SUMMARY

ANNEALING INFLUENCE ON THE ELECTRICAL PROPERTIES OF GaP SINGLE CRYSTALS

Influence of annealing conditions on the properties of undoped gallium phosphide crystals obtained from the melt: near stoichiometric, with gallium excess or phosphorus excess, as well as with different carbon concentration was investigated. Monocrystalline blocks with a thickness of 10 – 20 mm and wafers with a thickness of ~ 700 μm were annealed. Annealing conditions such as the temperature, time and phosphorus vapor pressure in the ampoule allowing for obtaining semi-insulating material, were determined. It was confirmed that as result of annealing undoped GaP crystals with the carrier concentration n = (2 – 5) × 10^{16} cm^{-3} and carbon concentration $N_C \leq 1 \times 10^{16}$ cm^{-3} we can obtain SI *n* – type material. At the carbon concentration $N_C \sim 5 \times 10^{16}$ cm^{-3} the SI material of *p* – type can be obtained.

Keywords: GaP, annealing, SI crystal, electrical properties

OPTICAL STUDIES OF UNDOPED GaP GROWN BY LEC METHOD

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The features of undoped LEC GaP crystals with particular emphasis on their luminescence properties are presented. Hall and GDMS measurements revealed that C and Si are the main residual shallow impurities. Semi-insulating features of the samples were controlled by the presence of the phosphorous anti-site defect, P_4P_{Ga}. Its presence was confirmed by ESR measurements as well as the emission at 1.05 eV. For p-type samples with phosphorous antisite defect, P_4P_{Ga}, and high carbon concentration an emission at 1.9 eV has been observed. We tentatively assign this emission to the recombination of the excitons bound with isoelectronic complex $P_{Ga}C_P$. A deep-centre luminescence with the maximum at 1.33 eV was dominant in n-type GaP and in electron-irradiated samples. The obtained results indicate that this emission results from native defect complex.

Key words: GaP, photoluminescence, native defects, Hall measurements, ESR

1. INTRODUCTION

Unintentionally doped 2 – 3" diameter GaP crystals recently became of great interest for their application as an optical material in the infrared spectral region. Despite the fact that optical and electrical features of GaP were intensively studied 30 – 40 years ago, problem of native defects creation in undoped GaP crystals grown by the liquid encapsulated Czochralski method (LEC) is still unsolved. It is known that electrical parameters of undoped GaAs [1] or InP [2 - 3] grown by the LEC method are controlled by isolated native defects [2] or by their complexes with residual impurities [4]. Among them, anion antisite defects are the most common defects in III-V compounds. Vacancies in the P sublattice with concentration of some 10^{17} cm^{-3} have also been observed in as-grown GaP [2]. Isolated antisite defects (P_{Ga}) with concentration of 4×10^{16} cm^{-3} have been detected in Zn-doped GaP by electron spin resonance experiments (ESR) [2]. In *n*-type GaP, however, the concentration of P_{Ga} defects has been found to be in the range below 10^{15} cm^{-3}. GaP is also known as a semiconductor in which isoelectronic (neutral) complexes are relatively easily formed [2, 5-6].

We found that electrical parameters of unintentionally doped LEC-grown GaP crystals can change markedly along the crystal, as well as among different crystals. This suggests that native defects or complexes associated with the native defects, can play an important role in defining the properties of undoped GaP crystals. It is commonly known that it is very difficult to control precisely the phosphorous pressure in LEC technique and consequently the

concentration and microscopic structure of native--defect related complexes. This is one of the reasons that the growth of undoped and semi-insulating (SI) LEC GaP crystals is still a challenging issue. The aim of this paper was to explain the observed differences in electrical parameters of undoped LEC grown GaP crystals. The paper concerns the features of these crystals with particular emphasis on their luminescence properties.

