Problem of saturation of excitation in relaxed optics

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The problems of saturation of the excitation in Relaxed Optics are discussed and analyzed. Structural and chemical bonds cases are analyzed. The problems of the creation of various structures are represented as phase transformations or chemical bonds transformations. Types of possible transformations are discussed. Problems of stability and applications proper phases are discussed too.

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1. Introduction

Problem of relation between of radiation and radiationless relaxation is one of the central problems of modern Quantum Electronics, Nonlinear and Relaxed Optics [1–5]. Processes of radiation relaxation are pure optical effects whereas processes of radiationless relaxation are caused the chain of irreversible transformations in irradiated matter. These phenomena may be explained with unitary point of view if we will be use kinetic approximation of Relaxed Optics in the regime of step-by-step saturation of excitation of proper types of light scattering centers [1]. These centers may be having stable or unstable nature. For first case of interaction of laser irradiation with matter (stable centers) we must take into consideration energetic and temporary conditions of the irradiation. For second case (unstable centers) we must take into account integral energetic condition of saturation of excitation, temporary characteristics of irradiation haven't significant influence.

According to these positions the kinetic model was created. This model allows explaining the results of interaction laser irradiation with indium antimonide, cadmium telluride, silicon, germanium and carbon. Two-dimensional lattice of sphalerite was used as basis for this modeling for InSb and phase diagram of silicon – for silicon and germanium.

Methods of this model would be used for the modeling possible laser-induced allotropic transformations in carbon, including transformations graphite – diamond, diamond – graphite, graphite – graphenes and other.

This model allows interpreting next phenomena of irreversible interaction laser irradiation with matter: laser radiation, subthreshold formation of damages in irradiated matter, chaotization of laser irradiation, superradiation, laser-induced formation of nanostructures and other effects of unitary point of view.

Usage methods of this model allow expanding the observation and interpretation nonlinear optical effects on "irreversible" part of relaxation and allow interpreting spectral characteristics of chaotization of laser irradiation in semiconductor lasers.

Perspectives of usage of represented model for interpreting other results of interaction laser radiation with matter are discussed too.

2. Modeling and discussion. Case of chemical bonds

With point of view of physics status solid the chain of possible irreversible formations in *InSb* after Ruby laser irradiation with increasing of level of irradiated intensity may be next: excitons; multiexcitons; excitons drops; diffusive, martensite or diffusive–martensite phases; destruction and evaporating materials [1]. These transformations may be modeled with help of various physical theories.

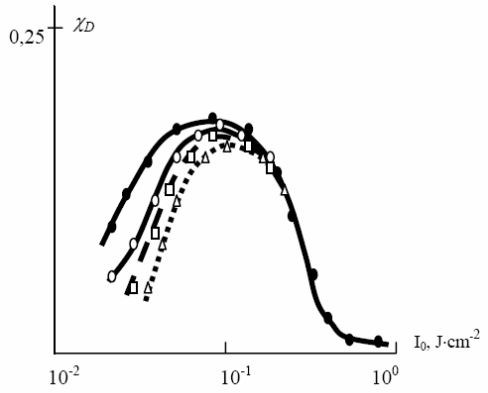

Fig 1. Dynamics of the behaviour the damages (keeping defectable χ_D in arbitrary units) in InSb after Ruby laser irradiation: • – 2-4 hours after irradiation; ° – 48 hours after irradiation; □ – one week after irradiation; Δ– two weeks after irradiation.

The problem of phase stability of structures on may be resolved in short-range action approximation as cascade processes [1]. Dynamics of the behaviour the damages (keeping defectable) in InSb after Ruby laser irradiation was observed with help method of Rutherford backscattering of protons with energy of 500 keV and represented in Fig.1 [1].

The process of scattering light in solid may be represented in the approximation of short-range action representation. Three approximations: spherical, cylindrical and straight were used [1]. When quantum energy $h\nu >> E_a$, where E_a – the threshold energy of ionization (a disruption) of proper chemical bond, then cascades of collisions (second order effects of scattering ionized electrons) are created. It may be cause of the creation of displacements of atoms (ionic subsystem of crystal). These damages may be having another nature as classic defects. Two-dimensional lattice of InSb (Fig. 2, sphalerite phase) was used. Energy of bond 1 is 0,18 eV (band gap); bond 2 – 1,95 eV and bond 3 – 2,15 eV [1].

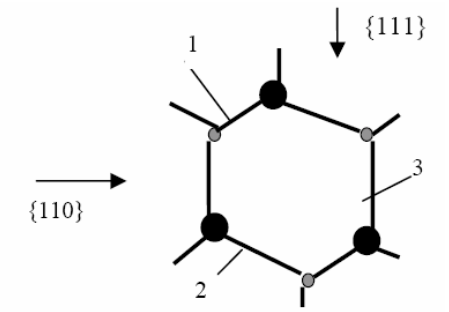

Fig. 2. Two-dimensional picture the crystal lattice A_3B_5 (including InSb and InAs) the cubic symmetry. Bond 1 is pure covalent [1].

