will diverge in a most probable sense above the critical concentration and $1/\tau$ will be nonzero or tend to zero slower than s, leading to a delocalization. (The series converges below the critical concentration; this means that $1/\tau \to 0$ as $s \to 0$, and we have localization.)

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Excitation and Temperature Dependence of Band-Edge Photoluminescence in Gallium Arsenide[†]

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Photoluminescent spectra of *n*-type GaAs were studied as a function of the excitation intensity, temperature, and doping level. The spectra consisted of two major bands representing radiative band-to-band recombination and radiative transitions through impurity centers, respectively. The intensity of the peak of the former went through a minimum and a maximum as the temperature was increased from 175 to 500 °K. The temperature corresponding to the above maximum increased as the excitation intensity was decreased or the doping level increased. These results suggest that the temperature dependence of the peak intensity in band-to-band transitions is primarily due to the thermal distribution of the carriers over the available energy states. The peak intensity would therefore normally be expected to decrease monotonically with an increase in temperature, while the above maxima and minima represent perturbations imposed by the presence of temperature-dependent transitions through radiative or nonradiative impurity recombination centers.

INTRODUCTION

Although the power output from luminescent GaAs *p*-*n* junctions generally decreases monotonically with an increase in temperature,[1] it has been found that the emission from GaAs diodes containing a high degree of compensation[2] in the *p*-type side of the junction passed through a maximum at a temperature which moved toward higher values as the current through the diode was reduced.[3,4]

This effect was explained in terms of a recombination mechanism which was governed by the position of the quasi-Fermi level for electrons which moved relative to radiative and nonradiative impurity levels in the forbidden gap, the former being attributed to donor states introduced by the compensating tellurium. However, the steep impurity gradients in the depletion region made it impossible to obtain unequivocal correlation of the above effects with the characteristics of the material in the emitting region, and there was always the possibility that the observed effects could be due to an injection[5] rather than to a recombination process.

In this work, direct correlation of these effects with the characteristics of the material and the recombination process was obtained by observing the photoluminescence emitted by the *n*- and *p*-type sides of the "junction-containing" wafers[2] where the epitaxial layers were sufficiently thick to permit these layers to be treated as bulk samples. The photoluminescent technique also permitted the investigation of the temperature dependence of radiative recombination in lightly doped samples prepared by the horizontal Bridgman crystal-growing technique.

SAMPLE SPECIFICATIONS AND EXPERIMENTAL PROCEDURES

Although the Bridgman sample had no deliberate doping, the material was found to be *n* type with a carrier concentration of 1×10^{16} electrons cm^{-3}.[6] This conductivity was attributed to contamination with silicon from the quartz reaction tube used during growth. The carrier concentrations in the two epitaxial tellurium-doped *n*-type layers used were assumed to be the same as those measured by the Hall effect in material grown identically on appropriate substrates, i.e., 3.6×10^{18} and 5.5×10^{18} electrons cm^{-3}, respectively. A similar technique was used to determine a carrier concentration of 2.1×10^{19} holes cm^{-3} in the *p*-type layer used. For brevity, the above samples will be identified by the symbols n, n^+, n^{++}, and p^+, respectively. The sandwiching of the thin compensated *p*-type layer between the *n*-type and the uncompensated *p*-type layers of the epitaxial wafers prevented access to it.

Since low optical injection rates (to conform with low diode current densities) were of particular interest, a high effective aperture optical system, shown schematically in Fig. 1, was used. Light from the mercury arc filtered through 2 mm of KG3 and 1 mm of BG18 Schott glass contained only wavelengths for which the absorption coefficient of GaAs was greater than 1000 cm^{-1}. This, together with the very short lifetime in GaAs, minimized penetration and internal absorption of the incident and emitted light, respectively.

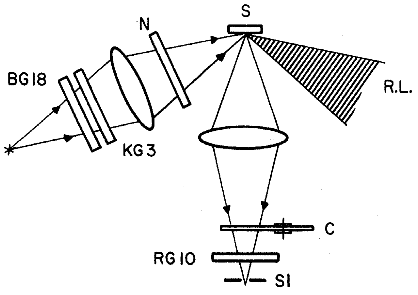

FIG. 1. Schematic diagram of the optical system used for illuminating the sample S, showing the positions of the BG18, KG3, and RG10 Schott glass filters preventing scattered light from entering the monochromator, and the position of the intensity-controlling neutral density filter N, the chopper blade C, and the monochromator entrance slit Sl.

