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LUMINESCENCE INVESTIGATIONS ON HEAVILY DOPED SEMICONDUCTORS (ON THE BASE OF GALLIUM ARSENIDE)

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Abstract. *The near band-edge luminescenee spectral distribution of heavily doped GaAs ($n = 10^{17} - 10^{19}cm^{-3}$) is studied. The correlation between the elcctrical and luminescence parameters is used for optical evaluation of the frec carrier and ionized impurities eoncentrations in degenerated GaAs LPE layers. Taking into account thc random impurity potential distribution a good quantitative accordancc with the theory is obtained practically without any fitting parameters.*

For strongly compensated samples an agreement between the experimental and theoretical values of the lumineseencc parameters calculated under the assumption of a correlated impurity distribution is also obtained.

It is found that the parameters of the emission bands due to recombination transitions through shallow donors and acceptors in lightly doped or undoped GaAs LPE layers ($n = 10^{14} - 5.10^{15}em^{-3}$) also depend on the random impurity potential. Thus they are discussed in terms of the theory of heavily doped semiconductors.

1. INTRODUCTION

The analysis of the luminescence spectra is widely used for investigations the physical processes of the radiative recombination in semiconductors. Usually these processes are severely affected by the defects in the real crystal, including impurity atoms. In this aspect the luminescence can be used as a method for evaluation of the basic materials parameters. The possibilities of this method combined with the modern experimental technique are illustrated in the invited paper reported by Dr H. J. Queisser on RECON' 79 [1].

In the present paper the luminescence investigations on heavily doped gallium arsenide allowing to determine the local values of some basic materials parameters are considered. The theoretical models are used which are valid in the effective mass approximation. That's why

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only near band edge luminescence spectra, called in this paper luminescence spectra will be considered.

In the first section the peculiarities of the luminescence spectra as a result of the specific energy diagram in heavily doped semiconductors — gallium arsenide in our case — and the influence of the random spatial impurity distribution in the real crystal at relatively lightly doping are discussed.

The second section is devoted to the analysis of the near band edge luminescence spectra — cathodo — and photoluminescence — in degenerated gallium arsenide.

The third section contains an exposition of the investigations on heavily doped and strongly compensated gallium arsenide where the interaction between groups of ionized impurity atoms determines the spectral distribution of the luminescence.

In the fourth section of the present paper the luminescence spectra of the samples with low impurity concentrations (10^{14}-$10^{15}cm^{-3}$) are discussed. Usually these samples are called "undoped" or "high purity".

SECTION I

The energy spectrum of heavily doped semiconductor at various degree of compensation is discussed in [2][1]. Some peculiarities of heavily doped and heavily doped and strongly compensated gallium arsenide will be noted because of their important role in the luminescence.

First in the agreement with the basic ideas of the theoretical models all shallow energy levels are spatial average broadened since they "follow" the impurity potential fluctuations. The amplitude of this broadening γ is equal to

$$\gamma = 2\sqrt{\pi}\,\frac{q^2}{\varepsilon\varepsilon_0 R_s}\,(N_I R_s^3)^{1/2} \qquad (1)$$

where N_I is the total ionized impurity concentration.

As in heavily doped semiconductors the values of γ are relatively high, one can expect that the luminescence spectra will consist of wide emission bands and any fine structure resolution will be impossible.

The theory of the near band edge luminescence in heavily doped

1. In the present paper the symbols for the impurity potential parameters ψ, R_s, R_c and R_0 introduced in [2] are used.

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semiconductors with direct band-to-band transitions at low and high degree of compensation is developed in [3]. The lack of long-range order in heavily doped semiconductors is taking into account, that's why the radiative transitions take place without k-selection rules. Moreover quasi Fermi-levels for the nonequilibrium carriers localized in the potential relief cannot be used. At whole the luminescence spectra are obtained by the solution the Boltzmann kinetic equation.

In heavily doped gallium arsenide the electron Bohr radius a_e is usually larger than the screening radius R_s, but the hole Bohr radius is smaller. So in n-type gallium arsenide as well as in p-type one can observe the radiative recombination transitions of free electrons with holes localized in the potential relief near the valence band edge. At low and very high compensation this allows the direct interpretation of the spectral shape which will be used and discussed in sections 2 to 4.

All theoretical models used here assume heavily doped semiconductor to the effect that the wave functions of neighbour majority impurity atoms are overlapped. This condition is expressed with the inequality

$$N\alpha_B^3 \gg 1 \tag{2}$$

where N is the majority impurity concentration.

At not very high compensation the same inequality $n\alpha_B^3 \gg 1$ is valid for the majority carriers. The reversed inequality is accepted as a condition for lightly doped semiconductor

$$Na_B^3 \ll 1 \tag{3}$$

For n-GaAs the electron Bohr radius $a_e \approx 10^{-6}$ cm and the condition (2) is realized at concentrations $N > 10^{18}cm^{-3}$. For p-GaAs the hole Bohr radius is $\alpha_h \approx 1,7.10^{-7}$ cm and the condition (2) is not fulfulfiled np to concentration $N = 5.10^{20}cm^{-3}$. Nevertheless the electrical [2] and optical processes typical for heavily doped semiconductors are observed in such samples. This is in agreement with the well-known theoretical considerations [2]. Probably the condition (3) is not enough to call a semiconductor lightly doped.