2. EXPERIMENTAL

Unintentionally doped GaP crystals were grown under stoichiometric P-rich conditions using LEC technique. Semi-insulating and *n*-type or *p*-type GaP crystals with free carrier concentration in the ranges (2×10^9 – 6×10^{15} cm^{-3}) and (2.3×10^8 – 2×10^{16} cm^{-3}), respectively, were studied. Wafers of thickness 0.5 – 0.7 mm were cut from different part of the crystals and subsequently cut into pieces for electrical, photoluminescence and electron spin resonance (ESR) measurements. Electrical parameters were calculated from Hall coefficient measurements using van der Pauw method. From the temperature dependent of Hall effect measurements (4 – 500 K), the residual donor (N_D) and acceptor (N_A) concentrations were calculated (Tabl. 1). Electron spin resonance (ESR) experiments were carried out using a Bruker ESP-300 X-band spectrometer with 100-kHz field modulation and phase-sensitive detection, which operated at the microwave frequency of about 9.4 GHz. The photoluminescence was excited by the 488 nm emission from Ar^+ laser. Low temperature luminescence at 6 K was measured by mounting the samples on the cold finger of the close-cycle cooling-system refrigerator. Some of the wafers were annealed under a phosphorous-vapour overpressure of 2×10^5 Pa at 1140°C for 8 – 88 h. After annealing the decomposed surface layer was removed and Hall measurements were performed. The intensity of the absorption lines at 12 K related to the local vibration modes of carbon (605.8 cm^{-1} [7]), oxygen (568.9 cm^{-1} [7]) and nitrogen (496 cm^{-1} [7]) was used to control the amount of these residual impurities. The concentrations were calculated using the calibration factors 1.6×10^{16} cm^{-2} and 5×10^{16} cm^{-2} for carbon and nitrogen, respectively. Since the correlation factor for oxygen is unknown, so far one can only compare the relative changes in the oxygen concentration.

3. EXPERIMENTAL RESULTS

3.1. Electrical measurements

The electrical parameters and the concentration of residual shallow donors and acceptors calculated from Hall and absorption measurements for samples from as-grown crystals are presented in Tabl 1.

Table 1. Basic parameters of as-grown crystals.
Tabela 1. Podstawowe parametry mierzonych kryształów.

Sample label	Distance from seed (mm)	Type	n_H * (cm^{-3})	Mobility (cm^2/Vs)	Carbon $\times 10^{16}$ (at/cm^3)	Oxygen absorption coefficient** (cm^{-1})	Nitrogen $\times 10^{16}$ (at/cm^3)	N_D*** $\times 10^{16}$ (cm^{-3})	N_A**** $\times 10^{16}$ (cm^{-3})	E_i***** (meV)
81I	-	n	6.8E16							
81II	125	SI-n	1.13E+8	31	20.2	1.8	12			1050
92-I	-	n	1.7E17							
92-102	102	p	1.4E16	83	20.5	5.8	3.4			
94-5	5	n	2.45E16	191	-	-	-	6.1	3	79
94-50	50	n	1.88E16	83	-	-	-	6	4.1	83
94-64	64	p	2.09E16	122	3.5	3.6	9.5	-	-	-
94-96	96	p	3.5E16		2.0	3.5	2.6	-	-	-
94-165	165	p	4.59E16	104	10	1.9	2.2	-	-	-
94-215	215	p	1.0E17	116		-	-	8.3	10.2	51
103-142	142	n	5e14	35	1.1	0.59	22	-	-	-
104-154	154	SI-p	2.30E+08	151	3.5	1.1	20	-	-	-
106-150	150	SI-n	2.00E+08	40-88	1.5	2	7.9	-	-	-

Sample label	Distance from seed (mm)	Type	n_H * (cm^{-3})	Mobility (cm^2/Vs)	Carbon × 10^{16} (at/cm^3)	Oxygen absorption coefficient** (cm^{-1})	Nitrogen ×10^{16} (at/cm^3)	N_D*** × 10^{16} (cm^{-3})	N_A**** × 10^{16} (cm^{-3})	E_i***** (meV)
139-5:P	5	n	4.80E14	42	-	-	-	-	-	-
139-165	165	n	4.60E11	42	<det	0.4	32.	-	-	400
143-107	107	n	1.6E15	142	-	-	-	-	-	-
143-125	125	n	4.5E4	7.5	7.4	2.3	2.9	-	-	1000
145-120:Ga	120	n	4.9E14	144	0.66	2.2	8.3	-	-	-
147-7:P	7	n	2.4E16	160	<det	7.6	<det	-	-	-
147-155	155	SI-n	1E11	156	<det	<det	31	-	-	-

* - free carrier concentration calculated from Hall measurements; ** - absorption coefficient for oxygen; *** - acceptor concentration; **** - donor concentration; ***** - energy of the electrical level calculated from Hall measurements

