Extrinsic photoluminescence from GaAs quantum wells

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Extrinsic photoluminescence has been observed from a number of undoped GaAs-$Al_xGa_{1-x}As$ multiquantum-well samples grown by molecular beam epitaxy. For quantum wells of width $L_z \lesssim 300$ Å this luminescence is typically only a few percent of the intrinsic luminescence and it decreases with decreasing L_z. Single quantum-well samples doped with [Be] $\sim 10^{17}$ cm^{-3} are found to exhibit extrinsic and intrinsic luninescence comparable in intensity. This extrinsic luminescence is believed due to the recombination of $n=1$ electrons with neutral acceptors in the quantum wells, carbon in the case of the undoped material. Estimates of the binding energy of the neutral acceptors $E(A^0)$ from the measured free heavy-hole exciton energy gap of the quantum wells, the heavy-hole exciton binding energy, and the energy of the peak of the extrinsic photoluminescence, show that $E(A^0)$ increases with decreasing L_z. These results on $E(A^0)$ are compared with the recent theoretical results of Bastard on the binding energy of hydrogenic acceptors as a function of L_z and position in the well. Other data on the extrinsic photoluminescence of single and multiquantum samples are also presented.

I. INTRODUCTION

Publications to date on the spontaneous photoluminescent properties of GaAs-$Al_xGa_{1-x}As$ quantum-well structures have been largely on undoped material and have emphasized that the resultant luminescence is mainly intrinsic in nature.[1-4] This is in marked contrast to undoped bulk GaAs of comparable quality where the luminescence is mainly extrinsic.[5,6] In the present work, a number of undoped superlattices have been examined carefully for extrinsic photoluminescence. In addition, several single quantum-well samples, both doped (p type) and undoped, have been studied. Extrinsic luminescence that is attributed to the recombination of free electrons in the $n=1$ quantum-well state with neutral acceptors (e-A^0), probably carbon, can frequently be observed with undoped material. This type of extrinsic recombination is also observed with [Be] $\sim 10^{17}$ cm^{-3}, doped single-well samples. The observed variations of the extrinsic luminescence with temperature and excitation intensity are believed to be consistent with e-A^0 recombination. The photoluminescent and excitation spectra are used to determine the neutral acceptor binding energy as a function of the GaAs quantum well width L_z. These results are compared with the recent theoretical calculations of the binding energy of acceptors in GaAs wells by Bastard.[7]

II. EXPERIMENTAL

The samples to be discussed were grown by molecular beam epitaxy (MBE) over a period of about two years using several different systems. Layers were grown on GaAs(100) substrates that were either Cr doped or Zn doped. A GaAs buffer layer was grown first, followed by the required number of alternating layers of $Al_xGa_{1-x}As$ and GaAs. In some cases the alternating layers were clad with thicker layers of $Al_xGa_{1-x}As$. All layers were undoped except for several single-well samples.

Optical excitation was with a cw-tunable dye laser whose output was at normal incidence to the plane of the layers and focused to a spot ~ 200 μm in diameter. The photoluminescence was detected 24° off normal incidence in the reflection (backward) direction, passed through a $\frac{1}{2}$-m monochromator, and detected using a cooled photomultiplier with a GaAs cathode. The detection bandwidth was ~ 0.3 meV. Circular polarization techniques were usually utilized in both excitation and detection to determine the electron-spin polarization

which can be useful for identifying transitions and estimating lifetimes.[1] The samples were mounted in a variable-temperature cryostat, but unless otherwise noted, the measurements reported herein were obtained at ~ 5 K. The apparatus and techniques utilized in these experiments have been described in detail previously.[1]

III. RESULTS

The evidence for extrinsic luminescence for a number of undoped samples is a relatively weak broad peak observed on the low-energy side of the main intrinsic photoluminescence peak which is usually at or very near the $n=1$ electron and heavy-hole, free-exciton transition E_{1h}.[1,3,8] A good example of this is given in Fig. 1 which shows the photoluminescent signal I_{PL} versus photon energy for a multiquantum-well sample at ~ 5 K with 46 periods of $L_z = 160$ Å GaAs wells and $L_B = 170$ Å $Al_{0.3}Ga_{0.7}As$ barriers. The integrated intensity of the lower-energy peak at 1.511 eV is about 8% of

