Experimental exciton binding energies in GaAs/$Al_xGa_{1-x}As$ quantum wells as a function of well width

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In the low-temperature photoluminescence excitation spectra of high-quality GaAs/$Al_xGa_{1-x}As$ single quantum wells, we have observed distinctive peaks arising from the first excited level (2*s*) in addition to the ground state (1*s*) of heavy- and light-hole excitons. We utilized this accurate determination of the 2*s*-1*s* splitting energies to derive the binding energies of the heavy- and light-hole excitons as a function of well width and found good agreement with other similar determinations and with recent theoretical calculations based on models of quantum wells which included valence-band coupling. The agreement with exciton binding energies derived from magneto-optical spectroscopic experiments is satisfactory when comparison is made with recent results.

INTRODUCTION

One of the more important questions regarding the effect of spatial confinement on excitons in semiconductor quantum wells (QW's) concerns free-exciton binding energies. It is clear that confinement increases binding energies (E_B), but the exact dependence of the magnitude of E_B on quantum-well width L_Z is less well understood. There have been many theoretical studies,[1-4] but only a few experiments. Miller *et al.*[5] have suggested that band edge-like structure seen in the photoluminescence excitation spectra (PLE) of high-quality QW's arose from the onset of excited levels (2*s*, 3*s*, etc.) of the excitons. Using relatively simple modeling, the energy difference between this "band edge" and the ground state of the exciton (1*s*) is a direct measure of E_B. Other experimental determinations of E_B have utilized magnetointerband spectroscopy, which requires nonlinear extrapolations to zero magnetic field.[6-8] These experiments usually, but not consistently, produced E_B magnitudes larger than reported by Miller *et al.*[5] More recent magneto-optical experiments[9,10] produced results more consistent with Miller *et al.*[5] In a further development, low-temperature PLE spectra of apparently higher-quality samples were reported which contained a distinctive peak (interpreted as the 2*s* exciton state) at the band edge.[11] Similar peaks have been seen by others as well.[12] We have also observed similar structure in the 5-K PLE spectra of several samples containing QW's with various L_Z's. Furthermore, as the temperature was increased, this peak structure disappeared at temperatures consistent with the binding energy of the 2*s* exciton and the "bare" band edge was observed to remain. In analyzing these spectra, we have derived E_B's for ground-state light- and heavy-hole excitons in quantum wells ranging in width from 3.8 to 21.8 nm. Our values of E_B are in good agreement with those determined by Dawson *et al.*[11] and are slightly larger than those reported by Miller *et al.*,[5] but are significantly different from those determined in the original magneto-optical experiments.[6-8]

EXPERIMENT

The sample structures were grown with a Riber 2300P molecular-beam-epitaxy (MBE) machine on undoped [100] GaAs substrates at a substrate temperature of 650 °C without growth interruption. The aluminum concentration in the 54-nm $Al_xGa_{1-x}As$ barrier layers was 22%, as determined by low-temperature photoluminescence (PL) spectra. In order to minimize variations due to growth conditions, several single quantum wells (SQW's), of differing thicknesses, were grown on the same substrate. Well thicknesses were determined from the measured rate of growth of the layers, the energies of the heavy-hole and light-hole excitons obtained from low-temperature PL and PLE spectra, and standard theoretical calculations. One of the advantages of PLE spectroscopy as opposed to absorption spectroscopy, which provides similar information, is the ability to isolate the signal from each SQW in a given sample by a judicious choice of the monitoring energy. This permitted us to individually investigate four SQW's in each sample. This would be impossible using absorption spectroscopy since the spectra of the four SQW's would overlap. Absorption spectroscopy has the added disadvantage of possibly introducing nonuniform stress into the sample structure during specimen preparation since, in our samples, removal of the substrate would be necessary.

The samples were excited with either a low-power HeNe laser (for PL studies) or a tunable dye laser (employing Oxazine 750 dye) pumped with a Kr-ion laser (for PLE studies). They were mounted, strain-free, in a continuous-flow liquid-helium cryostat. Their PL emission was dispersed with a double-grating spectrometer and the PL intensity was measured with a cooled GaAs photomultiplier coupled to a photon-counting system.

