Optical Properties Changes at Low-Temperature Annealing of $ZnGeP_2$ Single Crystals Irradiated by Fast E-Beam

A.I. Gribenyukov, G.A. Verozubova, A.Yu. Trofimov

Institute of monitoring of climatic and ecological systems SD RAS, 10/3 Academicheskii, Tomsk, 634021, Russia, phone:(3822)492589, fax:(3822)492950, e-mail: loc@imces.ru

Abstract – To improve the optical quality of the $ZnGeP_2$ crystals it is used both thermal annealing as well the fast e-beam irradiation. To estimate a reliability of the optical elements working at high intensive pump radiation and to determine the limit of temperature range allowable for post-irradiation treatments it is necessary to know areas of temperature stability of optical properties of irradiated crystals.

Influence isochronal anneal of $ZnGeP_2$ crystals irradiated by 4 MeV electrons on optical absorption coefficient has been investigated.

It was established that optical losses changes take place in two temperature ranges depending on spectral region of optical radiation. Near-to-edge absorption (0.7–1.0 μm) indicates strong reduction at 200–220 °C. In region 1.0–2.5 μm the optical absorption rises beginning from 250–260 °C and coming to saturation at 340–350 °C.

It was found difference in behavior of optical absorption coefficient anneal for the $ZnGeP_2$ crystals irradiated by electrons with different energy.

The results obtained are explained in the frames of interconnection between radiation-induced defects with native point defects of the $ZnGeP_2$ crystals.

1. Introduction

The $ZnGeP_2$ single crystals are the most effective non-linear media for frequency conversion of IR radiation. Recently it was shown that the crystals are also very prospective to obtain tunable radiation in far infrared region (100–1000 μm). Fast e-beam irradiation of the $ZnGeP_2$ single crystals is one of the most effective ways to reduce optical absorption losses down to level acceptable for use in work with laser optical beams of high intensity typical for nonlinear optics applications.

The temperature stability of optical properties of the irradiated $ZnGeP_2$ crystals presents an interest for estimation of capacity for work and reliability of nonlinear optical elements. To clear these questions were measured optical transparency spectra of the $ZnGeP_2$ crystals preliminary irradiated by 4 MeV electrons and then thermally treated in temperature range from 120 °C up to 400 °C with interval 20 °C and exposition 20 min at each temperature.

2. Absorption coefficient of the $ZnGeP_2$ crystals

The most correctly total description of the optical absorption coefficient spectra should be done on base of theoretic model of optical transition cross-section for deep level centres developed by authors [1]. Unfortunately, in solids the absorption coefficient spectra are never single ones. The absorption coefficient spectra of separate deep level centres always overlap each another and, therefore, in high-energy parts of the spectra there is a risk of incorrect use of obtained data for deep level parameter estimations. To minimise possible mistakes related to overlap of the single level absorption spectra one can estimate the deep level parameters on base of low energy parts of absorption coefficient spectra.

For the low energies the precise integral presentation of optical absorption cross-section spectra [1] is very close to the Boltzman approximation which can be used also for express analysis of measured data:

$$\alpha = \alpha_0 + (\alpha_1 - \alpha_0) \times \left[1 + \left(\exp \frac{h\nu - x_0}{\Delta x} \right) \right]. \quad (1)$$

Here α_0, α_1–α_0, x_0, and Δx are the characteristic parameters of the Boltzman function. The first two parameters have sense of a non-selective background level (α_0) and an amplitude of optical absorption (α_1–α_0), respectively. The last presents the product of concentration of deep level centres and its photons capture cross-section. The second pair of the parameters relates to energy characteristics of the deep level centres. Herewith x_0 is referred to the characteristic of energetic position of deep levels in forbidden gap, and Δx is a dilatation parameter proportional to the first order derivative of absorption coefficient spectrum at x_0.

By using known [2] theoretical value of ratio for effective masses of electrons and holes in the $ZnGeP_2$ it was made calculations of families of the optical cross-section spectra for different types of optical transitions and energies of these transitions. The low energy parts of these calculated spectra were approximated by the Boltzman's (sigmoid) curves what allows to establish following relations taking in account p-type conductivity of the $ZnGeP_2$ crystals:

a) Transitions Valence-band – deep acceptor (Type I):

x_0=0,03238+0,88898·E_{0PT},

Δx=0,00675+0,37855·ΔE,

where E_{0PT} and ΔE are accordingly the energy of deep level regarding to V-band and energy gap within which the optical cross-section changes from level $1/(2e)\approx 0.184$ up to $(1-1/(2e))\approx 0.816$ and

b) Transitions Valence band – deep donor (Type III):

x_0=–0,08734+1,06624·E_0,

Δx=–0,00301+0,40104·ΔE.

