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Effect of $ZnGeP_2$ annealing in Zn vapor on the laser spectrum

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The work is devoted to experimental investigation of the band structure, deep local centers and complexes as well as of generation/recombination processes in the $ZnGeP_2$ semiconductor crystal. The crystals grown by Bridgeman technique, annealed in Zn vapor and unannealed were studied. The dynamics of the defect structure change in the $ZnGeP_2$ crystal due to annealing in Zn vapor has been considered as well as the presumable identification of impurity centers.

Статья посвящена экспериментальному исследованию зонной структуры, глубоких локальных центров и комплексов, а также генерационно-рекомбинационных процессов в полупроводниковом кристалле $ZnGeP_2$. Исследовались кристаллы, выращенные методом Бриджмена: отожженные и неотожженные в парах Zn. Рассмотрена динамика изменения дефектной структуры в кристалле $ZnGeP_2$ после отжига в парах Zn, а также возможная идентификация примесных центров.

Semiconductors A^2B^5 form the development base for the modern optoelectronics and solar power engineering. A further investigation in diamond-like semiconductors makes it possible, on the one hand, to reveal new physical phenomena and regularities, and at the other hand, to satisfy the constant demands of the semiconductor electronics in creation of novel devices and improvement of the existing ones. It is just the $A^2B^4C^5_2$ compounds that are the closest ternary analogs of binary A^2B^5 semiconductors. These compounds are to be studied at a new level to realize in practice the unique properties thereof revealed at the initial stage, in particular, in $ZnGeP_2$, thus offering more possibilities in the practical use of the potentials found in those substances. The aim of this work is to study the effect of annealing in Zn vapor on $ZnGeP_2$ with chalcopyrite lattice grown by Bridgeman technique.

Varying the crystallization conditions and dopant type, one can control the photosensitivity, radiative recombination (RR) and optical absorption of the crystals. In the intentionally undoped samples grown from gas phase, the short-wavelength RR component (1.55 to 1.75 eV) and the long-wavelength one (1.4 eV) dominate. As the crystals are enriched in Zn, the 1.55–1.75 eV emission becomes weakened while the 1.33 eV one is intensified. Introduction of excess Ge into the raw material is accompanied by broadening of the 1.4 eV band, while the short-wavelength emission is weakened and observed as an extended "tail" only [1]. The presence of two volatile components and one amphoteric element (Ge) in $ZnGeP_2$ is a real precondition to various types of intrinsic lattice defects at all high-temperature processes involving this substance. The evaporation will result in formation of zinc (V_{Zn}) and phosphorus (V_P) vacancies in the crystal. In the course of thermal annealing (TA) in an evacuated space together with zinc, the number of V_{Zn} must decrease. In fact, at high zinc vapor pressure, the phosphorus vapor pressure must decrease, thus resulting in increasing

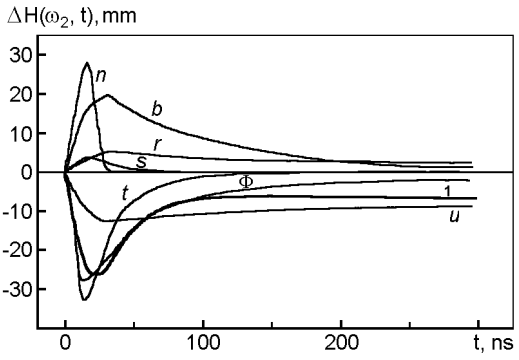

Fig. 1. $\Delta H(\omega_2,t)$ oscillograms for tetragonal-syngony $ZnGeP_2$ crystals grown by Bridgeman technique and annealed in zinc vapor. The oscillograms are obtained at $\hbar\omega_2$ = 1.45 eV (1) and 1.84 eV (2) and I_l = 9 MW·cm^{-2}, $\mathbf{q}_1\|\mathbf{q}_2\|\mathbf{ce}_1\|$ $\mathbf{e}_2$ without the sample illumination. *b*, *u*, *s*, *t*, Φ, and *r* are components of the oscillogram 1.