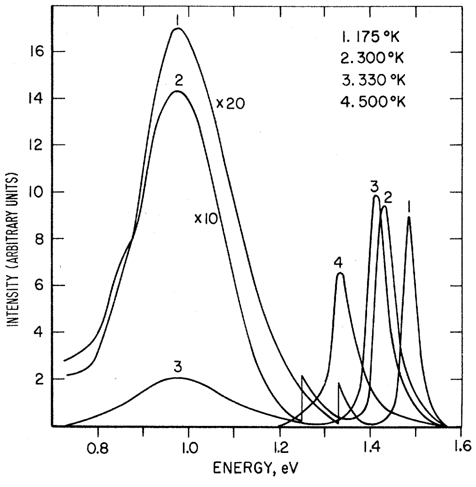

FIG. 2. Curves showing the temperature dependence of the photoluminescent spectrum of lightly Si-doped *n*-type GaAs.

The stray-light level in the monochromator was further reduced by collecting the photoluminescent emission in a direction which prevented light specularly reflected from the sample (shown shaded in Fig. 1) from entering the monochromator. By the use of a special small-aperture photomultiplier with an S-1 response, adequate signal-to-noise ratios were obtained without cooling. Since the spectra frequently extended to 0.7 eV, the low-energy portions of the spectra were measured with a lead sulphide cell and the results corrected by cross calibration of the lead sulphide and photomultiplier responses to the emission from a globar.

The dependence of the spectrum on the excitation intensity was determined by varying the latter over two orders of magnitude with neutral density filters.

RESULTS AND ANALYSIS

The general form of the photoluminescent spectrum for *n*-type material and its temperature dependence is shown in Fig. 2 which represents the characteristic spectrum of the lightly silicon-doped sample. This sample exhibited two main bands, one of which peaked at a constant photon energy of 0.97 eV at all temperatures, while the other peaked at a photon energy which corresponded to the band gap of intrinsic material and shifted with temperature in a manner which was characteristic of the temperature dependence of the band gap of GaAs,[7] as shown by curves 1–4 in Fig. 2, obtained at constant high excitation intensity.

These curves also show that at low temperatures most of the emission occurred in the low-energy band. As the temperature increased from 175 to 330 °K, the emission in the low-energy band decreased rapidly while that in the high-energy band increased slightly. The emission in the low-energy band became vanishingly small and disappeared at temperatures above ≈ 350 °K. As soon as this happened, further increases in temperature produced a decrease in the emission in the peak of the high-energy band, and an asymmetric broadening of this band toward higher energies as shown in curve 4 of Fig. 2.

All of the above main characteristics of the photoluminescent spectra of the lightly doped *n*-type material were also observed in samples heavily doped with tellurium, except that the low-energy band in the latter peaked at 1.2 instead of 0.97 eV, and both bands of the heavily doped material were considerably broader than in the case of the lightly doped sample.

Since the low-energy bands in these samples clearly originate in radiative transitions through impurity levels, and the temperature dependence of such transitions has already been discussed in some detail,[3] the present work is addressed toward the understanding of the temperature dependence of the high-energy band, attributed to band-to-band transitions.

Since the low-energy bands produced by the n^+ and n^{++} samples at low temperatures overlapped into the high-energy band, the temperature dependence of the latter was studied at the higher temperatures where the intensity of the low-energy band was low enough to permit good resolution between the two bands.

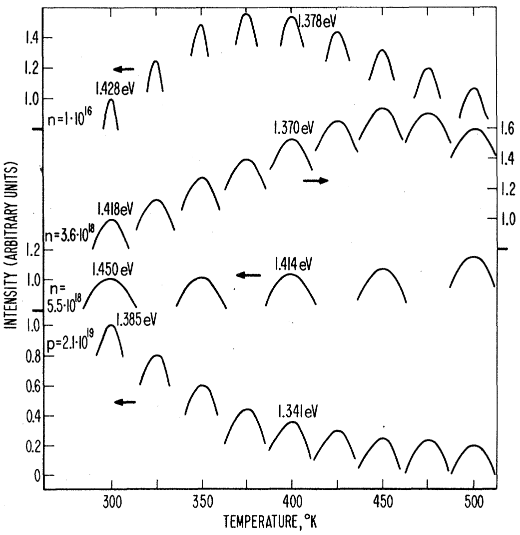

FIG. 3. Curves showing the dependence of the intensity and the curvature of the high-energy peak of the photoluminescent spectrum of GaAs on the concentration of the dopant and temperature. (The energy scale along the abscissa, not shown, was the same for all the curves.) See text for details.

The effect of the dopant and doping concentration on the temperature dependence of the high-energy band (under the same constant high-intensity excitation conditions) is shown in Fig. 3, where the series of curves stretching from left to right represent portions of the spectra in the vicinity of the high-energy peak, obtained at temperatures indicated by the intersection of the ordinate through the peak with the abscissa.

