Effects of electronic coupling on the band alignment of thin GaAs/AlAs quantum-well structures

K. J. Moore, P. Dawson, and C. T. Foxon
Philips Research Laboratories, Redhill, Surrey RH1 5HA, England
(Received 1 February 1988)

We report the results of a systematic investigation of the effects of decreasing the AlAs layer thickness from 41 to 5 Å on the band alignment of GaAs/AlAs quantum wells in which the GaAs thickness was kept constant at nominally 25 Å. Combining the techniques of photoluminescence and photoluminescence excitation spectroscopy we have mapped out both the direct Γ-related band gap and the X-Γ band gap as a function of AlAs thickness. We observe a reversal of the band alignment from the type-II to the type-I arrangement when the AlAs thickness is reduced below ∼13 Å. In addition, we present further evidence which confirms that the type-II emission process is related to the X_z-Γ pseudodirect band gap. In the structures with very thin (<10 Å) AlAs layers we note a significant modification of the type-I excitation spectra where the $n=1$ exciton peak can be hundreds of times stronger than the apparent absorption in the continuum region.

INTRODUCTION

The ability of molecular-beam epitaxy to grow very-high-quality heterostructures of $Al_xGa_{1-x}As$/$Al_yGa_{1-y}As$ whose constituent layers are very thin has led to the study of a range of new physical phenomena based on quantum confinement. In particular there have been extensive optical investigations of the subband structure and valence-band alignment of such quantum-well or superlattice structures. Detailed studies of the band alignment at the $Al_xGa_{1-x}As/Al_yGa_{1-y}As$ heterointerface has led to evaluation of the fraction of the direct energy gap difference Q_v accommodated at the valence-band step to lie in the range 0.3–0.4. For a comprehensive review of this subject, see the article by Duggan.[1] This range of values for Q_v has important consequences in structures where the $Al_yGa_{1-y}As$ is indirect ($y>0.45$). In particular it is possible to engineer a type-II quantum-well structure where the lowest-energy conduction-band minimum and highest valence-band maximum are not in the same material. Initial confirmation of this effect was provided by Dawson *et al.*[2] who made photoluminescence studies of an $Al_{0.37}Ga_{0.63}As$/AlAs multiple-quantum-well structure where the high aluminum content of the $Al_xGa_{1-x}As$ was used to push the lowest direct confined electron state above the X minimum of the AlAs. The luminescence from this structure was assigned to recombination involving electrons confined at the AlAs X point and $n=1$ heavy holes confined in the $Al_xGa_{1-x}As$. Further evidence for such type-II behavior was provided by Wolford *et al.*[3] who used hydrostatic pressure to drive the $n=1$ confined electron state of a GaAs/$Al_{0.28}Ga_{0.72}As$ multiple quantum well above the X minimum of the $Al_xGa_{1-x}As$. Above a certain critical pressure they observed recombination involving electrons at the X minimum in the $Al_xGa_{1-x}As$ with heavy holes in the GaAs.

Work on type-II systems has been extended to include purely binary structures of GaAs/AlAs. In this system it has been shown[4–7] that a type-II band alignment is produced when the GaAs thickness is less than ∼35 Å, so that the $n=1$ electron subband lies above the AlAs X valleys. In these reports extensive use was made of photoluminescence (PL) and photoluminescence excitation (PLE) spectroscopy to identify not only the pure GaAs Γ transitions (type I), but also transitions related to the type-II band gap. The main conclusion from the work of Finkman, Sturge, and Tamargo[4] was that in all three samples they studied the type-II exciton emission was an indirect transition involving $n=1$ heavy holes in the GaAs and electrons in the X_{xy} valleys of the AlAs, i.e., those electrons with momenta in the layer planes, along the [100] and [010] directions. Their assignment of the type-II emission as an indirect process was based on fitting the PL decay curve of this line, which was nonexponential, to an expression for the time dependence of the decay of localized zone-boundary excitons made allowed by scattering from a random interface potential. Support for this interpretation was provided by Ihm[8] who predicted that indeed X_{xy} can be the lowest minima in some circumstances.

In our earlier work[5] we reported similar features in the PL and PLE spectra as observed by Finkman and coworkers from samples consisting of 60 periods of 70 Å of AlAs with either 28 or 22 Å of GaAs. However, we presented a different interpretation of the emission data. We ascribed the type-II process as zero-phonon and phonon-assisted recombination of excitons involving $n=1$ heavy holes in the GaAs and X_z electrons in the AlAs, i.e., those electrons with momentum parallel to the growth direction, along [001]. This has the important consequence that because only the X_z state is mixed with Γ by the superlattice potential, we believe the type-II emission process is a pseudodirect transition and not an indirect transition arising from the unmixed X_{xy} states. More recently, Minami *et al.*,[9] who have studied the

