Band-gap narrowing in highly doped *n*- and *p*-type GaAs studied by photoluminescence spectroscopy

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Band-gap narrowing of GaAs as a function of doping concentration has been measured using photoluminescence spectroscopy on samples grown by molecular beam epitaxy. Both *n*- (Si) and *p*- (Be) doped samples with concentrations varying from 3×10^{17} to 3×10^{18} cm^{-3} have been measured. The experimental results obtained from a line-shape analysis of the spectra taking tailing effects into account are in good agreement with recent theoretical calculations. A simple expression for the band-gap narrowing as a function of concentration for both *n*-and *p*-doped GaAs is given.

INTRODUCTION

The spontaneous radiative recombination of electrons and holes across the fundamental edge (E_0 gap) has been extensively studied in bulk GaAs material.[1–16] Especially the influence of high impurity concentrations on the emission and absorption spectra has been investigated both theoretically and experimentally and the optical properties of heavily doped GaAs are relatively well understood. One of the effects of high doping, namely, band-gap narrowing, has received much attention owing to its basic and practical interest. Quantitative data have been derived from photoluminescent, cathodoluminescent, and electroluminescent measurements.

Photoluminescence (PL) spectroscopy is a direct way to measure the band-gap energy as a function of the carrier concentration. This technique measures the spectrum emitted by the radiative recombination of photogenerated minority carriers. The emission band extends from the reduced band-gap energy which is the difference between the top of the valence band and the bottom of the conduction band, to the energy of the optical absorption gap which is determined by the band filling.

We have derived the band-gap narrowing in both *p*- and *n*-type GaAs grown by molecular-beam epitaxy (MBE). A doping interval ranging from 3×10^{17} to 3×10^{18} cm^{-3} has been investigated. This interval has not been extensively covered in the literature and is of great importance for practical devices. The measured experimental curves have been analyzed performing line shape analysis based on an approach used for data extraction of PL spectra of silicon[17] assuming a constant matrix element. To include band-tailing effects we assumed a Kane-type[18] density of states with parameters defined by the experimental data. Although we realize that the Kane theory overestimates the magnitude of the band tails, we use a Kane-like expression because it has the advantage of yielding a simple analytical formula. The agreement with the experimental data is then obtained by adjusting a fitting parameter. The energy difference between the experimental Fermi level, shifted due to heavy doping effects, and the calculated Fermi level assuming parabolic density of unperturbed states is derived and compared with published experimental and theoretical values for the shrinkage of the reduced band gap.

EXPERIMENT

Samples were grown by MBE. The growth temperature was constant during epitaxy and taken the same for all samples. This was controlled by a calibrated pyrometer measuring the temperature of the molybdenum block at the backside of the pyrometer for the transparent GaAs substrate. Samples were glued with In on a Mo block. A buffer layer of 0.5 μm was followed by a 1–2-μm-thick doped layer. The maximum concentration for the Si doping was 3×10^{18} cm^{-3}. Above this value an increase in the Si concentration will cause an occupation of the As positions by the Si atoms instead of the Ga positions resulting in the *p*-type doping. This reveals the amphoteric character of the Si dopant and induces compensation. To avoid these complications, we limited doping at the above-mentioned value. Also *p*-type (Be-doped) samples were maximum doped at 3×10^{18} cm^{-3}. A total of ten samples was grown.

The doping concentration of the samples was measured by chemical capacitance voltage measurements (Polaron). This instrument has been calibrated by Hall measurements. Some ambiguity exists for *p*-type samples with concentrations higher than 3×10^{18} cm^{-3} due to a discrepancy between Hall and capacitance-voltage (*C-V*) measurements. A secondary-ion mass spectroscopy (SIMS) measurement calibrated by implanted samples could not remove this ambiguity. For this reason we limited the *p* concentration to the above-mentioned maximum value. We estimate the overall accuracy of the doping concentration at 10%.

The PL spectra were taken at 30 K. A constant temperature was carefully assessed for all measurements. An Ar$^+$ ion laser with an intensity of 300 mW cm^{-2} excited the sample; luminescent light was collected and focused on the slit of a 60-cm focal length monochromator. Signals were detected by a GaAs photocathode detector and recorded on a plotter or data were transferred directly and fitted with the central computer.

