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Comparative study of the effect of an electric field on the photocurrent and photoluminescence of GaAs-GaAlAs quantum wells

L. Viña,* R. T. Collins, E. E. Mendez, and W. I. Wang
IBM Thomas J. Watson Research Center, P. O. Box 218, Yorktown Heights, New York 10598
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The effects of an electric field on the excitons in GaAs-GaAlAs quantum-well heterostructures have been studied by means of low-temperature photoluminescence and photocurrent spectroscopy. Increasing the electric field causes a red shift of the excitonic luminescence to energies well below the bulk GaAs band edge and a corresponding decrease of the total luminescence efficiency. We find very good agreement between the energy thresholds obtained by luminescence and photocurrent measurements. A significant shift of the luminescence relative to the photocurrent is observed at high fields as a result of enhanced bound-exciton luminescence when electrons and holes move closer to the interfaces.

In previous studies, without an electric field as external parameter, a Stokes shift of the photoluminescence (PL) relative to the absorption in GaAs-$Ga_{1-x}Al_xAs$ quantum wells (QW) has been reported.[1-3] This shift depends on sample thickness and on sample preparation; shifts from 5 meV, for a 50-Å QW,[3] to 1–2 meV, for a 260-Å QW,[1] have been measured. These Stokes shifts have been interpreted in terms of exciton trapping on random interface defects,[2] before the exciton recombines. The influence of a static electric field on the optical properties of GaAs-$Ga_{1-x}Al_xAs$ QW has received considerable attention in recent years. Different techniques such as PL,[4-7] time-resolved PL,[3,8] optical absorption,[9-12] photocurrent spectroscopy (PCS),[7,13] and electroreflectance[14] have been employed. If an electric field perpendicular to the layers is applied, in addition to a red shift of the excitonic recombination with increasing field, a spatial separation of conduction- and valence-band electrons, with the electronic distributions shifted closer to the well edges, has been predicted.[15] Therefore, an increasing discrepancy between the PL and absorption thresholds would be expected if the photogenerated carriers are somehow shifted toward the well interfaces, where more defects and impurities are present. In order to confirm this point, we have studied in detail the electric field dependence of the PL and PCS of a 160-Å-thick QW. The effects of the electric field should help to clarify the role that the impurities or defects play in the Stokes shift between PL and absorption.

The sample used in our measurements was grown by molecular-beam epitaxy on a Si-doped GaAs (100) substrate and consisted of five GaAs-$Ga_{0.65}Al_{0.35}As$ QW's. The wells (160 Å) and barriers (250 Å) were sandwiched between 0.1-μm $Ga_{0.65}Al_{0.35}As$ layers. The first 500 Å of the $Ga_{0.65}Al_{0.35}As$ buffer layer adjacent to the substrate were doped with Si, while the rest of the layers were nominally undoped. An electric field perpendicular to the interfaces was applied via a semitransparent Schottky contact formed by evaporating a $\sim$50-nm-thick Ni-Cr film on the top of the cladding layer. The flat-band condition was estimated to occur very close to a bias of 0.8 V based on the agreement, at this voltage, in line shape and energy position, of the PL peaks measured on and off of the electrode, and on the decrease and small shift to lower energies of the luminescence as the applied voltage was further increased.

For the PL measurements, the sample was mounted on a variable temperature cryostat and kept in a He-gas atmosphere at 5 K. The QW luminescence was excited either indirectly with the 5145-Å line of an Ar^+ laser or selectively, well below the $Ga_{0.65}Al_{0.35}As$ band gap, with the 6471-Å line of a Kr^+ laser. The beam was focused on a spot 400 μm in diameter, and excitation powers from 50 μW to 1 mW were used. The PL signal was analyzed with a $\frac{3}{4}$-m Spex double monochromator and detected with a cooled GaAs cathode photomultiplier. Observation of the luminescence on and off the electrode, with the sample held at flat-band condition, showed that the Ni-Cr film reduced the PL by about one order of magnitude. The PCS spectra were taken at 10 K using the light from a tungsten lamp source dispersed from a grating monochromator and focused on the electrode. The light-induced current flowing through the sample was detected using standard lock-in techniques. External dc voltages ranging from 1 to -2.5 V and from 0.8 to -2 V ($\sim$77 kV/cm) were used in the PL and PCS measurements, respectively, where positive corresponds to forward bias.