 ©1988 The American Physical Society

time dependence of the type-II emission, have questioned the analysis of Finkman and co-workers. They conclude that the nonexponential character of the decay could be explained by the recombination of excitons involving X_z electrons, in agreement with our interpretation of the emission data. The assignment of the lowest-lying conduction-band state as being the X_z valley is also in line with the theoretical predictions of Ruden, Englehardt, and Abrokwah[10] and Duggan and Ralph.[11]

In this paper we report the results of a systematic investigation of the effects of electronic coupling of the GaAs Γ states on the band alignment of type-II GaAs/AlAs multiple-quantum-well structures. We have studied a series of samples in which the thickness of the GaAs layers was fixed at $\sim$25 Å and the AlAs thickness varied between samples from 41 to 5 Å. Using the techniques of PL and PLE spectroscopy we have followed the positions of both the Γ-related direct gap and the X-Γ type-II band gap as a function of AlAs thickness. We also present further evidence to support our original assignment of the type-II emission as a pseudodirect process involving electrons at the X_z minimum. In addition, we note a significant modification of the PLE spectra in samples in which the AlAs thickness is less than about 10 Å.

EXPERIMENTAL RESULTS

The samples reported on in this study were grown by molecular-beam epitaxy in a Varian Associates Gen II system; full details of the procedures used have been published elsewhere.[12] The layers were deposited on (001) orientated semi-insulating GaAs substrates at a temperature of 630 °C. The growth sequence was as follows: (a) 1.0 μm of GaAs buffer material; (b) 60 periods of nominally 25 Å of GaAs and AlAs layers varying in thickness from sample to sample but nominally 42.5, 25.5, 17, 8.5, and 5.7 Å as given in Table I; and (c) a capping layer of 1000 Å of GaAs. The samples were undoped, GaAs samples grown under the same conditions have background donor and acceptor concentrations of about 2×10^{14} cm^{-3}.[12]

The samples were mounted in a variable temperature (4–300 K) continuous-flow cryostat. The luminescence was excited by either a Kr-ion laser or an Ar-ion-laser-pumped dye [4-dicyanomethylene-2-methyl-6-p-dimethylaminostyryl-4H-pyran (DCM) or pyridene] laser. The luminescence was analyzed by a Spex Industries 1404 spectrometer and detected by a GaAs photomultiplier (C31034) and associated photon-counting system. The photoluminescence-excitation-spectroscopy (PLE) experiments were performed by exciting the samples with light from either a lamp and scanning spectrometer or the tunable dye laser and monitoring the luminescence intensity as a function of excitation energy. The period d of each superlattice was measured by x-ray diffraction and the GaAs thickness d_1 was determined by comparison of the type-I exciton peaks in the PLE spectra with effective mass calculations. Details of both these procedures are described by Orton *et al.*[13] The values of d, d_1, and the deduced AlAs layer thickness d_2 are all given in Table I. We note the excellent agreement, to within one monolayer, between the nominal growth parameters and the measured values of layer thickness.

The results of our photoluminescence (PL) and PLE investigations are presented in Figs. 1, 2, and 3. A preliminary report showing some of this data can be found in Ref. 7. First, consider the low-temperature PL (Fig. 1) from the quantum-well structures in which the thickness of the AlAs layers are 41, 28, and 19 Å. We identify the main PL transition labeled as ($E1X$-HH1) in these three samples as zero-phonon recombination of type-II excitons involving electrons confined at the lowest X point of the AlAs and holes at the Γ point in the GaAs. The sidebands on the low-energy side of the main line we assign as phonon replicas of the same transition. In our earlier work on this subject[5] we reported the observation of three phonon replicas in samples with AlAs layers $\sim$70 Å. In those samples the strengths of the phonon replicas were comparable to the strength of the zero-phonon line. Reducing the AlAs thickness to 41 Å has produced a significant decrease in the relative intensity of the phonon-assisted transitions and this trend continues as the AlAs thickness is reduced further to 28 and 19 Å. In these samples only two replicas are resolvable in the emission spectrum. We measure the splitting of these lines with respect to the zero-phonon line as 30±2 meV and 50±2 meV for all these samples and identify the phonons involved to be LA and LO AlAs X-point phonons, respectively.[14] We have found that the decrease in strength of the phonon assisted transitions with decreasing AlAs thickness can be correlated with an increase in the radiative decay rate of the zero-phonon line. Contrary to other reports,[4] our lifetime measurements on these samples show that the type-II emission has an exponential decay at 4 K. At the lowest temperatures the decay is slow, $\sim$0.1–7 μs, but becomes faster as the temperature is increased. A detailed analysis of the decay

TABLE I. Sample parameters (nominal GaAs thickness is 25 Å, nominal AlAs thickness is given in brackets) and energy positions of peaks measured from Figs. 1, 2, and 3.