Basic cascade characteristics were estimated with application theory of cascade creation in Radiation Physics of Status Solid to process of "irreversible photoionization" [6]: energy of damage creation was changed on the energy of activation of proper chemical bond, energy of falling particle – on photon energy of laser irradiation [1].

Density of centers of light scattering for case of Ruby laser irradiation of InSb was determined as a density of proper chemical bonds.

For modeling of these processes we must consider nature of scattering: scattering on stable or unstable centers.

Now we'll use straight method [1]. Straight method of the estimation the energetic characteristics this processes may be realized in the next way. Energy of "disruption" of chemical bonds of one type is equaled

$$\mathrm{E}_{di} = N_i E_i ,$$

where N_i – a density of proper bonds; E_i – energy of a disruption (ionization) one bond.

For the $InSb$ $N_1 = N_2 = N_3 = N_0/2$ and are equaled $1,4 \cdot 10^{22} cm^{-3}$, $E_1 = E_g = 0,18eV$ and therefore $\mathrm{E}_{d1} = N_1 E_g = 403,2 \frac{J}{cm^3}$ and $\mathrm{E}_{d2} = N_1 E_2 = 4368 \frac{J}{cm^3}$. Surface density of irradiation may be determined with the help of next formula

$$\mathrm{E}_{sis} = \frac{\mathrm{E}_{di}}{\alpha_i},$$

where α_i – proper absorption factor, for the first bonds of $InSb$ $\alpha_1 = 2 \cdot 10^5 cm^{-1}$, for second – $\alpha_2 \sim 10^5 cm^{-1}$. Second absorption factor is nonlinear and take into account the effect of blooming. For $InSb$ these values are next $\mathrm{E}_{s1s} = 0,002 \frac{J}{cm^2}$ and $\mathrm{E}_{s2s} = 0,04368 \frac{J}{cm^2}$. These values must be multiplied on 2 (with including reflection) and therefore real values are next $\mathrm{E}_{s1sr} = 0,004 \frac{J}{cm^2}$, $\mathrm{E}_{s2sr} = 0,08797 \frac{J}{cm^2}$ and $\mathrm{E}_{\Sigma r(2)} \approx 0,092 \frac{J}{cm^2}$ (bonds 1 and 2 together). Energy of "disruption" of third chemical bonds (Fig.2) is equaled $\mathrm{E}_{d3} = N_1 E_3 = 4816 \frac{J}{cm^3}$. If $\alpha_3 \sim 10^5 cm^{-1}$ we have $\mathrm{E}_{s3s} = 0,04816 \frac{J}{cm^2}$ and $\mathrm{E}_{s3sr} = 0,096 \frac{J}{cm^2}$. Summary surface density of energy of three bonds is equaled $\mathrm{E}_{\Sigma r(3)} \approx 0,188 \frac{J}{cm^2}$. Value $\mathrm{E}_{\Sigma r(2)} \approx 0,092 \frac{J}{cm^2}$ is represented of curve 2 on Fig.3 and $\mathrm{E}_{\Sigma r(3)} \approx 0,188 \frac{J}{cm^2}$ – curve 3 on Fig.3.

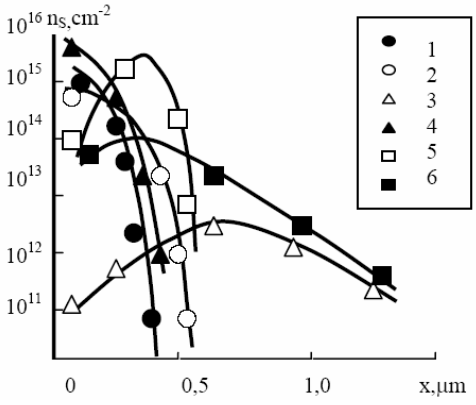

Fig.3. The profiles the distribution the layer concentration of the donor centers (electrons) in inverse layers InSb and InAs after ruby laser irradiation with various density of energy (monoimpulse regime): 0,07 (1); 0,1 (2); 0,16 (3); 0,16 (4); 0,25 (5); 0,5 J·cm^{-2} (6). 1-3—InSb, 4-6—InAs.

For scattering on stable centers we must include timing data of irradiation and process of saturation of excitation proper centers of scattering. The chain of proper relaxation times was constructed and used for the explanation experimental data of Fig.1.

The question of stability of receiving layer may be explained as increasing of relaxation time of firstly photoexcitations. The time of optical excitation of covalent bond with energy $0{,}18eV$ may be determined from uncertainty principle

$$\tau_{ex} = \frac{\hbar}{E_g}. \qquad (1)$$

For *InSb* $\tau_{ex} = 3{,}7 \cdot 10^{-15} s$. The chain of relaxation times may be determined as:

1) Time of adiabatic relaxation

$$\tau_{ar} = \tau_{ex} \cdot e^{\frac{h\nu}{E_g}}. \qquad (2)$$

This time of relaxation electronic subsystem of irradiated materials only. For *InSb* $\tau_{ar} = 8{,}1 \cdot 10^{-11} s$.