The PL and PCS spectra for an applied voltage of 0.8 V, corresponding to flat-band condition, are plotted in Fig. 1 with solid and dashed lines, respectively. The PL spectrum was taken with the 5145-Å line of the Ar^+ laser with a power density of 0.2 W/cm^2. Three structures are observed, at 1.540 eV ($1e1lh$), 1.533 eV ($1e1hh$), and 1.532 eV (D,X) (donor-bound exciton). The first two, with half width at half maximum of 1 meV, are identified as the free-exciton recombination between the electron and light- and heavy-hole ground states, respectively. This identification is based on a comparison of their energies to those calculated in the envelope-function approximation,[16] where masses

$$m_e^*(\mathrm{GaAs}) = 0.067m_0,\ m_e^*(\mathrm{Ga_{0.65}Al_{0.35}As}) = 0.092m_0\ ,$$
$$m_h^*(\mathrm{GaAs}) = m_h^*(\mathrm{Ga_{0.65}Al_{0.35}As}) = 0.45m_0\ ,$$

and a 60–40% rule for the conduction- and valence-band discontinuities were used. The rapid decrease of the third structure, together with an increase of the $1e1lh$ and $1e1hh$ peaks, when the temperature is raised to 20 K, as well as its dependence on excitation power, allows us to assign it to a bound exciton. From the difference between the $1e1hh$ and (D,X), 1.1 meV, similar to the difference between free and donor-bound exciton in bulk GaAs, we attribute this structure to a donor-bound exciton. The PCS spectrum exhibits

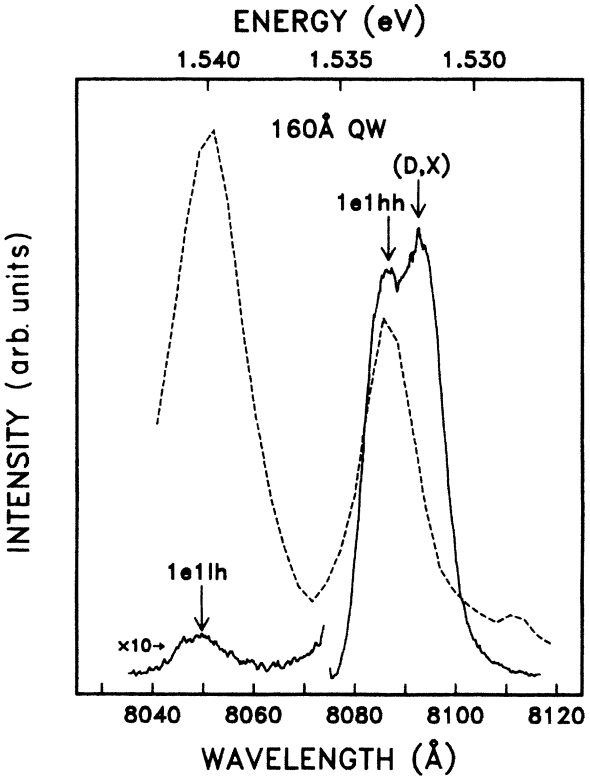

FIG. 1. Low-temperature ($T=5$ K) photoluminescence (solid line) and ($T=10$ K) photocurrent (dashed line) spectra of a 160-Å GaAs-$Ga_{0.65}Al_{0.35}As$ quantum well. The free light-hole, heavy-hole, and bound excitons have been labeled $1e1lh$, $1e1hh$, and (D,X), respectively. The spectra were taken at 0.8 V, very close to flat-band condition, as explained in the text.

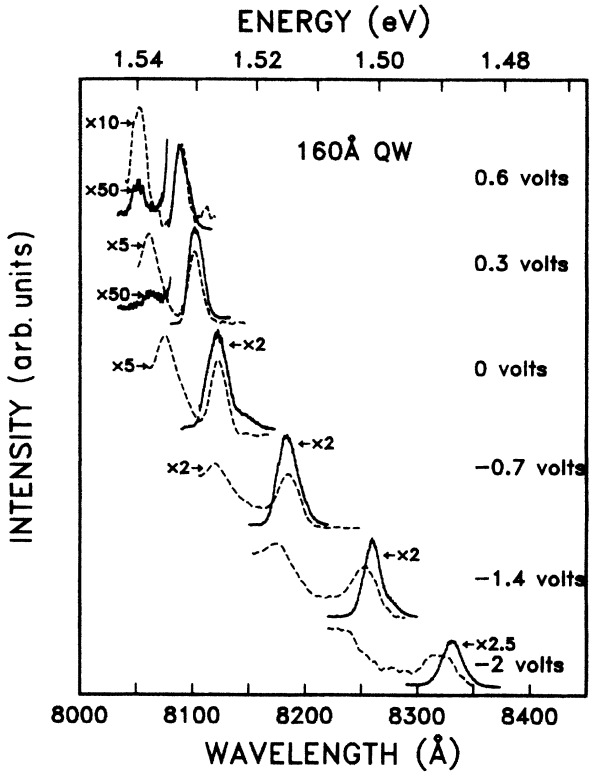

FIG. 2. Photoluminescence and photocurrent spectra at different external voltages. The measurements were done at the same temperatures as in Fig. 1. The spectra are displaced vertically with respect to each other for clarity; the high-energy peaks correspond to $1e1lh$, while those at lower energies correspond to $1e1hh$ excitons. The vertical scale of some of the spectra has been enhanced by the factors indicated with arrows beside the spectra.