DATA ANALYSIS

The form used to fit the experimental spectra is derived from the following equation:

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$$I(E) \sim \int_0^\infty \rho_c(E_e)\rho_v(E_h)|M(E_e,E_h)|^2 f_c(E_e) f_v(E_h)\,dE_e, \quad (1)$$

where $\rho_c(\rho_v)$ is the density of states for electrons (holes). $E = E_e - E_h$, $E_e(E_h)$ being the energy of the electrons (holes), and $f_c,(f_v)$ is the Fermi–Dirac distribution function for electrons (holes).

$$f_c = \frac{1}{1+\exp[(E_e - E_F)/kT]},$$
$$f_v = \frac{1}{1+\exp[(E_F - E_h)/kT]}. \quad (2)$$

The matrix element determining the oscillator strength of the transition is given by $|M(E_e,E_h)|^2$.

The photocreated minority carriers are assumed to be thermalized completely before radiative recombination with one of the electrons in the conduction band for an *n*-doped semiconductor or holes in case of *p*-type material. The excitation intensity of the laser light determines the quasi-Fermi level of the minority carriers and for high laser intensities this may cause a shift of the energy of the emission peak. This of course will influence the deduced band-gap narrowing, especially for *p*-doped GaAs because a filling of the electron states in the conduction band produces the highest shift. The pair density in our experiments is less than 10^{14} cm^{-3} for a carrier lifetime of 10^{-9} s and therefore the spread of the population of the minority carriers is neglected. Moreover, due to the complete thermalization and for low intensity of the photoexcitation, the minority carriers taking part in the recombination process are energetically situated at the extremum of the band tail.

Equation (1) can, for the case of *n* doping (the derivation for *p* doping is analog), be written as

$$I(E) \sim \rho_c(E_e) f_c(E_e)|M(E_e,E_h)|^2. \quad (3)$$

For heavily doped semiconductors the *k*-selection rule is relaxed. Due to the doping concentration, the potential fluctuations destroy the translational symmetry of the crystal and deform the wave functions[6] so that they no longer resemble plane waves. Nonvertical transitions are possible in the no *k*-selection rule transitions. The matrix element determining the oscillator strength is energy or *k* dependent but the exact form of the matrix element is not known. Although good results have been obtained explaining the experimental absorption coefficient using a well-defined *k*-dependent matrix element, deviations from experiment both at the low- and high-energy sides of the spectra are mentioned in literature. A combination of *k*-allowed and *k*-nonallowed contributions to explain the experimental luminescence spectra[6] has also been used.

To fit our spectra and especially to determine the experimental Fermi level we assume the matrix element constant. The agreement with theoretical and experimental results and the internal consistency of our results indicates that this approach is very acceptable.

Equation (3) may now be written as

$$I(E) \sim \rho_c(E_e) f_c(E_e). \quad (4)$$

In other words, the spectra reflect directly the electron population in the conduction band as a function of energy.

The distorted density of states in semiconductors which are sufficiently heavily doped that the impurity levels have merged with the adjacent bands is approximated by a Kane[18] form. This conduction-band density of states is given by

$$\rho_c(E_c) \sim \int_{-\infty}^{(E_e - E_c)/\eta_c} \left(\frac{E_e - E_c}{\eta_c} - z\right)^{1/2} \exp(-z^2)\,dz, \quad (5)$$

where E_c is the conduction-band edge for parabolic density of states, in absence of narrowing effects. In the same way a valence-band density of states is defined. When the unperturbed valence-band maximum is taken as the zero of energy, $E_c = 1.515$ eV at 30 K.

Although there is some discussion over the existence of a tail of localized states below the conduction-band edge and/or above the valence-band edge[12–14] we found that Eq. (5) gives a good fit to the experimental results if we use $\eta_{c,v}$ as a fit parameter in our data analysis.

