Effect Isothermal Annealing on Optical Properties of the $ZnGeP_2$ Single Crystals Irradiated by Fast E-Beam

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

Institute of Monitoring of Climatic and Ecological Systems SB RAS, 10/3, Academichesky ave., Tomsk, 634021, Russia
E-mail: loc@imces.ru

Abstract – The $ZnGeP_2$ single crystals are an effective non-linear media to develop OPOs with tunable output radiation wavelength from 2.4 to 12 microns at pump by laser radiation near 2-micron region. These crystals are also very prospective material to obtain tunable radiation in far infrared region (100–1000 microns). Fast e-beam irradiation is often used for final optical enlightenment of the $ZnGeP_2$ crystals in spectral range near 2-microns.

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

It was established that annealing of irradiated $ZnGeP_2$ crystals result in restoration of absorption coefficient in near-to-edge spectral range (0.7–1.0 microns) at temperatures 180–220 °C. This process can be described by the general hyperbolic law with variable migration energy. It was found also appearance optical absorption band in spectral range 1.0–2.5 microns at temperatures 320–340 °C.

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

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. Besides data needed for application, it is interesting to know information about kinetics of transformations of energy spectrum of optically active deep level centers at post-irradiation isothermal anneals. To clear these questions were measured optical transparency spectra of the $ZnGeP_2$ crystals preliminary irradiated by 4 MeV electrons and then isochronally annealed in temperature range 150–350 °C [1]. The studies of isochronal anneals allow us to choose the temperatures 160–220 and 300–350 °C as the most appropriate them for isothermal anneals.

The measured optical absorption spectra of the $ZnGeP_2$ samples and their changes with anneal expositions were analyzed on base of the Boltzmann's approximations just as [1] because this procedure turns out much stable as compared with the least squares fitting to the results of model calculations for optical absorption cross section for different types of electrons transition under optical excitation [2].

2. Isothermal annealing technique

Post-irradiation anneals were made by conventional techniques. The irradiated $ZnGeP_2$ samples were placed in a pre-heated furnace kept at the assigned temperature T chosen in accordance with the results of the isochronal anneals [1].

The most interesting points of temperature scale are 180 and 320 °C for isothermal anneal. Taking in account that anneals can be partially carrying out during samples heating and cooling (about 3 min each), the shortest exposition time, Δt_1 was selected as 10 min. The treatment of measurements was assumed on base of solutions for well-known differential equation describing relaxation process for disappearance of non-equilibrium defects [3]:

$$d(\Delta N)/dt = -\Delta N^{x}\, W(T), \qquad (1)$$

where power x is the generalised characteristics of drains ($x = 1$ in case of "infinite" drains power and x is equal to the order of chemical reaction reduced on 1), $W(T)$ is function of anneal temperature T and the migration energy Em of non-equilibrium defects

$$W(T) \sim A \exp[-Em/(k_B T)]. \qquad (2)$$

Here k_B is the Boltzmann constant; A is the pre-exponential numerical factor.

The measurements of absorption coefficient were performed for each sample consequently: firstly at one temperature and then after saturation of changes for measured values at used temperature another temperature of anneal was applied.

3. Absorption coefficient spectra behavior for the $ZnGeP_2$ crystals under e-beam irradiation

Figure 1 presents the changes of optical absorption coefficient spectra of the $ZnGeP_2$ crystals under influence of e-beam irradiation. These spectra indicated the typical behavior of absorption spectra for ZGP samples produced by IMCES SB RAS.

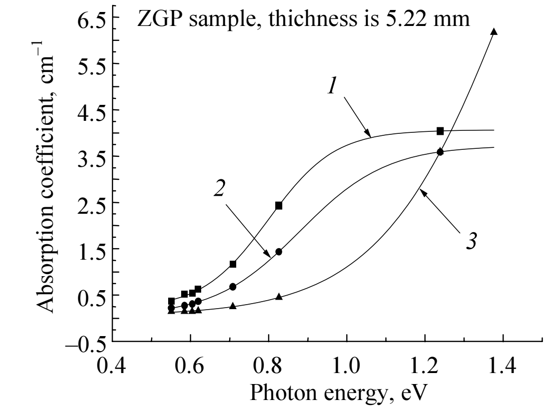

Fig. 1. Optical absorption spectra for ZGP sample with thickness of 5.22 mm: *1* – after post growth anneal; *2*, *3* – after two-sides e-beam irradiation with flux of $0.55 \cdot 10^{17}$ and $3.1 \cdot 10^{17}$ cm^{-2}, accordingly. Solid lines are approximations by Boltzmann functions

From Fig. 1 one can easy to see that optical absorption spectra changes due to amplitude factor what can be explained by the Fermi level move and additionally in connection with the energetic parameters of absorbing centers what together result in “disappearance” of optical absorption in 2 microns region.