For all investigated $ZnGeP_2$ slices the values of the Boltzman approximation parameters x_0 are varied from 0.75 eV to 0.85 eV. Such way the low energy parts of optical absorption coefficient spectra in accordance with the Boltzman approximation could be caused by either deep acceptors with energy location $E_A=E_V+(0.81–0.92)$ eV or deep donors placed at $E_D=E_V+(0.79–0.88)$ eV. For the estimated energy position of deep levels, the dilatation parameters dx for the Boltzman approximation of measured absorption coefficient spectra should be expected as $\Delta x_A=0.17\cdot E_A+0.007\sim 0.15$ eV for optical transitions of Type I (V-band – acceptors) and $\Delta x_D=0.203-0.106{*}E_D\sim 0.07$ eV for optical transitions of Type III (V-band – donors), accordingly. The last value is better accorded with the fitting parameter Δx of the Boltzman approximation of optical absorption coefficient spectra obtained from measurements. Therefore we conclude that in $ZnGeP_2$ crystals the optical absorption origin can be attributed to optical transitions: Valence band – deep donor with energy position $E_d=E_v+(0.79–0.88)$ eV.

3. Changes of absorption coefficient spectra for the $ZnGeP_2$ crystals under e-beam irradiation

An example of e-beam irradiation influence on absorption coefficient in $ZnGeP_2$ crystals is presented in Fig. 1. As it clearly seen e-beam irradiation results in a sharp enlightenment of the $ZnGeP_2$ crystals in spectral region of 0.4–1.3 eV. But simultaneously with optical losses reduction in this spectral range we found increase of near-to-edge optical absorption (1.5–1.8 eV). As it turned out the amplitudes of Boltzman approximations of absorption spectra for irradiated $ZnGeP_2$ samples have nonlinear dependence with e-beam fluence and therefore they should be described by polynomial regression curves. The result of polynomial regression analysis for the Boltzman amplitudes shows that the optimal e-beam fluence for $ZnGeP_2$ crystals can be calculated in accordance with following empiric expression:

$$F_{opt}=(0,01486+0,3986\cdot A_{init})\cdot 10^{17},$$

where A_{init} – is amplitude of the Boltzman approximation of absorption coefficient spectra in state "before irradiation". It should be noted that the optimal e-beam flux value F_{opt} can be estimated as $0.4\cdot 10^{17}$ cm^{-2} on each 1 cm^{-1} of the Boltzman amplitude for the initial absorption coefficient spectra. Efficiency of irradiation will reduce with decrease of the Boltzman amplitude of the initial absorption spectra.

As to energy parameter that regression analysis indicates linear dependence between the middles x_0 of the Boltzman approximations of absorption spectra of the $ZnGeP_2$ samples and e-beam fluence:

$$x_0=0,85674+9,83117\cdot 10^{-19}\cdot F.$$

Here it is worth to note that indicated relations concern to the Boltzman amplitude for optical absorption spectra depending on e-beam flux. The amplitude is rather characterising the absorption coefficient values at 1 mkm region. The 2 mkm absorption coefficient of irradiated $ZnGeP_2$ samples must have the linear dependence from the current Boltzman amplitude of absorption spectra and nonlinear dependence from position of the middle of Boltzman approximation due to exponential dependence from energy of the low energy "tail" of absorption cross-sections. This exponential dependence is determinant as compared with linear one. Therefore the absorption at 2 microns important for efficiency of optical parametric oscillator is mainly function of deep defects spectrum and their nature.

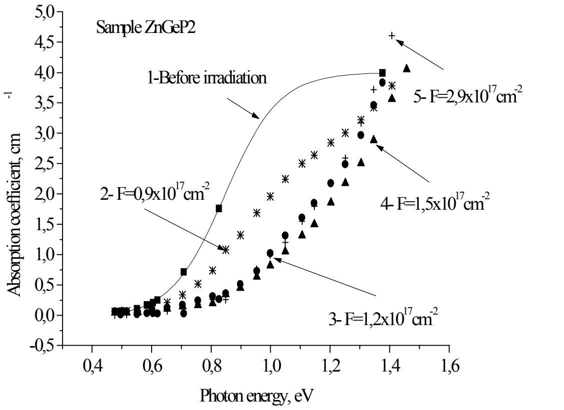

Fig. 1. Influence on Optical absorption spectra of ZGP sample vs fluence (F) of e-beam with energy 4 MeV: 1–before irradiation, 2 – F= $9\cdot 10^{16}$ cm^{-2}, 3 – F=$1.2\cdot 10^{17}$ cm^{-2}, 4 – F=$1.5\cdot 10^{17}$ cm^{-2}, 5 – F=$2.9\cdot 10^{17}$ cm^{-2}