RESULTS

Spontaneous emission spectra for *p*-type and *n*-type GaAs are shown in Figs. 1(a) and 1(b), respectively. It is clear from the figures that, as a function of doping concentration, the *n*-type spectra shift to higher energies while the *p*-type shift to lower energies than the undoped band-gap value: the contribution of the Burstein–Moss effect overrules the band-gap narrowing in *n*-doped GaAs, contrary to *p*-doped GaAs. The energy difference due to band-gap filling for *n* type is roughly $(m_{hh}^*/m_e^*)^{3/2}$ times that of *p*-type material (using Boltzmann statistics and neglecting contributions of the light holes) or for an effective electron mass $m_e^* = 0.067 m_e$ and an effective heavy hole mass $m_{hh}^* = 0.35 m_e$, where m_e is the electron mass, a ten times smaller contribution of the Burstein–Moss shift in *p*-doped than in *n*-doped GaAs is obtained.

The spectral linewidth for the most heavily doped samples is also much smaller for *p*-type spectra than for *n*-type as a consequence of the smaller spread in energy of the holes in the valence band. Besides the central peak stemming from the band-to-band (*B–B*) transition, two features are revealed from the *n*-type emission spectra.

At 1.49 eV is a peak corresponding to a band-to-acceptor (= carbon) or donor-to-acceptor recombination (*e–A*). The intensity of this peak is related to the background contamination and is an indication of the purity of the MBE-grown material. This band-to-acceptor recombination is only present in the lowly *p*-doped samples as, e.g., clearly shown in Fig. 2. The intensity of this peak is, for the *p*-type samples, stronger than the *B–B* recombination, but the peak disappears almost due to complete merging when the band-to-band recombination peak shifts over the *e–A* position and when the carbon acceptors seem to lose their identity. It is interesting to note that this is not the case (for the applied doping concentrations) for *n*-type material where the *e–A* peak does not disappear. The intensity of the *B–B* peak also becomes smaller when doping is increased as can be seen from Fig. 1(a). To fit the spectra where the *e–A* transition was clearly visible, a Lorentzian line shape was included in the fit, giving good results as can be appreciated from Fig. 2

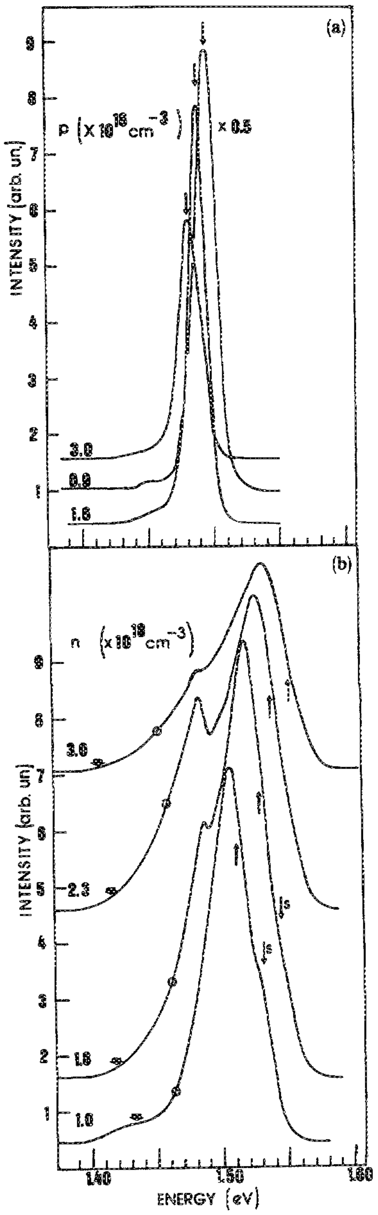

FIG. 1. (a) Photoluminescence spectra of *p*-doped GaAs. The arrows indicate the experimental Fermi level. An increase of the doping level shifts the peaks to lower energies and lowers the intensity. (b) Photoluminescence spectra of *n*-doped GaAs. An increase of the doping shifts the peaks to a higher energy. The arrows indicate the experimental Fermi level. The open circles indicate the energy value of the band gap if the narrowing would only be due to a rigid shift. The thick arrows point to the experimentally position of the band gap. *S* indicates a shoulder observed in the medium doped *n*-type spectra and possibly due to a Fermi edge radiative transition enhancement.

for *p*-doped GaAs. Figure 3 shows a fit for *n*-doped GaAs where the *e–A* contribution in the experimental spectrum is small but still visible.

