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# Decrease of exciton radiation intensity in compensated gallium arsenide single crystals under influence of low electric field

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Variations of edge photoluminescence characteristics of high compensated undoped gallium arsenide single crystals under influence of an electrical field (EF) has been investigated. It is established that at liquid nitrogen temperature, the decreasing of exciton radiation intensity in the material takes place at abnormal low values of field strength in comparison with uncompensated material. It is shown that the result obtained cannot be explained by known mechanisms of exciton state decay in EF. A new mechanism of EF influence on decreasing of the exciton photoluminescence intensity is proposed. This mechanism is due to GaAs structural features associated with its charge compensation.

Изучено изменение характеристик краевой фотолюминесценции монокристаллов сильно компенсированного нелегированного арсенида галлия под влиянием электрического поля (ЭП). Установлено, что при температуре жидкого азота в данном материале имеет место снижение интенсивности экситонного излучения при аномально низких, по сравнению с некомпенсированным материалом, значениях напряжённости поля. Показано, что полученный результат невозможно пояснить известными механизмами распада экситонных состояний в ЭП. Предложен новый механизм влияния ЭП на снижение интенсивности экситонной фотолюминесценции, который обусловлен структурными особенностями GaAs, связанными с его зарядовой компенсацией.

## 1. Introduction

The theoretical statements allowing to analyze the exciton spectra of semiconductors in electric fields (EF) of different force have been worked out long ago [1–3]. So, in stationary conditions, the intensity of exciton photoluminescence (PL) in a field with electric strength $E$ is defined by the probability impact ionization $Q(E)$ and exciton decay probability $(1/\tau)$ resulting from others radiative and non-radiative processes [2]:

$$I(E) = I_0[1 + Q(E)\tau]^{-1}, \qquad (1)$$

where $I_0$ is the PL intensity. In this case, $Q(E)$ can be found as

$$Q(E) = \int_{W_i}^{\infty} Q_e(W)\rho(W)f(W)dW. \qquad (2)$$

In the latter expression, $Q_e(W)$ is the probability of ionization with one electron detachement; $\rho(W)$, density of states in the conductivity band; $f(W)$, the energy distribution function for electrons, and the integral is takes over all energy values exceeding the ionization energy $W_i$. At the same time, it is known that the experimental data for structurally inhomogeneous crystals [4, 5] may differ essentially from the calculated values given by expressions (1), (2). The binary undoped semiconductors, such as

Table. Parameters of SIU GaAs samples at $T$ = 300 K

| Sample No. | $\rho$ ($\cdot 10^7$ $\Omega\cdot$cm) | $\mu_n$ (cm$^2$/V$\cdot$s) | $N_{EL2}$ ($\cdot 10^{16}$, cm$^{-3}$) | $N_C$ ($\cdot 10^{15}$, cm$^{-3}$) |
|---|---|---|---|---|
| 1 | 8.2 | 5800 | 1.4 | 4 |
| 2 | 11.4 | 6100 | 1.7 | 7 |
| 3 | 7.7 | 5200 | 1.2 | 9 |
| 4 | 22.1 | 5500 | 2.0 | 12 |
| 5 | 9.5 | 5100 | 2.3 | 30 |

undoped gallium arsenide, show an essentially inhomogeneous distribution of the background impurity and intrinsic point defects (IPD) [6]. Now, few investigations of edge recombination in GaAs crystals in relatively low ($E$ < 300 V/cm) EF under similar experimental conditions are characterized by significant discrepancy of results. This concerns both the field parameters causing the edge emission suppression, and interpretation of the results obtained [7–9].

Therefore, it is expedient to study the EF influence on the edge emission of undoped GaAs crystals with the preset structure features. In this work, change of the edge emission characteristics of high compensated undoped gallium arsenide single crystals at presence of EF is investigated at temperature of liquid nitrogen. The most probable mechanisms causing suppressions of exciton radiation in such crystals under influence of low electric fields are considered. The new mechanism of EF influence on decreasing of exciton PL intensity is offered.