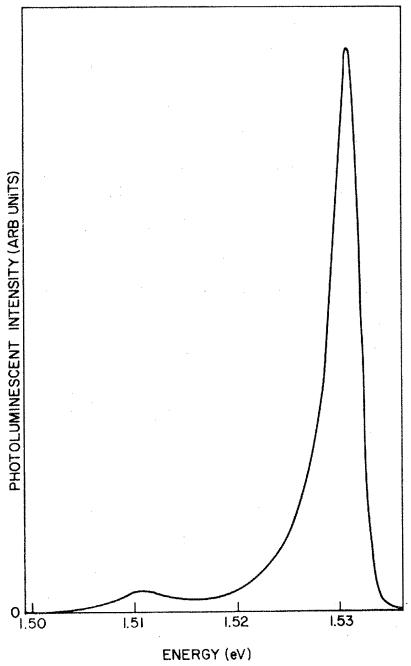

FIG. 1. Photoluminescent intensity at ~ 5 K vs photon energy for a multiquantum-well sample ($L_z = 160$ Å) excited at 1.624 eV with 55 mW/cm^2. The main peak is intrinsic luminescence at the energy of the $n=1$ electron and heavy-hole exciton (1.531 eV). The smaller peak is extrinsic luminescence.

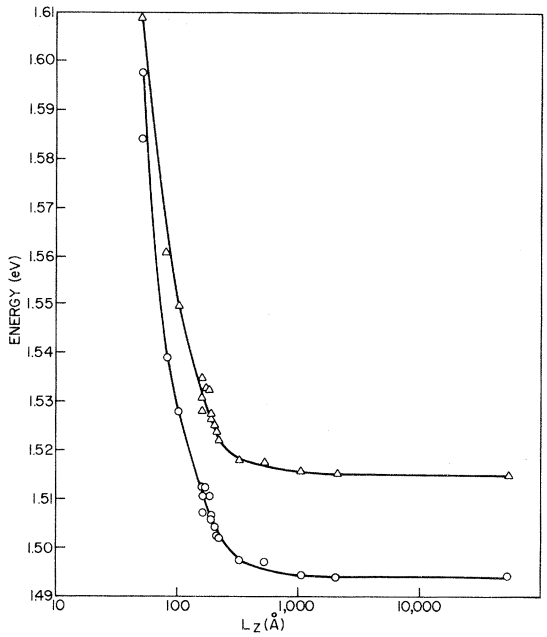

FIG. 2. Energies of the peaks of the intrinsic free exciton (Δ) and the extrinsic (○) photoluminescent spectra vs width of the GaAs layer.

that of the main peak, which is essentially at E_{1h} (1.531 eV). Excitation spectra show that both of these peaks are due to the GaAs wells. Data obtained in this manner for a number of different undoped quantum-well samples are shown in Fig. 2. The upper curve shows the energy of E_{1h}, or in the case of very wide wells, the energy of the free exciton versus the GaAs well width L_z. The lower curve gives the corresponding energy for the lower-energy peaks attributed to an $n=1$ electron recombining with a neutral acceptor, e-A^0. An additional shoulder is observed for the sample with $L_z = 51$ Å so that two points for e-A^0 are plotted for this sample. The scatter is due in part from the variation in x from sample to sample, $\sim 0.30 \pm 0.05$, and the uncertainty in L_z, $\pm 5\%$. Observations of the "two-hole transition,"[5] i.e., a transition of an exciton bound to a neutral acceptor (A^0-X) in which the acceptor is left in the $n=2$ excited state, via resonant excitation of A^0-X in undoped bulk material grown by MBE, show that carbon is always the main shallow acceptor impurity.[6] Thus it is believed that this extrinsic photoluminescence from the quantum wells is also due to C as the main acceptor.

A series of multiquantum-well structures with $L_B \approx L_z \approx 200$Å and $x \sim 0.3$ barriers were grown under the same conditions except that the substrate

temperature during the growth of the layers, T_s, was varied from run to run. Earlier work[2] has shown that for this system $T_s = 690\,^{\circ}\mathrm{C}$ produces the highest peak photoluminescence intensity and also the narrowest width for the E_{1h} peak in the excitation spectrum, i.e., under these growth conditions, $T_s = 690\,^{\circ}\mathrm{C}$ produces the "best" multiquantum-well structures from a photoluminescent point of view. The present authors have repeated these measurements and obtained results in good agreement with the earlier work. However, during these measurements the present authors were also able to observe extrinsic luminescence with some of these samples and have determined its peak intensity versus T_s. These data are shown in Fig. 3. The extrinsic photoluminescence also peaks at 690 °C but its variation with T_s is more rapid than that of the intrinsic luminescence.