The change in the conductivity type from *n*-type at the seed to *p*-type at the tail of the crystal was observed for most studied crystals. In the middle part of the length the crystals were usually semi-insulating (SI) or slightly *n*- or *p*-type conductive due to compensation process. The ionisation energy of the electrical levels calculated from the temperature dependence of the Hall effect measurements was 79 – 83 meV for *n*-type samples and 51meV for *p*-type (Fig. 1). These values correlate well with the energy of 85 meV for shallow Si_{Ga} donor [8] and 53.2 meV for shallow C_P acceptor [9], respectively. The sources of background carbon and silicon impurities are graphite heaters and quartz crucibles, respectively, and it is usual for the LEC technique. It is reported that the segregation coefficients for Si and C in GaAs and InP should be ≤ 0.5 [10]. The observed change in the type from *n*- type at the seed to *p*-type at the tail for studied GaP crystals, suggests that the segregation coefficient of carbon in GaP is somewhat higher than that of silicon. It is interesting, however, that in some cases (e.g. samples 81II and 92-102) the carbon concentration obtained from the absorption measurements is inconsistent with carrier concentration in *p*-type material and the concentrations of background shallow impurities calculated from Hall measurements. One can see that despite the high carbon concentration, the 81II crystal still remains SI at the tail, while the 92-102 crystal is *p*-type with hole concentration above 10^{16} cm^{-3}. At the seed both crystals were *n*-type with electron concentration 6.8 × 10^{16} cm^{-3} and 1.7 × 10^{17} cm^{-3}, respectively (Tabl. 1). The energy level calculated from Hall effect measurements for the SI 81II sample was 1.05 eV. The thermal activation energy of free carrier concentration lies within 1 – 1.1 eV as men-

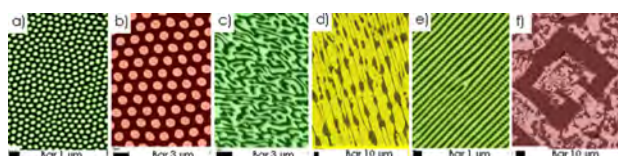


Fig. 1. Free carrier concentration n_H calculated from Hall effect measurements versus temperature for the samples cut from a 94 GaP crystal at the distances 5 mm, 50 mm and 215 mm from the seed. From the slope of the curves the ionization energy E_i was calculated.

Rys. 1. Koncentracja swobodnych nośników określona z temperaturowych pomiarów hallowskich dla próbek wyciętych z kryształu 94 w odległości 5 mm, 50 mm i 215 mm od zarodzi. Na rysunku podane są również energie termicznej aktywacji swobodnych nośników określone z nachylenia krzywych.

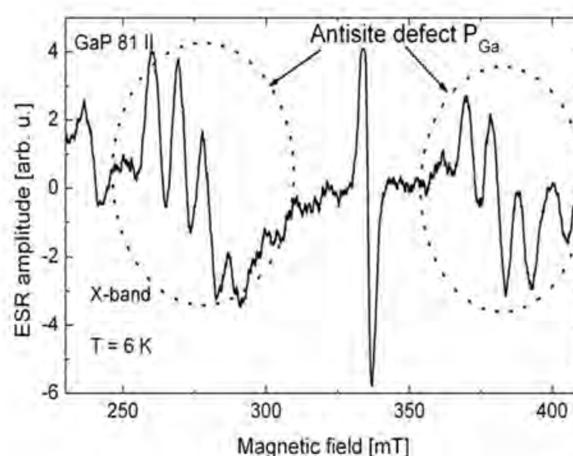


Fig. 2. ESR spectrum for a 81II GaP sample with visible lines related to phosphorus antisite.

Rys. 2. Widmo ESR dla próbki 81II z widocznymi liniami związanymi z obecnością antystrukturalnego defektu P_{Ga}.

tioned earlier for SI GaP [2] and has been assigned to a deep mid-gap, singly ionized double-donor related to an antisite defect of phosphorous atom located at gallium sublattice (P_{Ga}^{+}) [4]. The ESR measurements confirmed the presence of this antisite defect in the 81II sample (Fig. 2).

3.2. Photoluminescence measurements

Deep-level photoluminescence in 2.1 – 0.75 eV spectral range for the selected GaP samples is shown in Fig. 3. For SI and for *p*-type GaP with the hole concentration up to 1×10^{16} cm^{-3}, a broad band with maximum at 1.05 eV was a dominant luminescence emission in this spectral range. On the high-energy side of 1.05 eV band an additional emission as a significant shoulder with maximum at about 1.3 eV appears for SI 81II sample. A similar shoulder of a lower intensity is also present for the *p*-type 92-102 sample but it is missing for the *p*-type 104-154 one. What differs these two *p*-type samples is the carbon and oxygen concentration (Tabl. 1). The concentration of carbon in 81II and 92-102 samples is almost the same and about 6 times higher than that of the 104-154 sample. On the contrary, the absorption coefficient for 568.9 cm^{-1} band related to oxygen atoms shows that the concentration of the oxygen atoms is similar in the 81II and 104-154 samples and is three times lower than that in the 92-102 sample. One can also notice that luminescence band at 1.05 eV is asymmetric in its shape on its high-energy side suggesting an overlapping at least two luminescence bands.