## 2. Experimental

The Czochralski-grown semi-insulating undoped (SIU) GaAs (100) single crystals with the $n$-type of conductivity and the carrier concentration of $n = 8\cdot 10^7$–$3\cdot 10^8$ cm$^{-3}$ were studied. Their dark conductivity is due to the deep donors — thermally ionized EL2 defects (the defect basis is an arsenic atom in the position of gallium, $As_{Ga}$ [10]). The main background impurities were shallow acceptors — carbon atoms occupying arsenic vacancies and shallow donors — silicon atoms in gallium vacancies. Their concentration ratio is $N_{Si} = (0.2$–$0.5)\cdot N_C$. Concentration of these impurities (to within ± 30 %) was determined by photoluminescence method considered in [11]. Parameters of the studied crystals at $T$ = 300 K are presented in Table ($N_{EL2}$ is total concentration of deep donor centers EL2). An optical method was used to determine $N_{EL2}$ (to within ± 22 %), considered in [10]; $\rho$, $n$ and $\mu_n$ values were determined by Hall method). For all crystals, specific resistance at 77 K $\rho \to \infty$, the majority carrier mobility $\mu_n \approx (2$–$6)\cdot 10^4$ cm$^2$/V$\cdot$s. The samples were sized as 10×5×3 mm. Four identical point nickel contacts of ≤0.5 mm diameter located along one line and spaced by ≤1 mm were formed on the sample surface. After annealing of the contacts, the surface of crystals was treated in polishing etchant $H_2SO_4$:$H_2O_2$:$H_2O$ (3:1:1).

A direct constant voltage was applied to the outer contacts. The whole part between inner contacts (≤0.5 mm) was illuminated evenly by a laser. The voltage drop $U$ in the illuminated area of the sample was determined by the compensation method. As at $T$ = 77 K, the nonequilibrium carrier concentration in such a part $\delta n >> n_0 \approx 0$, then the voltage applied to outer contacts of the crystal exceeded by two order the values registered in the laser-illuminated part. The voltage drop determination error did not exceed 5 %. To eliminate the additional carrier injection from contacts, those were coated with an optically opaque lacquer.

A He–Ne laser (quantum energy 1.96 eV, absorption factor $\chi = 4\cdot 10^4$ cm$^{-1}$) with radiation strobbing at a frequency of $\nu$ = 2 kHz was used to excite the crystal PL at $T$ = 77 K. That has permitted to reduce essentially the possible warming-up of the sample, since in dark phase of strobbing, the current is close to zero (electron lifetime $\tau_n \sim 10^{-7}$ s <<1/$\nu$ [12]). Intensity of laser irradiation was $I_0 \sim 10^{17}$ cm$^{-2}\cdot$s$^{-1}$. PL spectra were registered by a standard technique [13] with using of MDR-3 monochromator at the spectral resolution not worse than 0.7 meV. PL intensity in energy range $h\nu$ > 1 eV was determined with the help of cooled FEU-68 (threshold sensitivity in the range of 1.51 eV ~ $10^{-10}$ lm), and at $h\nu$ < 1 eV — by cooled FD-9G photo diode. Integral in-

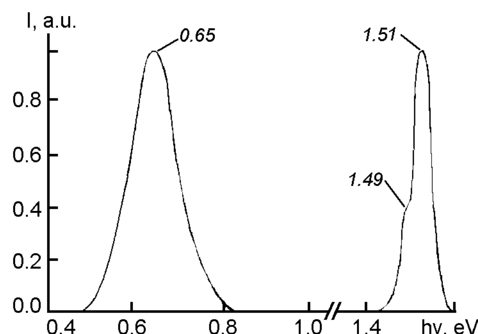


Fig. 1. General view of PL spectra of SIU GaAs single crystals.

tensity of PL was as an area, limited in the spectrum by the corresponding luminescence bands.

The narrow surface of crystal was a source of effective PL (more than 80 % of recombination is generated in this area). Extension of this area in the sample depth was $s = 1/\chi$, if $l_d < \chi$ ($l_d$ being the electron diffusion path at $T = 77$ K), and $s = l_d$, if $l_d \geq \chi$. Accordingly, the average value of electric field strength in the illuminated crystal area, starting from exponential decreasing of electric strength deep into the sample, was determined as:

$$E = \frac{1}{s}\int_0^s E_0 \cdot e^{-y/s}dy, \quad (3)$$

where $y$ is the coordinate in the light passing direction; $E_0$, the electric field strength on the spot. Using criterion of low electric field [14]:

$$E << 3k \cdot T/2e \cdot l_e, \quad (4)$$

where $e$ is the electron charge; $l_e$, average electron free path (it is accepted to be $l_e \cong 5 \cdot 10^{-5}$ cm at $T = 77$ K, that is typical of sufficiently "pure" crystals [4]; deterioration of the crystal quality reduces this value and, respectively, increases $E_{cr}$), we get the condition $E << E_{cr} \cong 200$ V·cm$^{-1}$ which well hold for all electric strength values in this work.