4. Isochronal annealing of irradiated ZGP samples

To have the well-founded choice of the conditions providing the maximum reduction in absorption of $ZnGeP_2$ crystals designated to extreme intense work it takes to study a stability of optical properties under post-irradiation annealing. There are two factors which not allow use one-wavelength data to estimate effects of low-temperature post-irradiation anneals. First of them is above mentioned difference in behaviour of low- and high-energy parts of absorption spectra under e-beam irradiation. The second relates to overlap of separate spectra of different origin. Both factors lead to necessity to consider whole absorption spectra what must give more reliable estimation of the most important parameters of defects resulting in the defect-related optical absorption: their energy position in energy gap of material and defects concentrations if to use reasonable assumptions concerning to optical absorption cross-section. An example of post-irradiation isochronal anneal presented in Fig. 2.

Performed investigation showed that there are at least two stages of anneal for defects created by e-beam irradiation what looks like the stages indicated earlier in [3]. One of the stages exists in the temperature range of 150–250 °C. Herewith the high-energy parts of optical absorption spectra of irradiated ZGP samples have reduced. Another stage becomes major at temperatures above 300 °C. At these temperatures it takes place changes of optical absorption coefficient in whole spectral range. Herewith two opposites directed process flow simultaneously. The high energy parts of the spectra continue to expose the tendency of the absorption reduction, but the low energy absorption band appears and grows with increase of anneal temperature and/or exposition time.

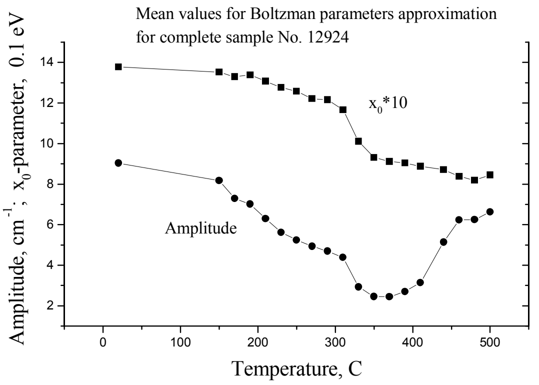

Fig. 2. The Boltzman amplitude and characteristic energy x_0 (multiplied in10 times) for approximations of absorption coefficient spectra functioned from temperature of isochronal anneal

The sample thickness was equal to 6.3 mm what allows us to carry out studies of the e-beam irradiation influence on the ZGP optical properties changes distributed on samples depth. For this purpose the sample was cut on three parts called as the "middle"(No. 2), and the "top "(No. 1) and the "bottom"(No. 3). The two last were named arbitrary because all conditions for them were the same. The cuts were made parallel to initially polished surfaces throughout e-beam irradiation was induced. The sample No 3 was then polished from two sides to indicate a possible influence of the mechanical treatment. The results of optical measurements for these three samples annealed simultaneously at the same thermal conditions are presented in Fig. 3, 4.

Evidently optical absorption coefficient has different types of changes with temperature for different wavelength and therefore one should to use more general characteristics of the spectra.

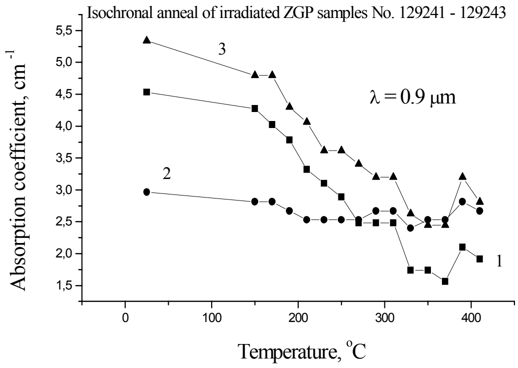

Fig. 3. Comparative data on isochronal anneal of absorption coefficient at 0.9 microns for different parts of ZGP sample irradiated by e-beam with fluence F of $1.5 \cdot 10^{17}$ cm^{-2} from two sides: 1– the top part; 2 – the middle part; 3 – the bottom part

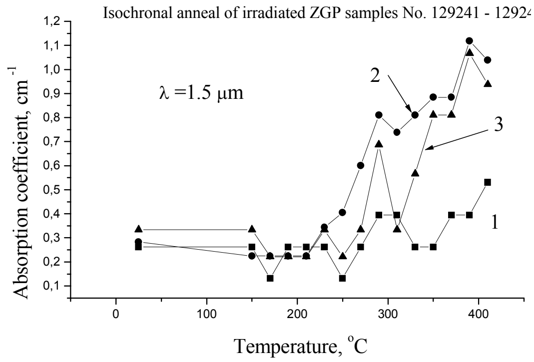

Fig. 4. Comparative data on isochronal anneal of absorption coefficient at 1.5 microns for different parts of ZGP sample irradiated by e-beam with fluence F of $1.5 \cdot 10^{17}$ cm^{-2} from two sides: 1– the top part; 2 – the middle part; 3 – the bottom part

It is clearly seen also that optical absorption coefficient indicates a different behaviour for the middle part of the $ZnGeP_2$ sample in comparison with its edges: top and bottom parts. Further, there are some differences between top and bottom parts. The absorption spectra measurements were then fitted by using the least square method to the Boltzman approximation curves. The results of this work are presented in Fig. 5, 6.

