

## **RADIATIVE RECOMBINATION IN ELECTRON-IRRADIATED GaP CRYSTALS**

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Photoluminescence measurements of S- and Te-doped GaP crystals, irradiated with 10-MeV electrons, are reported. The observed quenching of green and red luminescence bands under irradiation and their recovery at subsequent isochronal annealing are discussed aiming to reveal the possible mechanisms of the relevant recombination centres transformation including vacancy-involved complexes and non-radiative recombination centres.

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### **1. Introduction**

The studies of irradiation-induced structural damage in gallium phosphide propose different models of behaviour for both point and complex defects which also depend on the type and energy of the irradiating particles. Deep level transient spectroscopy [1], optical absorption [2–4], Raman scattering [5], optically detected magnetic resonance [6], positron annihilation [7, 8] techniques are effectively applied for the studies of irradiation effects in GaP. Gallium phosphide is a well-known luminescent material and its luminescence spectra have been studied thoroughly for a wide variety of dopants [6–23]. However, much less papers are devoted to the studies of radiation effects on GaP luminescence, mostly electro- and cathodoluminescence [24–26], and they deal with rather narrow set of impurities and smaller irradiating electron fluences. Neutron irradiation effect on GaP luminescence was also studied [23, 27]. Since the problem of degradation of GaP-based light emitting diodes is important not only in view of the effects of electric field and temperature [28], but also due to the possible irradiation effects, such studies seem to be interesting from the point of view of investigation of carrier recombination processes, radiation defect formation and possible applications.

### **2. Experimental**

Here we report the results of photoluminescence (PL) measurements for high-energy electron-irradiated Czochralski-grown Te- and S-doped GaP ( $n_0 \sim 10^{17} \text{ cm}^{-3}$ ) single crystals, irradiated with fluences  $\Phi$  up to  $10^{18} \text{ cm}^{-2}$  of 10-MeV electrons. The irradiation was carried out at room temperature on a M-30 microtron of the Institute of Electron Physics, Ukr. Nat. Acad. Sci. (Uzhhorod, Ukraine). In order to avoid overheating in the course of irradiation the samples were cooled by evaporating liquid nitrogen, the temperature being controlled by copper-constantane thermocouple.

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Isochronal annealing studies were carried out from 340 to 915 K with a 25-K step and 20-min duration of each annealing session.

PL spectra were measured at 4.2 and 77 K on LOMO DFS-12 and DFS-24 monochromators with a FEU-79 phototube and a photon counting system, He-Cd ( $\lambda=441.6$  nm) and Ar<sup>+</sup> ( $\lambda=488.0$  nm) lasers being used for excitation.

### 3. Results and discussion

The most intense luminescence bands of GaP, located in the visible spectral range, are generally referred to as "green" and "red". In the green part of the spectrum below the energy gap at low temperatures exciton bands are revealed, their position depending on temperature and on the impurities on which the excitons are localized [11, 12]. As seen from Fig. 1, the recombination of exciton localized on tellurium in GaP gives rise to an intense narrow band centred at  $h\nu=2.309$  eV ( $T=4.2$  K) and its several phonon sidebands, much weaker and somewhat broader (curve 1). A broad intense band near 2.20 eV whose position decreases with temperature more rapidly than the energy gap, can be related to the radiative recombination of free holes on neutral Te donors [11]. In [15] this band, observed in GaP with intermediate donor concentration, is attributed to recombination on donor-acceptor pairs involving tellurium donors and carbon acceptors. A similar band is observed in GaP doped with S donors.

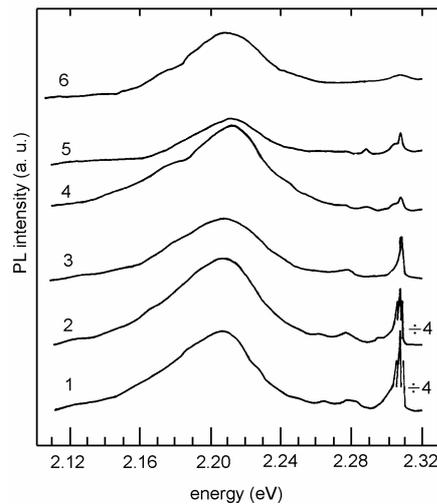


Fig. 1. Green photoluminescence spectra at 4.2 K of Te-doped GaP crystals irradiated with 10-MeV electron fluences  $\Phi = 0$  (1),  $5 \times 10^{15}$  (2),  $1 \times 10^{16}$  (3),  $3 \times 10^{16}$  (4),  $5 \times 10^{16}$  (5),  $7 \times 10^{16}$  (6)  $\text{cm}^{-2}$ .