A stronger and, perhaps, more precise condition for lightly doping is proposed in [4]:

$$\gamma / E_0 \ll 1 \tag{4}$$

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where E_0 is the hinding energy of the majority impurity atom. It can be shown that if $\gamma << E_0$ the inequality (3) is valid too. Fig. 1 shows that it is possihle $\gamma > E_0$ even though $Na_B^3 << 1$.

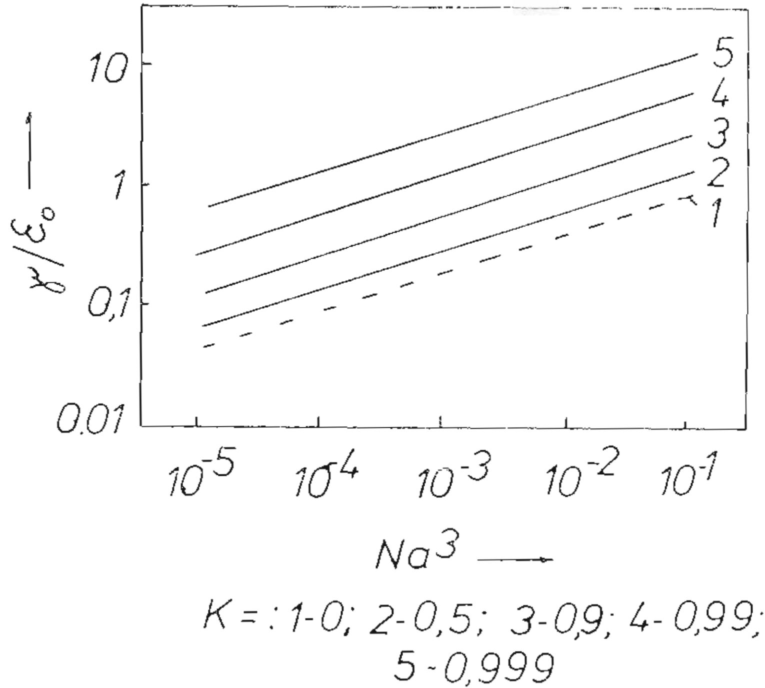

Fig. 1

As a result some of parameters of the near band edge luminescence in lightly doped or "high purity" [5] gallium arsenide must be discussed in terms of the theory of heavily doped semiconductors.

SECTION II

The near band edge luminescence in degenerated gallium arsenide is studied in [6 to 10] including the absorption investigations. The main question in these works is to obtain the Fermi level E_F. It is accepted that the energy of the maximum of the luminescence spectra E_{max} corresponds to the radiative transitions from the Fermi level. Fig. 2 shows that as the carriers concentration n increases the energy E_{max} (respectively E_F) increases too, but this increase remains

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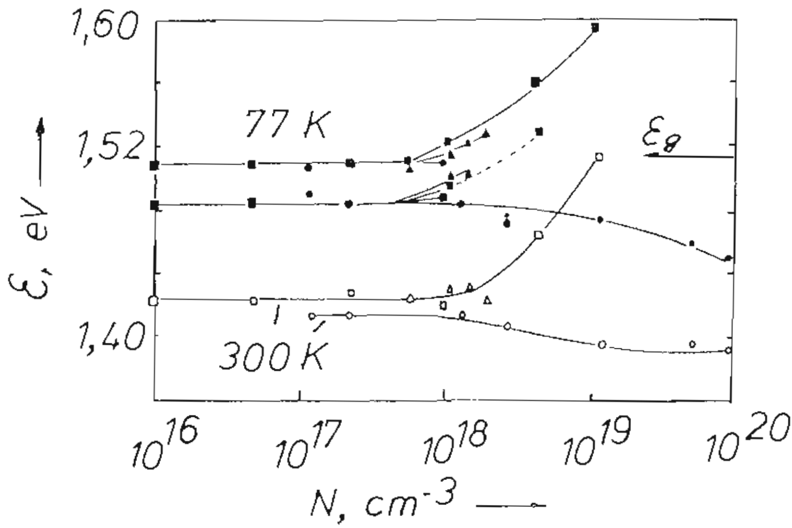

Fig. 2

considerably lower than the theoretically predicted Burstein - Moss-shift. Because of this discrepansy the values of n cannot be directly obtained from the results shown on Fig. 2. An empirical dependence of E_{max} as a function of n is given in [8] (Fig. 3) but the authors point