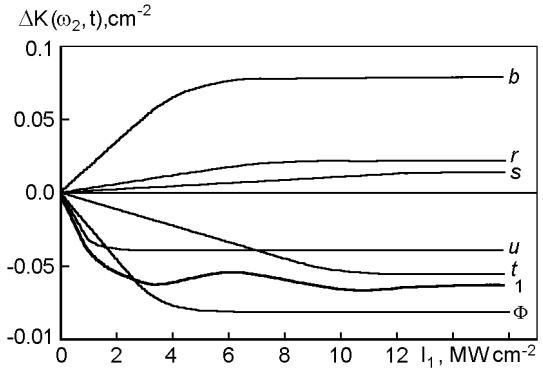

Fig. 2. Intensity dependences $\Delta K(\omega_2,t) = f(I1)$ at $\hbar\omega_2$ = 1.69 eV, $\mathbf{q}_1\|\mathbf{q}_2\|\mathbf{ce}_1\|$ $\mathbf{e}_2$; t = 35 ns, *b*, *u*, *s*, *t*, Φ, and *r* are components of the intensity dependence.

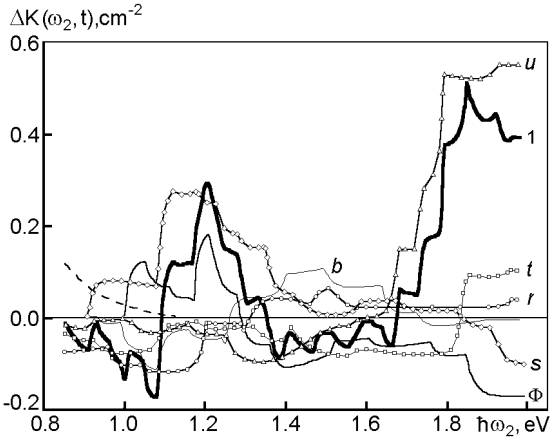

Fig. 3. Spectral dependences $\Delta K(\omega_2,t)$ (1) obtained at $\mathbf{q}_1\|\mathbf{q}_2\|\mathbf{ce}_1\|$ $\mathbf{e}_2$, t = 35 ns, I_l = 9 MW·cm^{-2}, without the sample illumination. *b*, *u*, *s*, *t*, *Φ*, and *r* are components of the spectrum 1 caused by transitions between the *v* and *c* bands and the corresponding *b*, *u*, *s*, *t*, Φ, and *r* extrinsic centers.

number of V_P while the V_{Zn} formation will be suppressed. In this case, the V_P concentration will be expected to exceed the V_{Zn} one. In [1], shallow donor levels ($E_D \le 10$ meV) have been found.

When analyzing the lattice defect model, the analogy principle is used as well as the available knowledge on that subject in an analogue compound $ZnGeP_2$–GaP where the vacancies in the gallium sublattice believed to be acceptors while V_P are donors. Basing on thermal association of $ZnGeP_2$, the V_{Ge} concentration can be assumed to be much lower than the V_{Zn} one. It is just V_P and anti-structure defects P_{Zn} that are to be considered as the main donor defects in $ZnGeP_2$, the concentrations thereof being close to one another.

The hole conduction type and low resistance of $ZnGeP_2$ crystals that interacted with Zn vapor may be due to the anti-structure defects Zn_P [1]. In fact, the TA in zinc vapor gives rise to V_P, the concentration thereof being increased in the absence of zinc. However, the donating action of V_P is now suppressed, since zinc occupies the free sites of phosphorus.

Fig. 1 shows oscillograms $\Delta H(\omega_2,t)$ obtained in the points $\hbar\omega_2$ = 1.45 eV (1) and 1.84 eV (2) at the laser radiation intensity I_l = 9 MW·cm^{-2}, $\mathbf{q}_1\|\mathbf{q}_2\|\mathbf{c}\perp\mathbf{e}_1\|$ $\mathbf{e}_2$ without the sample illumination. The $\Delta H(\omega_2,t)$ and $H_0(\omega_2)$ were measured at the probing beam energy $\hbar\omega_2 \in$[1.10 eV; 2.00 eV] at 0.005 to 0.02 eV steps both without illumination and under illumination by third source. Fig. 2 presents the intensity dependence obtained for $ZnGeP_2$ crystals annealed in Zn vapor in the point $\hbar\omega_2$ = 1.69 eV (1). The intensity dependences were measured within the energy range $\hbar\omega_2 \in$ [1.10 eV; 2.00 eV] at 0.01 to 0.05 eV steps. The intensity dependences $\Delta H(\omega_2,t)$ answer to the values at the time moment t = 35 ns.