Irradiation of GaP:Te crystals with 10-MeV electrons results in gradual decrease of the PL band intensities with the irradiation dose. It is seen from Fig. 1 that the intensity of the broader green band near 2.20 eV decreases much slower than the exciton band intensity. Note that the phonon sidebands of the latter also decrease in intensity with  $\Phi$ , however, not so rapidly, a slight shift of their energy position and some redistribution of intensities being also observed. This fact can be, in our opinion, related to the redistribution of phonon-assisted transitions involved into exciton radiative recombination due to disorder-induced selection rule relaxation which is also observed in Raman scattering studies [5].

A more intense red PL band centred in our case at 1.70 eV for intentionally undoped GaP, 1.72 eV for GaP:Te and 1.78 eV for GaP:S, is often related to the charge carrier recombination on the pairs of a VI-group donor and an acceptor of questionable origin [10–12, 17]. However, a number of investigations have revealed a complex character of this band following from the time-decay studies [10], correlation of luminescent and electric measurements [19], annealing studies [21]. Note that the

above noticed difference in the band maximum energy position does not exactly correlate with the difference between S and Te donor ionization energies known from [11, 29], what can be related to the fact the relevant acceptor level being different for the S- and Te-doped samples. A similar discrepancy was observed in [21].

As seen from Fig. 2, the red PL band intensity also decreases with  $\Phi$ . Note that its decrease rate is more rapid than that for the green PL band (2.20 eV) intensity.

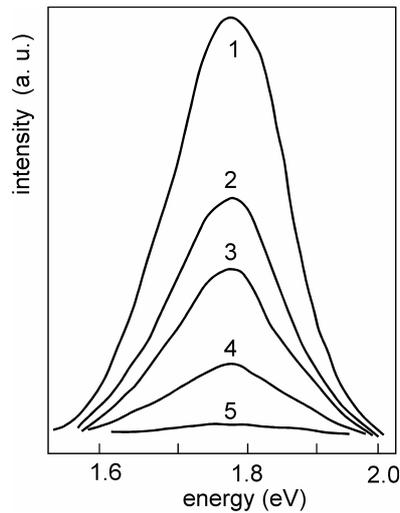


Fig. 2. Red photoluminescence spectra at 77 K of S-doped GaP crystals irradiated with 10-MeV electron fluences  $\Phi=0$  (1),  $10^{16}$  (2),  $10^{17}$  (3),  $3 \times 10^{17}$  (4),  $10^{18}$  (5)  $\text{cm}^{-2}$ .

It is worth notice that PL intensities were normalized by the intensities of the first-order Raman scattering bands, measured simultaneously. Since the exciting light wavelength (488 nm) was within GaP fundamental absorption range, resonant Raman effects could be expected which are known to be revealed as interaction between the electron subsystem of a crystal and LO phonons [30]. Note that in our case the redistribution of intensities between TO and LO phonons with  $\Phi$  was observed (Fig. 3).

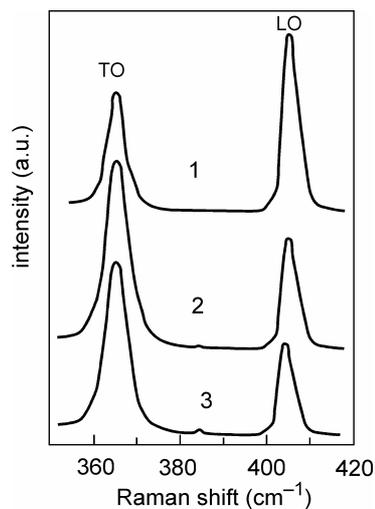


Fig. 3. Unpolarized first-order Raman spectra backscattered from the (111) plane for non-irradiated (1) and irradiated with  $\Phi=2 \times 10^{18}$   $\text{cm}^{-2}$  (2) and  $7 \times 10^{18}$   $\text{cm}^{-2}$  (3) 10-MeV electrons GaP crystals, measured at 80 K with the excitation of  $\lambda=488.0$ -nm laser light.