2) First time of nonadiabatic relaxation

$$\tau_{nr_1} = \tau_{ex} \cdot e^{\frac{h\nu}{E_g} + \frac{E_g}{kT}}. \qquad (3)$$

This time is included nonadiabatic relaxation to room temperature. For *InSb* $\tau_{nr_1} = 1{,}1 \cdot 10^{-7} s$.

3) Second time of nonbadiabatic relaxation

$$\tau_{nr_2} = \tau_{ex} \cdot e^{\frac{h\nu}{E_g} + \frac{E_g}{kT} + \frac{r_k}{r_{mc}}}. \qquad (4)$$

This time is included the process of saturation the excitation of one level, in our case one chemical bond. For *InSb* $\tau_{nr_2} = 3{,}9 \cdot 10^{-2} s$.

4) Third time of nonbadiabatic relaxation

$$\tau_{nr_3} = \tau_{ex} \cdot e^{\frac{h\nu}{E_g} + \frac{E_g}{kT} + \frac{2r_k}{r_{mc}}}. \qquad (5)$$

This time is included the process of saturation the excitation of two levels, in our case two chemical bonds. For *InSb* $\tau_{nr_3} = 1{,}4 \cdot 10^{4} s$.

5) Fourth time of nonbadiabatic relaxation

$$\tau_{nr_4} = \tau_{ex} \cdot e^{\frac{h\nu}{E_g} + \frac{E_g}{kT} + \frac{3r_k}{r_{mc}}}. \qquad (6)$$

This time is included the process of saturation the excitation of three levels, in our case three chemical bonds. For *InSb* $\tau_{nr_4} = 6{,}9 \cdot 10^{8} s$.

The estimations of relaxation times with help formulas /3/ – /6/ are rough and approximate because it aren't included the collective dynamical processes (heating, melting and other).

The hierarchy of values these times is corresponded to the experimental data of Fig.1.6. The problems of the stability the creation damages in Ruby laser irradiated indium antimonite may be have next explanation. For the low intensities of the irradiation we have relaxation times τ_{r1} and τ_{r2}, from $\sim 10^{-7} s$ to $\sim 10^{-2} s$, these values are corresponded to lifetime of nonequilbrium carrier (τ_{r1}) and exciton drops (τ_{r2}) in *InSb*. For the intensities of Fig.1.6 we can use relaxation times of τ_{r3} and τ_{r4}. These relaxation times are meat of the changes of intensities of irradiation from $0{,}02\,J/cm^2$ to $0{,}1\,J/cm^2$. Density $0{,}1\,J/cm^2$ has maximal value and meets to emptying of two from three chemical bonds in two-dimensional representation. In this state irradiated material has crystal (solid state) structure and therefore we have maximum displaced atoms. After increasing of intensity of irradiation to $0{,}16\,J/cm^2$ (curve 3 on Fig.1.4) we have melting of material, maximum of distribution of donor centers is displaced on $0{,}7\,\mu$ in depth of irradiated material [393].

After further increasing of intensity of the irradiation to $0{,}22 - 0{,}26\,J/cm^2$ we have creation of five phases with trigonal, tetragonal, hexagonal, polycrystalline and amorphous symmetries [1]. Visual destruction of irradiated materials is realized for the intensity of irradiation $0{,}3\,J/cm^2$ [1]. For the explanation these results we can use the theory of phase transitions and methods of irreversible kinetics.

Analogous explanation may be used for *InAs* (curves 4-6 on Fig.3).

The estimation of relaxation time in form /3/ is included exponential term $e^{\frac{h\nu}{E_g}}$. This term is increased the relaxation time. Therefore it must be minimized for the transformation femtosecond laser impulses in picosecond impulses. This procedure is realized with the help photon energy of pumping near to band gap *InSb* and *InAs* [1]. This condition must be realized and for the receiving laser irradiation with possible short impulses under optical pumping [1].

The chain of relaxation times and chain nature of processes of interaction laser irradiation with InSb allow explaining a difference between creation of donor centers after 5 ms pulses of Ruby laser and 10 ns series of pulses of Nd laser irradiation (Fig. 4) [7].

For millisecond regime of irradiation (curves 1 and 2 of Fig.4) we have on one order less concentration as for nanosecond regime (curver 3 of Fig.4). The proper maximal volume concentration of electrons after 20 ns pulse Ruby laser irradiation is 10^{20} – 10^{21} cm^{-3}. This difference may be explained as reemission on bond 1 of Fig.2 (lasing effect) [1]. The number of reemission may be having value 30 – 300 [1]. It allows explaining the different slope of subsurface and tailing parts of curves 2 and 3 of Fig.4. Subsurface parts are corresponded to absorptive indexes of falling radiation $10^5 – 2\cdot10^5$ cm^{-1}; tailing parts are corresponded to absorptive indexes of reemission with $h\nu=E_g \sim 10^2 – 5\cdot10^2$ cm^{-1}.