Using the intensity dependences and the values of the absorption coefficient change $\Delta K(\omega_2,t)$ in the intermediate points, the spectrum $\Delta K(\omega_2,t) = \varphi(\hbar\omega_2)$ presented in Fig. 3 was obtained. Here, *b*, *u*, *s*, *t*, Φ, and *r* are components of the kinetics, intensity points and spectral dependences. Each ex-

perimental point answers to several tens of measurements. The confidence intervals answer to the confidence probability of 0.8.

Comparing the results obtained for the samples annealed in Zn vapor with those for unannealed ones, one can see that the same extrinsic centers are present in the band gap of those crystals. However, the $\Delta K_a^{(1)}(\omega_2,t)$ and $\Delta K_r^{(1)}(\omega_2,t)$ spectra change the signs under annealing. In unannealed samples grown by the vapor phase synthesis technique, the extrinsic centers are emptied by laser pulses, thus evidencing the formation of compensating donor extrinsic centers; as a result, the Fermi level is shifted towards the band gap middle. Under annealing in Zn vapor, the Fermi level is lowered, and as a result, the laser pulses favor the additional occupancy of the extrinsic centers *a* of unannealed samples. The displacement of the Fermi level explains also the inversion of $\Delta K_r^{(1)}(\omega_2,t)$ under the crystal annealing in Zn vapor. Prior to the annealing, the laser pulses empty the *r* centers with a high initial occupancy level in $ZnGeP_2$, while after the annealing, the occupancy level of the *r* centers is low and the laser pulses provide an additional occupancy thereof.

For the annealed samples, the bands peaked at $\hbar\omega_2 = 1.21$ and 1.325 eV show a higher intensity as compared to the unannealed ones. This can be explained by the fact that it is just acceptors that are deep components of donor-acceptor pairs that answer to those bands. In this case, when the Fermi level is lowered, the occupancy of the acceptor components will decrease, resulting in a more intense filling thereof by the laser pulses and thus in an increased additional absorption of the probing light in the donor-acceptor pairs. The crystal annealing may result also in an increased concentration of the donor-acceptor pairs; however, as that concentration decreases, it is just the consequences of the Fermi level lowering that are predominant.

As to the absence of *b* centers in the crystals grown by the Bridgeman technique, this fact can be interpreted in the fashion that the *b* defects of the lattice interact with the lattice defects appearing in the course of growth. As a result, the position of the *b* level in the band gap may be changed. Most likely, the *b* centers interact with the lattice defects appearing in the course of growth, resulting in formation of complexes corresponding to the *r* energy levels. Those centers differ insignificantly from the *b* ones in the depth of occurrence, kinetics, and maximum bending.

Bearing in mind that, as the crystal is annealed in zinc vapor, the zinc vacancy concentration must decrease thus resulting in a lowered intensity of the $\Delta K_f^{(1)}(\omega_2,t)$ spectrum corresponding to those vacancies, the comparison of the spectra for annealed and unannealed samples would permit us to determine the center corresponding to the zinc vacancies. However, the absorption at the acceptor centers is intensified at the annealing due to the Fermi level lowering. Such an intensification can compensate the weakening caused by the reduced concentration of the centers. But the intensity of the spectrum corresponding to the zinc vacancies become reduced at a considerable reduction of their concentration. Comparing the spectrum in Fig. 3 with the similar spectral dependences for unannealed samples [2], it is seen that the intensities of the *o*, *p*, *e* spectra for unannealed samples are increased while that of the *d* one is reduced. The increased intensity of the *p* and *e* spectra and reduced one of the *d* spectrum could be explained by the Fermi level lowering due to the crystal annealing in zinc vapor. But that lowering at an unchanged concentration of *p* centers would result in a reduced *p*-spectrum intensity. Thus, the increased *p*-spectrum intensity due to the annealing may be caused by a considerable increase of the *p* center concentration.

Thus, the enrichment of the samples in zinc causes an increased concentration of the *p* centers. This fact evidences that it is just the associative defects capturing zinc atoms that can be such *p* centers. Such associates can be exemplified by the $V_P^+ + Zn_i$ ones possessing the energy level in the band gap close to that of the *p* centers.

The studies of defects in $ZnGeP_2$ using EPR and ENPR [4–6] have revealed the V_P^+, P_{Ge}, V_{Zn}, V_P^0, Ge_{Zn}, V_{Zn}^-, V_{Zn}^0, Zn_{Ge}, Ge_P defects as well as those consisting of Zn atoms and V_P, the V_{Zn} and V_P defects dominated.