RESULTS AND DISCUSSION

In Fig. 1 we present 5-K PL and PLE spectra of two of the narrower SQW's present in one of our samples. QW1 and QW2 have well thicknesses of 4.5 and 6.4 nm, respectively. The PL for each QW is dominated by free-exciton emission with weaker-intensity, impurity-related shoulders at lower energies. The PLE spectrum for each well consists of two strong and narrow peaks (labeled E_H^{1s} and E_L^{1s}) which are due to ground-state heavy- and light-hole excitons in the quantum well. The half-widths of the ground-state exciton peaks in these samples are comparable to the narrowest half-width reported in the literature and their temperature dependencies will be reported on fully elsewhere.[13] For SQW's of these widths, the continuum of heavy-hole–exciton excited states is expected to begin at an energy between that of E_H^{1s} and E_L^{1s}. This is, in effect, the "band-gap" energy of the ground-state heavy-hole exciton. (Throughout this work we will not discuss any effects due to exciton transitions involving higher quantum levels within the wells. We will concentrate on the ground-state heavy- and light-hole excitons and their excited levels.) Thus, the ground-state light-hole exciton and its excited levels lie on top of the heavy-hole continuum of states and this, in fact, leads to the observed Fano broadening of E_L^{1s}. This is the reason why E_L^{1s} is much broader than E_H^{1s} in high-quality narrow QW's.[14]

The structures of interest here lie at the edge of the continuum of excited levels due to the ground-state heavy- and light-hole excitons. We interpret the distinctive peaks seen in these locations with the first-excited levels of the heavy- and light-hole–exciton ground states and label them E_H^{2s} and E_L^{2s}, respectively, in each QW in Fig. 1.[15] This is in agreement with the interpretation of Dawson *et al.*[11] of similar PLE peaks in their samples.

Additional evidence in support of this designation is provided by the temperature dependence of these peaks. The binding energy of the 2*s* exciton state is known to be much smaller than that of the ground state (about a factor of 7 for wells of these width[11]). Thus, at temperatures high enough that the 2*s* exciton is completely thermally ionized, the 1*s* exciton should still be present. Evidence for this occurring is given in Fig. 2. The top two curves are the PLE spectra of QW2 at 5 and 80 K in the vicinity of the 1*s* light-hole exciton (E_L^{1s}) and the band edge of the heavy-hole–exciton continuum of excited states. The energy abscissae of the two spectra have been adjusted so as to line up the E_L^{1s} peaks for easier comparison. The peak labeled as first-excited level of the heavy-hole exciton (E_H^{2s}) in the 5-K spectrum is absent in the 80-K spectrum, while the E_L^{1s} peak is still clearly observed. We take this as evidence of thermal ionization. Not only is the E_H^{2s} peak missing, but the band edge has apparently shifted to a slightly higher energy at the higher temperature. Actually, at lower temperatures, the real band edge (defined as the lowest-energy nonexcitonic transition between the lowest conduction-band level and the highest heavy-hole level in the QW) is hidden by emission from E_H^{2s} and other higher excited levels of the ground-state heavy-hole exciton. Only at higher temperatures, at which these states have become ionized, is it possible to observe the real "bare" band edge. In addition, at higher temperatures, higher-lying transitions such as the heavy-hole continuum and E_L^{1s} become weakly thermally populated and give rise to photoluminescence emission. This is illustrated by the bottom PL spectrum of Fig. 2. The steplike band edge in the 80-K PLE spectrum produces a peak in the 80-K PL spectrum since, at this temperature, the lower-energy states, to the left in Fig. 2, are more heavily populated than higher-energy states to the right. This unequal population distribution changes a steplike density-of-