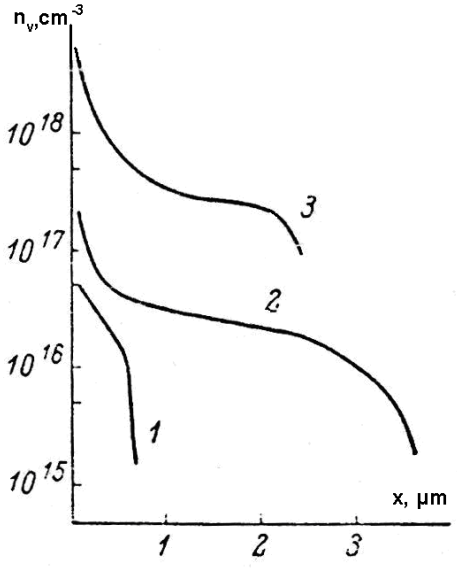

Fig 4. Profiles of the volume distribution electrons in InSb after laser irradiation. 1, 2 – Ruby laser; 3 – YAG:Nd laser. Energy density in pulse J/cm^2 *: 1 – 5; 2 – 40.*

The proper kinetic characteristics of irradiated relaxation may be received in next way. Roughly speaking a relaxation time t_{nn_1} is the time, which is used for the determination of the threshold intensity of laser power of the irradiation. For *InSb* and *InAs* these threshold values are equaled $7,8\cdot10^7 \frac{W}{cm^3}$ and $3,1\cdot10^7 \frac{W}{cm^3}$ respectively [1].

Good proof of our physical and chemical modeling of processes of Relaxed Optics is the process of solid state recrystallization of ion-implanted layers $Mg^+ / InSb$ under pulse and stationary CO_2-laser irradiation (with activation acceptor impurity [1]) and sublimation this materials under CO_2-laser irradiation with more high power density [1]. Effect of CO_2-laser annealing is basically photostimulated (photochemical) phenomenon because value of integral energetic characteristics for stationary regime of the irradiation is more on ~10% than for impulse regime of irradiation. In this case basic mechanism of light scattering (absorption) is the absorption on deep metastable and unstable states [1]. Relaxation time of excited states is infinite practically. Therefore integral intensity of irradiation must be less as for the Ruby laser irradiation.

After further increasing of intensity of the irradiation to $0,22 – 0,26$ J/cm^2 we have creation of five phases with trigonal, sphalerite, hexagonal, polycrystalline and amorphous symmetries [1]. Visual destruction of irradiated materials is realized for the intensity of irradiation $0,3$ J/cm^2 [1]. For the explanation these results we can use the theory of phase transitions and methods of irreversible kinetics.

Results of its modeling allow uniting in one system basic effects of interaction laser irradiation with crystals (equilibrium, nonequilibrium and irreversible).

The saturation of excitation bond one is the optical pumping semiconductor laser [5]. For *InSb* wavelength of this laser irradiation is equaled the value its band gap or energy of bond 1 (this crystal has straight band gap [1]).

The saturation of the excitation of bond 2 (Fig.2) is caused of the creation long-lived state (dangling bonds) and cancellation of laser irradiation. Thus for the creation damages in the regime of the saturation only two bonds with three must be cut. This result is corresponded maximal value of curves on Fig.1. It may be represented as addition to the famous Lindeman and Zeitz criteria [6] of creation defects in solid.

The saturation of the excitation all three bonds is caused regime of free collective motion of solid, including melting. In this case the redistribution of indium and antimony atoms in *InSb* must be realized. These atoms have various self-diffusion coefficients. These coefficients are less as for equilibrium processes; therefore this process may be called photostimulated diffusion [1].

In this case curves on Fig.1 go to minimum. But the restoration of initial electrophysical properties of materials hasn't place. The restoration dangling bonds may be caused the generation of optical irradiation with various wavelengths. This effect is famous as eximer laser effect. It are caused the creation old and new phases of irradiated materials. An appearance of new phases may be modeled with help catastrophe theory [1].

All these effects are caused of straight ionization of respective chemical bonds. Therefore it must be take into account for the laser annealing of ion-implanted semiconductors. The nature of light scattering (stable or unstable centers) must be include in the explanation of receiving negative results of Ruby and Neodymium laser annealing of ion-implanted layers indium antimonite, cadmium mercury telluride and lead tin telluride [1]. For the effective laser annealing of semiconductors we must select laser irradiation with maximal absorption in impurity (ion-implanted defect structure) spectral region of absorption. For this case thermal effects are second order range effects of relaxation of irradiated materials. Therefore we must estimate all possible mechanisms of relaxation: kinetic and dynamical; and possible

mechanisms of excitation: hierarchical photoionization. In this case we must include respective chain of relaxation times. It is necessity for the more full representation and modeling real and possible physical processes for the respective regimes of interaction.