two well-resolved excitonic structures in this energy region, which agree, within 0.3 meV, with the light- and heavy-hole excitons seen in PL. This agreement represents the best reported up to now between PL and absorption (or absorption-related) measurements, and confirms our assignment of the structure at 1.533 eV to the heavy-hole exciton. It is also worth mentioning the very good agreement in the linewidth observed in both spectra, which indicates that both techniques are sampling the same electronic states. These results and the sharpness of the excitonic structures demonstrate the excellent quality of our samples.

Figure 2 shows the PL and PC spectra for six selected voltages. As the field is increased (i.e., the external voltage decreased) three main effects can be observed in the PL: The (D,X) peak decreases slightly and can be seen only as a shoulder at 0.6 V, all the structures shift to lower energies, and the total luminescence efficiency decreases. The rate of decrease of the (D,X) peak is sample dependent and also varies with the laser-power density. Otherwise, we did not observe any significant dependence of the variation of the PL with electric field on laser wavelength or intensity. We believe, as will be discussed later, that both structures, $1e1hh$ and (D,X), remain throughout the whole range of applied voltages, although they cannot be resolved separately. The light-hole exciton quenches very quickly in PL, and could only be followed up to 0.3 V. On the other hand, the light- and heavy-hole excitons change at a similar rate in the PCS, indicating that the effect of the electric field on the matrix elements involved in the absorption mechanism is comparable for both kinds of holes. The faster decrease of the light-hole exciton compared to that of the heavy-hole exciton in PL can be explained by an increase in the rate of sweep-out of the light holes in the QW and possibly by a faster decrease of the light-hole exciton binding energy. These effects have been predicted to occur at much lower fields for the light hole than for the heavy hole.[17] The decrease of the heavy-hole PL intensity by a factor of ~ 5 from 0.6 to -2 V is accompanied by an increase of the photocurrent between those voltages. However, we did not find, in contrast to Ref. 7, that their intensities add to a constant value.

The energies of the light- and heavy-hole excitons in the PL and PCS spectra are plotted in Fig. 3 as a function of applied voltage. Both excitons move at similar rates, with the former shifting slightly slower than the latter. An interesting observation in our measurements is that the heavy- and light-hole excitons shift to energies below the band gap of bulk GaAs, indicating that the electrons and holes have been pushed apart by the electric field and are localized at the interfaces. Therefore, their recombination is indirect in real space, similar to the case of n-i-p-i heterostructures.[18] The energy thresholds found in both measurements (PL and PCS) agree to within 0.3 meV up to voltages of ~ -1 V. For higher fields, the shifts in the luminescence are larger than those in the PCS, the difference amounting to 2.5 meV at -2 V, the largest reverse bias voltage used for

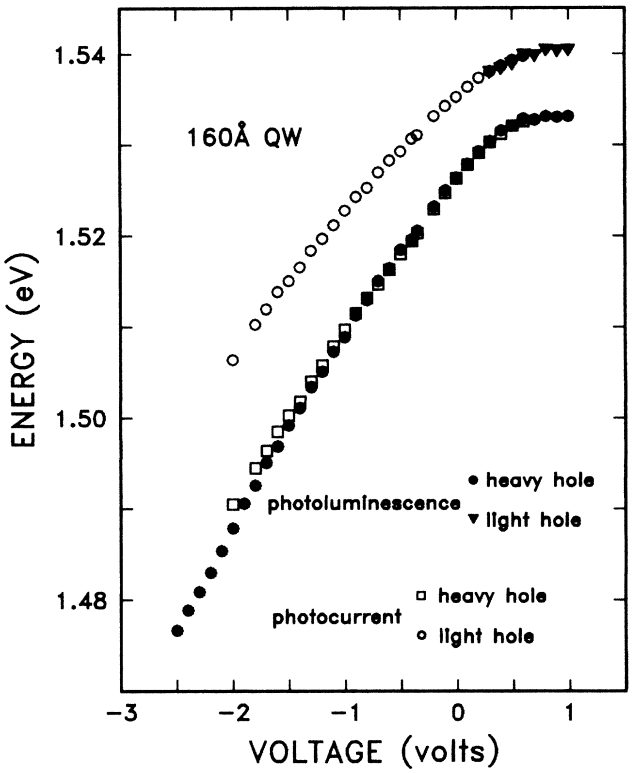

FIG. 3. Energies of the excitonic peaks as a function of applied external voltage obtained by photoluminescence (●, heavy hole; ▼, light hole) and photocurrent (□, heavy hole; ○ light hole) spectroscopy. Note that for voltages smaller than ~ -1 V, both structures shift below the bulk GaAs band edge.

the PCS measurements.