A difference between edges and the middle part is evident: the energy spectrum of the optical defects monotonously changes for the middle part of the investigated sample from values of near 1.35 eV down to 0.8 eV. At the same time for the top and bottom parts of this sample the defect energy is close to constant (1.35 eV) up to temperature 300 °C and only then the characteristic energies have a relatively fast decrease down to the same values as in the middle part. Note, that the amplitudes of the Boltzman approximations indicate (Fig. 5) a good total similarity for the edges but they differ from the middle part. Very wide range of isochronal anneal from 150 to 350 °C, can be explained by existence of two relaxation processes overlapped on temperature. As result of these studies and calculations one can find the most preferable temperature range for low-temperature annealing of irradiated ZGP samples, namely, this temperature range is 350±20 °C. It is easy to see that besides the minimum of the Boltzman approximations amplitudes reached in above mentioned temperature range the uniformity of material has the highest level what is very important for laser applications.

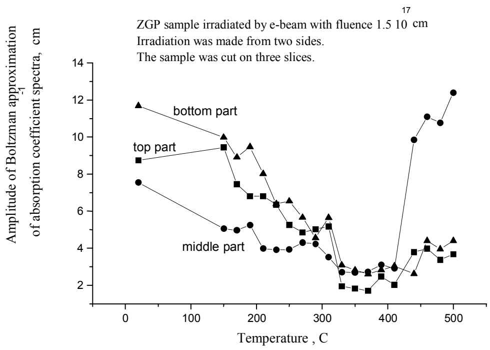

Fig. 5. Behavior of characteristic energy of deep centers in e-beam irradiated ZGP crystals under influence of low temperature isochronal anneals (Δt=20 min. ΔT=20 °C): Squares – for the top part of sample (shifted up on 0.1 eV); Circles – for the middle part of sample; Up triangles – for the bottom part of sample

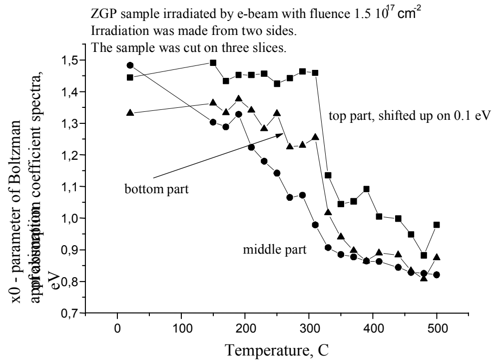

Fig. 6. Amplitudes of the Boltzman approximation of absorption spectra as functions of temperature of isochronal anneals for different parts of the ZGP sample No.12924 irradiated by e-beam with fluence of $1.5 \cdot 10^{17}$ cm^{-2}

5. Conclusion

Thus, the present stage of our investigation allows to say about the presence of following groups of deep levels taking part in formation of spectra of optical absorption coefficients in $ZnGeP_2$:

- Low energy optically active defects working in spectral range of 1.7–1.0 microns (optical transitions with energies from 0.65 eV up to 1.2 eV) have the donor-type nature. Both fast e-beam irradiation and low temperature post-irradiation anneal result in changes of the optically active deep levels energy. These changes can not be explained by the Fermi level movement. We believe our results to be more consistent with attribution of the absorption to cation substitution defects-GeZn or complete defects with its participation – (GeZn GeP).
- The high energy defects look like the deep acceptors which supply electrons in Conduction Band under influence of optical radiation with energies of 1.3–1.7 eV. Behaviour of these deep centres under e-beam irradiation and at post-irradiation anneals allows us to connected optical absorption in the spectral range of 0.7–1.0 microns with $ZnGeP_2$ vacancies.

The most significant data of these isochronal anneals investigations are the certified temperature ranges (near 200 °C, 310–320 °C, and above 380 °C) for further isothermic anneals which could give information about kinetics of transformations of energy spectrum of optically active deep level centres. The kinetics data could help in more founded identification of deep centres nature. In particular there is hope to make more certain conclusion concerning to optical transitions with energy close to a half of the ZGP forbidden gap.

References

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