k, \quad k = s, l. \quad (34)$$

In Eqs. (33),(34) ϵ_0 is dielectric constant of vacuum, m_e and m_h are masses of electron and hole. Free carrier absorption is expressed as [31]:

$$[\alpha_{FCA} = 4\pi k / \lambda_v]_k, \quad k = s, l. \quad (35)$$

Surface absorptivity. Absorptivity of optically thick homogen material is determined by the well-known Frenel formula:

$$R_{sur} = 1 - A_{sur} = \frac{(n_{kv} - 1)^2 + k_{kv}^2}{(n_{kv} + 1)^2 + k_{kv}^2}. \quad (36)$$

In our case this formula is correct also for the liquid silicon reflectivity if the $\alpha_{FCA, l} H_l \gg 1$ relation is true, H_l been the liquid phase thickness. In the opposite case the liquid phase reflectivity can be defined from solution of problem of thin layer reflectivity [31]:

$$\begin{aligned} A_{sur} &= 1 - R_{sur} \\ R_{sur} &= \left(\delta_1 + \frac{a_1 \gamma_1 \exp(-\alpha_{FCA, l} H_l)}{\gamma_1^2 + \gamma_2^2} \right)^2 + \left(\frac{a_1 \gamma_2 \exp(-\alpha_{FCA, l} H_l)}{\gamma_1^2 + \gamma_2^2} \right)^2, \\ \gamma_1 &= \delta_1 (\delta_1 - \delta_s) \exp(-\alpha_{FCA, l} H_l) + (\delta_s \delta_1 - 1) \cos \left(\alpha_{FCA, l} H_l \frac{n_l}{k_l} \right), \\ \gamma_2 &= -(\delta_s \delta_1 - 1) \sin \left(\alpha_{FCA, l} H_l \frac{n_l}{k_l} \right), \\ a_1 &= (\delta_1 - \delta_s) (1 - \delta_1^2), \quad \delta_s = \sqrt{R_s}, \quad \delta_l = \sqrt{R_l}. \end{aligned} \quad (37)$$

Intrinsic indexes of refraction are equal to $n_{0, s} = 3.55$ [5] and $n_{0, l} = 11.27$ [15].

Recombination. Auger recombination time for equal carriers concentrations can be calculated as [5, 9]:

$$\left[\tau_n = \frac{1}{C_a N^2} \right]_k, \quad k = s, l, \quad C_a = 4 \cdot 10^{-31} \text{ [cm}^6/\text{s]} \quad (38)$$

For the considered radiation wavelength the Auger recombination process is slowed down for concentrations above $N < 6.5 \cdot 10^{20} \text{ cm}^{-3}$ due to recombination screening phenomenon [5, 9, 32], therefore for higher concentrations we use constant value 6ps for the recombination time.

Equilibrium carrier concentration. Equilibrium concentration of the carrier N_0 is calculated as [5, 33]:

$$\left[N_0 = 5 \cdot 10^{15} T_e^{1.5} \exp(-E_g / k_B T_e) \right]_k, \quad k = s, l \quad (39)$$

where the expression before the exponent is effective density-of-state term. The formula ((39) is accurate only for equilibrium conditions $T_g = T_e$, but we also use it for $T_e > T_g$ because of the absence of better estimation.

Energy relaxation. The energy relaxation time is evaluated as [5]:

$$\tau_{e,k} = \tau_{e,0} \left[1 + (N_k / N_{\text{crit}})^2 \right], \quad k = s, l \quad (40)$$

Second term in square braces corresponds to screening of energy relaxation process [5, 8, 9]. When concentration N reaches its critical value N_{crit} , the energy relaxation slows down the slowing rate been proportional to the square of concentration. We use the value of 10ps for $\tau_{e,0}$, the critical concentration is equal to $N_{\text{crit}}(\lambda_v) = 2 \cdot 10^{21} \text{ cm}^{-3}$.

1.5. Solution method and numerical algorithm.

The main difficulty of the formulated problem from the numerical point of view results from the presence of two moving boundaries whose locations are unknown a priori. Also phase subdomains can change in size by several order of magnitude in a process of solution. While modeling the fast phase transformations in laser action problems with volumetric energy release it is necessary to apply numerical methods with *explicit front-tracking*. The most efficient of such a techniques is finite-difference method on dynamically adaptive grids [17, 34]. According to this approach, transition is performed from initial variables (x, t) to arbitrary unsteady-state coordinate system (q, τ) by means of general form coordinate transformation $x = f(q, \tau)$, $t = \tau$. Dynamics of the initial coordinate x is described in the new coordinate system by the additional differential equation:

$$\left[\frac{\partial \psi}{\partial \tau} = - \frac{\partial Q}{\partial q} \right]_k, \quad k = s, l, \quad \psi = \frac{\partial x}{\partial q}, \quad (41)$$

where ψ is metric coefficient, Q is function which determines specific form of the transformation in accordance with peculiarities of a problem. For the considered problem the function Q is defined in form $Q = -D \partial \psi / \partial q$, which ensures the grid nodes distribution in each subdomains to be quasi equidistant. The partial derivatives $\partial / \partial x$, $\partial / \partial t$ in the new coordinate system (q, τ) are expressed as:

$$\frac{\partial}{\partial x} = \frac{1}{\psi} \frac{\partial}{\partial q}, \quad \frac{\partial}{\partial t} = \frac{\partial}{\partial \tau} - \frac{Q}{\psi} \frac{\partial}{\partial q} \quad (42)$$