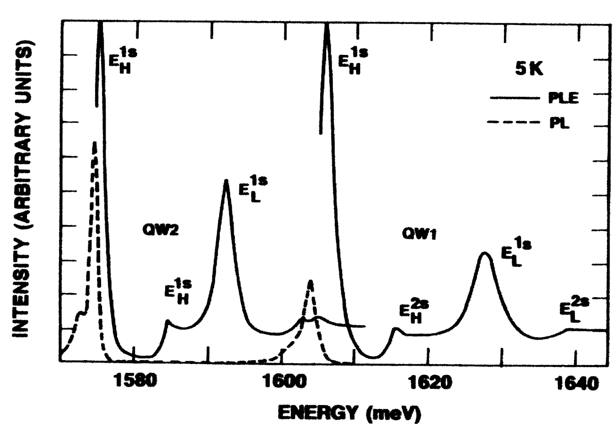

FIG. 1. 5-K photoluminescence (PL) and photoluminescence excitation (PLE) spectra of two narrow single quantum wells (QW1 and QW2) with widths 4.5 and 6.4 nm, respectively. E_H^{1s} and E_H^{2s} label the ground state and first-excited level of the heavy-hole exciton, while E_L^{1s} and E_L^{2s} identify similar states for the light-hole exciton.

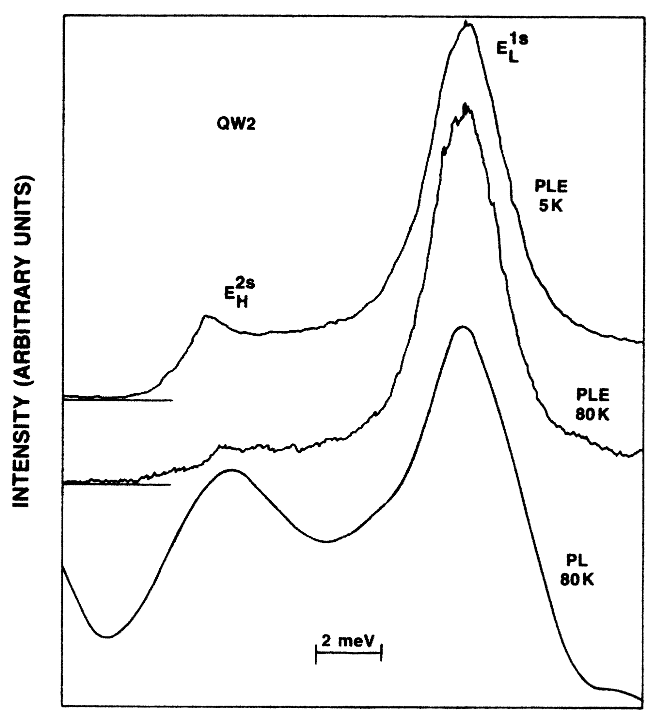

FIG. 2. Optical spectra of QW2 in the vicinity of E_L^{1s} and E_H^{2s} at two different temperatures. Top curve, PLE at 5 K; middle curve, PLE at 80 K; bottom curve, PL at 80 K. Note the *x* axis (energy) has been adjusted to line up E_L^{1s} in the spectra at each temperature for easier comparison.

states (observed in the PLE spectrum) into a peak in the PL spectrum. This peak cannot be due to emission from E_H^{2s} since the PLE spectrum provides evidence for its thermalization. At lower temperatures, weak photoluminescence emission from E_H^{2s} is possible and, in fact, has recently been observed.[16]