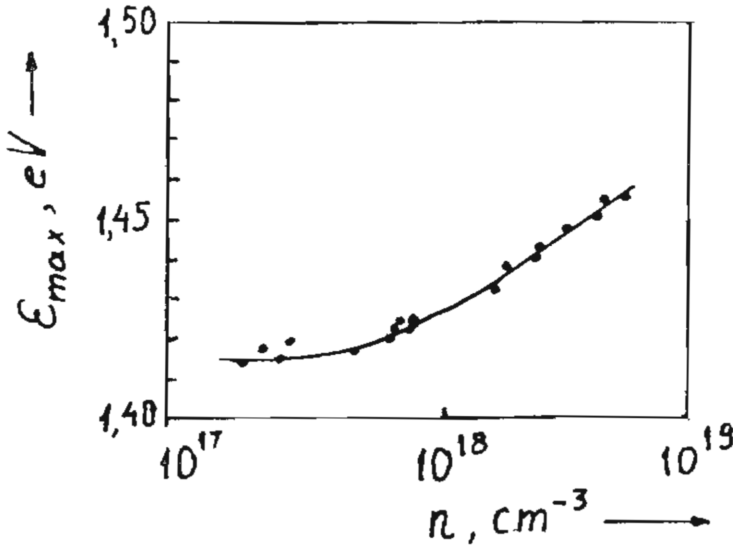

Fig. 3

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out the curve is not appliable for crystals with various compensation.

The luminescence spectra of heavily tellurium doped gallium arsenide liquid phase epitaxial layers with carrier concentrations from $5.10^{17}cm^{-3}$ to $1,1.10^{19}cm^{-3}$ are interpreted in [11, 12] on the basis of the described in [3] theory.

The supposed mechanism of radiative transitions in such objects in accordance with the ideas from section 1 is shown on Fig. 4-a. In

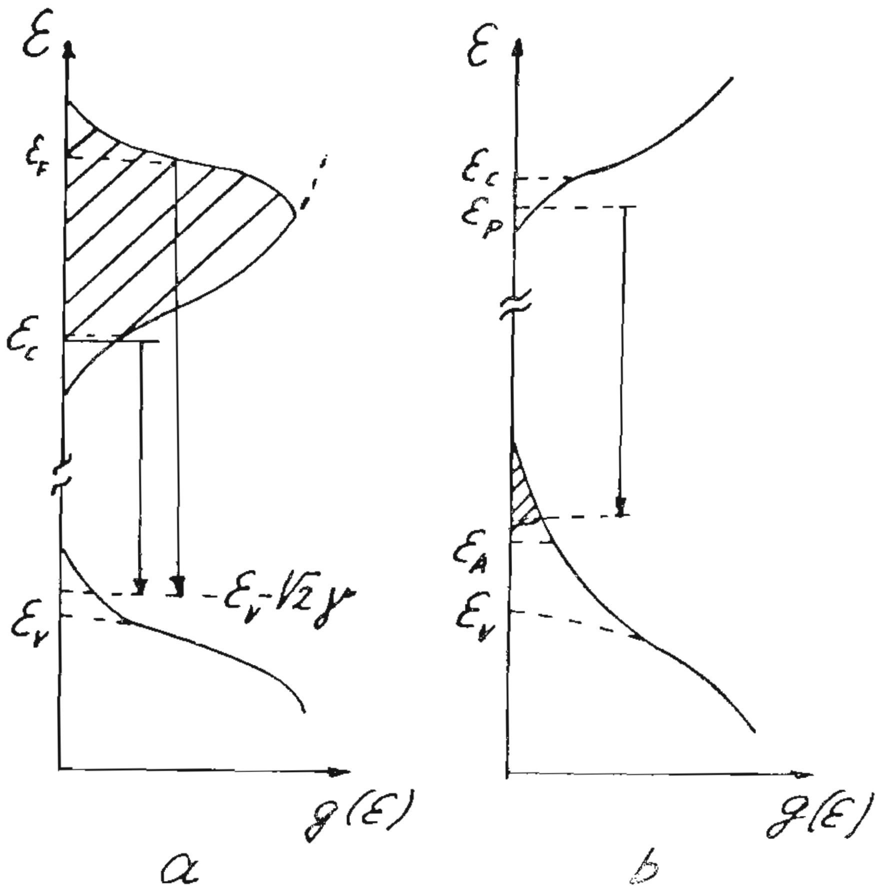

Fig. 4

the studied concentration range γ is from 25 to 75 meV and the derived in zero approximation values of the Fermi level are $E_{F_0} = 40 - 250$ meV. As a result at 77 K for all investigated samples a relation $E_{F_0} >> \gamma >> kT$ is realized and in accordance with [3] the nonequilibrium holes

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are localized in a narrow energy range (of about kT) near the acceptor type fluctuation level $Eg - \sqrt{2}\,\gamma$. Then the spectral shape will follow the free electrons distribution in the conduction band. As it is shown in [11] the radiative transitions from the Fermi level correspond to the half-intensity energy $E_{1/2}$ of the high energy band side.

