Radiative recombination in GaAs/$Al_xGa_{1-x}As$ quantum wells

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(Received 12 August 1991; revised manuscript received 22 October 1991)

An experimental study at room temperature of the rate of radiative recombination in a range of *p*-type $GaAs/Al_{0.33}Ga_{0.67}As$ quantum-well samples using both transient photoluminescence (PL) and photoconductivity (PC) techniques is reported. The PL measurements provided the small-signal time constant and the PC measurements probed the nonlinear excitation regime, providing quantitative evidence of excitonic involvement at hole densities less than about 3×10^{11} cm^{-2}. The intensity dependence of the PC gave the variation of effective mobility with excitation density. This mobility variation was used to successfully relate the PL and PC time constants. These time constants, corrected for photon recycling, had the same values as bulk material over a volume-hole-density range 8×10^{16} to 3×10^{18} cm^{-3}, described by a recombination coefficient $B=1.8\times10^{-10}$ cm^3s^{-1}. A comparison with a theoretical model, which included excitonic effects, photon recycling, and reduced electron-hole overlap in the well, highlighted the importance of the magnitude of the effective density-of-states mass in the valence subbands. Experimental evidence suggests that the latter is 0.32 m, which is over twice the value of the heavy-hole mass at the band edge. For degenerate excited populations the time constant, corrected for photon recycling, was found to be 0.8 ns, which is in reasonable agreement with the theoretical prediction of 0.7 ns.

I. INTRODUCTION

The study of radiative recombination in quantum wells has most frequently been carried out using photoluminescence (PL) techniques.[1–11] There has been, however, little attempt to compare the results with those found using photoconductivity (PC) techniques in quantum wells nor with the well-known behavior in bulk material. We address both issues in this paper, basing our approach on a theoretical model of the kinetics of radiative recombination that includes excitonic effects, photon recycling, quantum confinement, and degeneracy.[12,13] It has recently been shown that this model successfully describes the form and temperature dependence of transient PC in $Ga_xIn_{1-x}As/InP$ lattice-matched multiple quantum wells (MQW's),[14,15] and is capable of resolving old disputes concerning the role of excitons at room temperature. The model is also applicable to the nonlinear regimes of excitation in which the photoexcited population of carriers exceeds that in the dark. These are just the regimes pertinent to the operation of quantum-well lasers. They are also where differences between radiative recombination via free carriers only, or via free carriers plus excitons, reveal themselves. This has motivated our study of the PC transients in electron-hole plasmas over a range of optically excited densities.

Experimental details are summarized in Sec. II. PL techniques were used to explore the small-signal regime, and PC techniques covered both the nonlinear nondegenerate and the degenerate regimes. The importance of measuring the intensity dependence of PC in order to obtain the mobility variation is emphasized. Section III contains the experimental results and their interpretation in terms of the theoretical model, and in Sec. IV comparisons are made with theoretical predictions of the magnitude of the recombination time and with experimental results in bulk material.

II. EXPERIMENTAL DETAILS

The study was made at room temperature with a series of *p*-type MQW samples of $GaAs/Al_{0.33}Ga_{0.67}As$ grown by MBE. All samples consisted of 60 periods of 5.5-nm GaAs wells and 17.0-nm $Al_xGa_{1-x}As$ barriers, between cladding layers of 140-nm $Al_xGa_{1-x}As$. The structures were grown on semi-insulating GaAs with a GaAs buffer layer. Samples No. 1–5 were uniformly doped, and samples No. 6–9 were doped in the wells only. The doping densities, which ranged over almost two orders of magnitude, were determined by *CV* profiling and by Hall measurements. There are well-known uncertainties attached to both techniques, and it was not surprising that only modest agreement was obtained. Table I lists the details where p_0, the dark-hole concentration at room temperature, is accurate to only 30%.

The transient decay of PL was measured in the small-signal regime using a dye laser to excite primarily in the wells, plus deep-level centers in the barriers. Excellent exponential decays were obtained over three orders of magnitude of signal.

The transient decay of the PC was measured in the large-signal regime using uniform illumination by a mode-locked, *Q*-switched Nd:YAG laser giving 100-ps pulses at 5 Hz of 1.17-eV photons or, if frequency doubled, 2.34-eV photons. Most of the measurements were performed with the higher-energy photons. When the

TABLE I. Sample characteristics.