### 3. Results

The main contributions to the PL spectrum of SIU GaAs single crystals at $T = 77$ K are: the edge luminescence band with a maximum in energy range $h\nu_m = 1.506$–$1.508$ eV (the maximum position depends on concentration of electrically active impurity

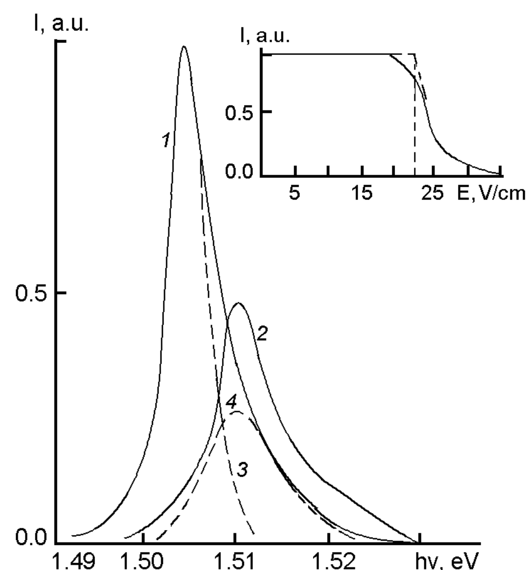


Fig. 2. Edge radiation of crystal (sample No.1) without (*1*) and with (*2*) EF. Dotted lines are expansion of a curve (1) on the radiation components caused by exciton (*3*) and free electrons and holes recombination (*4*). Inset: Dependence of exciton radiation intensity on EF strength (sample No.1).

[15]); the extrinsic luminescence band with $h\nu_m = 1.490$ eV caused by the shallow acceptor centers — carbon atoms occupying the arsenic vacancies $C_{As}$ involved in the emissive transitions; and the band with $h\nu_m \approx 0.65$ eV induced by emissive transitions through EL2 deep donor centers [10] (Fig. 1).

A decrease of the edge PL intensity was observed at electric strength values $E \geq 28$ V·cm$^{-1}$ (inset in Fig. 2). At $E \geq 35$ V·cm$^{-1}$, there was no emission with the maximum at $h\nu_{m0} = 1.506$–$1.508$ eV, and the edge band maximum fell on the energy range $h\nu_{m1} = 1.513$–$1.515$ eV (Fig. 2). At the same time, the energy difference $\Delta h\nu = h\nu_{m1} - h\nu_{m0}$ was $6.6 \pm 0.4$ meV for all studied samples. Values of $E_\Gamma$ (the procedure of $E_\Gamma$ determination is shown in the inset in Fig. 2) were varied non-trivially with change of $N_C$ (inset in Fig. 3).

In accordance with decreasing intensity of luminescence band with a maximum $h\nu_{m0}$, the intensities of bands with $h\nu_m = 1.490$ eV and $h\nu_m \approx 0.65$ eV increased, so that the emission intensity $I_{in}$ integrated over the whole spectral band was practically constant (Fig. 3). The further increase of electric

strength up to 50 V/cm did not cause any essential changes in the PL spectra.

### 4. Discussion

According to theoretical statements [16] and corresponding calculations [15], the edge emission band of undoped GaAs at 77 K can be expanded into two components. The first one, with a maximum at $h\nu_m$ = 1.514 eV, is due to recombination of free electrons and holes (Fig. 2 (4)). The second component of a higher intensity which show a long-wave shift of maximum with increasing $C_{As}$ concentration [13] ($h\nu_m$ = 1.5082–1.5059 eV), is caused by radiative annihilation of free excitons (Fig. 2 (3)). When comparing the curves *1* and *2* in Fig. 2, it is seen that exciton radiation is quenched in electric field at $E \geq 10$ V·cm$^{-1}$, and the residual edge radiation (from here on, the edge radiation in field) is determined by "band-to-band" carrier recombination.

The following mechanisms causing the quenching of exciton luminescence are known: (i) thermal dissociation of excitons; (ii) increasing probability of the nonradiative exciton recombination; (iii) impact ionization; (iv) tunneling of an electron from the bound state into the conductivity band. Let the realization probability of each mechanism be considered. (i) The thermal dissociation of excitons (as a result of sample heating) can be excluded from reviewing, on the one hand, due to low currents and the corresponding experimental technique (see section "Experimental") and, on the other hand, due to absolutely another changing character of the edge radiation parameters at $T \approx 77$ K [17]. (ii) The absence of any essential changing of the integrated PL intensity in EF (Fig. 3) testifies to a constant value of integrated (over all the wavelengths) quantum efficiency of radiation in the crystals. This implies that the probability of non-radiating electron-hole recombination in low EF is not increased. (iii), (iv) The $E_\Gamma$ values obtained in this work are too low for realization of both mechanisms. Really, additional energy which the electron gets in EF in the free path

$$W = e \cdot E \cdot l_e \qquad (5)$$

in the presented experiment does not exceed 1.8 meV (see Note 2). This value is much less than the exciton binding energy $W_e$ = 4.1 meV, that makes impossible its impact ionization. The tunneling probability of electron to the conductivity band is $P \sim \exp(-E_t/E)$ [14],