The alternate left and right intensity scales relate the intensities of these portions of the high-energy band to the intensity at 300 °K, the latter being arbitrarily chosen as unity. All the curves were corrected for photomultiplier response and illustrate the broadening of the spectra as the carrier concentration increased from 1×10^{16} to 5.5×10^{18} electrons cm^{-3} as noted above.

The upper two series of curves, representing *n*-type samples having carrier concentrations of 1×10^{16} and 3.5×10^{18} electrons cm^{-3}, clearly show that the intensity of the band-edge photoluminescence passes through maxima at ≈ 350 and 450 °K, respectively, while the emission from the more heavily doped sample showed a monotonic *increase* as the temperature was increased up to 500 °K (the limit used in these experiments).

In contrast with this, as shown by the lowest series of curves in Fig. 3, the Zn-doped *p*-type sample exhibited only a single band, the peak of which *decreased* monotonically with increase in temperature.

Within the temperature range used (100–500 °K), changing the exciting light intensity by two orders of magnitude did not produce any shift in the energy of either peak, i.e., there was no evidence of band-filling phenomena in any of the samples used.[8] However, as shown by the curves in Fig. 4, changes in the excitation light intensity produced marked effects on the temperature dependence of the intensity of the *peak* of the high-energy band. These curves, derived from curves similar to those shown in Fig. 3 obtained at different excitation intensities, show the temperature dependence of the intensity of the *peak* of the high-energy band at three doping levels *n*, n^+, and n^{++}, and three different excitation intensities as indicated in the figure.

The results obtained with the *n* and n^+ samples show that the intensity at the peak increased as the temperature increased from 250 °K and passed through a maximum at a temperature which shifted toward lower values as the excitation intensity was increased. The peak intensity of the more heavily doped n^{++} sample *increased* monotonically with temperature up to 500 °K (the maximum temperature used) at low excitation intensities and *decreased*

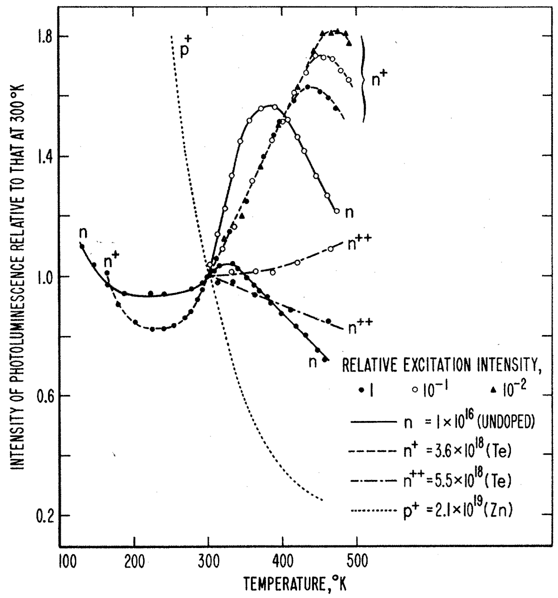

FIG. 4. Curves showing the dependence of the intensity of the high-energy *peak* of the photoluminescent spectrum of GaAs on the intensity of excitation as a function of dopant concentration and temperature.

monotonically when a high excitation intensity was used.

In general, the above excitation intensity effects on the temperature dependence of the band-edge photoluminescence in the three n-type samples are in agreement with the effect of the current density on the temperature dependence of the emission from GaAs p-n junctions.[3,4] However, it should be noted that, while it was assumed that the emission from the diode occurred in the compensated p-type side[2] of the junction, the temperature dependence of the peak emission from uncompensated p-type material shown by the dotted curve in Fig. 4 showed a steep monotonic decrease with increasing temperatures at all excitation light intensities.

At low temperatures, the peak emission from the n and n^+ samples passed through a minimum at ≈ 250 °K and then increased with further cooling. Overlap of the low-energy band into the high-energy band in the n^{++} sample prevented the study of the temperature dependence of the band-edge emission from this material at the lower temperatures.

DISCUSSION

Inspection of Fig. 2 clearly shows that the total emission is not constant for all temperatures and that the recombination process consists of at least three parallel mechanisms: (i) a radiative band-to-band process responsible for the high-energy or band-edge emission; (ii) a radiative recombination process between two states, the energy difference of which is independent of the temperature dependence of the band gap (these may arise from transitions between states in impurity-vacancy complexes[6,9] or between ground and excited states of an impurity); and (iii) a nonradiative recombination process, the efficiency of which increased with increasing temperature.

