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Subsurface modification of semiconductor materials by laser nanosecond pulses with a wavelength from tail of the absorption edge

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Abstract

The results are presented of numerical and experimental investigation of modifying transparent semiconductors structure induced by focusing into the material the nanosecond laser pulsed with a wavelength at the edge of intrinsic absorption band. The modification process is based on the thermal shifting of the absorption edge and increasing the radiation absorption in the focal area that, in turn, results in a local heating and modifying the material structure. It was obtained, when focusing nanosecond laser pulses into a transparent semiconductor, the following structural changes may occur: point-type and line-type modifications. Depending on the energy, duration and parameters of the laser pulse focusing, the first or second modification type can appear.

Keywords: semiconductor materials; absorption edge; laser processing

Introduction

Well-known methods of laser-induced structural modifying optically transparent materials are based on effects of nonlinear absorption of pico- or femtosecond laser pulses focused into a material bulk [Gamaly E. et al., 2006]. At the same time, some modification of transparent semiconductors structure may be achieved, as well, by using thermal effect of increasing the material absorption for laser wavelengths in spectral region at the intrinsic absorption edge [Daly R.T., 1970]. The absorption changes because the material band gap decreases as a result of its heating by the laser radiation.

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As shown in [Grigorev A., 2018], action on semiconductor materials of nanosecond laser pulses with the wavelength at the absorption edge is a threshold process. Significant changing in the temperature and material structure takes place, when the intensity of the laser pulse focused on the material surface exceeds the threshold. Results, obtained in [Grigorev A., 2018], allow to suppose the possibility of structural modification inside semiconductor materials caused by laser pulses with wavelengths near the absorption edge. However, at focusing the pulse inside a semiconductor, conditions of its propagation can change within the pulse duration. The pulse energy is absorbed and heats the material along the entire path from the material surface to area of focusing that results in increasing the absorptance and changing terms of the radiation propagation. The problem of material heating the laser pulses becomes unsteady and nonlinear and must be solved by numerical modelling.

Model of heating

Let us suppose that an axisymmetric laser beam with the uniform intensity distribution is focused inside the material, and the pulse has the rectangular temporal profile with the duration less than 100 ns. In such conditions the material thermal conductivity may be neglected [3]. The laser beam is focused along axis X. The problem of material heating should be reasonably solved with the use of finite-difference method. In numerical calculation the laser pulse is divided into k equal time intervals with duration Δt and serial indices j: $1 \leq j \leq k$. By analogy, the distance of the pulse propagation inside material to the focal plane is divided into m equal spatial slices with thickness Δx. The slices are numbered from the material surface with serial indices i: $1 \leq i \leq m$. At focusing a single laser pulse inside the absorbing material the temperature change inside i-th slice is related with changing the radiation intensity in this slice by the following equation:

$$c\rho\left(\frac{T_{i,j} - T_{i,j-1}}{\Delta t}\right) = \left(\frac{I_{i,j} - I_{i+1,j}}{\Delta x}\right)$$

Here, c and ρ are the specific heat and density of the material, respectively.
From this, the temperature of i-th slice of the material at j-th moment of time is determined by expression:

$$T_{i,j} = T_{i,j-1} + \frac{1}{c\rho}\left(\frac{I_{i,j} - I_{i+1,j}}{\Delta x}\right) \cdot \Delta t$$

Relation $\left(\frac{I_{i,j}-I_{i+1,j}}{\Delta x}\right) \cdot \Delta t$ is the energy density of laser radiation $w_{i,j}$, absorbed in an unitary material slice Δx during unitary time interval Δt.

$$w_{i,j} = (I_{i,j} - I_{i+1,j}) \cdot \Delta t/\Delta x = I_{i,j}\left[1 - \exp\left(-\alpha_{i,j-1} \cdot \Delta x\right)\right] \cdot \Delta t/\Delta x$$

Here $\alpha_{i,j-1}$ is the absorption coefficient.
The value of intensity $I_{i,j}$ in the last formula is the result of focusing laser radiation inside the material by a positive lens with numerical aperture *NA* and can be determined by expression:

$$I_{i,j} = \frac{W_p}{\pi \cdot \tau_p \cdot \left[\left(\frac{d}{l} - \frac{NA}{n}\right) \cdot \Delta x \cdot i + \frac{l \cdot NA}{n}\right]^2}$$

Here W_p and τ_p are the energy and duration of the laser pulse, respectively, d is the beam spot diameter in the focal plane, *n* is the material refraction index, and *l* is the distance from the material surface to the focal plane.

So, the temperature and the temperature change of i-th slice of the material at j-th moment of time will be:

$$T_{i,j} = T_{i,j-1} + \frac{w_{i,j}}{c\rho} \; ; \quad \Delta T_{i,j} = \frac{w_{i,j}}{c\rho}$$

This temperature change leads to increasing of the slice absorptance [Grigorev A., 2016.].

$$\alpha_{i,j} = \alpha_{i,j-1} \cdot \exp\left(\frac{\xi}{E_U} \cdot \Delta T_{i,j}\right)$$

The sequence of calculations is as follows. For each time interval in the order of increasing and for each slice of material, beginning from the first and ending to i, the following parameters are calculated: energy absorbed $w_{i,j}$, temperature raise $\Delta T_{i,j}$ caused by this energy, and absorption coefficient $\alpha_{i,j}$. The calculations result in the spatial distribution of the temperature inside material along axis X from the surface to the focal plane for each moment up to the end of laser pulse.