Thus this representation of the modeling dangling bonds, which are created with help laser irradiation, is very effective method. It allows including in consideration effects of equilibrium, nonequilibrium and irreversible relaxations.

3. Modeling and discussion. Case of structural phases

The question about the influence of saturation of excitation on effects of RO may be represented as process of transitions between metastable phases too. Now we'll estimate the influence of parameters of irradiation (including spectral) on irreversible changes and transformations in Si and Ge. Spectral dependences of absorptance of various structural modification of Si are represented on Fig.5 [1]: curve 1 – crystallic silicon; curve 2 – amorphous Si; curve 3 – amorphous Si with Ga impurity.

Now we'll be estimated intensities of Ruby and Neodymium laser irradiation (wavelengths of irradiation are 0,69 μm and 1,06 μm properly) of silicon and germanium, which are necessary for the creation of proper irreversible changes in irradiated semiconductor. As shown from Fig. 5, absorptance of the Neodimium laser radiation in silicon is equaled 60 cm^{-1}, Ruby – $2 \cdot 10^3$ cm^{-1}.

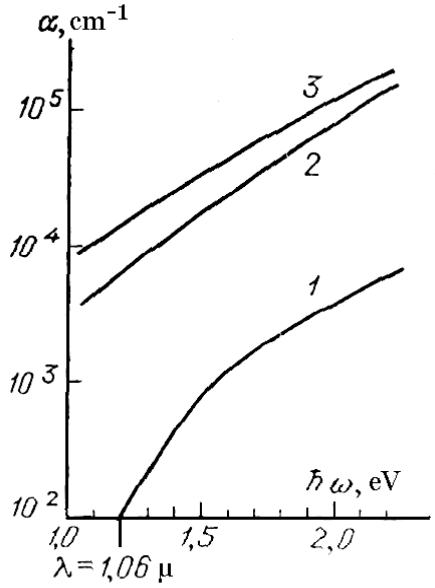

Fig. 5. Spectral dependence of absorptance: crystal (1), pure amorphous silicon (2) and amorphous silicon with Ga impurity (3) [1].

Crystal semiconductors Si and Ge have, basically, the structure of diamond. Elementary lattice have 8 atoms. Volume density of elementary lattices may estimate according to formula

$$N_L = \frac{\rho N_A}{8A}, \qquad (7)$$

where ρ – density of semiconductor, N_A – Avogadro number, A – a weight of one gram-atom. For Si $N_{LSi} = 6,26 \cdot 10^{21} см^{-3}$, and fo Ge $N_{LGe} = 5,68 \cdot 10^{21} см^{-3}$.

But Si and Ge may be crystallized in lattices with hexagonal, cubic and tetragonal symmetry. Phase diagram of Si as function of coordination number is represented on Fig. 6 [8,9]. Coordination number (CN) 8 is corresponded of diamond lattice, CN 6 – hexagonal lattice, CN 4 – tetragonal lattice, CN 3 – trigonal lattice. It should be noted that melting temperatures of these phases are various.

Roughly speaking, transition from one phase to another for reqime of saturation of excitation may be modeled as one-time breakage of proper number of chemical bonds, which are corresponded to the difference of CN of proper phases. For example, two bonds breakage is caused the phase transition from diamond to hexagonal structure. One bond breakage in the vregime of saturation is caused to generation of laser radiation.

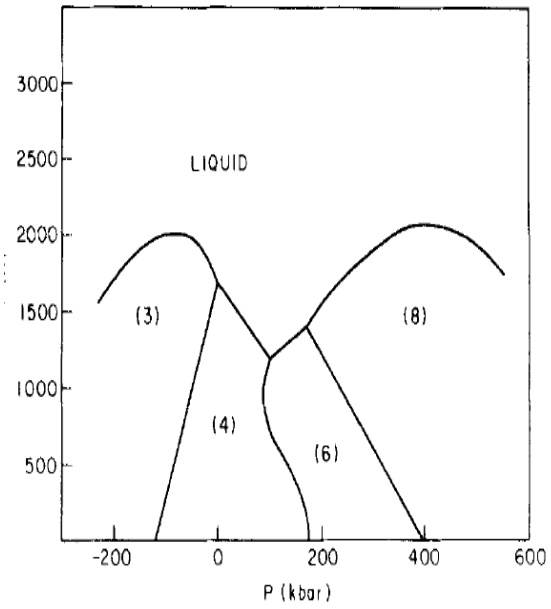

Fig. 6. A schematic phase diagram for Si(CN). The coordination numbers (CN) of the various phases are indicated. The diagram is based on common features of the phase diagrams of column IV elements as described by the references cited in Pistorius's review [8]. Starting from a high temperature $>3 \times 10^3 K$ and subject to a constraint of average density $\langle \rho \rangle = \rho(4)$, a hot micronucleus will tend to bifurcate into the most stable phases (highest T_m) which straddle Si(4) in density. These are Si(3) and Si(8), as indicated by the diagram [8].