The second feature is a shoulder at the high-energy side visible for $n = 1.0 \times 10^{18}$ cm^{-3} and also slightly for the $n = 1.8 \times 10^{18}$ cm^{-3} and situated at the Fermi-level energy. This feature is not visible for the higher values and is not seen for our *p*-type samples. It is on the other hand, clearly observed for *p*-doped GaAs[4,9] for concentrations higher than 10^{19} cm^{-3}. It is described in literature[4,9-11] in different ways

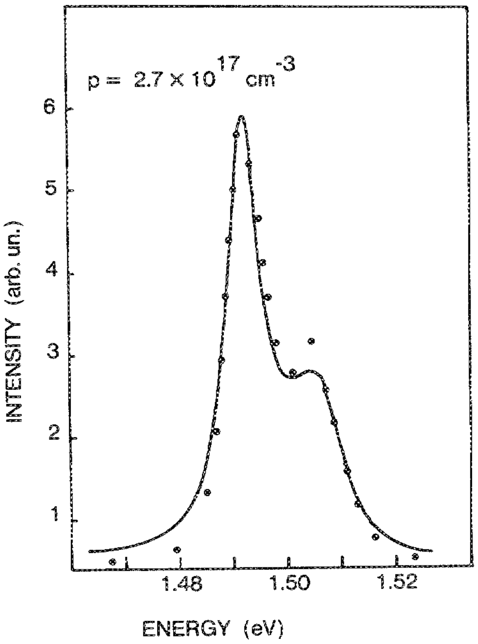

FIG. 2. Fit of an experimental spectrum of a low-doped *p*-type sample. At the low-energy side the intense peak is a donor–carbon related transition. The shoulder at the high-energy side is the band-to-band transition.

and will be discussed more in detail in the last section of this paper.

The results are shown in Table I. The peak maxima tabulated in Table I are also shown in Figs. 4 and 5 together with low-temperature values from literature.

The temperature derived from the fitted *kT* values is in good agreement with the real temperature for the *p*-type samples. A *kT* value of 3(1) meV is found to be compared with the expected value of 2.5 meV for 30 K. But for the *n*-

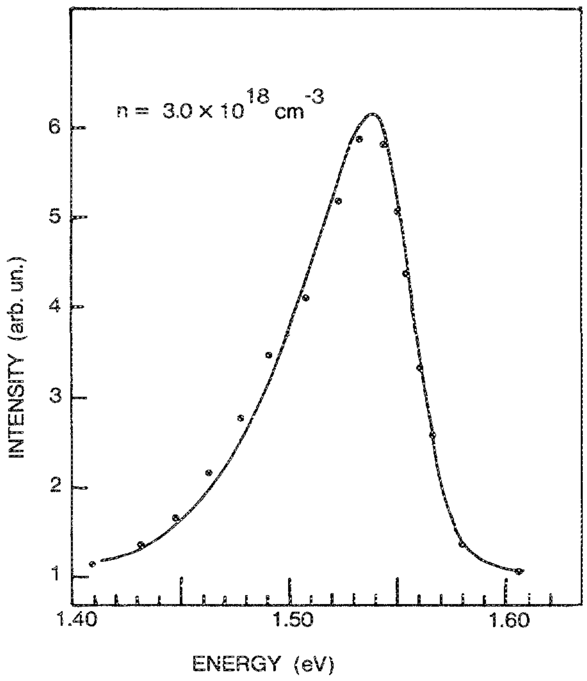

FIG. 3. Fit of an experimental spectrum of a high-doped *n*-type sample. The shoulder at 1.485 eV is due to a donor–carbon related transition.