To identify the defects revealed by means the measured spectra, we have studied also the samples enriched in zinc and those enriched in germanium. That enrichment was attained by the melt stoichiometry deviations. As the melt is enriched in zinc, the intensities of the *o*, *p*, *d*, and *e* spectra are increased as well as those of donor-acceptor transitions corresponding to $\hbar\omega_2$ maxima at 1.210 eV and 1.325 eV. As the melt is enriched in germanium, the

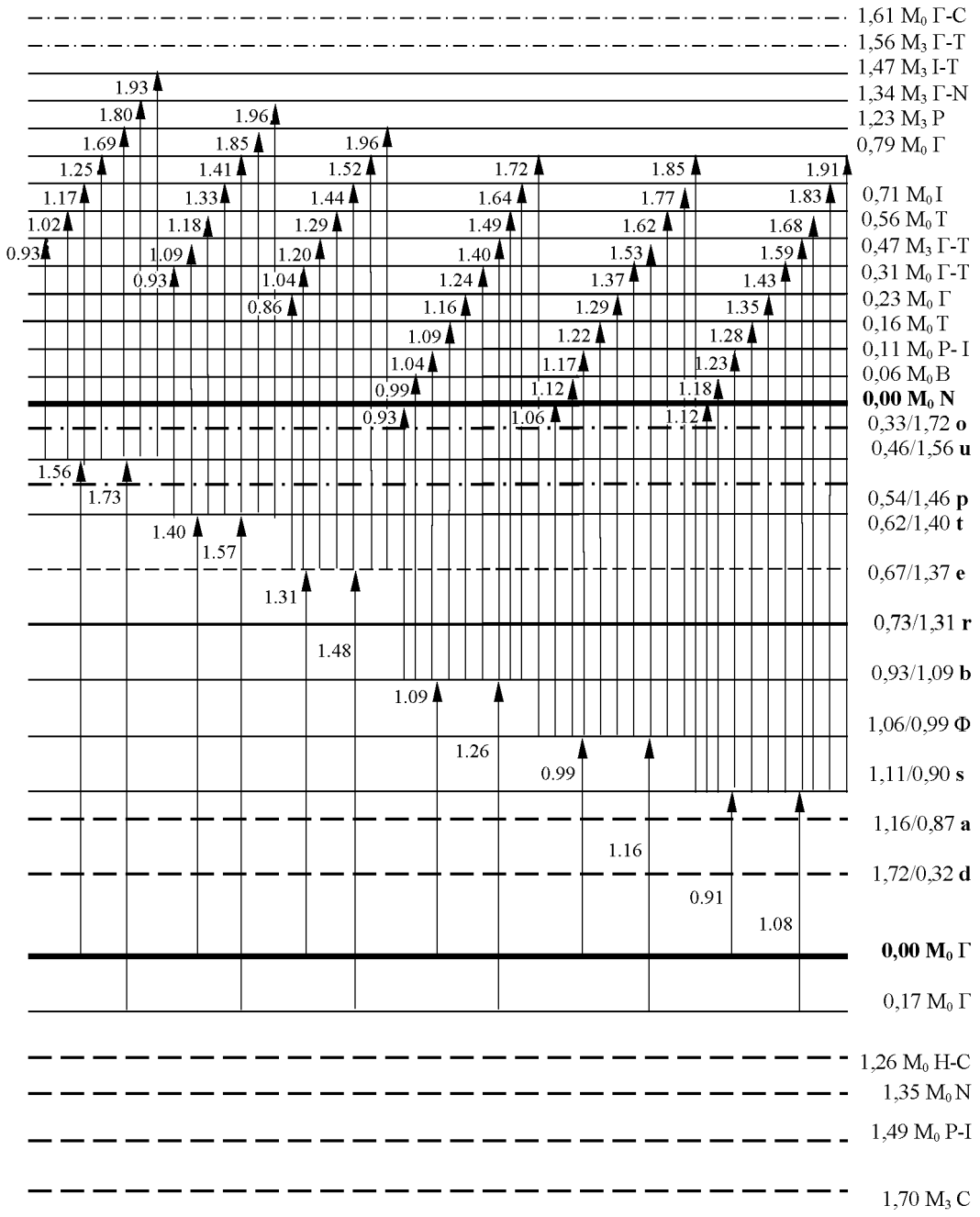

Fig. 4. Energy diagram of extrinsic levels and first order critical points for $ZnGeP_2$ crystals grown by Bridgeman technique and annealed in zinc vapor.

b spectrum appears while *e* and *r* ones are weakened. According to [1, 4–6], V_P, P_{Ge}, Ge_{Zn}, P_{Zn} defects are donors and V_{Zn}, Zn_{Ge}, Zn_P are acceptors.