Sample	p_0 (cm^{-2})	τ (ns)	Doping
No. 1	1.2×10^{10}	55	well and barrier
No. 2	1.2×10^{11}	17	well and barrier
No. 3	1.8×10^{11}	13	well and barrier
No. 4	5.0×10^{11}	4.9	well and barrier
No. 5	1.7×10^{12}	1.4	well and barrier
No. 6	4.4×10^{10}	36	well only
No. 7	7.2×10^{10}	27	well only
No. 8	3.7×10^{11}	9.5	well only
No. 9	6.1×10^{11}	7.3	well only

lower-energy photons were used, however, little difference in the form of the PC decay was detected. The latter could produce photoconductivity only by excitation of deep-level centers, the most likely candidate being *DX* centers in the $Al_xGa_{1-x}As$. Excitation would therefore be principally in the $Al_xGa_{1-x}As$, as it is for the higher-energy photon.

Hall bars, with Au-Zn:Ni contacts, in series with a 50-Ω resistor were used for the PC measurements with the current flowing parallel to the layers. A constant low dc voltage V_B gave currents within the Ohmic regime. The transient signals were recorded using a sampling oscilloscope. The rise time of the system was less than 100 ps. Changing the bias changed the amplitude but not the form of the PC decay.

It is always important to measure the dependence of the PC signal on illumination intensity, doubly so in the nonlinear regime. If it is observed that

$$V \propto I^S , \tag{1}$$

where V is the PC signal at some fixed time, then $\mu \propto n^{s-1}$.[14] A mobility dependence of this sort affects the form of the PC transient and must be allowed for when deducing radiative-recombination time constants. In the system analyzed here, the mobility was expected, in general, to be some average associated with conduction in both well and barrier. In practice, it will be predominantly determined by the photoexcited electrons (as distinct from holes). Ionization of *DX* centers will be expected to play some part in determining the mobility variation, as indeed will contact effects and the vertical nonuniform population distribution in the wells, which occurs as a result of the most intensive excitation being in the uppermost cladding layer. All of these factors make the situation in GaAs/$Al_xGa_{1-x}As$ samples more complex than that in $Ga_xIn_{1-x}As$/InP. A more thorough discussion of these matters has been given previously.[13]

III. EXPERIMENTAL RESULTS

As mentioned above, the PL transient decays were all exponential, corresponding to the response expected in the small-signal regime in the absence of competing processes such as trapping. Time constants derived from these results, which are given in Table I, showed the expected trend of decreasing with increasing p-type doping. The relative contributions from excitons and free carriers could not be obtained from these small-signal results.

An example of the PC decay in the nonlinear regime is shown in Fig. 1, for one of the lighter-doped samples (No. 3). Similar results were obtained for all but the most heavily doped sample (No. 5), irrespective of the location of the doping. The decay consisted of a roughly exponential fall (visible only at the highest intensities) followed by a nonexponential region whose form was independent of intensity. It could be fitted extremely well by the expression

$$\frac{n(t)}{[n(t)+p_0]^{1-r}} = \frac{n(0)}{[n(0)+p_0]^{1-r}} \exp(-t/\tau) , \tag{2}$$

where $n(t)$ is the electron density at time t, p_0 is the background hole density, r is the exciton factor, and τ is the small-signal radiative recombination time constant in the nondegenerate regime. The exciton factor ranges between 0 and 2 and is given to a good approximation by[13]

$$r = \frac{4\phi_x p_0}{N_{cv} + 2\phi_x p_0} , \tag{3}$$

where N_{cv} is the reduced effective density of states. The exciton trapping factor ϕ_x is given by

$$\phi_x = \exp(E_x/k_BT)\{\mathrm{erf}[(E_x/k_BT)^{1/2}] - 2(E_x/\pi k_BT)^{1/2}\exp(-E_x/k_BT)\} , \tag{4}$$

where E_x is the exciton binding energy, assumed to be time independent over the applicable range (nondegeneracy) of Eq. (2). When $E_x \ll k_BT$, then $\phi_x \approx 0$ and $r \approx 0$, and the decay is predominantly via free-carrier recombination. Conversely, when $E_x \gg k_BT$, then $\phi_x \to \infty$ and