The dependence of the luminescence from a multiquantum-well sample on the excitation intensity I_p has been determined over the range of I_p from 3 to 220 mW/cm^2. It is found that the intrinsic luminescence is nearly linear in I_p, whereas the extrinsic luminescence tends to saturate as might be expected due to a limited number of acceptor centers. As I_p is increased to 220 mW/cm^2, the peak of the extrinsic luminescence shifts to higher energies by about 1 meV. When the sample temperature is increased from ~5 to about 40 K, the intrinsic luminescence decreases by about 25% and extrinsic luminescence decreases by about a factor of 3.

The photoluminescent spectrum for a single quantum-well structure with $L_z = 255$ Å and $x = 0.20$ excited at 1.600 eV is shown in Fig. 4. The well was doped throughout with Be at a concentration of a few $\times 10^{17}$ cm^{-3}. The peaks at 1.521 and 1.499 eV are due to the single quantum well as shown by the excitation spectra. The other peaks are due to either the GaAs substrate or the GaAs buffer layer. An excitation spectrum for the luminescent peak at 1.499 eV is shown in Fig. 5. Detection was at 1.499 eV and the level of excitation was about 6 W/cm^2. The prominent exciton transitions involving electrons with heavy or light holes with the same quantum number n (allowed transitions), denoted by E_{nh} and E_{nl}, respectively, are labeled in the figure.[8] Also shown is a forbidden transition E_{13h} (parity allowed) involving the $n=1$ electron and $n=3$ heavy hole. Electron-spin polarization measurements using circular polarization techniques give opposite polarization for the photoluminescence from light and heavy holes[9] and have confirmed the hole assignments given. This excitation spectrum proves that the luminescence peak at 1.499 eV originates in the GaAs well and not in the substrate or buffer layer.

As expected from Fig. 5, resonant excitation at E_{1h} leads to an enhanced emission from the well as is shown in Fig. 6. Since in this case E_{1h} is very

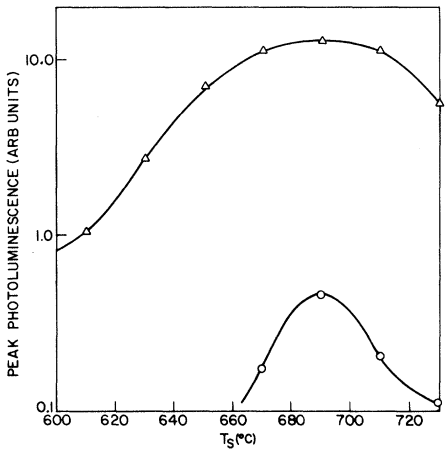

FIG. 3. Intensities of the peaks due to intrinsic (Δ) and extrinsic (○) photoluminescence vs substrate temperature T_s during the growth of the layers with $L_z \approx 200$ Å.

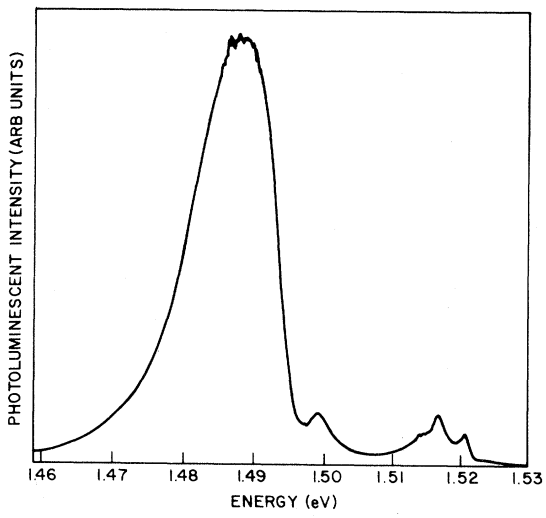

FIG. 4. Photoluminescent spectrum for a single-well sample, $L_z = 255$ Å, excited at 1.600 eV with 2.2 W/cm^2. The GaAs well was doped with Be at a concentration of a few $\times 10^{17}$ cm^{-3}. Excitation spectra show that the peaks at 1.521 and 1.499 eV are due to the single well.