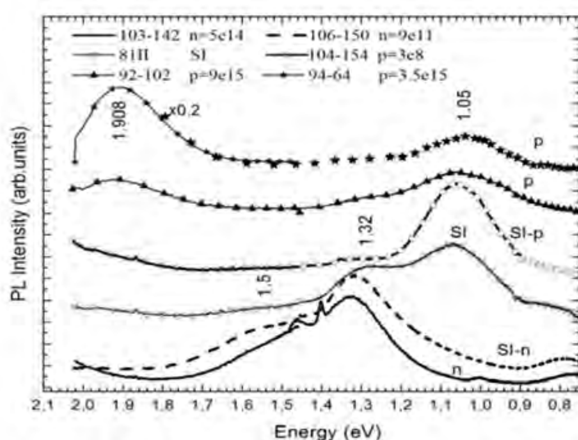
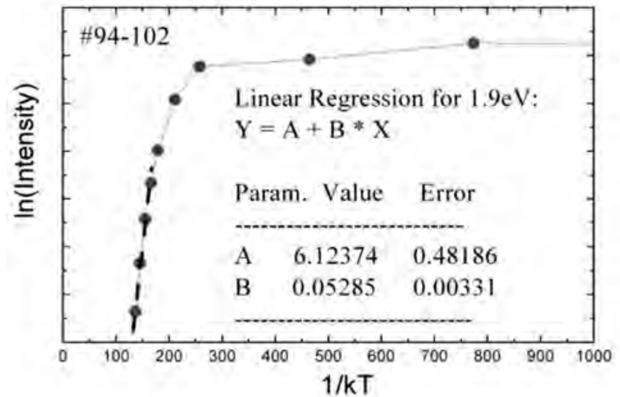


Fig. 3. Deep-level light emission spectra measured at 12 K for the samples cut from different intentionally undoped as-grown GaP crystals.

Rys. 3. Emisja w 12K związana z obecnością głębokich defektów dla wybranych próbek GaP pochodzących z niedomieszkowanych kryształów GaP.

For the 92-102 and 94-64 samples, an additional emission with a maximum at around 1.9 eV has been observed. The activation energy for thermal quenching of the 1.9 eV band calculated from Arrhenius plot was found to be 52.8 meV (Fig. 4). This value coincides with thermal activation energy for carbon acceptor what suggests that carbon acceptors can be involved in this radiative recombination process.



Rys. 4. The thermal energy for quenching the 1.9 eV light emission calculated from the Arrhenius plot for the 94-102 GaP sample.

Rys. 4. Termiczna energia gaszenia pasma emisyjnego leżącego przy 1.9 eV określona z krzywej Arrhenius'a dla próbki GaP nr 94-102.

The emission of 1.9 eV band at different excitation power for the 94-64sample is presented in Fig. 5. The 1.9 eV band does not show the characteristic for donor-acceptor recombination blue shift of the maximum with an increase of the excitation power. Such behavior is observed when one of the species participating in the radiative recombination

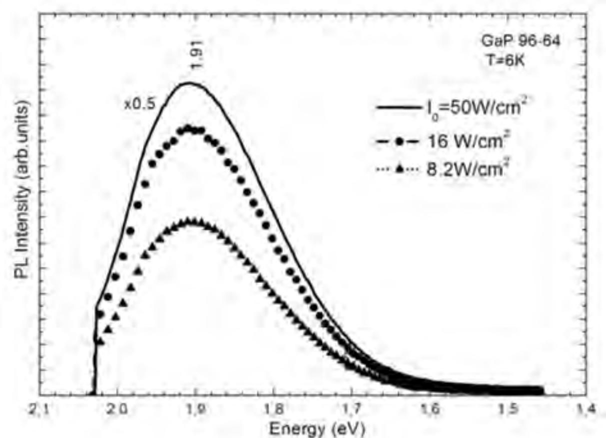


Fig. 5. 1.9 eV light emission spectra for a 94-64 GaP sample for various excitation intensity.

Rys. 5. Pasmo 1.9 eV dla próbki GaP nr 94-64 zmierzone przy różnych intensywnościach wzbudzania.

is an isoelectronic centre and no Coulomb interaction between species occurs [16].

Deep-level luminescence feature for *n*-type material is a broad band emission with the maximum at 1.33 eV. Similar luminescence band has been also found for neutron-irradiated *n*-type GaP (Fig. 6). Samples labeled as 139-5 and 139-165, as well as 147-7 and 147-155 were cut, respectively, from the top and the bottom of GaP crystals labeled as 139 and 147 for which an additional injection of phosphorous was applied at the initial stage of the growth process. As it is shown in Fig. 7 for the sample 139-5 two emission bands with maxima at 1.05 eV and 1.58 eV are present while for the sample 147-7 a very weak emission with two maxima at 1.56 eV and 1.33 eV has been revealed. The emission at 1.33 eV is also present for the sample 145-120:Ga coming from the crystal that was grown from Ga-rich solution. The lack of 1.33 eV emission has been stated for the 139-5:P sample that originates from the top part of the crystal when an additional phosphor has been injected. A weak emission at 1.33 eV was also found in the case of higher oxygen concentration (samples 143-125 and 143-107).

