Exciton Recombination Radiation of GaAs:Zn

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The identification of recombination radiation from excitons bound to ionized- and neutral-zinc centers has been confirmed, and the energy of these radiations has been found to be independent of Zn concentration up to $\approx 10^{16}$ acceptors/cc. Comparison with theory leads to an electron-to-hole effective-mass ratio for exciton considerations in GaAs of 0.28. For more heavily Zn-doped GaAs, the photoluminescence changes character, indicating that the nonlocalized state is involved.

IN a previous paper[1] we reported on the photoluminescence of lightly doped epitaxial GaAs and, among other results, identified emission lines associated with excitons bound at ionized- and neutral-zinc impurities. Correlations were made between these photoluminescence results and extrapolations of published results[2,3] for zinc activation energy, E_A, using the available theories[4–6] for the binding of excitons to these impurities. Since that time we have determined E_A for Zn in GaAs from Hall-effect measurements[7] on purer specimens than those previously available, and we report here on photoluminescence of these specimens leading to improved correlation with theory.

The theoretical studies of the binding of excitons to impurities treat σ, the electron-to-hole effective-mass ratio for the exciton, as a parameter and determine over what range of this parameter the binding occurs. The recent work of Levy-Leblond[8] implies a more restricted range for binding in certain cases than do the previous theories. He concludes that there exists a critical mass ratio $\sigma_c \lesssim 1$, such that the ionized acceptor cannot bind an exciton if σ is less than that value. The present study indicates that σ for GaAs is 0.28, so that σ_c must be less than 0.28.

The results for the Zn-related emission lines are given in Table I. The energies of the radiation related to an exciton bound to an ionized-zinc impurity and neutral-zinc impurity are, respectively, E_{Zn^-} and E_{Zn^0}. For all but the most heavily doped sample, the spectra contained other weaker but identifiable lines, including the $n=1$ free-exciton line and the donor-related line at 1.5141 eV. The presence of these lines in their proper places tells one that the band gap is essentially unchanged, at least up to these concentrations. Photoluminescence at 77°K[9,10] indicates that the band gap is probably unchanged up to concentrations greater than that of the most heavily doped sample used here. This last sample will be discussed later.

The identification of the lines listed in Table I, with the addition of Zn to the synthesis, is very clear. Note that the relative efficiency of the 31-meV line in general increased with Zn concentration N_A. Data of this type are somewhat uncertain, however, since the relative efficiencies depend on the quality of the sample surface. All samples were cut ultrasonically and treated similarly, except 629803-3-*H*3, which was cleaved to shape. The higher efficiency of the latter sample is explained by the more nearly "as-grown" condition of the surface, which has been found to give the best efficiency. The involvement of a bound exciton in the 31-meV peak is implied by the existence of one sample[1] for which this line is much narrower than kT.

Under high resolution, the 8-meV peak is found to be a doublet, the two lines being of nearly equal intensity and separated by 0.17 meV. The energy of this peak given in Table I is the average of the positions of these two lines, and the half-width is that of the combined doublet. The half-width of each of the two lines is approximately 0.15 meV, again less than kT. This peak was previously[1] reported to be a triplet for one sample. Subsequently, this sample was reexamined and lightly etched. This caused one line to vanish, presumably by the relieving or removing of strains, leaving a doublet, as observed with the present samples and as reported by others.[11]

Note that the relative-efficiency ratio of the 8-meV to the 31-meV line decreases with increasing Zn concentration. Such behavior is expected, since the radius of the exciton-Zn^0 complex is larger than that of the exciton-Zn^- complex. This causes a reduction of efficiency of the 8-meV line from overlapping of wave functions to occur at Zn concentrations for which the 31-meV line is still unaffected.

The energy of the radiation from excitons bound to Zn^- and Zn^0 changes less than $\frac{1}{3}\%$, even though E_A decreases by about 10% as the impurity concentration increases by one order of magnitude. This points out the basic differences in the two phenomena and leads

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TABLE I. Photoluminescence results at 4.2°K.

Sample No.	N_A [a]	E_A (meV)[a]	$E_G-E_{Zn^-}$ (meV)[b,c]	Width (meV)	Rel. eff.[d]	$E_G-E_{Zn^0}$ (meV)[a,c]	Width (meV)	Rel. eff. ratio E_{Zn^0}/E_{Zn^-}
629805-2	···		31.0	2.4	0.31	8.1	0.30	0.30
629803-2	1.65×10^{15}	29.1	31.1	2.5	0.39	8.1	0.41	0.20
629803-3-*H3*	1.12×10^{15}	28.7	31.1	2.4	0.70	8.1	0.30	0.23
619995-1	4.13×10^{15}	26.3	31.1	2.5	0.36	8.1	0.33	0.16
629801-2	5.15×10^{15}	27.4	31.0	2.5	0.64	8.0	0.33	0.14
620000-2	1.43×10^{16}	26.9	31.0	2.5	1.00	8.0	0.43	0.04
*G*5-20-14.9	3.08×10^{17}	16.2	(37.5)[e]	11	0.35	···	···	···

[a] See Ref. 7.
[b] $E_G=1.5202$ eV at 4.2°K.
[c] The uncertainty of these values is about ±0.4 eV, including the uncertainty in E_g. The precision is at least twice that good.
[d] Rel. eff. ∝ line height×width.
[e] This result is listed here for comparison only. Discussion of possible mechanism is contained in the text.

one to the conclusion that the limiting low-concentration values of E_A are the proper ones to relate to the theories and the photoluminescence results.

We consider first the binding of an exciton to a neutral acceptor. The stability of this complex is not critically dependent on the mass ratio in the region of interest, and the binding energy has been calculated in terms of E_A by Kohn[5] and Munchy[6] as a function of the mass ratio. Using the present data and the low-concentration limit of $E_A=30.8$ meV for Zn,[7] one finds an effective-mass ratio for the exciton of 0.28. Similarly, using the calculations of Sharma and Rodriguez[4] and our data for the exciton bound to Zn^-, we find an effective-mass ratio of 0.29. If we use an electron effective mass of 0.068 m_0, the ratio yields an effective hole mass of about 0.24 m_0, lying between the light and heavy hole masses for GaAs, which is a reasonable value. The value is not too different from the one previously reported[1] of $\sigma=0.2$, but is somewhat more accurate and self-consistent, due to the use of more appropriate values for E_A. This kind of consistent picture suggests that the identification of the Zn-related photoluminescence is correct, that the appropriate σ for exciton considerations in GaAs is about 0.28, and that σ_c must be less than this value.

Finally, for the most heavily doped sample, G5-20-14.9, the difference E_G-E_{PL} has increased by 6 meV, while the E_A has decreased by nearly 13 meV from the low-concentration values. From Table I we see that the photoluminescence is much broader and the efficiency lower, relative to the Zn concentration for this sample. Further, the presence of impurity-band effects[7] indicates that overlapping of wave functions for the hole bound to Zn^- is already considerable. Photoluminescence of samples with Zn concentration between the last two in Table I shows a single line with intermediate energy. It seems very likely that this change in energy is caused by increased overlapping, or the loss of local character of the wave functions. One should not necessarily expect the localized and nonlocalized states of the same impurity to have the same energy,[12] and we have here a relatively clear demonstration of such a difference for Zn in GaAs.

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