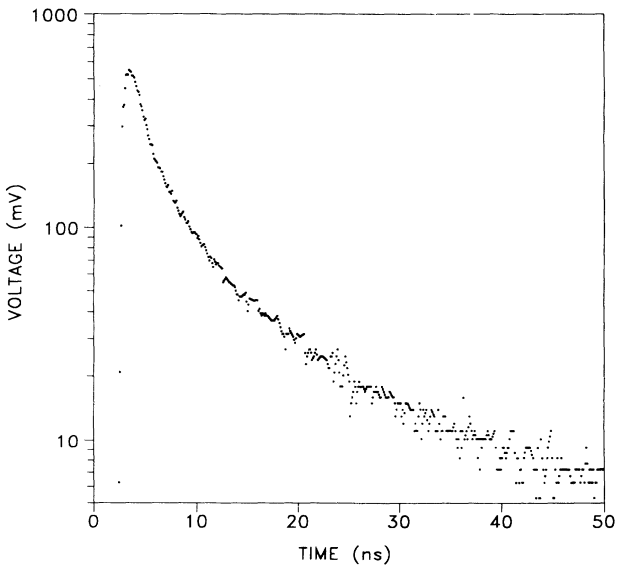

FIG. 1. An example of the transient photoconductivity in sample No. 3 ($T = 292$ K, $\lambda = 0.53$ μm, $V_B = 5$ V).

$r \rightarrow 2$, and the decay is via exciton annihilation. At room temperature, the former condition is very nearly applicable and $r \ll 2$, implying the dominance of free-carrier recombination. Nevertheless, we have found that neglecting excitonic effects entirely [putting $r=0$ in Eq. (2)] did not provide acceptable fits to the decay curve. Theoretical curves identical to the observed transients were generated only if the value of r estimated from Eqs. (3) and (4) was used. This indicated that excitonic recombination, though a small component at room temperature, affected the shape of the nonlinear transients.

Theoretical fits to the observed nonlinear transients were initially made assuming a constant mobility, giving values for the PC time constants. The most heavily doped sample (No. 5) gave an exponential decay, as shown in Fig. 2, indicating that in this case we were in the degenerate regime over the entire decay.

A comparison of the PL and PC time constants showed a marked discrepancy, except for the most highly doped sample, as shown in Fig. 3. With this exception the PC time constants were almost a factor of 2 larger than the PL time constants.

Figure 4 shows the peak value of the PC versus intensity for sample No. 3. In the presaturation regime, Eq. (1) was obeyed with $s=0.55$. The same exponent was obtained in sample No. 3 if, instead of the peak value, the PC amplitudes at times 10 and 20 ns were taken. The PC decays were lengthened compared with the PL decays by the factor s^{-1}. (As the carrier density falls with time, the mobility rises, and this tends to keep the PC high.) The intensity dependence was obtained for all samples. The PC time constants, when corrected for the mobility variation, were in good agreement with the PL time constants. In the case of the most highly doped sample there was a substantial region where $s \approx 1$, as shown in Fig. 5, and hence no correction was required. It was notable that using 1.17-eV photons did not change the intensity dependence, i.e., s was the same. The same dependence was observed in another set of experiments in which the photon energy, 1.49 eV, was such as to produce intrinsic excitation in the wells but not the barriers.[16]

The most striking feature of the intensity dependence was the approach to saturation. Saturation has been observed by us in MQW samples of $Ga_xIn_{1-x}As/$

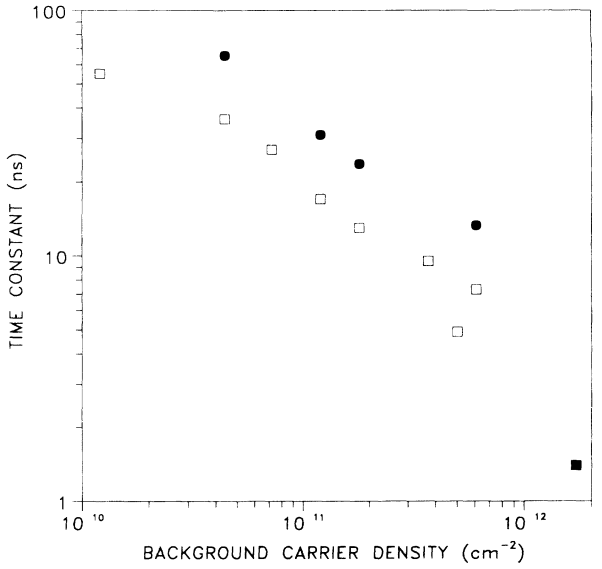

FIG. 3. The experimentally determined time constants as a function of background carrier density. Closed circles, photoconductivity; open squares, photoluminescence. (Closed square: points coincide).