In accordance with Raman scattering selection rules for zincblende-type structures for backscattering from the (111) surface TO and LO phonons are observed simultaneously, hence from their intensity ratio Faust-Henry coefficient  $G$  can be estimated [30]:

$$\frac{d_{LO}}{d_{TO}} = \left( 1 - \frac{\omega_{LO}^2 - \omega_{TO}^2}{G\omega_{TO}^2} \right), \quad (1)$$

$\omega_{LO}$  and  $\omega_{TO}$  being the phonon frequencies,  $d_{LO}$  and  $d_{TO}$  – the corresponding components of the Raman scattering tensor. As follows from Eq. (1), Raman efficiency for LO phonon scattering is enhanced ( $G < 0$ ) or reduced ( $G > 0$ ) with respect to that of TO phonon depending on the sign and value of  $G$ . The calculated value of this coefficient for GaP crystals  $G_{\text{theor}} = -0.37$  and the experimental one  $G_{\text{exp}} = -0.64$  are known from [30]. We have obtained for the non-irradiated sample from the experimental Raman spectra (Fig. 3)  $G_{\text{exp}} = -0.45$ . With the increase of the irradiation dose the Faust-Henry coefficient changes its sign (at  $\Phi \geq 2 \times 10^{18} \text{ cm}^{-2}$   $G_{\text{exp}} = 0.48$ ).

As follows from [30], the value  $G$  is given by

$$G = \frac{e^* (\partial\chi/\partial u)}{\mu\omega_{TO}^2 (\partial\chi/\partial E)} \quad (2)$$

where  $e^*$  is the dynamical charge of one of the atoms,  $\mu$  is the reduced mass ( $\mu^{-1} = M_{\text{Ga}}^{-1} + M_{\text{P}}^{-1}$ ),  $\partial\chi/\partial u$  is the deformation potential,  $\partial\chi/\partial E$  is electrooptical coefficient.

Since according to Eq. (2)  $G$  is a measure of the ratio of the "mechanical" strength of bonds (the deformation potential) to the electric (Fröhlich) one in the electron-phonon interaction [30], it is seen that disorder induced in GaP by high-energy electron irradiation at high fluences results in the redistribution of these contributions.

Hence, due to the above discussed effects, affecting LO phonon scattering, only TO phonon intensity was chosen appropriate for the normalization of the luminescence intensity.

The irradiation-induced decrease of intensities of all the observed PL bands as well as different quenching rates for different bands are consistent with the majority of earlier electroluminescence and cathodoluminescence studies for MeV-electron- [24, 26] and neutron-irradiated [27] GaP. Only the authors of [25] observed the increase of cathodoluminescence under 13-keV electron irradiation which they attributed to recombination-enhanced defect reactions. However, the mechanism of keV-electron interaction with crystal is strongly different from that for much more energetic MeV-electrons and neutrons which result in the formation of vacancies, interstitials and antisite defects or even of defect clusters in the crystal lattice. A strong increase of red PL in neutron-irradiated GaP is related to recombination centres being formed by transmuted impurities [23].

Generally two main mechanisms of luminescence quenching under irradiation are considered. The first one is related with the radiation-induced formation of non-radiative recombination centres, the second one concerns transformation of the existing luminescence centres due to the interaction with the radiation-introduced primary defects which are known to be mobile in gallium phosphide not only at room temperature but even at much lower temperatures [3, 4]. Which of the mechanisms is predominant, is still a question, the answer to which obviously depends on a number of factors, in particular, on the irradiating particles type and energy. The first mechanism is considered to be predominant in the case of neutron irradiation when the defect clusters are formed which are known to favour the non-radiative recombination [27]. However, the issue seems more doubtful for MeV-electron irradiation. Recombination channels involving vacancies are supposed to be the competitors of the green-band transitions, and therefore the green PL intensity should decrease at the radiation-induced growth of vacancy concentration [14, 20], what is consistent with our experimental results. On the other hand, as supposed in [20] on the base of comparison of cathodoluminescence, scanning electron microscopy and positron annihilation studies, vacancies in GaP form a recombination centre, probably a vacancy-donor complex, associated with the red emission. Such assumption can hardly correlate with

our results since we observed the red PL quenching with  $\Phi$  even more rapidly than the green one what would not be expected in case the red PL centres involving vacancies whose amount should increase under irradiation.