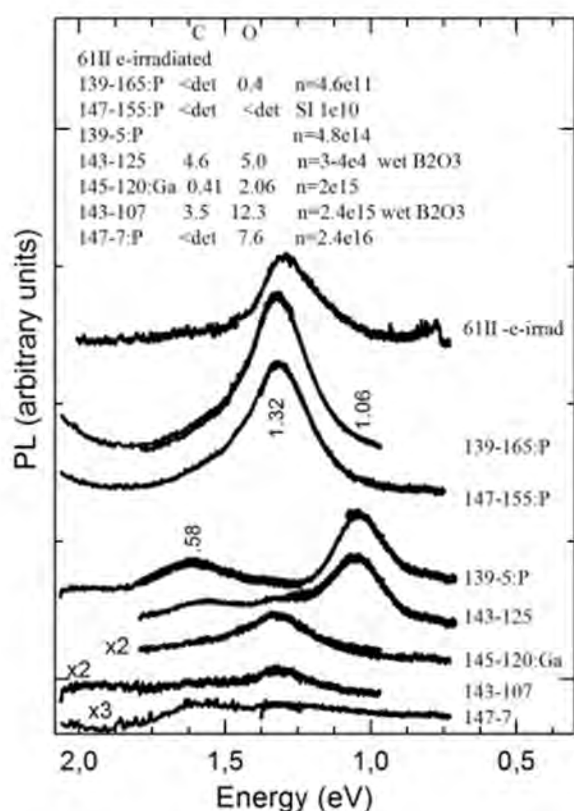


Fig. 6. Deep-level light emission spectra for *n*-type intentionally undoped GaP crystals. All spectra are vertically moved for clarity but plotted in the same vertical scale. Mark x2 means that the intensity of the PL signal was magnified two times. The values of absorption coefficients for LVM absorption related to C_P and O_P are also shown.

Rys. 6. Luminescencja pochodząca od głębokich centrów dla wybranych próbek GaP typu *n* i naświetlanej elektronami. Dla lepszej jasności widma PL są przesunięte w skali pionowej ale przy zachowanej jednostce skali. Oznaczenie x2 oznacza, że przedstawiona intensywność widma została powiększona 2x. Na rysunku przedstawione są również wartości współczynników absorpcji określone z intensywności pików absorpcyjnych związanych z modami drgającymi atomów węgla i tlenu.

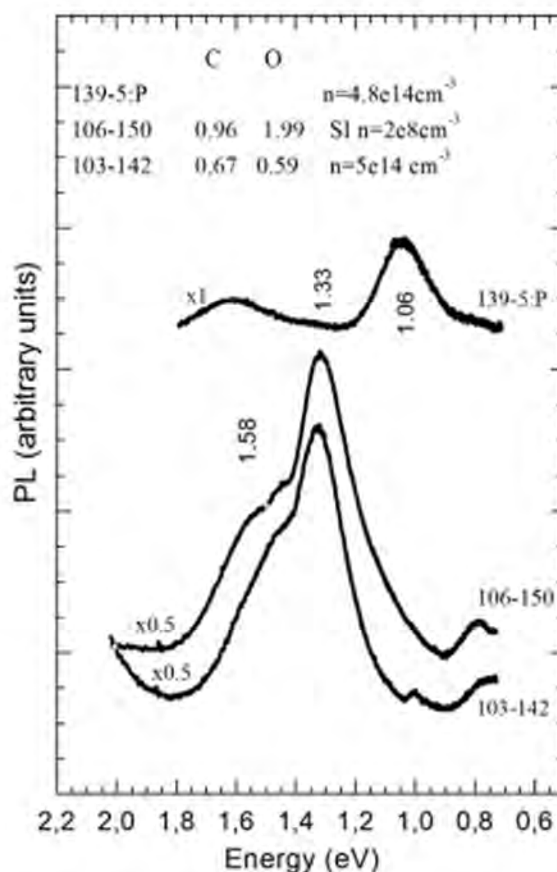


Fig. 7. The influence of an phosphorous injection during the crystal growth on the deep-level light emission spectra for *n*-type undoped GaP crystals. The different spectrum for the semi-insulating material, sample 139-5, is not related to the different Fermi level position but is due to an excess of phosphorous atoms resulting in a different material defect structure.