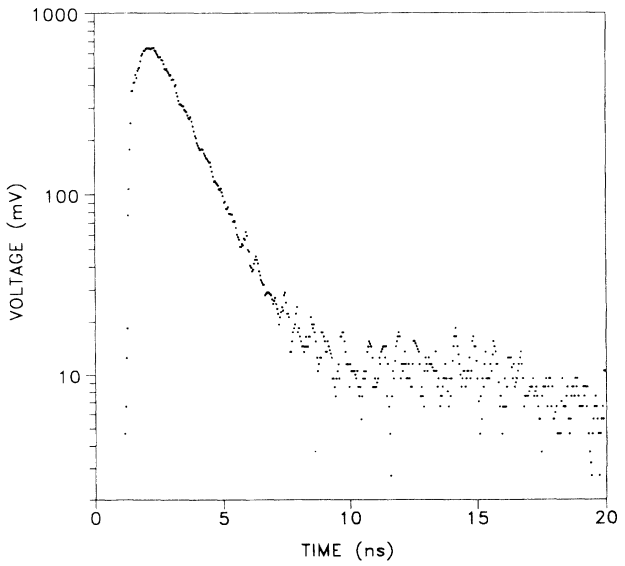

FIG. 2. An example of the transient photoconductivity in sample No. 5 ($T=291$ K, $\lambda=0.53$ μm, $V_B=4.8$ V).

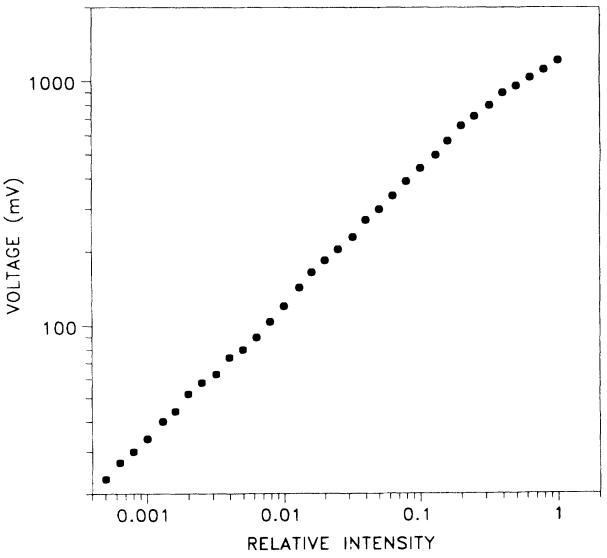

FIG. 4. The peak transient photoconductivity as a function of laser intensity for sample No. 3 ($T=292$ K, $\lambda=0.53$ μm, $V_B=9.7$ V).

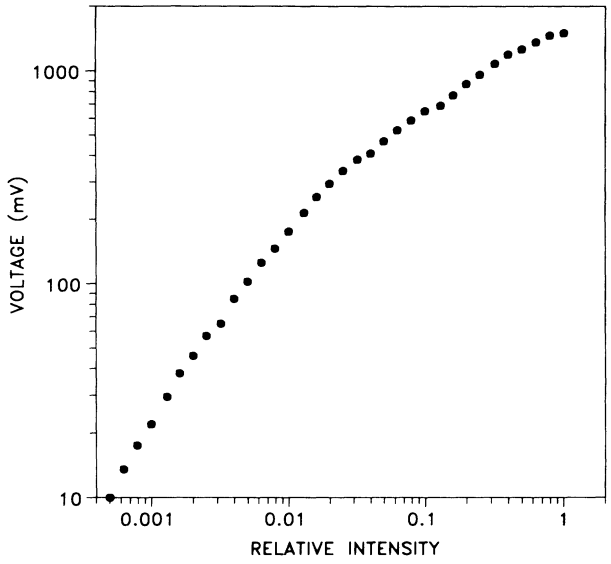

FIG. 5. The peak photoconductivity as a function of laser intensity for sample No. 5 ($T=291$ K, $\lambda=0.53$ μm, $V_B=9.7$ V).