TABLE I. Experimental values obtained from the fitted PL spectra and calculated Fermi levels (FL) for the different doping levels. ΔE_g is not a fitted value but directly deduced from the spectrum. For p-type material the difference between ΔE_F and ΔE_g is negligible.

n (10^{18} cm^{-3})	Max. pos. (eV)	Exp. FL (eV)	η (eV)	Calc. FL (eV)	ΔE_F (meV)	ΔE_g (meV)
1.0(1)	1.507(2)	1.511(2)	0.04(1)	1.564	53(2)	83
1.8(2)	1.520(2)	1.533(2)	0.06(1)	1.589	56(2)	96
1.9(2)	1.520(2)	1.534(2)	0.06(1)	1.592	58(2)	98
2.3(2)	1.530(2)	1.544(2)	0.06(1)	1.602	58(2)	98
3.0(2)	1.535(2)	1.554(2)	0.07(1)	1.619	65(2)	105
p (10^{18} cm^{-3})	Max. pos. (eV)	Exp. FL (eV)	η (eV)	Calc. FL (eV)	ΔE_F (meV)	
0.27(3)	1.503(2)	1.503(2)	⋯	1.516	16(2)	
0.50(5)	1.495(2)	1.495(2)	⋯	1.518	25(2)	
0.90(9)	1.492(2)	1.492(2)	0.024(5)	1.520	31(2)	
1.6(2)	1.489(2)	1.490(2)	0.031(5)	1.522	38(2)	
3.0(3)	1.483(2)	1.487(2)	0.028(5)	1.523	48(2)	

type samples a value of 7(2) meV is found, larger than the expected value of 2.5 meV. For the n type the deviation for the temperature may be explained by a broadening of the spectra due to an incomplete thermalization of the holes apart from a general broadening of the electron levels. This is in contradiction with our assumption for a δ-like distribution of minority carriers, and a slight underestimation of the shift of the Fermi level is the consequence. On the other hand, the experimentally determined Fermi-level position is influenced less than a few meV by fitting with inclusion of a Gaussian distribution function to account for both effects, and we analyzed our spectra with the less time consuming equation (4).

Also added in Table I are the Fermi-level position values calculated assuming parabolic density of states. The obtained difference between conduction band (valence band) and the Fermi level is added to the energy gap of 1.515 eV corresponding to the value for intrinsic GaAs at 30 K. The values for the Fermi level are calculated using expression (6) assuming complete ionization.

$$n = N_c(T)F_{1/2}[(E_F - E_c)/kT], \tag{6}$$

where

$$F_{1/2}(y) = \frac{2}{\sqrt{\pi}}\int_0^\infty \frac{x^{1/2}\,dx}{1+e^{x-y}}. \tag{7}$$

The difference between the experimental value and the theoretical value ΔE_F is tabulated in Table I. This value would be exactly the band-gap narrowing ΔE_g if doping would cause a rigid-band shift. Due to the stretching of the band tails ΔE_F will be smaller than ΔE_g. This is made clear in Fig. 1(b) where the difference between the intrinsic band gap of 1.515 eV and ΔE_F is marked with open circles for the n-type spectra and represents the band gap if no stretching would occur. It can be seen that the spectrum extends to much lower energy values, demonstrating the stretching. For $n = 3.0\times10^{18}$ cm^{-3} a difference of 40 meV is noticed between the open circle and E_g. E_g corresponds to the intersection between the tangent to the low-energy tail of the emission band and the background. The band-gap narrowing ΔE_g is the difference between this value and 1.515 eV and is tabulated in Table I.

For lowly doped p-type samples tailing is much smaller and within the experimental linewidth as derived from the e–A peak ΔE_F equals ΔE_g.

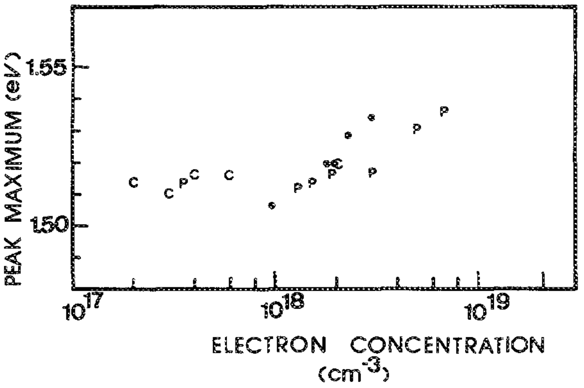

FIG. 4. Compiled data of the peak position of p-type samples. Our data are indicated by a dot. Other data are from Pankove (see Ref. 4) (P), Cusano (see Ref. 7) and (C), Olega and Cardona (see Ref. 9) (O).