Rys. 7. Wpływ wstrzykiwania fosforu w procesie wzrostu kryształu na widmo pochodzące od głębokich defektów dla niedomieszkowanych kryształów GaP typu *n*. Zmiana charakteru widma dla półizolującej próbki GaP 139-5 nie jest wynikiem zmiany położenia poziomu Fermiego, ale wywołana jest jedynie nadmiarową koncentracją atomów fosforu.

3.3. Discussion

3.3.1 Emission at 1.05 eV

The luminescence band with a maximum at 1.07 -1.1 eV has been already observed in a number of papers [2, 11-12] and is related to the presence of an antisite defect $P_{Ga}P_4$. ESR studies showed that the defect $P_{Ga}P_4$ acts in GaP as a double donor [14]. If P atom substitute Ga atom in GaP lattice three of the five valence electrons of P are needed or complete tetrahedral bonds with the four P ligands. So P_{Ga}^{3+} ion can be viewed as neutral state, D^o, of P_{Ga} double donor. The singly ionised double donor P_{Ga}^{4+} (D^+) has one unpaired electron and this paramagnetic state gives rise to the ESR spectrum. In the *p*-type material, when Fermi level lies in the lower part of the energy gap, the equilibrium state for this antisite defect is in the diamagnetic doubly ionised charge state, P_{Ga}^{5+}. The ESR signal in the *p*--type GaP appears after the photo-emission of hole from P_{Ga}^{5+} to the valence band, P_{Ga}^{5+}/ P_{Ga}^{4+}, with the energy threshold at 1.25 eV [14]. The binding energy for the second electron, P_{Ga}^{4+}/ P_{Ga}^{3+}, was found to be 1.07 eV - 1.1 eV, [12,14]. The thermal activation energy calculated from the temperature dependence of the electron concentration for undoped SI LEC GaP falls within 1.0 – 1.1 eV. [2] and is related to the thermal emission of an electron from P_{Ga}^{4+} to the conduction band.

The ODMR spectrum for p-type GaP:Zn, detecting changes in spectral range 0.7-1.4 eV, revealed that 1.07 eV emission is a superposition of two bands with maxima at 0.97 eV and 1.1 eV [12] or 0.97 eV and 1.2 eV [14]. The 0.95-0.97 eV [12-13] emission with threshold energy 1.25 eV [13] was related to the defect of tetrahedral symmetry and was interpreted as donor-acceptor recombination involving electronic transition from isolated P_{Ga}^{4+} donors to distant shallow acceptors [12-13]. The emissions at 1.1 eV and 1.2 eV were confirmed to be the recombination in which $P_{Ga}Y_P$ complex is involved. O'Donnell [12] suggested that 1.1 eV emission derives from the defect with C_{3v} symmetry that is characteristic for a complex $P_{Ga}Y_P$ and can be regarded as internal transition (localised electron-hole recombination) when nearest neighbours phosphorous site is occupied by Zn atom. The line with maximum 1.2 eV had threshold energy 1.55 eV for luminescence spectrum and 1.77 eV for ODMR signal [13]. It has been proposed that the emission derives from the donor-acceptor recombination when the complex $P_{Ga}Y_P$ acts as a deep donor. A possible candidate is the pair of antisites $P_{Ga}Ga_P$ which is prevalent defect in compound semiconductors [15]. But in such configuration the defect acts as an isoelectronic complex and additional electron can derive from an interstitial Fe^{2+}_I which stabilize an extra electron at the antisites pair and gives the complex $(P_{Ga}Ga_P)^-$ - Fe^{2+}. Upon excitation after capture electron-hole pair an exited state is formed ,$(P_{Ga}Ga_P)^{2-}$ - Fe^{3+}, that can be treated as an donor-acceptor pair responsible for the emission at 1.2 eV.

In view of this data the emission at 1.05 eV observed in our samples can be interpreted as related to the recombination at the complex in which the antisite defect $P_{Ga}P_4$ is involved. The presence of $P_{Ga}P_4$ defect in P_{Ga}^{4+} charge state was confirmed by ESR measurement for sample 81II (Fig. 2). In *p* type samples, the $P_{Ga}P_4$ defect is in P_{Ga}^{5+} charge state which is a diamagnetic and no ESR signal assigned to this defect is detected, contrary to the still present emission at 1.05 eV confirming the presence of the antisite gallium defect. The 1.05-eV emission is observed only in the *p* type or SI GaP when Fermi level lies in the lower half of the band gap or is close to its middle. This fact suggests that in the recombination processes responsible for this luminescence, the shallow acceptors being in the neutral state upon excitation or any deep acceptors that capture holes upon excitation can participate. Presented above short review of the features of the 1.1 eV emission makes it evident that the structure of the complex may be different and is dependent on the crystal origin or, in other words, on the growth conditions. In our samples the main residual shallow impurities were carbon and silicon. From Glow Discharge Mass Spectroscopy (GDMS) analysis the concentration of Zn atoms was two or three orders of magnitude lower (< 10^{13} at/cm^3) than carbon atoms and below < 3-5 ppb for Fe atoms. It is worth to note that despite relatively high carbon concentration in sample 81II or 92kII not any shoulder at around 0.95 eV for the 1.05 eV emission was observed confirming the $(P_{Ga}^{4+}C^0)$ donor –acceptor transitions.