Results of calculation of volume densities of energy, which are necessary for breakage of proper number of bonds in regime of saturation of excitation, are represented in Table 1. It conceded that energies of all chemical bonds for elementary lattice are equivalent (Si and Ge are pure homeopolar semiconductors). For silicon energy of covalent bonds Si-Si are equaled 1,2–1,8 eV; for germanium energy of covalent bonds Ge–Ge are equaled 0,9–1,6 eV. Minimal values of these energies are corresponded of Pauling estimations.

Table 1. Volume density of energy I_{vi} (10^3 J/cm^3), which is necessary for the breakage of proper number of chemical bonds in the regime of saturation of excitation in Si and Ge

	I_{v1}	I_{v2}	I_{v4}	I_{v5}
Si	1,18–1,76	2,36–3.54	4,72–7,08	5,90–8,84
Ge	0,80-1,42	1,60-2,84	3,20-5,68	4,00-7,12

These estimations are very rough and it may be used for the qualitative explanation and prognostication of proper data.

Surface density of energy of Ruby and Nedimium lasers irradiation may receive after division of results of Table 1 on proper absorptances. Results of these calculations are represented in Table 2.

Table 2. Surface density of energy I_{si} (J/cm^2), which are necessary for the breakage of proper numbers of chemical bonds in Si and Ge crystals after Ruby and Nd lasers irradiation in regime of saturation the excitation

	I_{s1}	I_{s2}	I_{s4}	I_{s5}
Si, Nd laser	20–30	39–60	79–120	98·–150
Si, Ruby laser	0,6–0,9	1,2–1,8	2,4–3,5	3,0–4,4
Ge, Nd laser	0,05–0,09	0,10–0,18	0,20–0,36	0,25–0,45
Ge, Ruby laser	0,004–0,007	0,008–0,014	0,016–0,028	0,020–0,035

Remark to Table 2: absorbtances of Si (Neodimium laser) –60 cm^{-1}; Si (Ruby laser) – $2\cdot10^3$ cm^{-1}; Ge (Neodimium laser) – $1{,}6\cdot10^4$ cm^{-1}; Ge (Ruby laser) –$2\cdot10^5$ cm^{-1}.

It should be noted that real regimes of irradiation must be more on 20 – 30 percents (process of light reflection wasn't included in our estimations). In addition we aren't including the relaxation (temporary) processes for the scattering of light on stable centers (self-absorption in crystals) as in previous chapter.

For light absorption on unstable centers (amorphous semiconductors) time characteristics haven't large observable influence on formation of irreversible changes in semiconductors. Here integral dose of irradiation has general meaning; therefore in this case photochemical ionizing processes give basic contribution and processes of radiated relaxation are neglected.

Calculated data of determination of regimes of Nd laser irradiation of pure amorphous Si and amorphous Si with impurity are represented in table 3. Volume data were used from Table 1. Calculation was done in "opposite" direction, another words we were calculated the density of energy, which is necessary for the creation of proper phase (structure) with help of renewal (reconstruction) of proper numbers of chemical bonds.

Table 3. Surface density of energy I_{si} (J/cm^2), which are necessary for the regeneration of proper numbers of chemical bonds in pure amorphous Si and amorphous Si with impurity after Nd and Ruby lasers irradiation in regime of saturation the excitation

	I_{s1}	I_{s3}	I_{s4}	I_{s6}	I_{s8}
Si, pure, λ=1,06μm	0,28–0,35	0,71–1,06	0,9–1,7	1,40–2,13	1,87–2,84
Si,with Ga λ=1,06μm	0,12–0,18	0,35–0,53	0,5–0,7	0,7–1,1	0,93–1,42
Si, pure, λ=0,69μm	0,09–0,14	0,28–0,42	0,38 – 0,57	0,56–0,85	0,75–1,13
Si, with Ga λ=0,69μm	0,06–0,09	0,12–0,26	0,28 – 0,36	0,35–0,53	0,47–0,71

Remark to Table 3: absorptances of pure amorphous Si (Neodimium laser) – $5\cdot10^3$ cm^{-1}; pure amorphous Si (Ruby laser) –$\cdot10^4$ cm^{-1}; amorphous Si with impurity (Neodimium laser) – $1{,}2\cdot10^4$ cm^{-1}; Ge (Ruby laser) –$2\cdot10^4$ cm^{-1}, accrding to Fig. 5.

With including of light reflection data of Table 3 must be increased on 20-30 percents.

Energetic dependencies of residual defectable in single crystals Ge and Si with amorphous layers with various depths after 50 ns Ruby laser irradiation is represented on Fig. 7 [1,10]. As apparently calculated data from Table 3 and experimental data of renewal of Si on Fig. 7 are coincided practically. Unfortunately data about absorptances of amorphous layers from Fig. 7 are absented.