In an idealized case, where only band-to-band radiative recombination is present, thermal redistribution of the free carriers in the conduction band over a wider range of energies with increasing temperature would be expected to result in a broadening of the spectrum and a corresponding decrease in the intensity at the peak. This effect is illustrated by the close equality of the integrated luminescence, i.e., areas, under the high-energy bands in spectra 3 and 4 of Fig. 2.

Such an idealized temperature dependence of the intensity of the peak of the band-to-band radiative recombination spectrum is shown schematically by curve ABEC in Fig. 5.

The presence of additional radiative or nonradiative recombination paths through impurity levels will effectively decrease the excess carrier concentration and therefore also the above band-to-band radiative recombination rate. However, the recombination rate through an impurity center would be expected to pass through a maximum[3,10-14] at a temperature T_c satisfying the equation

$$E_{F_p} - E_{F_n} = -kT_c \ln(C_p/C_n) \ , \qquad (1)$$

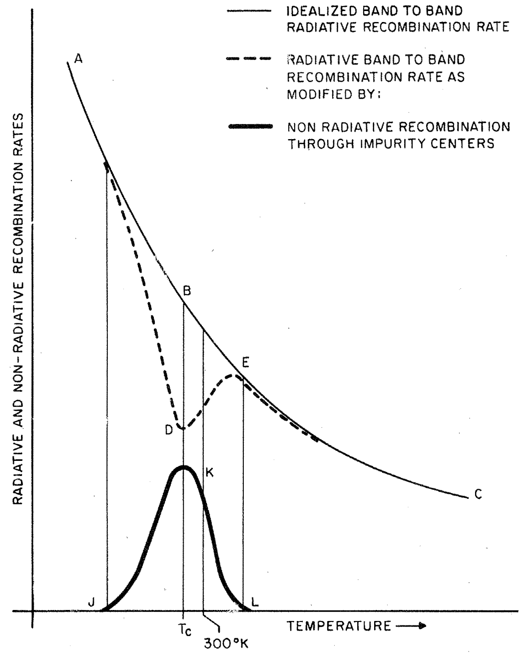

FIG. 5. Schematic curves relating the shape of the curves shown in Fig. 4 to the perturbation of an idealized band-to-band recombination process ABEC by a parallel recombination process through an impurity center represented by curve JKL.

where E_{F_p} and E_{F_n} are the quasi-Fermi levels for holes and electrons, respectively, k is Boltzman's constant, and C_p and C_n are the capture probabilities for holes and electrons, respectively, by the impurity level.

The recombination rate through the impurity can thus be schematically represented by curve JKL in Fig. 5, while the effect of such transitions in depleting the carrier concentration available for band-to-band transitions is shown schematically by curve ADEC in the same figure.

The experimental curves obtained with the n and n^+ samples (Fig. 4) show good qualitative agreement with the shape of curve ADEC in Fig. 5, both sets of curves exhibiting maxima and minima corresponding to E and D in Fig. 5.

A more explicit expression for the temperature dependence of the recombination rate through the impurity can be obtained by expressing the quasi-Fermi levels in terms of the carrier concentrations. This procedure is greatly simplified by assuming parabolic band edges and low carrier concentrations when

$$n_0 + \Delta n = N_c \, e^{(E_{F_n} - E_c)} / kT \tag{2}$$

and

$$p_0 + \Delta n = N_v \, e^{(E_v - E_{F_p})} / kT \ , \tag{3}$$

where n_0 and p_0 are the electron and hole concentrations at thermal equilibrium, Δn is the excess carrier concentration generated by optical excitation, N_c and N_v are the effective density of states, and E_c and E_v are the energy levels of the conduction- and valence-band edges, respectively.

Equations (1)–(3) then yield

$$\ln\left(\frac{n_0 p_0 + \Delta n \, (n_0 + p_0) + \Delta n^2}{N_c N_v}\right) + \frac{E_g}{kT_c} = \ln \frac{C_p}{C_n} \ , \tag{4}$$

where $E_g = E_c - E_v$ is the band gap. In n-type material, $n_0 \gg p_0$, and at low intensities $\Delta n \ll n_0$. Under these conditions, since

$$n_0 p_0 = N_c N_v \, e^{-E_g / kT}$$

and

$$N_c N_v = (2\pi k T / h^2)^3 \, (m_n m_p)^{3/2}$$

(where h is Plank's constant and m_n and m_p are the effective masses of the electrons and holes, respectively), Eq. (4) may be rewritten as

$$\frac{n_0 \, \Delta n \, e^{E_g / kT_c}}{T_c^3} = A\left(\frac{C_p}{C_n} - 1\right) \ , \tag{5}$$

where

$$A = (2\pi k / h^2)^3 \, (m_n m_p)^{3/2}$$

and is a constant for a given material.