In the coordinate system (q, τ) two phase subdomains $[\Gamma_{kv}, \Gamma_{sl}], [\Gamma_{sl}, x_s]$ with moving boundaries Γ_{kv}, Γ_{sl} are mapped onto two computational subdomains $[0, q_{sl}]$ and $[q_{sl}, q_s]$ with fixed boundaries. Until formation of liquid phase one physical domain $[\Gamma_{kv}, x_s]$ is mapped onto one computational interval $[0, q_s]$. After coordinate transformation we write implicit finite-difference approximation for the considered differential problem. The resulting system of nonlinear algebraic equations is solved using Newton method with two-level iteration cycles [17].

2. SIMULATION RESULTS.

Let us consider main peculiarities of nonequilibrium heating and melting of Si induced by Nd-YAG laser radiation at 1.06 μm . Numerical experiments have been executed using Gaussian shape (10) with a FWHM of 30ns and a G_0 of 110MW/cm² for the laser pulse. Curves on Figs. 1-8 shows the dynamics of processes involved.

2.1. Absorption dynamics.

Fig. 1 shows the temporal profiles of incident $G(t)$ and absorbed $A_{\text{sur}} G(t)$ intensity of the laser radiation. Drop on the second plot corresponds to dramatic decrease (from 0.7 to 0.3) of the absorbed radiation fraction. Such a behaviour of absorptivity means the surface have been transformed to the melted state. The melting of the surface occurs at the point $t \approx 0.7 \tau_v$ on the

trailing edge of the laser pulse, when the pulse energy is already mainly exhausted. But despite the late melting and the decreasing of the absorptivity the rest part of the laser pulse continues to effectively heat the surface, Fig. 3, curve $T_g(t)$.

Fig. 2 shows temporal profiles of absorption $\alpha(t)$, as well as $\alpha_L(t)$ and $\alpha_{FCA}(t)$ dependencies of lattice absorption and free carrier absorption which illustrate nonlinearity of laser radiation absorption in silicon. Free carrier absorption is greater than lattice absorption until melting begins. From this time point both quantities are of the same order of magnitude. After the melting has begun α_L remains constant, α_{FCA} changes slowly following changes of concentrations, and total value of absorption α reaches 10^5 cm^{-1} . Thus the silicon sample becomes strongly absorbing medium after the melting of the surface.

Let us analyze absorption dynamics before melting. The rate of α_{FCA} increase is maximum at the onset of the laser pulse. The rate of α_L increase is minimum at the onset, then gradually increases following the increase of the temperature. Such a behaviour results from a complicate coupling of the two processes [5]. At the outset of the pulse the small lattice absorption $\alpha_L \approx 10 \text{ cm}^{-1}$ is enough to create some free carriers. These carriers then absorb radiation which is converted to heat. That causes the band gap to shrink and lattice absorption to increase. Thus more carriers are generated, which means stronger free carriers absorption and so on. The process is thus self-regenerative. It should be noted that the regenerative process could never start without free carrier absorption.

2.2. Surface temperature.

Fig. 3 shows temporal profiles of the carrier temperature $T_e(t)$, the lattice temperature $T_g(t)$, and the difference of two quantities $\Delta T(t) = T_e - T_g$ on the surface of the sample. During the main part of heating period before melting (approximately to $t \approx 0.5\tau_v \approx 15\text{ns}$) the temperatures slowly rises. Then both temperatures increase dramatically during short time period which indicates the avalanche-type development of the processes to take place. Then break is well observed on both $T_e(t)$ and $T_g(t)$ plots which results from surface melt formation. Temperatures then continue to increase and reach their maximum values at the instant $t \approx 35\text{ns}$. The T_e , T_g temperatures maximum shifts with time relative to the maximum of absorbed radiation intensity $A_{\text{sur}}G(t)$, Figs.1, 3. This fact is due to peculiarities of volumetric energy absorption, which is characterized by the $\alpha(t)A_{\text{sur}}(t)G(t)$ quantity, as well as by the influence of phase transformation.