Typical luminescence spectra at 77 K are shown on Fig. 5. The

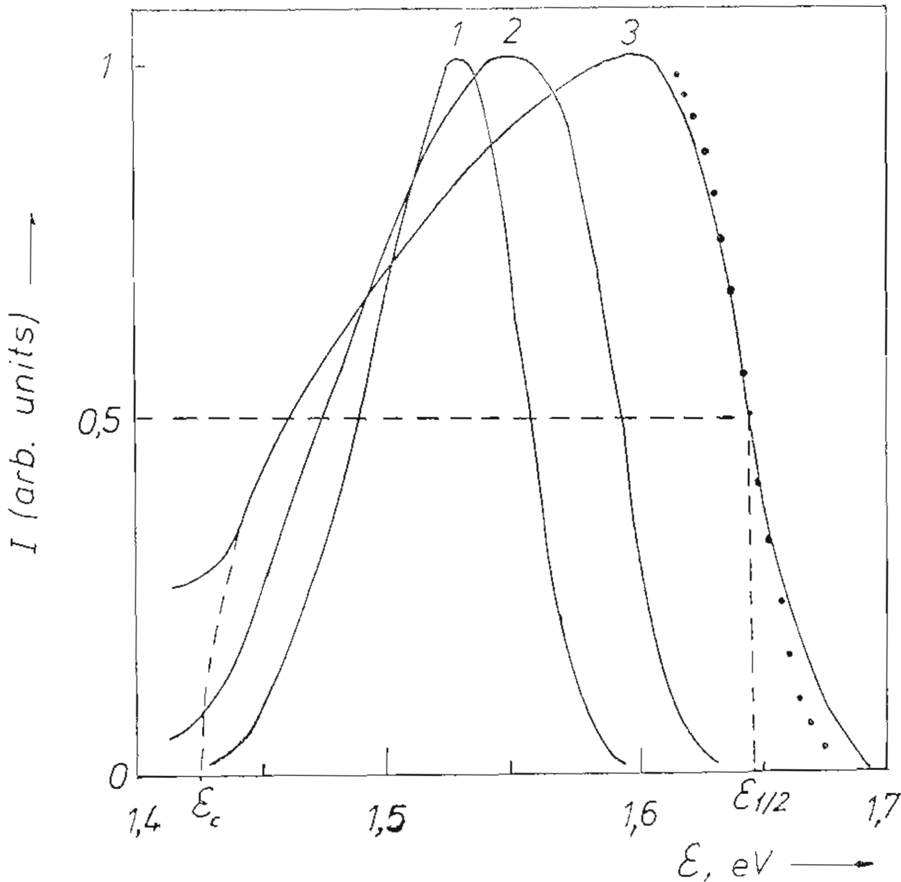

Fig. 5

points mark the Fermi-Dirac function at the corresponding concentration n. In this way a good quantitative explanation of Burstein-Moss effect in gallium arsenide is obtained in [11].

An analysis of the shape of low energy side of the luminescence

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spectra in these samples is made in [12]. As it is known [13] the density of states for heavily doped gallium arsenide is nearly parabolic in the vicinity of the Fermi level. For all spectra a parabolic range is observed, as can be seen on Fig. 6. Extrapolating the lines from the

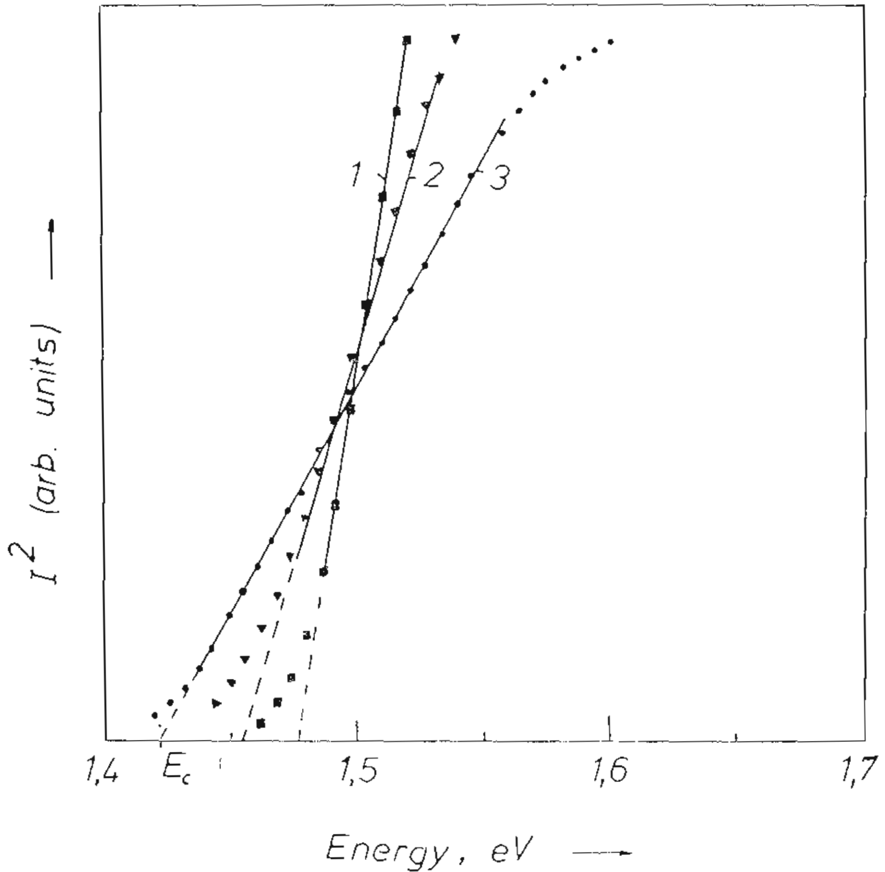

Fig. 6

dependences $I^2(E)$ to zero intensity the energy positiou of the radiative transition from the unperturbated conduction band bottom E_c is obtained. The free carrier concentration n can be directly determined from the experimental value of E_c using the equation