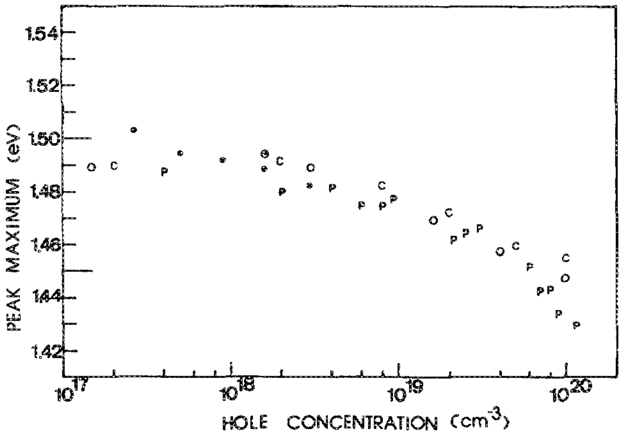

FIG. 5. Compiled data of the peak position for n-type samples. Our data are indicated by a dot. Other data are from Pankove (see Ref. 3) (P) and Cusano (see Ref. 7) (C).

DISCUSSION

The presence of a large concentration of free carriers and impurity ions in a semiconductor can cause a significant reduction of the band gap. At low doping levels there are well-defined bound states associated with each dopant ion. As the dopant density increases, the bound states broaden into a distinct impurity band because of overlap among the dopant-ion orbits. As the density increases still further, the impurity band merges with the main band. At the same time, the conduction-band edge moves downward and the valence-band edge moves upward. On the whole, the band gap narrows and the density of state curve is distorted because the states in each band do not shift with the same amount. The band-gap narrowing is caused by carrier impurity ions interaction and by many-body effects. The many-body effects result from the spin-spin interaction (exchange) and Coulomb repulsive interaction (correlation) between the free carriers. Also the minority carriers (involved in each optical experiment) are influenced both by the ionized doping ions and the majority carriers.[11–13] Possibly also band-tailing effects occur due to a random distribution of impurities.

Casey and Stern[6] have attempted to give a theoretical explanation of the band-gap narrowing using a model where the many-body change in the band gap is not included, but is determined empirically by rigidly shifting the theoretical curves to give the best fit to the experimental data. The agreement is found to be quite good and for p-type material they give an empirical gap shrinkage for optical absorption measurements.

$$\Delta E_g = -1.6\times 10^{-8} p^{1/3}, \tag{8}$$

with ΔE_g in eV and p in cm^{-3}. We represent our results in a graph (Fig. 6) where, for the p-type material, we also included the results of PL measurements by Olego and Cardona.[9] For the doping concentrations $p \geqslant 10^{18}$ cm^{-3} a least-squares linear fit gives

$$\Delta E_g = -2.6(2) 10^{-8} p^{1/3}, \tag{9}$$

different from the absorption measurement results.

The theoretical results that are represented in Fig. 6 for both p- and n-type doping are from Bennett and Lowney.[16] In their calculations they have used Klauder's multiple scattering theory which is capable of determining the distortion of density of states at lower concentrations. For p-type material their theoretical calculations are in good agreement with the experimental values. Also the theoretical results of Sernelius,[11–13] not shown in Fig. 6, are in good agreement.