4. Isothermal annealing of irradiated $ZnGeP_2$ samples

To estimate the relaxation characteristics of anneal we have used the changes of amplitude parameters optically active centres fitted to the Boltzmann curves.

Smoothed curves for measured spectra are presented in Fig. 2.

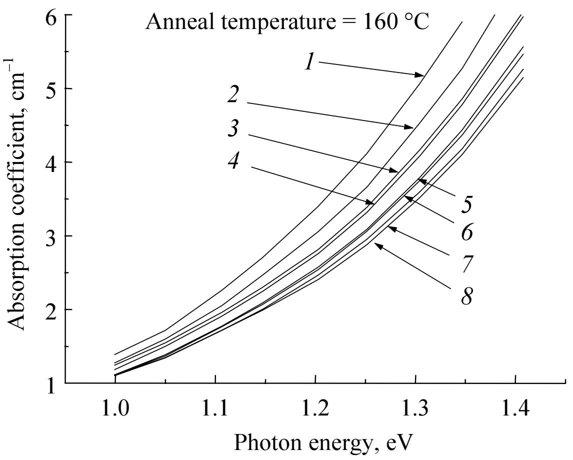

Fig. 2. Behavior of absorption coefficient spectra of $ZnGeP_2$ sample initially irradiated from two sides by e-beam flux of $3.1 \cdot 10^{17}$ cm^{-2} under isothermal anneal at 160 °C: *1* – initial spectrum; *2–8* – spectra obtained after total exposition time of 470, 2000, 4400, 8700, 17000, 32900, and 69500 s, accordingly

The energetic position of middles of the Boltzmann approximations E_{X_0} = 1.32–1.37 eV was varied less than 3% of the estimated values therefore the amplitudes ($A_{1.35}$) of optical absorption spectra at energies quantum of 1.35 eV were taken for following analysis.

Because of absorption coefficient amplitudes at fixed wavelength can be functions of two main parameters of defects such as concentration and energy position that we had used also an equivalent of concentration which was calculated by integration of spectra on energy $S_{1.35}$.

Results of the least squares fitting of measured spectra obtained at post irradiation anneal at 160 °C to the Boltzmann approximations are presented in Table 1.

Table 1. Characteristics of optical absorption spectra of $ZnGeP_2$ crystal depending on the total exposition time of post irradiation anneal at temperature 160 °C

No. spectra	*t*, s	$A_{1.35}$, cm^{-1}	*dE*, eV	$S_{1.35}$, eV/cm
init	0	5.905	0.225	1.37
1	470	5.27	0.229	1.246
2	2000	4.855	0.244	1.179
3	4400	4.780	0.232	1.140
4	8700	4.436	0.232	1.062
5	17000	4.368	0.243	1.060
6	32800	4.180	0.238	1.027
7	69500	4.035	0.243	1.007

The values of time decay for measured amplitudes and areas calculated of absorption spectra were fitted by two ways: firstly to Exponential Decay approximation (ED1) and then to the Generalised Hyperbola (HG):

$$y = a - b/(1 + ct)^{1/d}, \quad (3),$$

where *a*, *b*, *c*, and *d* are the parameters of fitting. Herewith *a* is the minimal value (background level) of function reached in infinite limit of variable; *b* is the total interval of function changes; *c* is the constant reciprocal to decay in power of *d*; *d* is the order of reaction reduced on 1.

As calculations showed, the data fitting to HG turned out much better from point of view of the sum for squares of discrepancies. This is clearly seen in Fig. 3 also.

Herewith the optimal value *d* is about 1.5. Such result means that relaxation mechanism of anneal is close to bimolecular one because reaction order $r = d + 1$. The deviation *d* from 1 can be related to either presence some drains of different power or variable migration energy of non-equilibrium defects introduced under irradiation.

The same studies and estimations were made for anneal temperature of 180 °C. According data are presented in Fig. 4 and Table 2.

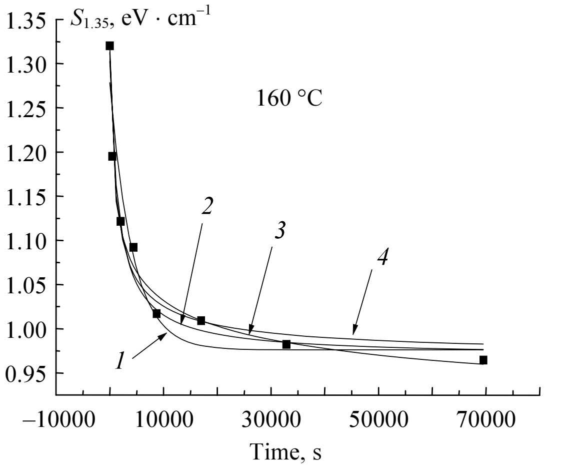

Fig. 3. The results of fitting to different basic functions for values $S_{1.35}$ depending on exposition time irradiated $ZnGeP_2$ sample annealed at 160 °C: *1* – ED1 approximation; *2* – bimolecular ($r = 2$, fixed); *3* – free parameters; *4* – fixed background (*2–4* – HG approximation)