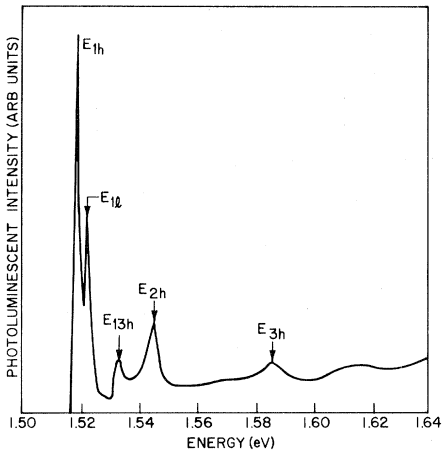

FIG. 5. Excitation spectrum for the luminescent peak at 1.499 eV shown in Fig. 4. Four allowed exciton transitions and one forbidden (parity allowed) transition, E_{13h}, are labeled.

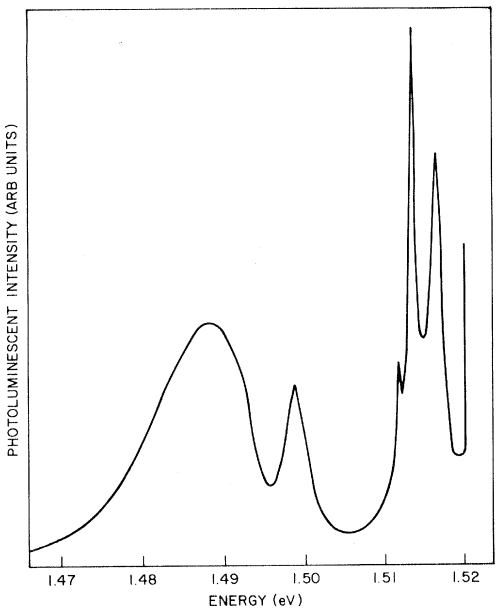

FIG. 6. Photoluminescent spectrum for the doped single-well sample described in Fig. 4, but with excitation resonant with the $n=1$ electron and heavy-hole free exciton, 1.520 eV. The peak due to the well at 1.499 eV is strongly enhanced. Since the exciting photons are also near the bulk GaAs band edge, the peaks due to buffer layer at ~ 1.515 eV are also enhanced. The rising intensity at ~ 1.52 eV is due to the detected wavelength approaching the excitation wavelength.

near the band gap of bulk GaAs, the luminescence at the bulk GaAs exciton edge from the buffer layer is also increased.

These and other data show that the luminescence in Fig. 4 at 1.521 eV is intrinsic and due to E_{1h}, and the peak at 1.499 eV is attributed to e-Be^0. In this case the extrinsic and intrinsic luminescence are comparable in intensity whereas the e-A^0 peaks in undoped wells with the same nominal L_z are usually a few percent of the intrinsic peaks; see, for example, Figs. 1 and 3.

The photoluminescence from one undoped single-well sample is of special interest since the extrinsic photoluminescence dominates the spectrum and it is in a spectral region where there is little other luminescence. The photoluminescence spectrum when this sample is resonantly excited at E_{1h} with 5 W/cm^2 is shown in Fig. 7. The large extrinsic peak at 1.534 eV is due to the single well with $L_z=114$ Å and $x=0.40$ barriers. It is observed that this peak shifts to higher energies, becomes more narrow, and its integrated intensity increases slightly superlinearly, with increasing I_p over the measured range of 0.36–24 W/cm^2. Also as shown in Fig. 7, the polarization of the luminescence from the well increases with increasing photon energy suggesting that the ratio of electron lifetime to the electron-spin relaxation time, τ/τ_s, decreases with increasing emission energy. The relaxation of this polarization in a transverse magnetic field[10] (Voigt geometry—Hanle effect) leads to estimates of τ and τ_s which show a decrease by factors of 5 and 2, respectively, as one goes from

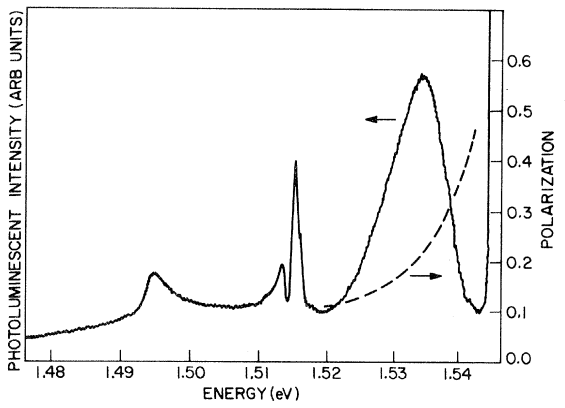

FIG. 7. Photoluminescent spectrum for a single-well sample, $L_z=114$ Å, when resonantly excited at the $n=1$ electron and heavy-hole free-exciton transition, 1.544 eV. The polarization of the luminescence from the well is shown by the dashed line.

the half-power point on the low-energy side of the peak to the half-power point on the high-energy side.