3.3.2 Emission at 1.9 eV

Zn and Cd impurities incorporated into a gallium site in GaP lattice form the "isoelectronic" complexes O_PZn_{Ga} and O_PCd_{Ga} that bound excitons. It is due the fact that the deep donor-acceptor pairs that occupy the nearest-neighbor sites form complexes that apparently are isoelectronic centers. These centers can trap electrons with a binding energy reduced from that of the isolated oxygen donors [16]. Recombination of excitons, X, from these isoelectronic

centers (e.g. O_PZn_{Ga},X) produces red luminescence band at about 1.9 eV. This band consists in fact of two components: (i) recombination of exciton (X) bound to the neutral center (e.g. O_PZn_{Ga},X) and (ii) recombination of the electron trapped at negatively charged complex with hole bound to a distant neutral acceptor (e.g. $O_PZn_{Ga}^-$,Zn^o). When shallow acceptor is located at phosphorous sublattice, as it is the case of C, such emission is not observed as donor and acceptor atoms are not located in a chemical bonding distance [17]. However, emission at around 1.9 eV was observed by us for some *p*-type samples. As has been shown above the activation energy for the quenching of 1.9 eV band was 0.053 eV. This value pretty well coincides with the one of 0.055 eV for thermal activation energy of carbon acceptor. This fact suggests that carbon acceptors should be involved in this radiative recombination process. Taking into account that Zn concentration is three orders of magnitude lower than that of carbon, we exclude the origin of this emission from radiative recombination involving isoelectronic ZnO centres. Emission at 1.9 eV accompanied by the emission at 0.97 eV has been also observed in the epitaxial layers grown by MOVPE technique under a high phosphorous pressure [18] and has been suggested that band at 1.9 eV can also involve the P_{Ga} antisite defect. Unchanged energy position of 1.9 eV band with increasing the excitation intensity (Fig. 5) suggests that lack of Coulomb interaction between the species responsible for this radiative recombination. It means that one of the species can be an isoelectronic centre. One of possible candidate for such isoelectronic centre can be a complex $P_{Ga}^+C_P^-$ by analogy to $Zn_{Ga}O_P$ one. Formation of the similar isoelectronic complex has been proposed earlier for $P_{Ga}^+Si_P^-$ in *n*-type GaP doped with Si. [19]. Upon excitation conditions an isoelectronic centre $P_{Ga}^+C_P^-$ could bound an electron (with energy considerably reduced from that of the isolated P_{Ga} donor that will recombine with hole trapped at shallow acceptor which in our case is a carbon atom.

3.3.3. Emission at 1.33 eV

Deep-level luminescence of the studied by us *n*-type undoped GaP crystals is dominated by the emission at 1.33 eV (Fig. 6) although it is also present in SI GaP (e.g. sample 81II in Fig. 3). This emission is prominent in the high-resistivity *n*-type samples while its intensity seems to decrease with the increase of the carrier concentration (see samples 147-7 and 143-107 in Fig. 6). On one side it can be due to the lower defect concentration responsible for this radiative recombination but on the other one due to the movement of the Fermi- level toward the bottom of the conduction band when at least one of the species involved in this recombination process would change its charge state. The same spectra of deep--level luminescence for two *n*-type GaP samples with the same free carrier concentration (samples 139-5:P and 103-142) but essentially different PL spectrum are shown in Fig. 7. What differs these samples it is an injection of phosphorus during initial stage of the growth of the 139 GaP crystal. Thus one can expect the lower concentration of phosphorus vacancies in the 139-5 sample originating from the upper part of this crystal. The appearance of the emission at 1.05 eV related to the presence of the phosphorus antisite defect for the 139-5 sample confirms the assumption that the phosphorus antisites are present. Expected higher concentration of V_P at the bottom of the crystal grown by LEC technique coincides with the higher intensity of 1.33 eV emission (samples 139-165 and 147-155 in Fig. 6). Higher concentration of V_P can also be expected in the 145-120:Ga crystal that was grown from Ga-rich solution. In contrast to this the emission at 1.33 eV seems to be reduced in the samples with higher oxygen concentration (compare the samples 143-125 and 143-107 in Fig. 6). In view of this one can suggest that in the recombination process responsible for 1.33-eV emission is observed when deficiency of phosphorus atoms occurs. For such case, formation of the defects involving V_P or Ga_P should be expected. The appearance of 1.33 eV emission after electron irradiation for 61II conductive *n*-type GaP sample also suggests the origin of this emission from the complexes that involve the native defects. However, at present there is no evidence that both emissions with maximum at 1.33 eV arise from the same complex. To make it clear further studies are necessary.