The temperature of the carriers subsystem is above the lattice temperature during the action of laser pulse until $t \approx 2\tau_v \approx 60\text{ns}$, Fig. 3. It means that heating process of Si goes on in nonequilibrium conditions. The $T_e - T_g$ difference increases until the beginning of melting, reaches its maximum value of 900K, and then slowly decreases. When $T_e(t)$ and $T_g(t)$ reach the maximum values its difference is approximately 150°K . Temperatures of two subsystems become equal to each other in 15ns after the cooling process on the surface has begun.

2.3. Carriers concentrations.

Fig. 4 shows temporal dependence of the concentration on the surface $N(t)$. Also presented on this figure are plot of equilibrium (for temperature T_e) concentration $N_0(t)$ and time dependence of the two concentrations difference, $\Delta N(t) = N - N_0$. The $N(t)$ curve behaves approximately the same way as the surface temperature does. It slowly increases first, then raises dramatically, has a break at the point of melting, reaches its maximum $N_{\text{max}} \approx 9 \cdot 10^{20} \text{ cm}^{-3}$ at $t \approx 33\text{ns}$ and slowly decreases. The carrier concentration is above it's equilibrium value $N_0(T_e)$ during the laser pulse action because the carrier generation is mainly due to photoionization. The $\Delta N(t)$ curve has two maximum and its behaviour is determined by the ratio of N_e and T_e rates of increase.

2.4. Melt thickness and melting front velocity.

Figs. 5,6 show time dependencies of melted layer thickness $H_l(t)$ and phase front velocity $V_{sl}(t)$, which are two main quantities describing dynamics of melting and crystallization processes. The melting process corresponds to leading edge of $H_l(t)$ curve and to positive values of $V_{sl}(t)$. The predicted duration of melting is equal to 70ns and maximum thickness of the melt is approximately $1.1\mu\text{m}$ for the considered value of radiation intensity, Fig. 5. The crystallization process is essentially longer and requires several hundreds of nanosecond to complete. The melting and crystallization processes in silicon are strongly nonsymmetric, which is apparently demonstrated by the behavior of $V_{sl}(t)$ curve, Fig. 6. The onset of the melting is characterized by dramatic increase of the front velocity, which reaches maximum (approximately 70m/s) in 2-3 ns after the

liquid phase has formed. Then the velocity slowly decreases and becomes negative. The maximum velocity of melting is more than one order of magnitude higher than the maximum velocity of crystallization.

2.5. Spatial profiles.

Figs. 7,8 show spatial profiles of temperatures $T_s(x), T_c(x)$ and concentrations $N(x), N_0(x)$ at the instance $t \approx 20\text{ns}$, which corresponds to the very onset of the melting. The temperatures of the two subsystems differ from each other only in thin surface layer (approximately $1.5\mu\text{m}$), Fig. 7. The concentration N deviates from the equilibrium at greater depth, Fig. 8. This peculiarity results from difference in reaching of the temperature and carriers concentration equilibrium. Energy relaxation is characterized by the energy relaxation time τ_e which only weakly depends on process parameters. However concentration equilization is determined by the Auger recombination time which is inversely proportional to the square of the concentration. As a result the farther from the surface, the less carriers concentration, the slower recombination and the longer equilization.

Presence of local maximum behind the melting front is another peculiarity of the temperature and concentration spatial profiles. Its formation corresponds to emergency of overheated metastable region. The maximum value of overheating is observed during the several nanosecond after the melting has begun, when the melt thickness is small and $V_{sl} / \alpha a > 1$ relation is true. In our case the maximum overheating of the solid phase is approximately 250K. As the melt thickness increases the value of the overheating diminishes and front location on the spatial profiles can be observed only in the form of small break, Fig. 7, similar to the case of surface absorption. Note that the period of existance of the overheated region and the period of dramatic rise of the melting front velocity are approximately synchronized, Fig. 6. This phenomenon occurs because in this period the energy is transfered to phase front not only from the surface, but from the overheated region as well. Heat flows in Stefan condition (15) are added to each other rather then subtracted, as in case of surface absorption.

3. CONCLUSION

In this paper the mathematical model of the nonequilibrium heating and phase transformations in Si is considered induced by the nanosecond pulse laser irradiation at $1.06\mu\text{m}$. Taken into account are two mechanisms of the radiation absorption, the electron-hole plasma dynamics including the processes of photogeneration, Auger recombination, impact ionization and ambipolar diffusion, as well as energy relaxation process in two-component system. The melting and crystallization are described by means of classic version of Stefan problem, and evaporation into media with negligible counterpressure is described by one-phase version of Stefan problem. By means of numerical analysis we established the following:

1. The processes taken place in Si under the considered conditions are nonlinear and nonequilibrium. The stage of heating before melting is characterized by avalanche-type carriers generation and absorption increase.
2. The melting process is characterized by dramatic increase of the front velocity on the onset, by the formation of overheated region in the solid phase and complicated dynamics of equilibrium establishing.

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