The decrease in the exciton binding energy as the field increases, due to the decrease in the Coulomb attraction between electron and hole as they move to opposite sides of the QW, which should be ~ 2 meV,[12,17] cannot be responsible for the discrepancy between PL and PCS because it affects both measurements in the same way. We explain this difference on the basis of enhanced bound-exciton luminescence as the carriers are brought closer to the interfaces, by the electric field, where more impurities exist. Since the bound-exciton luminescence is very sensitive to temperature and should decrease rapidly as the temperature is increased above ~ 10 K, we have measured the temperature dependence of the PL at different voltages to confirm this explanation. At voltages for which the free and bound excitons could be resolved ($0.8 \leq V \leq 0.5$), a rapid decrease of the (D,X) exciton with increasing temperature was found. It was observed only as a shoulder at a temperature of 20 K. At voltages smaller than -1 V, where the PL peak could no longer be resolved into its two components, a pseudoshift to *higher* energies was observed as the temperature was increased. The observed pseudoshift of ~ 1.2 meV at the highest field corresponds to the energy difference between the free- and bound-exciton measured at flat band (Fig. 1). Thus, we can conclude that, although unresolved, both lines are present in the PL spectra at higher fields, and as the temperature is increased the contribution of the bound exciton decreases compared to that of the free exciton. This results in an apparent shift to higher energies (towards the free exciton), which improves the agreement between PL and photocurrent.

As far as the temperature effect on the energy position of the excitonic peak is concerned, one should keep in mind that an increase of temperature from 5 to 20 K produces a small shift (≤ 0.5 meV) of the band gap to lower energies,[1] which would improve the agreement between PL and PCS if it were taken into account. We should also mention that a complicated behavior, as a function of electric field, of the relative amplitudes of free and bound excitons was found by Miller and Gossard[5] in their photoluminescence study of a p-doped GaAs-$Ga_{1-x}Al_xAs$ QW. They also observed that PL structures due to free and bound excitons were still present at their highest field, although no significant Stark shift of these peaks was found.

The fact that bound-exciton recombination dominates the PL spectra both at flat band and at high fields seems to be directly related to the density of states of the impurity band in a QW. A calculation by Bastard[19] predicted two singularities, at the center and in the vicinity of the edges of the well, in the density of impurity states per unit binding energy. Thus, the impurity-related bound exciton is expected to be more easily resolved at flat-band condition, when the electronic distribution peaks at the center of the well, as well as at high fields, when it is closer to the interfaces, consistent with our experimental results.

A difference of ~ 1.3 meV at -2 V between the PCS and the PL is still present when the sample is held at 20 K. This difference could be due, in part, to temperature effects, as mentioned above, but an increase of the contribution of acceptor-bound excitons to the PL line shape, which would shift the PL to lower energies with respect to the photocurrent, cannot be ruled out. Unfortunately, we cannot resolve this structure; we therefore only speculate that a possible explanation for this discrepancy could be the enhancement of acceptor-bound excitons with respect to free and donor-bound excitons as the holes are brought closer to the interface. This is very plausible since, because of the smaller valence-band-edge discontinuity and the larger heavy-hole effective mass, the holes are expected to shift faster than the electrons toward the interface.[15]

In summary, we have shown that good agreement between the excitonic energies in GaAs-$Ga_{1-x}Al_xAs$ QW obtained by photoluminescence and photocurrent spectroscopy can be achieved with the use of high quality samples. The use of a static electric field as an external parameter helps to clarify discrepancies previously found in the literature and to confirm the role that the impurities play in these Stokes shifts. Our measurements show that as the electron and hole distributions are skewed toward the interfaces, the luminescence shifts to lower energies with respect to the absorption, and the amount of this shift coincides with the energy difference between free and bound excitons. A significant red shift of the excitonic structures in GaAs-$Ga_{1-x}Al_xAs$ QW, of the order of 50 meV for ~ 3 V, bringing the QW photoluminescence energy well below the bulk-GaAs band edge, has also been measured.

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*Permanent address: Instituto de Ciencia de Materiales, Consejo Superior de Investigaciones Científicas, Universidad de Zaragoza, 50009 Zaragoza, Spain.

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