The Fermi level lowering at the crystal annealing in zinc vapor may be due to increased concentration of the Zn_P anti-structure defects. In fact, the annealing in zinc vapor promotes the formation of V_P, but the donor action is now suppressed as a consequence of the fact that zinc occupies the free phosphorus sites. This results in the Fermi level lowering.

The results obtained allow us to suppose the nature of *a*, *b*, *d*, *e*, *o*, *p*, *r* centers in the unannealed samples. The *a* centers may be zinc vacancies V_{Zn}; the *b* ones, the anti-structure Ge_{Zn} defects; *d*, phosphorus vacancies V_P; *e*, the Zn_{Ge} or Ge_P anti-structure defects; *o*, the anti-structure defects; *p*, the associates of phosphorus vacancies with interstitial zinc atoms; and *r*, the anti-

structure P_{Ge} defects. The above-mentioned defects may be included in associates forming the corresponding centers.

In [7], the optical properties of $ZnGeP_2$ have been studied using photoluminescence and absorption. The revealed spectral band peaked at 1.2 eV was ascribed to transitions in the donor-acceptor pairs. In [8], a luminescence band at 1.33 eV was observed in p-$ZnGeP_2$ crystals (grown by low-temperature crystallization technique) excited by a He–Cd laser ($\lambda = 441$ nm). This band was observed also in the radiative recombination spectra of the crystals grown from the melt enriched in zinc [1]. The association of that band with the donor-acceptor transitions has been discussed neither in [1] nor in [8].

In [1], a radiative recombination band peaked around 1.4 eV was observed. This band coincides with the distance from the o energy level to the conduction band bottom and from the energy position of the M_0 type critical point being 0.45 eV under the conduction band bottom. Since this bend intensity is increased as a germanium excess id introduced into the raw material, it is most likely that the band corresponds to the b centers. In the same work, a pronounced plateau at the quantum energy about 0.80 eV and a wide structureless band at $\hbar \cong 1.80$ eV (300 K) are reported. The plateau position is in accordance with the occurrence depth of the e defect level while the 1.8 eV band corresponds to p, d, and a plateaus in our spectra. Since the 0.8 eV plateau is most pronounced in the photoconductivity spectra of the samples obtained at minimum pressures of phosphorus vapor, the e centers could be believed to be the Ge_P anti-structure defects. The observed pronounced photoconductivity band with the long-wavelength $\hbar\omega \cong 0.70$ eV corresponds to the distance between the o level and the top of the second valence subband (Fig. 4). In [1], observed was also a considerable increase of photocurrent starting from $\hbar\omega > 0.6$ eV. The author [1] associates this fact with the photoactive excitation of the carriers at the acceptor level $E_v + 0.6$ eV that is revealed by the Hall coefficient change [9]. Those acceptor levels coincide with the defect o energy levels formed by the anti-structure acceptor defects Zn_P revealed in this work.

Thus, taking into account the available literature data, Ge deficiency and the crystal annealing in Zn vapor, it can be assumed that the u, t, r, b, Φ, s centers in the annealed crystals are $P_{Zn} + Zn_i$; P_{Ge}; $V_P^+ + V_{Ge}^-$; O; Zn_{Ge}; Zn_P, respectively. The disappearance of the o centers at the annealing can be explained by the P_{Zn} entering into $P_{Zn} + Zn_i$ associates while the disappearance of p centers, by occupancy of germanium vacancies by zinc atoms. As a result, the o (P_{Zn}) and p (V_{Ge}) disappear and new u ($P_{Zn} + Zn_i$) and Φ (Zn_{Ge}) ones appear.

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Вплив відпалу $ZnGeP_2$ у парах Zn на спектр лазерної спектроскопії

Стаття присвячена експериментальному дослідженню зонної структури, глибоких локальних центрів і комплексів, а також генераційно-рекомбінаційних процесів у напівпровідниковому кристалі $ZnGeP_2$. Досліджувалися кристали, вирощені методом Бріджмена: відпалені і невідпалені разом з парами Zn. Розглянуто динаміку зміни дефектної структури у кристалі $ZnGeP_2$ після відпалу в парах Zn, а також можливу ідентифікацію домішкових центрів.