This evidence strongly suggests that the peaks observed at the band edges of the continua of the heavy- and light-hole–exciton excited states are due to 2*s* excitons. As pointed out previously,[11] the observation of a 2*s* peak yields a more precise measure of experimental 2*s*-1*s* splittings, and thus of exciton binding energies, than was possible in the earlier work since distinctive peaks were not observed at the band edge.[5] It also answers a question raised concerning the accuracy of the determination of 2*s* exciton energies.[7] Since the 2*s* energies of Miller *et al.*[5] were taken as the midpoint of the rising portion of their steplike band edge, there 2*s*-1*s* splitting energies were somewhat underestimated. Thus, it is not surprising that our values, and those of Dawson *et al.*,[11] are slightly larger than those of Miller *et al.*[5] We have observed distinctive 2*s* peaks in the low-temperature PLE spectra from many of our high-quality narrow SQW's. 2*s* peaks were not so readily observable in wider wells. The reason is not completely clear, although it may be related to thermalization effects since the binding energy of 2*s* excitons decreases monotonically with increasing well width. If this is the reason, 2*s* peaks in these wider QW's may be observable at still lower temperatures. Further, over a considerable L_Z range (in the vicinity of 14 nm), the overlap of E_L^{1s} and E_H^{2s} precludes accurate determination of the energy of E_H^{2s}. However, steplike band edges can usually be observed, even in wider wells, and, since we know from our study of narrower wells that the 2*s* state occurs very near the band edge, we can accurately determine 2*s* exciton energies for most our SQW's.

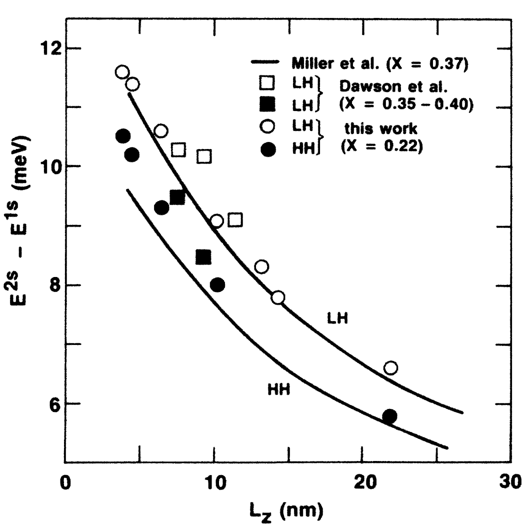

FIG. 3. 2*s*-1*s* splitting energies in GaAs/$Al_xGa_{1-x}As$ SQW's as a function of well width (L_Z). Experimental data are from Miller *et al.* (Ref. 5) (solid lines), Dawson *et al.* (Ref. 11) [open (LH) and solid (HH) squares], and this work [open (LH) and solid (HH) circles].

Our experimental values for 2*s*-1*s* splitting energies for heavy- (HH) and light- (LH) hole excitons in seven SQW's ranging in width from 3.8 to 21.8 nm are presented in Fig. 3 (errors are estimated to be of the size of the points in the figure, i.e., about a few percent). For comparison, we also show calculated curves from Miller *et al.*[5] (which agree well with their experimental values) and experimental points from Dawson *et al.*[11] These new values of 2*s*-1*s* splitting energies are in good agreement with each other (the small difference may be related to different values of *x* in the $Al_xGa_{1-x}As$ barriers) and both are consistently slightly larger than those of Miller *et al.*[5]

Following theoretical models given before,[5,11] we have derived exciton binding energies from our experimental splitting values and plotted them (along with the equivalent values from Refs. 5 and 11) versus L_Z in Fig. 4. Again, our values and those of Dawson *et al.*[11] agree well with each other and both sets of values are slightly larger than the calculated curves of Miller *et al.*[5] The