It follows that if, for a given light intensity, C_p/C_n can be regarded as a constant, then the temperatures T_{c1} and T_{c2} at which the impurity recombination rates in samples having carrier concentrations n_{01} and n_{02}, respectively, pass through maxima are given by

$$\frac{n_{01} \, e^{E_g / kT_{c1}}}{T_{c1}^3} = \frac{n_{02} \, e^{E_g / kT_{c2}}}{T_{c2}^3} \ . \tag{6}$$

For simple graphical solution, this may be rewritten in the form

$$\frac{E_g}{kT_{c2}} - \frac{E_g}{kT_{c1}} = 3 \ln \frac{T_{c2}}{T_{c1}} - \ln x \ , \tag{7}$$

where $x = n_{02}/n_{01}$.

In applying the above calculations to the experimental curves shown in Fig. 4, it must be emphasized that the schematic representation of the proposed model, shown in Fig. 5, is greatly oversimplified.

The temperatures corresponding to the minimum D and maximum E will, of course, depend on the relative slopes of curves ABEC and JKL. In the configuration shown, a shift of the curve JKL toward higher temperatures to a position J′K′L′ will displace the minimum D and maximum E to new positions D′ and E′, respectively, on the temperature scale. If the temperature shift of the maximum K′ − K is written as $T_{c2} - T_{c1}$, then, in general, the temperature shifts of the minimum D′ − D and maximum E′ − E will be such that D′ − D $< T_{c1} - T_{c2} <$ E′ − E.

Since the minimum D occurs at a temperature close to that of the maximum K in Fig. 5, the minimum in the radiative recombination rate for sample n at 240 °K, Fig. 4, may be used as a measure of T_{c1}.

The value of T_{c2} for the n^+ sample can then be derived from Eq. (7) by putting $x = n_{02}/n_{01} = 3.6 \times 10^2$. Graphical solution of Eq. (7) then yields $T_{c2} = 261.5$ °K.

Since the experimental displacements of the minimum and maximum for the n^+ sample relative to that of sample n shown in Fig. 4 are 12 and 60 °K, respectively, for the same intensity of illumination indicated by the open circles, the above inequality

$$\mathrm{D}' - \mathrm{D} < T_{c2} - T_{c1} < \mathrm{E}' - \mathrm{E} \tag{8}$$

is confirmed.

Assuming that the ratio C_p/C_n remains constant, Eq. (5) predicts that an increase in n_0 would shift the minimum D and maximum E toward higher temperatures. Such a shift in the maximum observed with n, n^+, and n^{++} samples is clearly shown in Fig. 4. Although Eq. (5) does not differentiate between increases in n_0 and Δn, the experimental curves in Fig. 4 show that increases in Δn resulting from increases in the intensity of the exciting light shift the maximum to lower temperatures. Since C_p is defined as the probability of the capture of a hole when all the impurity levels are filled with electrons and C_n is similarly defined as the probability for the capture of an electron when all the impurity states are empty, it is clear that excitation and stimulation processes will modify the ratio C_p/C_n.

In general, an increase in the intensity of the light will increase C_p/C_n. Writing Eq. (6) in the form

$$\frac{n_0 \Delta n e^{E_g/kT_c}}{T_c^3}\left(\frac{C_p}{C_n}-1\right)_I^{-1}=A \qquad (9)$$

to indicate the intensity dependence of C_p/C_n, it follows that an increase in the intensity must be associated with a reduction in T_c, and consequently with a movement of the maximum in the radiative recombination rate towards lower temperatures, as shown in Fig. 4.

The model proposed for the temperature dependence of the radiative recombination rate is in good agreement with the experimentally observed characteristics; however, it must be emphasized that the use of parabolic band edges and nondegenerate statistics in discussing the behavior of highly doped GaAs characterized by exponential density-of-states tails extending the band edges into the forbidden gap can at best only represent an order of magnitude calculation.

CONCLUSIONS

In general, the temperature dependence of band-to-band radiative recombination in GaAs appears to be governed by the thermal distribution of the carriers in the two bands. An increase in temperature results in the spreading of the carriers over a wider range of energies with a resultant decrease in the intensity at the peak of the spectrum.

The presence of radiative or nonradiative recombination through impurity centers results in a modification of the above band-to-band recombination rate in such a way that the intensity at the peak of the band-to-band recombination passes through a maximum and a minimum at temperatures which depend on (a) the excitation intensity, i.e., the excess carrier concentration; (b) the thermal free-carrier concentration; and (c) the nature of the dopant.

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