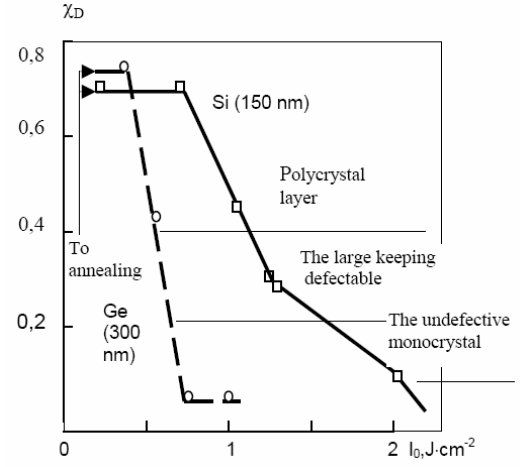

Fig. 7. The keeping defectable (relative units) in monocrystals Ge and Si with amorphic layers of various thickness after irradiation 50 ns pulsesRuby laser [10].

Comparative analysis of results of Table 2 and Table 3 show that intensity for ionizing processes of creation structures from crystal phase much more as for amorphous phase. Therefore Nd-laser annealing of ion-implanted layers of silicon is effective.

In addition we must remember that Ruby laser radiation for crystallic silicon has absorptance on order less as for amorphous, therefore for short regimes of irradiation the processes of bonds breakage may give more influence as for case of Nd laser irradiation. Polycrystall layer may include various crystallic phases. We can select condition of irradiation with creation on surface of silicon the nanostructures with various its fourth crystallographic modifications.

This method may be used for the realization of phase transformations of various allotropic modifications of pure carbon. Here we are represented the estimations of results of irreversible interactions laser irradiation and diamond and graphite in the regime of saturation of excitation.

Diamond may be transformed analogously to silicon and germanium. Therefore carbon may be have four crystal phases too. These phases are next: with coordination number 8 – a diamond; CN 6 – graphite; CN 4 and CN 3 [1,8,9]. A transition from diamond to other crystal phases may be represented as breakage of proper numbers of chemical bonds in the regime of saturation of excitation. Results of calculation of volume densities of energy, which are necessary for breakage of proper numbers of bonds in regime of saturation of excitation, are represented in Table 4. It conceded that energies of all chemical bonds for elementary lattice are equivalent (diamond as Si and Ge i pure homeopolar semiconductor). For carbon energy C–C covalent bond is equaled 2,5–2,9 eV [1]. Elementary lattice of diamond have 8 atoms. Therefore volume density of lattice may be determined with help formula /7/. We have for a diamond $N_{LC_{Dia}} = 2,2 \cdot 10^{22} cm^{-3}$.

Table 4. Volume densities of energy I_{vi} (J/cm^3), which are used for the breakage of proper chemical bonds in diamond for the regime of saturation of excitations.

	I_{v1}	I_{v2}	I_{v4}	I_{v5}
Diamond	(8,8–10,2)10^3	(1,76–2,04) 10^4	(3,52–4,08) 10^4	(4,4–5,1) 10^4

We are estimated surface density of energy of laser radiation, which is necessary for the breakage of proper number of bonds. For this data of Table 4 must be divided on proper absorptance. Two values of absorptance, α = 200 cm^{-1} and α = $2 \cdot 10^4$ cm^{-1} will be used for the receiving of our estimation. These results are represented in Table 5.

Table 5. Surface densities of energy I_{si} (J/cm^2), which are used for the breakage of proper chemical bonds in diamond for the regime of saturation of excitations for two regimes of absorption of radiation.

α	I_{s1}	I_{s2}	I_{s4}	I_{s5}
200 см$^{-1}$	44–56	88–102	176–204	220–255
$2 \cdot 10^4$ см$^{-1}$	0,44–0,56	0,88–1,02	1,76–2,04	2,20–2,55

Physical phenomena, which are corresponded to breakage of proper number of bonds, are next: population depletion of one bond is caused the laser effect; two bonds – a creation of graphite; four bonds – a creation crystal structure with CN=4 and breakage of five bonds – a creation crystal structure with CN=3. But it is true for the regime of saturation of excitation only. Under further increasing of intensity of an irradiation may be realized next processes: melting of semiconductor, creation various nanostructures, including nanohills, nanotubes and fullerens.

Analogous estimations may be realized for amorphous carbon too. A calculation must be organized in “reverse” direction: from structures with low symmetry to structures with high symmetry. In this case we can have various phases of carbon too.

Now we are analyzed question about possible phase transformations in graphite under laser radiation. Wellknown [1] that for temperature >1000 °C a diamond is transformed to graphite. Fourth covalent bond of diamond structure is changed on Van der Waals chemical bond in graphite structure. We are used for the receiving of an estimations value of energy of this bond 0,1 – 0,3 eV.

The closeness of elementary lattices in a graphite can be determine after correlation /*/ taking into account that a coordinating number for the hexagonal lattice of graphite is equal 6, a density of graphite 2,23 g/cm^3. Then $N_{LC_{Graph}} = 1,9 \cdot 10^{22} см^{-3}$. The corresponding volume density of energy that is needed for the breakage of these bonds is equal 304 – 912 J/cm^3. We should to mark that the top limit of volume density of energy is some overpriced. For the saturation of excitation of this connection we must select an irradiation in the infrared area of spectrum of from 4,1 to 12,4 μm.