$Al_{1-x}In_xAs$ and $Ga_xIn_{1-x}As/InP$.[17,14] In the present system of 5.5-nm GaAs wells there was only one confined subband and saturation was associated with well filling, which was estimated to occur at an electron density in the well of about 6×10^{12} cm^{-2}. Above this density the PC became rather insensitive to carrier recombination. In the density range 6×10^{12} cm^{-2} to about 9×10^{11} cm^{-2} the carrier population in the wells was degenerate. The decay in this degenerate regime was predicted by theory to be exponential, with a time constant given by the electron–heavy-hole minimum value τ_m, where

$$\tau_m=\tau_0/G \tag{5}$$

and

$$\frac{1}{\tau_0}=\frac{2e^2\eta p_{cv}^2 E_g}{3\pi\varepsilon_0\hbar^2c^3m^2}\ . \tag{6}$$

Here G is the electron-hole squared overlap integral, η is the refractive index, p_{cv}^2 is the squared momentum matrix element, E_g is the transition energy, and the rest are fundamental constants. (At densities above about 4×10^{11} cm^{-2}, excitons are screened out and so do not play a role in degenerate recombination.)

We observed an approximately exponential component in the degenerate regime for all samples, all with the same PC time constant of about 2 ns. A mobility exponent of about 0.5 was obtained from the intensity dependence, giving a true time constant of 1.0 ns. This is in reasonable agreement with the theoretical value of 0.88 ns derived below. There was no indication of Auger processes up to densities of the order of 6×10^{12} cm^{-2}, which places an upper limit of 10^{-29} cm^{6}s^{-1} on the Auger coefficient.

Unlike the situation of $Ga_xIn_{1-x}As/InP$, attempts to use the theoretical model to fit *absolute* magnitudes of PC were not successful. We attribute this to a combination of contact effects and vertical nonuniformity of excitation in the MQW. However, the independence of *shape* on intensity does suggest that nonuniformity was not a major factor.

IV. DISCUSSION

The nonlinear dependence of PC on intensity, explicable in terms of an effective mobility that varied with carrier density, was used to resolve the discrepancy between the small-signal time constants measured by PL and those deduced from the nonexponential PC decay. An exponent s [Eq. (1)] of about 0.8 can be explained by electron-hole scattering,[14] but that observed here (≈0.5) denotes a significantly larger effect that appeared to be independent of whether excitation was primarily in the wells or in the cladding layer. We have no explanation of this behavior which we have also observed in other $GaAs/Al_xGa_{1-x}As$ samples.

Nevertheless, the agreement between PL and PC results obtained by our assumption of a density dependent mobility encouraged us to make a comparison with theory. Our model gives the following expression for the small-signal radiative-recombination rate in nondegenerate p-type quantum wells:

$$\frac{1}{\tau}=\frac{1}{\tau_0}(1-\phi_v)\frac{m_r}{M}\left[G+\frac{8E_x}{k_BT}\phi_x\right]\frac{p_0}{N_{cv}+2\phi_x p_0}\ , \tag{7}$$

where τ_0 is given by Eq. (6), ϕ_v is the photon recycling factor, m_r is the reduced mass, M is the total mass of the exciton, and N_{cv} is the reduced density of states associated with the electron subband (there is only one in a 5.5-nm well) and the first heavy-hole subband. The exciton binding energy was assumed to be dependent via many-body effects on the background hole density p_0 via the simple model

$$E_x=E_{x0}e^{-q_sa_x}\ , \tag{8}$$

where E_{x0} is the unscreened exciton binding energy, q_s is the 2D screening factor, and a_x is the exciton radius (which is related to E_x), and this expression is roughly in accord with the results of elaborate many-body calculations. The exciton trapping factor ϕ_x is given by Eq. (4).

Coulomb enhancement and recombination explicitly involving light holes are ignored. The light-hole band is expected to lie some 30 meV above the heavy-hole band[18] (in hole energy) and will be lightly occupied at room temperature. Its contribution to the recombination is subsumed in our one-band model. Coulomb enhancement of free-carrier absorption and exciton formation are closely linked, and we have assumed that the excitonic term in Eq. (7) adequately accounts for the electron-hole attraction.