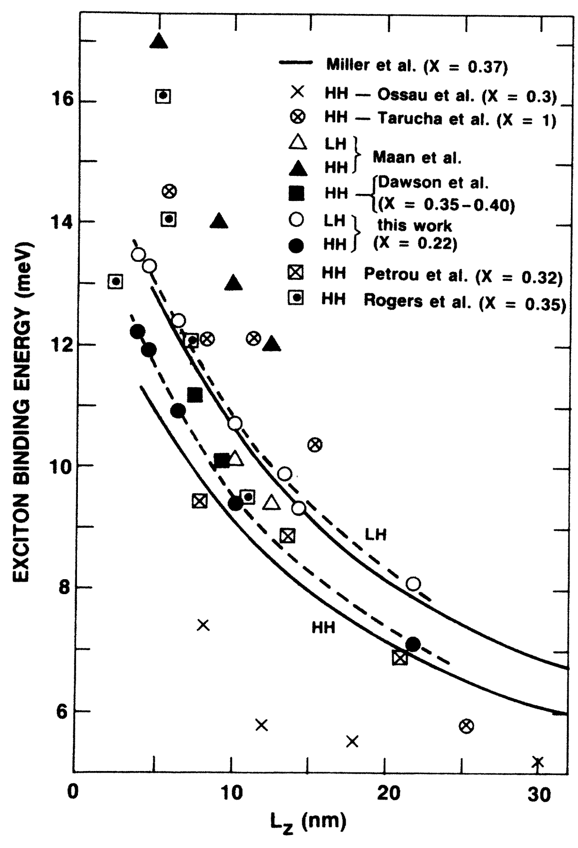

FIG. 4. Exciton binding energies in GaAs/$Al_xGa_{1-x}As$ SQW's as a function of well width (L_Z). Data are from Miller *et al.* (Ref. 5) (solid lines), Ossau *et al.* (Ref. 8) (crosses, HH), Tarucha *et al.* (Ref. 7) (circled ×'s, HH), Maan *et al.* (Ref. 6) [open (LH) and solid (HH) triangles), Dawson *et al.* (Ref. 11) (solid squares, HH), Rogers *et al.* (Ref. 9) (boxed points, HH), Petrou *et al.* (Ref. 10) (boxed crosses, HH), and this work [open (LH) and solid (HH) circles]. The dashed lines through the open and solid circles are empirical fits to the data.

dashed lines are empirical fits of third-order polynomials to the data. The coefficients for the three terms are (14.47, −0.0645, 0.000 141) and (15.74, −0.0611, 0.000 119) for the heavy- and light-hole–exciton binding energies, respectively.

Theoretical models based on infinite quantum-well depths generally provided E_B's in good agreement with these experimental data.[2,5] Surprisingly, early attempts to improve the model by including realistic well depths led to much poorer agreement.[3] In fact, for narrow QW's ($L_Z < 5$ nm), the improved theory predicted E_B's of light-hole excitons to be smaller than those of heavy-hole excitons. We see no evidence for this reversal in our results in agreement with Miller *et al.*[5] However, recently, more exact and complete calculations,[1,4] taking into account valence-band coupling between heavy- and light-hole excitons, as well as finite well depths (with the new 60-40 band-offset rule[4]), have yielded results in good agreement with the 2*s*-1*s* splitting energies of Miller *et al.*[5] Thus, they are also in substantial agreement with Dawson *et al.*[11] and the experimental results presented here.

A comparison of these three sets of experimental E_B's derived from 2*s*-1*s* splittings energies and values derived from magnetospectroscopy measurements is informative. There is significant disagreement between E_B's obtained using these two experimental techniques and, further, even among the three original magneto-optical experiments as is evident in Fig. 4. For instance, one set of values[7] is significantly smaller (by about a factor of 2) than the other two.[6,8] In one work, E_B's of heavy-hole excitons are reported to be larger than those of light-hole excitons, in contradiction to our work and that of Miller *et al.*[5] Not all of these discrepancies can be ascribed to differences in the aluminum concentrations of the well barriers, although the change in dielectric constant which results from increased aluminum concentrations does produce a discernible effect on E_B.[1,11] It is more likely that the procedure utilized to extract E_B from the measurements of exciton and Landau levels energies as a function of magnetic field is the problem. To obtain E_B energies requires nonlinear extrapolations back, from 10–20 kG, to zero magnetic field, of several transitions with different magnetic field dependencies. In more recent work, the agreement with Miller *et al.*[5] and values obtained here was significantly improved.[9,10] In Fig. 4 the results of Petrou *et al.*[10] are seen to be in good agreement with our results, especially if note is taken of their error bars (approximately ±10%). The values of Rogers *et al.*[9] are also closer to our results than previous magneto-optical work [again, the error bars are large, especially for the narrow QW's (as much as ±25%)]. The reason for the improved agreement is not clear, although the range over which extrapolation to zero field is necessary was somewhat larger (∼4 kG) in the earlier work[6–8] compared with that of the more recent work[9,10] (∼2 kG). Thus, it appears that the effect of even weak magnetic fields on spatially confined excitons seems to be a more complicated problem than previously suspected.