IV. DISCUSSION

The smooth transition of the energy of the peak of the extrinsic photoluminescence with L_z as it varies from micrometers, where it has been demonstrated to arise from e-C^0 transitions, to less than 100 Å is consistent with this luminescence from the multiquantum wells being attributed to the recombination of $n=1$ electrons with neutral carbon acceptors in the quantum wells. In addition, doping a quantum well with Be has been shown to enhance this extrinsic luminescence. The absence of a rapidly decreasing intensity with increasing temperature along with a shift to higher energies of the peak of the photoluminescence, especially with the wider well samples, argues against donor-acceptor pair emission (D^0-A^0) which is so prevalent in bulk GaAs.[5,6] As discussed in more detail below, a comparison of the binding energy of the neutral acceptors estimated from the present data with the recent theoretical calculations of the binding energies of acceptors in GaAs quantum wells,[7] also supports the origin of the extrinsic luminescence studies herein as being due to e-A^0 recombination and not D^0-A^0, a point of view which will be adopted for the following discussion.

Excitation spectra were obtained for all samples, which when supplemented by calculations of the transitions energies[8] and a knowledge of the growth parameters, provided values for E_{1h} (the $n=1$ free-heavy-hole exciton transition) and estimates of L_z. With this information and the binding energy $B(h)$ of the heavy-hole exciton as a function of L_z,[11] one can estimate the binding energy of the neutral acceptor, namely

$$E(A^0)=E_{1h}-E(e-A^0)+B(h)\ ,$$

or (1)

$$E(A^0)=E_g'-E(e-A^0)\ ,$$

where E_g' is the $n=1$ quantum-well energy gap and $E(e-A^0)$ is the energy of the peak of the e-A^0 luminescence. $E(A^0)$ is the energy required to take a hole from the neutral acceptor to the $n=1$ heavy-hole level in the valence-band well. Equation (1) is not generally regarded as an accurate method to determine the equivalent quantity in bulk GaAs since the position of the e-A^0 peak may vary by several meV.[5] However, in the present case, e.g., Fig. 7, this method frequently gives values for the $E(C^0)$ in bulk GaAs grown by MBE that are within 1 meV of the accepted value, 26.0 meV.[5] In any event, $E(A^0)$ has been estimated from Eq. (1) and is plotted as a function of L_z in Fig. 8. The circles are for undoped material, hence presumably C^0. The one square point is the average of two Be-doped samples, and note that it lies somewhat above the other points as expected since $E(\mathrm{Be}^0)$ for bulk GaAs is 28.0 meV.[5]

Also shown in Fig. 8 are some theoretical results from Bastard,[7] who calculated the binding energies with infinite potential barriers and for hydrogen-like donors and acceptors in GaAs as a function of L_z and the position of the impurity in the GaAs well. The results for C^0, with $E(C^0)\equiv R_0=26.0$ meV for the bulk value,[5] and a Bohr radius a_0 of 21.1 Å, are shown in Fig. 8 for C^0 at the interface and at the center of the well, in qualitative agreement with the data. For $L_z\rightarrow\infty$, the asymptotic values of $E(A^0)$ for an acceptor at the center of the well or at the interfaces are R_0 and $R_0/4$,

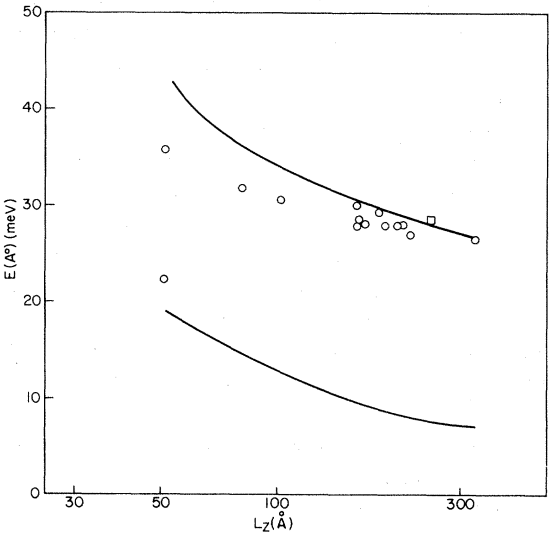

FIG. 8. Values of the binding energy of neutral acceptors determined from the present data vs the GaAs well width L_z. The circles are for undoped multiquantum-well samples and the one square point is for a Be-doped single-well sample. Experimental uncertainties in these data are estimated to be approximately ± 1 meV. The upper and lower solid curves represent the theoretical prediction of Bastard (Ref. 7) for the binding energy of carbon acceptors in the center of the well and at the interface, respectively.

respectively. For $L_z \rightarrow 0$, the binding energy becomes $4R_0$. Actually, this model must be modified quantitatively to take into account finite barrier heights and the central-cell correction,[12] but for the present purposes only the qualitative differences between well-center and interface binding energies are considered.