$$E_{1/2} - E_c = E_{F0} = (3\pi^2)^{2/3}(\hbar^2 / 2m_e)n^{2/3} \tag{5}$$

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The ionized impurity concentration N_I can be determined from the relation $E_g - E_c = \sqrt{2}\,\gamma$ using equation (1).

A good agreement between "optically" determined concentrations n^o and N_I^o and determined by the Hall coefficient and Hall mobility analysis values of n and N_I respectively is shown on Fig. 7-a.b.

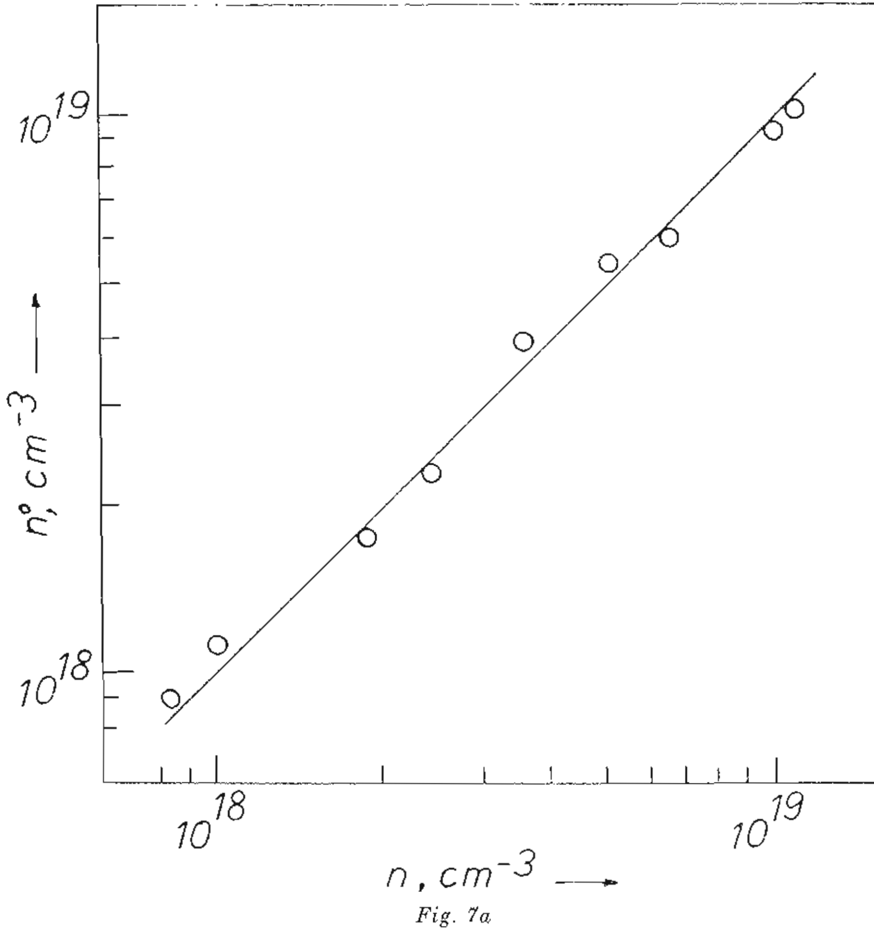

Fig. 7a

SECTION III

The luminescence spectra of heavily doped and compensated e-pitaxial gallium arsenide layers are widely studied in connection with their application in infrared light emitting diodes, for example in [14 to 16]. Usually they consist of one wide emission band, which shape

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and energy position varies with the variation of the generation rate. Attempts are made to explain the luminescence parameters by means of several shallow acceptor levels and density of state tails in the conduction band as well as with the influence of the density of state tails as a whole [15, 16].