Calculation results

The numerical modelling of heating process showed that at focusing inside semiconductor materials of a nanosecond laser pulse with the wavelength at the absorption edge, two types of heating can be obtained: a spot-like or extended (line-like). Realization of the first or second types depends on the energy and duration of the laser pulse. Figure 1 presents graphs of temperature distributions inside the material irradiated by a 100 ns-laser pulse in different moments within its duration.

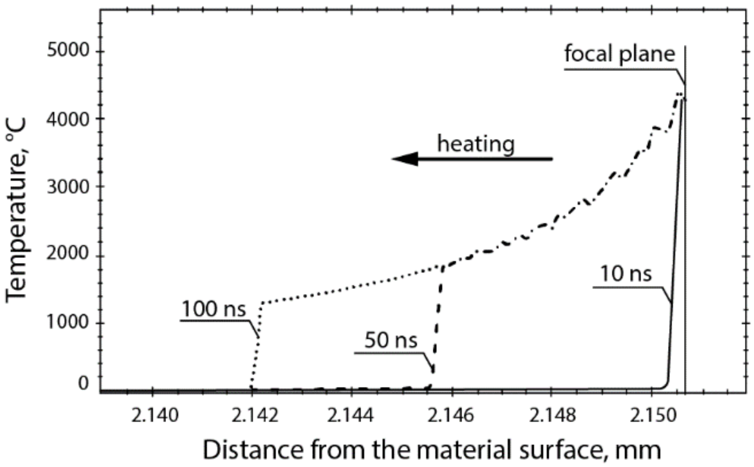

Fig. 1. Propagation of heating inside material within the laser pulse duration.

Evidently, that when the pulse starts, the heating is localized in the focal plane, but in some time the heated area begins to expand toward the laser radiation. Analogically, the moving of heated area toward the radiation is obtained when the pulse duration is kept constant and its energy increases. It is worth to note that the temperature in the focal area enlarges only at the beginning of the pulse and after that keeps stability up to the pulse end. Such a behavior results from blocking the laser radiation propagation to the focal area, which is caused by significant raising the absorption coefficient in material regions in front of the focus. That is why, from the moment, when regions, located before the focal plane, begin their heating, the focal temperature stops its raising and keeps constant during the residual pulse duration.

Experiment

Laser pulses with the duration of 30 ns at the wavelength of 495 nm were focused inside a semiconductor zinc selenide to the depth of 2 mm by a lens with the focal distance of 100 mm. Wavelength 495 nm corresponds to the beginning of the absorption edge of zinc selenide. It was obtained that the character of structural modifications inside the material is governed by the pulse energy. Under action of laser pulses with the energy of 5×10^{-6} J, the local modified structure occurs inside the sample, which cross size corresponds to the focused laser beam diameter.

When the pulse energy exceeds 10^{-5} J, the modification looks like a line-type structure oriented along the beam direction inside material. Photos of the local and linear modifications are shown in Fig. 2.

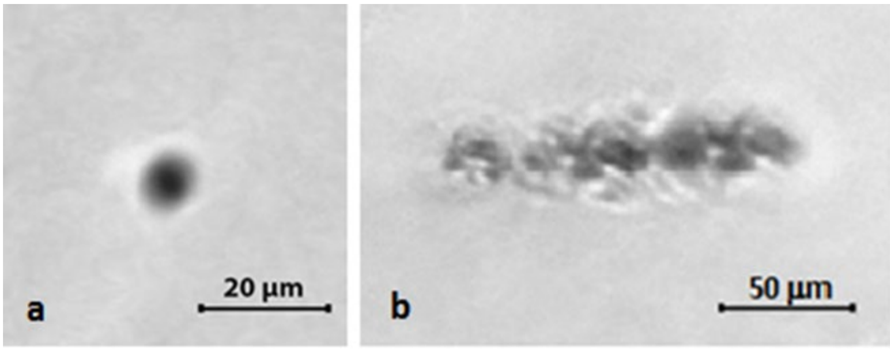

Fig. 2. Structural modifications: a – spot-like, b – line-like.

The linear modification has the length about 150 microns and comprises a plurality of micro cracks that confirms the numerical modelling results on expanding the heated area from the focus toward the laser beam. Temperature difference between the heated area and surrounding cold material can vary in the limits from several hundred to several thousand degrees. In these conditions the strong thermomechanical tensions occur, which value can be estimated by formula:

$$\sigma = E\gamma\Delta T/(1-\nu)$$

Here, E is Young's modulus, γ is the coefficient of linear expansion, ΔT is the temperature difference between the heated zone and surrounding material, ν is Poisson's ratio.

For experimental conditions the calculated temperature difference between the heated and surrounding material is from 2000 to 3000 degrees, that results in occurrence of tensions about 2 – 3 HPa. Crystalline semiconductor materials typically have the limit of elasticity in the region of 40 – 100 MPa. Apparently, the limit of elasticity is significantly less than the tensions induced in material by laser pulses. As a result, a track of micro cracks, directed from the area of focusing laser pulse to the surface of material, occurs. Hence, the experiment confirms the results of numerical modelling on possibility of realizing two types of material structure modification (spot- or line-type).

Conclusion

The results of numerical calculation and experiments evidently demonstrate the possibility of local heating and modifying structure of transparent semiconductor materials by focusing into material the pulsed laser radiation with the wavelength at the intrinsic absorption edge. The structure changes as a result of local heating caused by thermal increasing of the absorption coefficient. The possibility of obtaining spot-like and linear structural modifications of semiconductor materials is experimentally verified. The both types of structural changes can be used to solve different practical problems. The spot-like modification of structure can be applied for optical recording the information, as well as for formation inside transparent materials with a band gap of various photonic or others microstructures with complicated topology, for example, Bragg gratings or light guides. The line-like modification can be applied for dividing semiconductor wafers to chips by stealth dicing method.

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