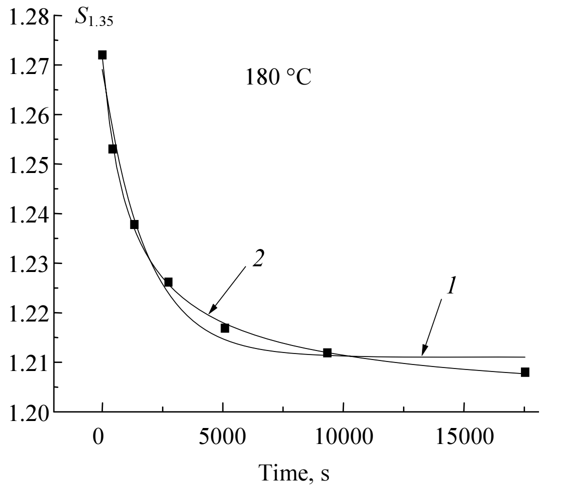

Fig. 4. The result of fitting to different basic functions for experimental data obtained under anneal at 180 °C: *1* – ED1 approximation; *2* – HG approximation

Table 2. Generalized characteristics of optical absorption spectra of $ZnGeP_2$ crystal depending on the total exposition time of post irradiation anneal at temperature 180 ^{o}C

No. spectra	t, s	$A_{1.40}$, cm^{-1}	dE, eV	$S_{1.40}$, eV/cm
init	0	5.249	0.2426	1.272
1	433	5.148	0.2437	1.253
2	1324	5.072	0.2443	1.238
3	2742	5.008	0.2449	1.226
4	5088	4.967	0.2451	1.217
5	9337	4.942	0.2451	1.212
6	17540	4.928	0.2448	1.208

The results of calculation for both anneal temperatures were joined in Table 3.

Table 3. Calculated results of the least squares fitting to Generalised Hyperbola for estimated amplitudes of optical absorption spectra depending on anneals exposition time at 160 and 180 °C

T, °C	Optimal fitting parameters			
	a	b	c	d
160	0.96455	–0.3484	0.00138	1.54089
180	1.19	–0.0722	0.00112	1.38347

From expression (3) and solution of equation (1) for bimolecular mechanism relaxation of non-equilibrium defects it can be obtained following relations allowing to carry out an estimation for the energy migration of the first stage of post-irradiation anneal of $ZnGeP_2$:

$$W(T) = c/[d(-b)^d] \tag{4}$$

and

$$E_m = k_B \ln [W(T_1) / W(T_2)] / (T_1^{-1} - T_2^{-1}). \tag{5}$$

Joint consideration of the results obtained at two isothermal anneals and the estimations described above applied to them gave the value of migration energy as much as $E_m = 1.35 \pm 0.2$ eV.

The obtained value of migration energy is intermediate one between typical values (about 1 eV) for of simple point defects (vacancies) created by irradiation [3] and effective migration energy of vacancy pairs consisting of the "true" migration energy and energy of bonds of two vacancies described as electrical interaction of point charges in continuous medium:

$$E_{electric} = q^2/(4\pi\varepsilon\varepsilon_0 R_{D\text{–}A}), \tag{6}$$

where q is the electron charge; ε and ε_0 are the relative dielectric susceptibility of $ZnGeP_2$ and the absolute dielectric susceptibility of vacuum, accordingly; $R_{D\text{–}A}$ is the distance between interacted donor and acceptor. The maximal value of the energy electrical interaction for *D–A* pairs can reach ~0.3 eV if to assume that the closest distance between defects in these pairs is determined by the radius of the second coordination sphere.

5. Conclusion

The optical absorption spectra for the $ZnGeP_2$ single crystals irradiated by fast e-beam were measured.

Behavior of optical absorption spectra under influence of isothermal anneals at 160 and 180 °C was investigated.

The obtained data makes us to explain anneals kinetics on base of bimolecular reaction non-equilibrium defects appeared under irradiation.

The migration energy of anneal was estimated as high as 1.35 eV

Both obtained reaction order and estimated value of the migration energy allow to propose that the vacancy pairs take sufficient participation in processes of defects anneal at 160–180 °C in irradiated $ZnGeP_2$ single crystals.

The estimated migration energy value disaccord significantly with data obtained on base of ED1 processing and contradicts to reported in [4] where data are obtained with samples of low perfection.

Estimation of this work agreed with conclusion about second order reaction for this stage of anneal of irradiated $ZnGeP_2$ crystals [5] made on base of electrical measurements.

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