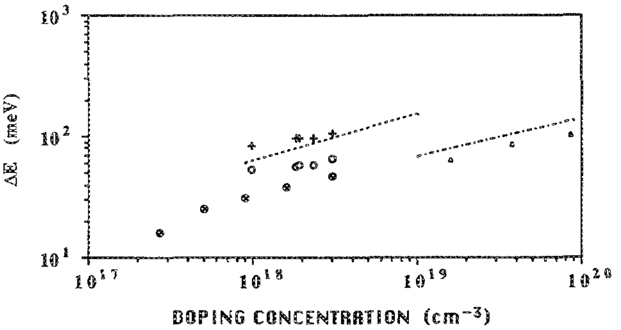

FIG. 6. Fermi-level shifts and band-gap narowing as a function of doping concentration of n- and p-doped GaAs. Highest p dopings (marked with Δ) are band-gap narrowing values from Olega and Cardona (see Ref. 9). Broken lines give theoretical values for band-gap narrowing derived by Bennet (see Ref. 16). Open circles = ΔE_F:n; full circles = $\Delta E_F(=\Delta E_g)$:p; crosses = ΔE_g:n.

For n-type material, the situation seems to be more complicated. The theoretical results of Sernelius seem to overestimate the experimental values. For 3×10^{18} cm^{-3} a theoretical value of $\Delta E_g = 190$ meV is obtained, to be compared with our 105 meV. On the other hand, the difference of 40 meV between ΔE_F and ΔE_g, as a consequence of Eq. (4) only due to the difference in the selfenergy of electrons in the conduction band, is in good agreement with Sernelius calculations. The too large theoretical value for ΔE_g may be due to the exceptionally large shift found for the carrier donor-ion interaction in the valence band. On the other hand, our experimental results possibly do not reveal the extraordinary stretching of the valence bands. As we already mentioned to explain the difference between the fitted temperature and the real one, it is possible that the holes are not thermalized completely. This will induce a shift towards a lower value for ΔE_g. Therefore, the very large hole donor-ion interaction is possibly not completely revealed due to the missing contributions of the $k = 0$ holes in the experimental spectra.

It must be pointed out that our ΔE_g values are in good agreement with the results of Bennet and Lowney.[16] The result of a fit through the data points gives for n doping:

$$\Delta E_F = -4.6(3) 10^{-8} n^{1/3}, \tag{10}$$

$$\Delta E_g = -7.3(4) 10^{-8} n^{1/3}. \tag{11}$$

Unlike for Si there is no determination of ΔE_g from device data. Recently[19] band-gap narrowing effects have been reported in Zn- and Be-doped GaAs solar cells. A study of band-gap narrowing effects in GaAs using capacitance-voltage measurements[20] shows good agreement with our results.

The peak or shoulder on the high-energy side of the spectra seems to be common to luminescent spectra from highly (p-) doped samples. In many papers this structure has been interpreted as coming from non-k-conserving processes due to presence of the acceptor ions. As explained by Sernelius[11] this interpretation is probably wrong. A feature resembling the peak we observed in our n-type spectra, which may have the same origin as for p-type spectra, is mentioned in the discussion of many-body effects in the absorption spectra of modulation-doped quantum wells,[21] the so-called Mahan peak. It is the Fermi edge radiative transition enhancement due to the many-body electron-hole correlation. Its appearance in the spectra at an energy close to the Fermi edge is a consequence of the Coulomb interaction between the photoexcited hole and the sea of electrons. This correlation peak becomes weaker and broader with increasing temperature as well as with increasing electron density. More data will be necessary to prove that this peak is also visible in bulk material and that it is indeed the peak we see in our spectra.

CONCLUSION

We have studied band-gap narrowing effects in heavily doped *p*- and *n*-type GaAs as a function of impurity concentration. The shift of the Fermi level is determined. It is the difference of an experimentally obtained fitted value, shifted due to doping effects, and the theoretical value. The theoretical value is obtained assuming a parabolic density of states function and no doping effects. This rigid-band shift value differs, especially for *n*-type doping, from the value obtained from the intersection between the tangent to the low-energy tail of the emission band and the background. This indicates a stretching of the bands. For the rather low doping concentrations studied here, the tails are very small for *p*-type material. For *n* type some care has to be taken in the interpretation of the tails as shown in the text. Our data for band-gap narrowing, for both *n* and *p* type, agree very well with the theory of Bennet and Lowney.[16] This approves the soundness of the approximations made in the text.

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