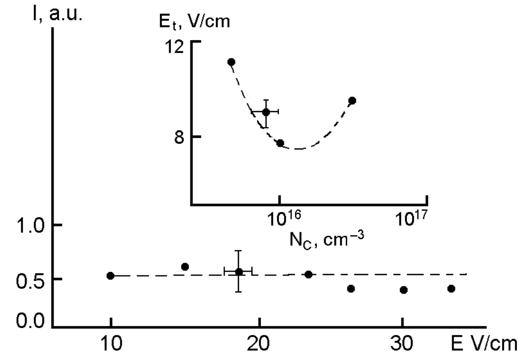


Fig. 3. Dependence of the total integrated PL intensity on EF strength (sample No.1). Inset: Dependence of $E_\Gamma$ on concentration of electrically active carbon in SIU GaAs crystals.

where $E_t$ is a tunneling constant which depends on the crystal parameters:

$$E_t = \frac{\pi \cdot W^{3/2} \cdot m_r^{1/2}}{2h \cdot e}. \qquad (6)$$

The equivalent effective electron and hole mass in GaAs $m_r \cong m_e$ (mebeing the effective mass of electron). There from, $E_t \approx 800$ V/cm. The experimental values $E_\Gamma << E_t$, hence, the probability of tunnel process can be neglected.

Thus, in very low EF, any mechanism of exciton luminescence quenching mentioned above cannot be realized. Moreover, it is known from [7, 8] that E values causing a drop of exciton radiation intensity in uncompensated GaAs exceed considerably the $E_\Gamma$ obtained in this work ($E$ values causing the PL quenching in EF for uncompensated GaAs also exceed $E_\Gamma$ considerably). It would be assumed that the results obtained are caused by structural features of GaAs associated with its charge compensation.

The "fatal" cause eliminating all displays of exciton states in bulk crystals is known to be the screening of the Coulomb electron-hole interaction thus preventing the electron-hole mutual attraction. The destruction of exciton states begins when the distance between the charged impurities $\delta \approx 1/(4 \cdot N)^{1/3} \geq R_B$ (where $N$ is the concentration of electrically active impurity, $R_B$, Bohr radius of the exciton). In GaAs, $R_B$ = 15 nm and the above requirement is satisfied at $N \geq 7 \cdot 10^{16}$ cm$^{-3}$. However, such a process is stochastic and the complete decay of exciton states takes place only at $N \geq 5 \cdot 10^{17}$ cm$^{-3}$ [16].

In highly compensated SIU GaAs, the state density "tails" are formed even at low doping due to spatial fluctuations of impurity density (negative carbon $N_C$, positive silicon $N_{Si}$, deep donors $N_{EL2}$, etc.) [16, 18]. The potential well parameters of the largest scale for the specified conditions (i.e. spatial width $r_i$ and the well energy depth $\gamma$) are defined by the relations [15]:

$$r_i = \sqrt{\frac{\varepsilon kT}{4\pi \cdot N_\Sigma \cdot e^2}}, \quad (7)$$

$$\gamma = \frac{e^2}{\varepsilon} \sqrt{N_\Sigma \cdot r} \quad . \quad (8)$$

At $T = 77$ K and $N_\Sigma = N_C + N_{EL2} + N_{Si}$ (where $N_{EL2} = 2{\cdot}10^{16}$ cm$^{-3}$; $N_C = 2{\cdot}10^{16}$ cm$^{-3}$; $N_{Si} \approx 1/3 {\cdot} N_C$), $r_1 \cong 3.9{\cdot}10^{-6}$ cm and $\gamma_1 \cong 5.2$ meV. Such parameters provide the localization condition for heavy holes

$$\frac{h^2}{m^* \cdot r^2} << \gamma, \quad (9)$$

while hardly providing the localization of electrons (the width and geometry of various wells can differ essentially, so the r.m.s. value $\gamma$ experimentally determined in [20] was ~1.5 meV). It is to note that concentration of the charged ODD ($N_{CODD}$) in GaAs, depending on the Fermi level position, can make a considerable proportion of the total ODD concentration [19] which reaches $10^{19}$ cm$^{-3}$. Therefore, the unhomogeneous distribution of $N_{CODD}$ in a crystal can contribute to the processes considered below. However, for compensated materials, in particular for SIU GaAs, the problem of the ratio between the charged and neutral ODD is investigated insufficiently. That is why the spatial fluctuation of $N_{CODD}$ will not be taken into account in this work.