Presented results show that the emission at 1.33 eV is not related to the concentration of the main residual carbon acceptors and thereby excludes the deep donor-shallow acceptor recombination. Theoretical calculations made by H. Xu [20] indicate that in *n*-type GaP phosphorus vacancies change their charge state from positive to neutral one when Fermi-level lies around 0.5 eV below the bottom of the conduction band. This fact coincides with observed by us the decrease of the intensity of 1.33 eV emission for a higher free carrier concentration. In e-irradiated material, when Femi-level is located at middle of the band gap, V_P should be also positively charged and 1.33 eV is observed.

From positron annihilation experiments [21], the concentration of V_p has been estimated to be of the order of 10^{17} cm^{-3} in *n*-type GaP. This is supported by theoretical calculations of point defects that resulted in maximum concentration of ≈ 10^{19} cm^{-3} vacancies in the P sublattice from fitting point defect model to the coulombometric data for stoichiometric or Ga- rich GaP crystals. It is suggested however, that most of them forms neutral complexes such as $V_{Ga}^{+}P_{Ga}^{2+}V_{Ga}^{-}$ and $V_P^{+}Ga_P^{2-}V_P^{+}$ [15]. Theoretical calculations of native defects concentrations as a function of stoichiometry predict that in *n*-type GaP with negative stoichiometry (excess of Ga) the gallium antisite defect, Ga_P, is dominant [22]. Taking into account these results, a complex $V_P^{+}Ga_P^{2-}V_P^{+}$ could be one of the candidates responsible for the 1.33-eV light emission.

3.4 Conclusions

Intentionally undoped GaP crystals grown by the LEC technique under stoichiometric and P-rich conditions have been studied. Silicon and carbon are found to be the main residual shallow donors and acceptors, respectively, in undoped GaP crystals. Semi-insulating features of the samples were controlled by the presence of the phosphorous anti-site defect, P_4P_{Ga}. Its presence was confirmed by ESR measurements as well as the emission at 1.05 eV. For *p*-type samples with phosphorous antisite defect, P_4P_{Ga}, and high carbon concentration an emission at 1.9 eV has been observed. We tentatively assign this emission to the recombination of the excitons bound with isoelectronic complex $P_{Ga}C_P$. A deep-centre luminescence with the maximum at 1.33 eV was dominant in *n*-type GaP and in electron-irradiated samples. The obtained results indicate that this emission results from native defect complex.

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BADANIA OPTYCZNE NIEDOMIESZKOWANYCH KRYSZTAŁÓW GaP OTRZYMYWANYCH METODĄ LEC

W pracy przedstawione są badania niedomieszkowanych kryształów GaP otrzymywanych w ITME metodą LEC ze szczególnym uwzględnieniem ich własności luminescencyjnych. Pomiary Halla, absorpcyjne i GDMS wykazały, że głównymi płytkimi domieszkami resztkowymi w otrzymywanych kryształach są węgiel i krzem. Półizolujące własności badanych kryształów determinowane były obecnością fosforowego antystrukturalnego defektu P_4P_{Ga}. Obecność jego została potwierdzona poprzez obecność linii rezonansowej w widmie ESR, jak również poprzez obecność emisji w podczerwieni z maksimum przy 1.05 eV. W kryształach typu *p*, w których potwierdzona została obecność defektu P_4P_{Ga} oraz stwierdzono relatywnie wysoką koncentrację węgla w widmie luminescencyjnym pojawiło się pasmo luminescencyjne z maksimum przy 1.9 eV. Nasza sugestia odnośnie pochodzenia tej emisji wiązana jest z wytworzeniem się isoelektronowego kompleksu $P_{Ga}C_P$. W niedomieszkowanych próbkach typu *n* jak również w próbce naświetlanej elektronami luminescencja pochodząca od głębokich centrów zdominowana była obecnością pasma leżącego przy 1.33 eV. Przeprowadzone badania wykazały, że jest ona związana z obecnością kompleksu wytworzonego przez macierzyste atomy sieci, natomiast nie zależy od koncentracji domieszek resztkowych.

Słowa kluczowe: GaP, fotoluminescencja, defekt samoistny, Hall, ESR