It should be noted that all got estimations on the results of irradiation do not take into account the reflection of light, and that is why must be increase on 10 – 20 percents.

At the irradiation of graphite with the regimes of irradiation α = 200 cm^{-1} surface density of energy of irradiation is equaled 1,52 – 4,56 J/cm^2, at an irradiation from α = $2 \cdot 10^4$ cm^{-1} – (1,52 – 4,56) $\cdot 10^{-2}$ J/cm^2. Depending on to the absorptance and intensity of irradiation in this case we can get the whole set of nanostructures, including fullerenes and carbon nanotubes [11–13]. It is conditioned by that at such regime of irradiation practically passes "stratification" of graphite on graphens, if to make an irradiation in direction perpendicular to the hexagonal layers. The density of these layers remains very high,

however at certain terms power formation of nanotubes becomes advantageous at an even light-striking and fullerenes at an uneven irradiation or at formation of interference pictures on a surface. The sizes of these nanostructures must depend on to the absorptance of light (deeper or less deep stratification of layers of graphite) and from intensity of irradiation. Practically, it the phenomenon is analogical to "swelling" of surface during ionic implantation [6].

We should be noted that these results are simple to the honeycomb model of laser annealing [1,9], but this model allow to receive quantitative estimations, which are explained experimental data. And, in addition, represented model allow estimating phase transformations amorphization – crystallization in both directions: laser irradiation may be caused a orderind and disordering of structures. The answer on question about generation of nanostructures may be next. A creation of δ-layers of Germanium on Silicon [11,14] may be explained with help thermodynamical [11] and photochemical [14] conceptions. Energy of bonds of Ge in SiGe films is less as Si. Other theories may be used for the explanation these results too. Kapayev-Kopayev-Molotkov theory allow to explaim metallization of subsurface irradiated region of semiconductor. Stafeev phason theory allow to determine the condition of the initiation new phase (phasons) and its evolution [1]. Last theory may be used for the modeling and initiation various nanostructures.

Thus in this chapter structural model of cascade excitation (breakage) of chemical bonds in Si, Ge and allotropic phases of carbon in regime of saturation is represented. This model allows explaining the proper experimental data, including creation of nanostructures.

4. Conclusions

The problems of modeling of irreversible pulse laser irradiation of matter in the regimes of saturation of excitation are discussed.

The model of “chemical bonds”, which is based on two-dimensional lattice of sphalerite, was used for the explanation of experimental data of interaction pulse Ruby laser radiation with InSb and InAs.

The model of case structural phase’s transitions, which is based on phase diagram of silicon, was development and used for the explanation and prognostication of experimental data of interaction pulse Ruby and Neodymium laser radiation with silicon and germanium.

Are shown that these models of Relaxed Optics may be used for the receiving proper allotropic phase of carbons, including diamond, graphite, graphemes and other.

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References

[1] P.P. Trokhimchuck, Foundations of Relaxed Optics, Volyn’ University Press “Vezha”, Lutsk (2011)
[2] R.H. Pantell, H.E. Puthoff Fundamentals of quantum electronics, John Wiley & Sons, Inc., New York a.a. (1969)
[3] I. M. Popescu, A. M Preda, C. P. Cristescu, P. E. Sterian, A.I. Lupaşcu, Probleme resolvate de fizica lazerilor, Editura technică, Bucureşti (1975, In Romanian)
[4] R.W. Boyd. Nonlinear optics, Academic Press, Amsterdam a.o. (2003)
[5] V.P. Gribkovskiy, Semiconductor laser, University Press, Minsk (1975, In Russian)
[6] P.P. Trokhimchuck, Radiation Physics of Status Solid, Vezha, Lutsk (2007, In Ukrainian)
[7] V. A.Bogatyryov, G. A. Kachurin, Phys. Tech. Semicond., 11, 100, (1977, In Russian).
[8] C.W.F.T.Pistorius, Progress in Solid State Chemistry **11**, 1 (1976).
[9] J. C. Philips, Journal of Applied Physics **52**, 7397, (1981).
[10] J. Foti, Laser annealing of the ion-implanted semiconductors, News of the Physics Status Solid, 10, 132, Mir, Moscow (1980, In Russian)
[11] Medvid’ A. Nano-cones Formed on a Surface of Semiconductors by Laser Radiation: Technology, Model and Properties, Nanowires Science and Technology, ed. Nicoletta Lupu, Inech, Vukovar, 61 (2010).
[12] J. Narayan, V. P. Godbole, C. W. White, Science, **252**, 416, (1991).
[13] A. Grigonis, A. Medvids, P. Onufrijevs, J. Babonas, A.Reza, Optical Materials, **30**, 749 (2008).
[14] M.S. Hegazy, H.E. Elsajed-Ali, J. Appl. Phys., **104**, 124302 (2008).

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