CONCLUSIONS

We report the observation of distinctive peaks at the band edges of the heavy-hole and light-hole–exciton continua of excited states when the low-temperature photoluminescence excitation spectra of high-quality $GaAs/Al_xGa_{1-x}As$ single quantum wells is measured. We interpret this structure as arising from the first-excited levels (2*s*) of ground-state (1*s*) excitons and utilize the accurate determination of the 2*s*-1*s* splitting energies this makes possible to derive binding energies of heavy- and light-hole excitons as a function of well width. Good agreement is found with other similar determinations of the binding energies and recent theoretical calculations based on a finite-well-depth model including valence-band coupling. The agreement with exciton binding energies derived from magneto-optical spectroscopic experiments is satisfactory only when comparison is made with recent results.

[1] For an extensive listing of theoretical work on exciton binding energies in quantum wells, see U. Ekenberg and M. Altarelli, Phys. Rev. B **35**, 7585 (1987).

[2] G. Bastard, E. E. Mendez, L. L. Chang, and L. Esaki, Phys. Rev. B **26**, 1974 (1982).

[3] R. L. Greene and K. K. Bajaj, Solid State Commun. **45**, 831 (1983); R. L. Greene and K. K. Bajaj, J. Vac. Sci. Technol. B **1**, 391 (1983); R. L. Greene, K. K. Bajaj, and D. E. Phelps, Phys. Rev. B **29**, 1807 (1984).

[4] D. A. Broido and L. J. Sham, Phys. Rev. B **34**, 3917 (1986).

[5] R. C. Miller, D. A. Kleinman, W. T. Tsang, and A. C. Gossard, Phys. Rev. B **24**, 1134 (1981).

[6] J. C. Maan, G. Belle, A. Fasolino, M. Altarelli, and K. Ploog, Phys. Rev. B **30**, 2253 (1984).

[7] S. Tarucha, H. Okamoto, Y. Iwasa, and N. Miura, Solid State Commun. **52**, 815 (1984).

[8] W. Ossau, B. Jakel, E. Bangert, G. Landwehr, and G. Weimann, Surf. Sci. **174**, 188 (1986).

[9] D. C. Rogers, J. Singleton, R. J. Nicholas, C. T. Foxon, and K. Woodbridge, Phys. Rev. B **34**, 4002 (1986).

[10] A. Petrou, G. Waytena, X. Liu, J. Ralston, and G. Wicks, Phys. Rev. B **34**, 7436 (1986).

[11] P. Dawson, K. J. Moore, G. Duggan, H. I. Ralph, and C. T. Foxon, Phys. Rev. B **34**, 6007 (1987).

[12] L. Vina, R. T. Collins, E. E. Mendez, and W. I. Wang, Phys. Rev. Lett. **58**, 832 (1987).

[13] Y. J. Chen. Emil S. Koteles, Johnson Lee, J. Y. Chi, and B. S. Elman, Proc. SPIE **792**, 162 (1987).

[14] D. A. Broido, Emil S. Koteles, C. Jagannath, and J. Y. Chi, Phys. Rev. B **37**, 2725 (1988).

[15] Coupling between quantum wells QW1 and QW2 in this particular sample produced the notch seen near E_L^{2s} in the excitation spectrum of QW2 in Fig. 1. This is analogous to similar effects seen by others [B. A. Wilson, R. C. Miller, S. K. Sputz, T. D. Harris, R. Sauer, M. G. Lamont, C. W. Tu, and R. F. Kopf, in *Gallium Arsenide and Related Compounds, 1986*, IOP Conf. Ser. No. 83, edited by W. T. Lindley (IOP, Bristol, 1987), p. 215], and will be discussed more fully elsewhere.

[16] K. J. Moore, P. Dawson, and C. T. Foxon, Phys. Rev. B **34**, 6022 (1986).