We have calculated the squared overlap integral G and find it to be 0.91. We have taken $E_{x0}=10$ meV. Figure 6 shows the density dependence of the excitonic factors that determine the shape of the transient decay and the magnitude of its small-signal time constant. At low densities, excitons are stable but few in number, and r [Eq. (3)] is small. With increasing density r rises, reaches a

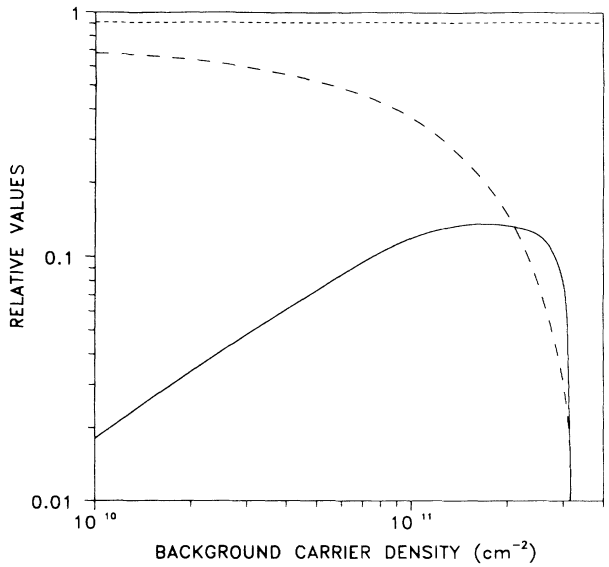

FIG. 6. The background carrier density dependence at 290 K of (a) the excitonic factors r (solid line) and $(8E_x\phi_x/k_BT)$ (dashed line) and (b) the squared overlap integral (dotted line).

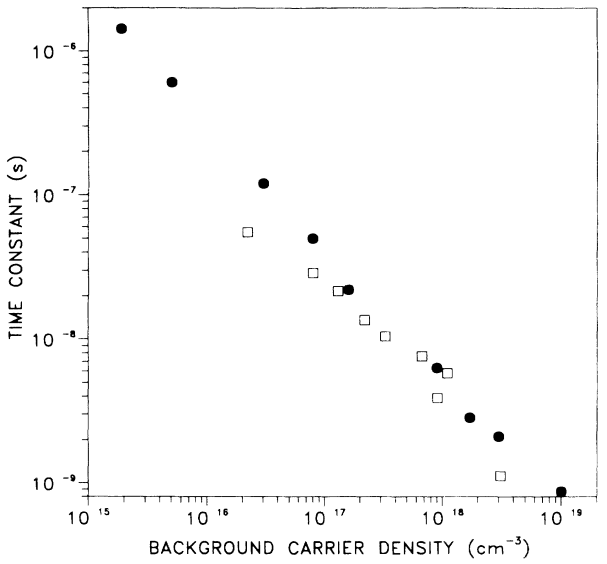

FIG. 8. The radiative time constants as a function of the background carrier density. Open squares, 5.5-nm GaAs/$Al_xGa_{1-x}As$ MQW; closed circles, epitaxial GaAs (Ref. 20).

maximum, and falls sharply, following the reduction in exciton binding energy. Above a density of about 3×10^{11} cm^{-2}, excitons play no role.

The curve in Fig. 7 shows the theoretical time constant as a function of the background carrier density, calculated using a photon recycling factor ϕ_v estimated by us to be 0.2.[13] The time constant τ_0 was taken to be 0.64 ns, corresponding to a transition energy of 1.51 eV, and we

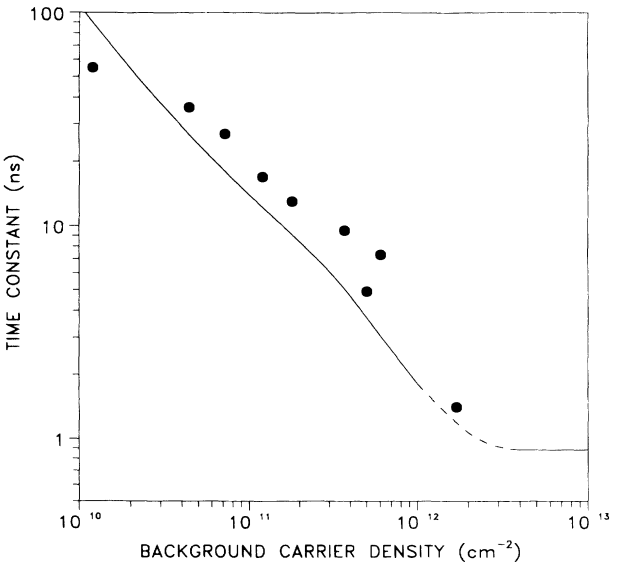

FIG. 7. The radiative time constant as a function of the background carrier density. The points are experimental values. The theoretical curve was calculated, using $G=0.91$, $E_{x0}=10$ meV, and $\phi_v=0.2$, in the nondegenerate (10^{10}–10^{12} cm^{-2}) and the degenerate (4×10^{12}–10^{13} cm^{-2}) regimes. The dotted line is an approximation in the weakly degenerate (10^{12}–4×10^{12} cm^{-2}) regime.