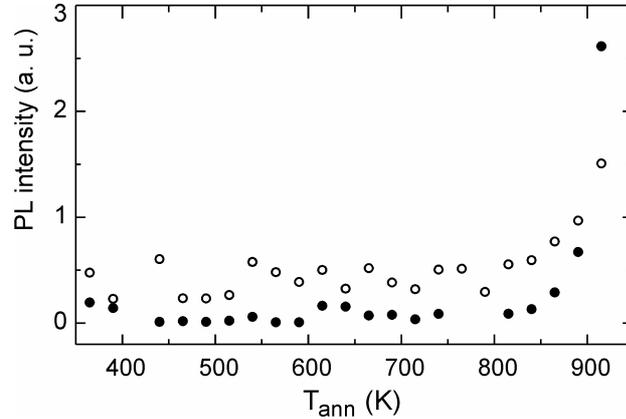


Fig. 4. Dependence of green (2.20 eV, dark circles) and red (1.78 eV, open circles) PL band intensity in the 10-MeV electron-irradiated ( $\Phi=10^{17}$  cm $^{-2}$ ) GaP:S on the subsequent isochronal annealing temperature. The PL measurements were performed at 77 K with excitation by 488.0-nm Ar $^{+}$ -laser line.

Additional information on the mechanisms of radiation defects formation can be obtained by isochronal annealing studies. Fig. 4 illustrates the results of annealing performed for S-doped GaP irradiated with 10-MeV electrons ( $\Phi=10^{17}$  cm $^{-2}$ ). As it is clearly seen, the recovery of both green and red PL band intensity is observed at the annealing temperature  $T_{\text{ann}}>850$  K.

It should be noted that optical absorption studies of electron-irradiated GaP have shown the annealing stages at much lower temperatures of 90 K, 240–260 K [3, 4] for the low-temperature irradiated samples and 420, 470–510, 540–580 (the main stage) and 650–670 K [31] for the room-temperature irradiated samples, the stages at 470–510 and 540–580 K being attributed to the annealing of phosphorus and gallium vacancies, respectively. Note that after the last stage ( $T_{\text{ann}}>670$  K) the absorption level for the non-irradiated sample is practically recovered [31]. Generally similar stages are reported for electron-irradiated (450–500 K and 570–670 K [32]) and proton-irradiated (450–500 K [8]) GaP. However, in proton-irradiated GaP there is also a pronounced annealing stage at 800–870 K [8], and in neutron-irradiated GaP a broad annealing stage at 600–1000 K (with the steepness increase at 850–950 K) is observed [7, 8]. Such transformation from lower-temperature to higher-temperature annealing stages with the increase of the irradiating particles energy is consistent with gradual transition from isolated defects to formation of defect clusters in GaP. Note that a similar trend is also reported in GaAs [8].

Hence, we may conclude that in electron-irradiated GaP radiation-induced optical absorption and PL quenching are caused by different types of radiation defects. The similar behaviour of irradiation-induced quenching and annealing-induced recovery for both green and red PL bands in our case enables us to relate these processes to non-radiative recombination centres formed under 10-MeV electron irradiation and annealed above 850 K. It is known that non-radiative recombination is often related to defect clusters which are reported to anneal in GaP in the same temperature range. It is possible that room-temperature 10-MeV electron irradiation in GaP gives rise not only to the isolated defects but also to their clusters what agrees with the radiation defects mobility at room temperature known from [3, 4] and with Raman scattering data indicating the increase of the contribution of the deformation potential into the electron-phonon interaction.

#### 4. Conclusions

Photoluminescence studies of 10-MeV electron-irradiated S- and Te-doped gallium phosphide have shown the decrease of both green and red PL band intensities with the irradiation dose, the different quenching rates being most likely related to the different initial concentration of the corresponding recombination centres. Isochronal annealing studies have shown the intensities of both bands to recover in the same temperature range. Comparison of the experimentally obtained results with our earlier optical absorption data and with luminescence and positron annihilation results of other authors enabled us to conclude that 10-MeV irradiation leads to the formation of non-radiative recombination centres which are annealed above 850 K. The role of such centres can possibly be played by defect clusters whose formation correlates with the mobility of radiation-induced defects in GaP at room temperature.

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