It is reasonable to assume that the impurities in the GaAs wells studied are randomly distributed. The data in Fig. 8 show that the position of the peak observed is most characteristic of impurities near the center of the well. This is as expected since for $L_z/a_0 \gtrsim 2$ impurities at the interface have little effect on the $E(A^0)$ observed.[7] In addition, the density of states per unit energy peaks for impurities at the center of a well since the binding energy is a maximum at the location.[7] However, as L_z becomes smaller, the strength of the emission due to the impurities at the interface gains relative to that of the remainder of the spectrum and so under certain conditions can lead to a second peak as shown by Bastard.[7] Thus, the second shoulder observed in I_{PL} versus energy for the sample with $L_z = 51$ Å, which leads to $E(A^0) = 22.3$ meV, may be due to impurities that are very close to the interface. A noticeable feature of Fig. 8 is that the variation with L_z of the well-center binding energy is less rapid than predicted by Bastard.[7] This can be explained either by a repulsive central-cell correction[12] (of order 14 meV for C compared to Ge[13] which on chemical or dielectric electronegativity grounds should be nearly hydrogenic), or by valence-band barrier heights smaller than indicated by previous work.[8]

There is considerable scatter in the luminescence intensities as a function of L_z, but it is clear that in general the e-A^0 luminescence for undoped multiquantum-well samples grown under good conditions decreases relative to the intrinsic luminescence with decreasing L_z. This is not understood, but it may be due in part to the increasing strength of the free exciton and its binding energy as it becomes more and more two dimensional.[11]

The data for the undoped single well, $L_z = 114$ Å, shown in Fig. 7, are anomalous in the sense that the extrinsic luminescence is dominant and the energy of the peak leads to the $E(A^0) = 23.4$ meV, and hence does not seem to fit in well with the bulk of the data from the multitude of other samples shown in Figs. 2 and 8. This sample, which had rather thick $Al_xGa_{1-x}As$ barriers, was grown under conditions that were known not to be ideal and its luminescence was broader than usual by about a factor of 2. These results when coupled with other data on two-quantum-well samples suggest that the first GaAs well grown after a relatively thick layer of $Al_xGa_{1-x}As$, $L_B >> L_z$, may contain significantly more impurities than subsequent GaAs wells grown after barriers with $L_B \simeq L_z$,[14] and that the impurities may be concentrated near the $Al_xGa_{1-x}As$-GaAs interface.[12] In any event, the decrease observed in both the electron lifetime τ and electron-spin relaxation time τ_s with increasing photon energy for the sample is consistent with earlier results[9] which strongly suggest that both of these times decrease with decreasing L_z due to nonradiative recombination and enhanced electron-spin relaxation at the interface and/or in the $Al_xGa_{1-x}As$ barrier. Thus, as the level of excitation is increased, it appears that the longer-lifetime sites near the center of the well, larger $E(e-A^0)$, tend to saturate first giving rise to the observed shifts of the peak photoluminescent intensity to higher energies with increasing I_p.

V. CONCLUSIONS

Photoluminescence attributed to the recombination of $n=1$ electrons with neutral acceptors in GaAs quantum wells has been observed in a number of undoped multiquantum-well samples and in Be-doped single-well samples. With the doped material the extrinsic and intrinsic luminescence can be comparable in intensity, whereas the extrinsic luminescence from undoped multiquantum-well samples is typically a few percent of the intrinsic luminescence and it decreases with decreasing L_z. Values of the binding energy $E(A^0)$ of the neutral acceptors, assumed for the undoped material to be carbon, which is the most prevalent acceptor in undoped bulk GaAs grown by MBE, have been determined from the photoluminescent and excitation spectra and are found to increase with decreasing L_z. Binding energies determined in this manner are in qualitative agreement with the theoretical predictions of Bastard.[7] There are data which suggest that the impurity distribution in some of the undoped quantum wells may not be uniform

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