assumed a heavy-hole in-plane mass of $0.14m$.[18] Theory predicts a kink in the curve at the background carrier density at which excitonic effects become weak, but otherwise an inverse linear dependence on hole density. There is some hint of such a break in the slope of the experimental data, but the experimental uncertainly is too great for this to be convincing. Theory consistently underestimates the time constants obtained experimentally.

In the degenerate regime, the time constant (including photon recycling) is predicted to be 0.88 ns if band-gap narrowing is ignored. Band-gap narrowing at densities in the degenerate regime probed here (roughly between 10^{12} and 6×10^{12} cm^{-2}) is expected to be less than 30 meV.[19] Renormalization effects, apart from the effect on the exciton binding energy, are assumed to be relatively insignificant in the present context. The experimental value of the degenerate time constant, 1 ns, was in reasonable agreement with the predicted value.

We can compare our results for a 5.5-nm GaAs quantum well with those of Nelson and Sobers for bulk GaAs,[20] after correction for photon recycling. The latter are in agreement with the predictions of Stern[21] and of Casey and Stern,[22] at least at high densities. Figure 8 shows this comparison with our areal hole densities converted to volume densities. At high densities (where our results lie) there is little difference in magnitude.

The increase in recombination rate caused by the larger band gap in the quantum well is almost completely offset by the slightly poorer overlap of the wave functions. Thus the radiative recombination coefficients for the high density, purely free carrier regime in two dimensions (2D) and three dimensions (3D) are as follows:

$$B_{2D}=\frac{1}{\tau_0}\frac{\hbar^2\pi L}{Mk_BT}G\ , \tag{9}$$

where L is the well width, and

$$B_{3D}=\frac{1}{2\tau_0}\left[\frac{2\pi\hbar^2}{k_BT}\right]^{3/2}\left[\left[\frac{m_{HH}}{M_{HH}}\right]^{3/2}+\left[\frac{m_{LH}}{M_{LH}}\right]^{3/2}\right]\times\frac{1}{m_{HH}^{3/2}+m_{LH}^{3/2}}, \quad (10)$$

where m_{HH}, m_{LH} are the heavy- and light-hole masses and M_{HH}, M_{LH} are the corresponding exciton masses. In our case, $B_{2D}=3.3\times10^{-10}$ cm^3s^{-1} and $B_{3D}=1.8\times10^{-10}$ cm^3s^{-1}, with $M=0.207m$, $M_{HH}=0.567m$, $M_{LH}=0.149m$, $m_{HH}=0.510m$, and $m_{LH}=0.082m$. According to this calculation, the time constant of the quantum well should be nearly half that of the bulk for the same density at room temperature. The calculated coefficient for the bulk agrees with that of Stern, which agrees with the data of Nelson and Sobers. Thus, the cause of the discrepancy appears to lie in our interpretation of the 2D data. Obvious uncertainties exist in the magnitude of the photon recycling factor, but they are unlikely to account for more than a small part of the difference between theory and experiment. A larger factor is the error in the estimation of the hole density. Perhaps the greatest source of error, however, is in the choice of the density-of-states mass of the holes. At room temperature, nonparabolicity of the heavy-hole band and perhaps occupation of the light-hole band is expected to increase the effective value of the density-of-states mass significantly. If, instead of the band-edge mass, the average of the latter and the bulk value are used, we obtain $0.32m$. This gives $M=0.387m$ and therefore $B_{2D}=1.8\times10^{-10}$ cm^3s^{-1}, which agrees with experiment. Clearly, a more elaborate calculation, taking into account the actual valence-subband structure, is required to obtain a well-founded value for the 2D radiative recombination coefficient. We note, finally, that the hole mass does not appear in the calculation of the time constant in the degenerate regime where agreement between theory and experiment was reasonably good. This supports the case for reassessing the hole mass in the nondegenerate regime.

ACKNOWLEDGMENTS

We are particularly grateful to Dr. P. Dawson (Philips Research Laboratory, Redhill, U.K.) for providing the PL data. We would like to thank the U.K. Science and Engineering Research Council for supporting this project.

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