Thus, in areas of ~$10^{-6}$ cm size (with higher value of $N$ than an average in the crystal) excitons cannot exist. Those exist in intermediate areas where $N$ is lower than average value.

In EF, an exciton has the dipole moment

$$P = \varepsilon_0 \alpha E, \quad (10)$$

where $\alpha$ is the exciton polarizability. A quantum-mechanical calculation shows [21] that the nondegenerate level with $n = 1$, $J = 0$, $m_J = 0$ ($J$, $m_J$ are quantum numbers of the atom total momentum and its projection onto the allocated axis) is not split, and a displacement depending on the field strength is observed for this level.

The component of the current carrier speed caused by field force is

$$\Delta\nu = \mu \cdot E, \quad (11)$$

and in our experiment its value reaches ~$10^6$ cm/s. Accordingly, the electron displacement along the field during the exciton lifetime ($\tau \approx 10^{-10}$ s) may amount $\Delta r$ ~ $10^{-4}$ cm. This value exceeds the electron free path $l_e$ ~ $10^{-5}$ cm, therefore, it is necessary to be limited by the $l_e$ value. Although the additional energy received by electron in EF at length $l_e$ is insufficient for transition of exciton into a quantum state with $n = 2$, the exciton gets a dipole moment and its orbit becomes extended along the field. If we accept that the sizes of areas with the lowered concentration of an impurity exceed $r_1$ no more than by one order [22], then in EF exciton orbits will get into areas with increased $N$ (areas of "tails"). This results in the exciton decay. The increase in impurity concentration results in increased $r_1$, decreased activation energy of such decay as well as the $E_\Gamma$ value (see inset in Fig. 3). However, with increasing impurity concentration, the carrier scatter is increased, the $l_e$ value is reduced, thus resulting in increased $E_\Gamma$. These two competing processes cause non-trivial dependence $E_\Gamma(N_C)$ (inset in Fig. 3). Also it is to note, that at $T = 4.2$ K, $r_2^2 \approx 0.05 {\cdot} r_1^2$ and $\gamma_2 \approx 0.5 {\cdot} \gamma_1$ from expressions (5), (6). Therefore, the localization condition (7) is realized worse and influence of "tails" can be much weaker.

The formation probability of the localized electron states in "tails" of conductivity band is low. Moreover, the majority of electrons and holes in the pairs are distant at $r_1$ and the radiative recombination probability for electrons and holes is negligible. That is why the electron entrapped in "tail" area is thrown out thermally into the band [15]. Value of $kT$ at $T = 77$ K is ~6.6 meV, that corresponds to an energy difference $\Delta h\nu$ between positions of the edge PL band maximum observed for all investigated crystals in EF and in absence of EF.

## 5. Conclusions

In the crystals of high compensated undoped gallium arsenide placed in low electric field (EF) at $T = 77$ K, the exciton ra-

diation intensity decreases at abnormal low electric strength in comparison with uncompensated crystals. Such a decrease cannot be explained basing on known exciton state decay mechanisms in EF. The most probable reason for the obtained effect is as follows. In EF, the exciton dipole moment is oriented along the field. In compensated material, even at low concentration of electrically charged background impurities, the "tails" of state density are formed as a result of fluctuations of the impurity concentration. The screening of the Coulomb interaction between electrons and holes when geting in area of such "tails" destroys the exciton states in the crystal placed in low electric field.

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# Зниження інтенсивності екситонного випромінювання під впливом слабкого електричного поля у монокристалах компенсованого арсеніду галію

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Досліджено зміну характеристик краєвої фотолюмінесценції монокристалів сильно компенсованого нелегованого арсеніду галію під впливом електричного поля (ЕП). Встановлено, що при температурі рідкого азоту у даному матеріалі має місце зниження інтенсивності екситонного випромінювання при аномально низьких, порівняно з некомпенсованим матеріалом, значеннях напруженості поля. Показано, що отриманий результат неможливо пояснити відомими механізмами розпаду екситонних станів у ЕП. Запропоновано новий механізм впливу ЕП на зниження інтенсивності екситонної фотолюмінесценції, обумовлений структурними особливостями GaAs, що пов'язані з його зарядовою компенсацією.