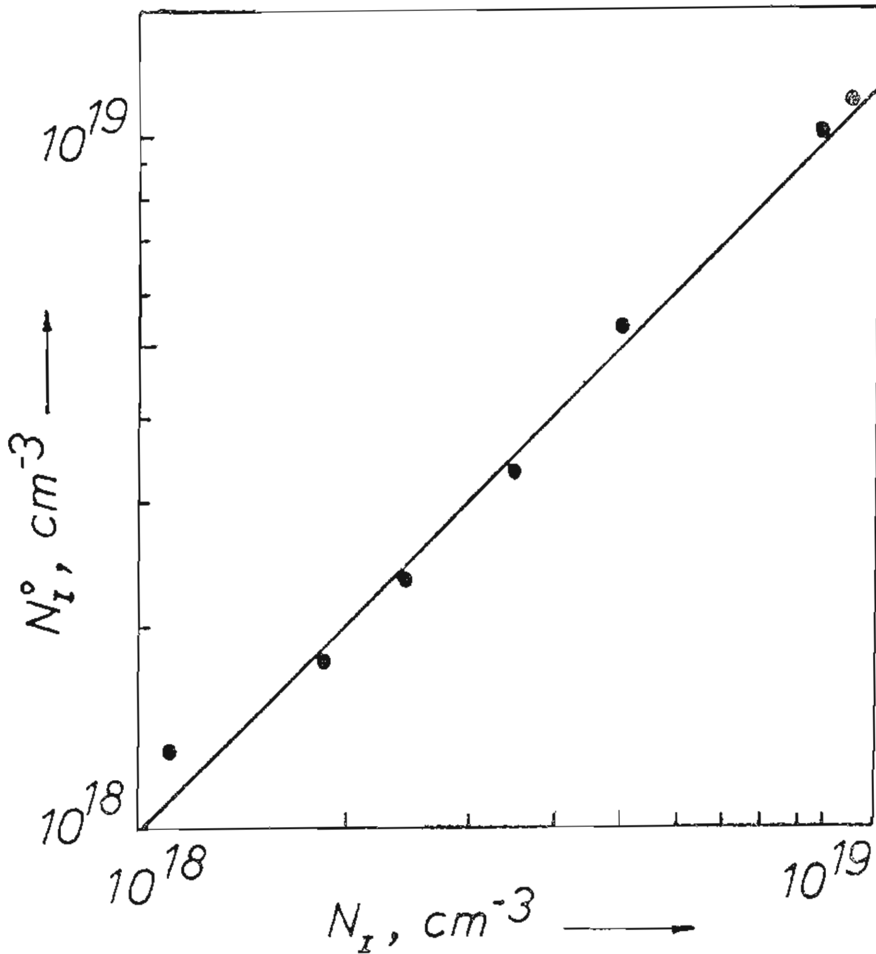

Fig. 7b

The theory [3] is taking into account the fact that at high degree of compensation K ($1 - K \ll 1$) the electron gas is not degenerated. At the same time the density of the bound states near the bottom of the conduction band is very low. The nonequilibrium electrons are

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localized in the narrow energy range near the percolation level E_p. As a result the shape of the spectral band will follow the holes energy distribution in the density of state tails of the valence band (Fig. 4-b).

The quantitative interpretation of these spectra is difficult due to the fact that at $1 - K << 1$ and random impurity distribution the degree of compensation K cannot be determined by the Hall coefficient. That's why $\gamma(R_e)$ cannot be derived. In the case of correlated impurity distribution, as it is shown in [2], the basic parameters of the potential relief can be calculated.

The luminescence in strongly compensated with shallow impurities liquid phase epitaxial layers at correlated impurity distribution is investigated in [17, 18]. The value of γ in the samples is previously determined from the electrical measurements, reported in [2]. It is found that the spectral shape is identical for n- and p-type samples at the same doping level (respectively γ). An exponential range with slope nearly kT is observed in the high energy band side. In the low energy

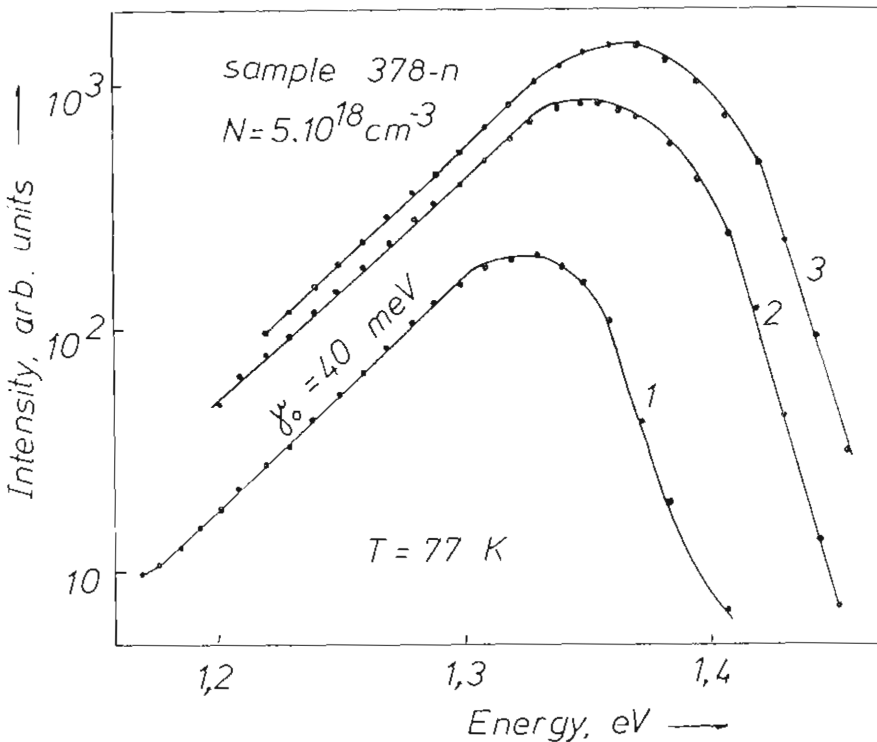

Fig. 8

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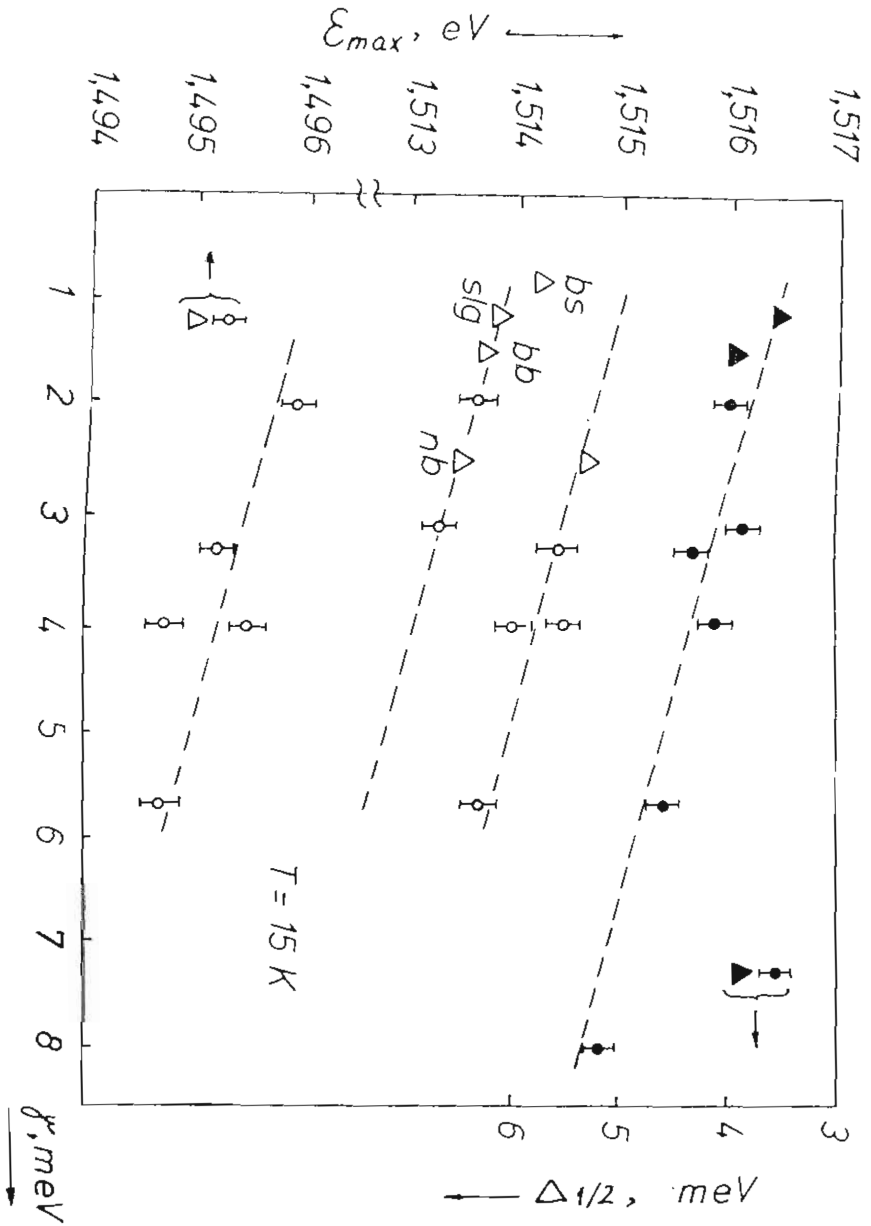

Fig. 9

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band side an exponential range is found with the characteristic slope γ_o (Fig. 8) equal to the calculated value $\gamma(R_o)$ from (1).

These facts are in agreement with the model illustrated on Fig. 4-b and allow nsing the luminescence for evalnation of the r.m.s. potential fluctuation in the case of correlated impurity distribntion.

Probably the analysis of the spectral shape can be used for determination of $\gamma(R_c)$ at random impurity distribution, too. But the experimental examination of the results by means of electrical or any other method is impossible for the moment.

SECTION IV

The near band edge luminescence of "high purity" or lightly doped gallium arsenide connected with the shallow impnrities is widely investigated [19 to 23]. It is established that E_{max} irregularly changes for the most of the bands in different samples, that's why the spectral explanation is difficult. A comparison between the thermal and optical ionisation energies E_0^τ and E_0^0, respectively is made in [5] by means of far infrared photoconductivity. It is found out that E_0^τ varies with the variation of the free electron concentration, while E_0 remains constant. The variation of E_0^τ in [5] is explained by means of random impurity potential fluctuation $\gamma(R_c)$ in [4]. It is shown that the experimental values of E_0^τ from [5] are in good agreement with the dependence

$$E_0^\tau = E_o - (1 + \alpha)\gamma(R_c) = E_o - (1 + \alpha)2(1 + k)\left(\frac{N\alpha^3}{1 - K}\right)^{1/3} \qquad (6)$$

where $\alpha\gamma = E_p (\alpha \approx 0{,}3)$ is the percolation level of the conduction band.

In the same way the energy position of the percolation level in the "far" band will reduce the E_{max} of the emission band according to the relation [3]:

$$E_{max} \approx E_g - E_o - E_p = E_g - E_o - \alpha\gamma(R_c) \qquad (7)$$

The experimental dependence of the energy of the maximum obtained in [24] follows the relation (7) (Fig. 9). It can be seen too that the

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ratio of the values of E_{max} for samples with different shallow donors can change depending on γ.

The data from Fig. 9 support the proposed criteria for lightly doping (4). As a result the luminescence can be used as a method for measurement the value of $\gamma(R_c)$ in lightly doped semiconductor and for estimation the degree of compensation in GaAs samples.

Attempts are made to determine the impurity concentration in gallium arsenide analysing the donor-acceptor recombination band [21 to 23]. It must be noted that a precise identification of the recombination mechanism by time-resolved measurements is made only in [21]. In gallium arsenide $a_e >> a_h$ and the amplitude of the potentinl relief in such "pure" samples can be relatively large, so the applicability of this method is quite limited.

CONCLUSION

The luminescence can be used for experimental determination of the local values of some basic parameters such as carrier and impurity concentrations for gallium arsenide samples. This is very important because of the well-known fact that the present state of the gallium arsenide technology — crystals and layers — cannot enable to achieve the necessary homogenity of these parameters on the surface of the wafer or in the crystal volume. The applicability of the luminescence as a method for measurement is possible taking into account the influence of the random impurity potential in the crystal.

At the end it will be pointed out that the main results in this paper are obtained practically without fitting parameters and this shows the good possibility for quantitative application of the theory of heavily doped semiconductors.

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ΠΕΡΙΛΗΨΗ

ΜΕΛΕΤΗ ΦΘΟΡΙΣΜΟΥ ΗΜΙΑΓΩΓΩΝ ΜΕ ΜΕΓΑΛΗ ΣΥΓΚΕΝΤΡΩΣΗ ΠΡΟΣΜΕΙΞΕΩΝ

(ΠΕΡΙΠΤΩΣΗ GaAs)

Ὑπὸ

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Μελετᾶται ἡ φασματικὴ κατανομὴ φθορισμοῦ κοντὰ στὴν ἀκμὴ τῆς ταινίας τοῦ GaAs μὲ μεγάλη συγκέντρωση προσμείξεων ($n = 10^{17} — 10^{19} cm^{-3}$) Ἡ συσχέτιση μεταξὺ ἠλεκτρικῶν παραμέτρων καὶ παραμέτρων φθορισμοῦ χρησιμοποιεῖται γιὰ τὴν ὀπτικὴ ἐκτίμηση τῆς συγκέντρωσης ἐλευθέρων φορέων καὶ ἰονισμένων προσμείξεων σὲ ἐκφυλισμένες LPE στρώσεις τοῦ GaAs Ἂν λάβουμε ὑπόψη τὴν τυχαῖα κατανομὴ τοῦ δυναμικοῦ προσμείξεων μιὰ καλὴ ποσοτικὴ συμφωνία μὲ τὴ θεωρία προκύπτει χωρὶς προσαρμογὴ τῶν παραμέτρων.

Γιὰ δείγματα μὲ ἰσχυρὴ ἀποκατάσταση παρατηρεῖται μία συμφωνία μεταξὺ τῶν πειραματικῶν καὶ θεωρητικῶν τιμῶν τῶν παραμέτρων φθορισμοῦ ποὺ ὑπολογίσθηκαν μὲ τὴ παραδοχὴ μιᾶς συσχετισμένης κατανομῆς προσμείξεων.

Ἐπίσης βρέθηκε ὅτι οἱ παράμετροι τῆς ταινίας ἐκπομπῆς ποὺ ὀφείλεται σὲ ἀνασύζευξη ρηχῶν κέντρων δοτῶν καὶ ἀποδεκτῶν σὲ LPE στρώσεις GaAs μὲ μικρὴ συγκέντρωση ἢ χωρὶς προσμείξεις ($n = 10^{14} — 5.10^{15} cm^{-3}$) εἶναι συναρτήσεις τῆς τυχαίας κατανομῆς τοῦ δυναμικοῦ προσμείξεων. Ὅλα αὐτὰ συζητοῦνται μὲ βάση τὴ θεωρία ἡμιαγωγῶν μὲ μεγάλη συγκέντρωση προσμείξεων.

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