Total period $d\pm1.5$ Å	GaAs thickness $d_1\pm0.5$ Å	AlAs thickness $d_2\pm2$ Å	PL (eV)	PLE (eV) $E1\Gamma$-HH1	PLE (eV) $E1X$-HH1
63	22	41(42.5)	1.792	1.947	1.809
50.5	22.5	28(25.5)	1.819	1.932	1.835
42	23	19(17.0)	1.845	1.897	1.860
33	25	8(8.5)	1.803	1.804	
30	25	5(5.7)	1.751	1.751	

rates of these systems will be the subject of a further publication.[15]

We can confirm our assignment of the emission spectrum as type-II recombination in the samples with AlAs layers of 41, 28, and 19 Å by recording the PLE spectra. At relatively low sensitivity we see type-I exciton transitions $E1\Gamma$-HH1 and $E1\Gamma$-LH1, involving $n=1$ GaAs Γ electrons ($E1\Gamma$) and $n=1$ heavy (HH1) and light holes (LH1), respectively, as illustrated in Fig. 2. These transitions occur at a much higher energy than the PL peak. At increased sensitivity, Fig. 3, we can see peaks in the PLE spectra which we identify as being due to the lowest type-II free-exciton transitions. For the sample with 19 Å of AlAs the type-II peak is less well resolved. This is because of the proximity of the lowest GaAs Γ subband in this sample, so that the weak type-II feature is sitting on the sharply rising absorption edge associated with the type-I ($E1\Gamma$-HH1) exciton peak. The small differences in energy (~ 15 meV) between the type-II excitons in the PL and PLE spectra at 4 K are critical to the detailed interpretation of our data and we will return to this point later. Important information about the nature of the type-II process can be gained by recording the temperature dependence of both the type-II PL and PLE features of these samples. In all cases we observe that the emission shifts to higher energy with increasing temperature between 4–40 K and then follows the temperature dependence of the X gap for $T>40$ K. Conversely the type-II

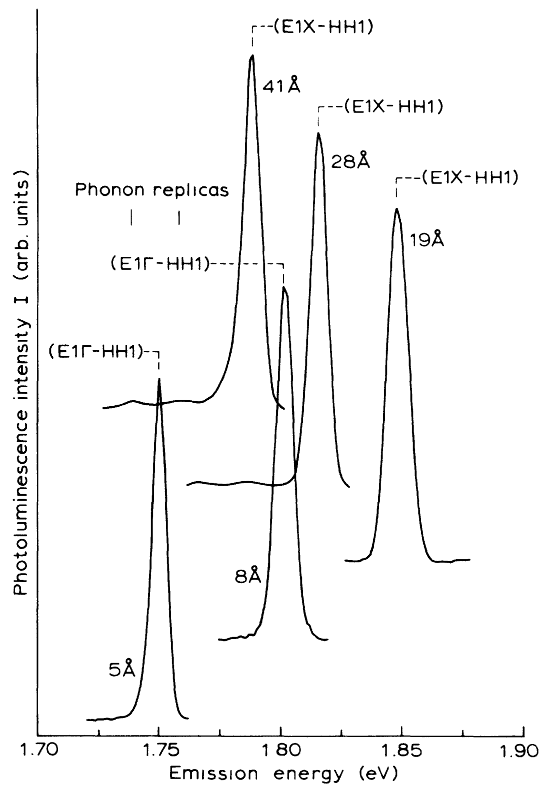

FIG. 1. Low-temperature (6 K) PL spectra. The emission from samples with AlAs layers of 41, 28, and 19 Å is associated with a type-II process. When the AlAs thickness is reduced to 8 and 5 Å the emission becomes type I. The curves have been displaced vertically for clarity.

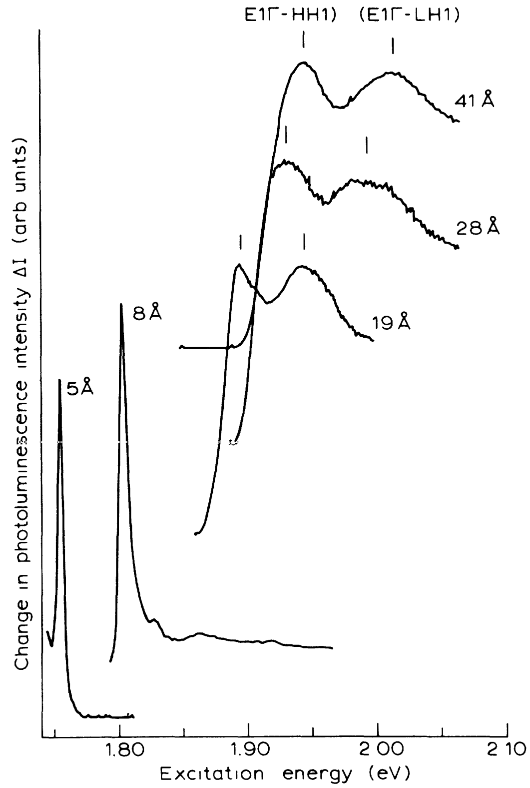

FIG. 2. Low-temperature (6 K) PLE spectra showing the type-I transitions for the samples described in Fig. 1. Notice the significant modification of the spectral shape for the samples with AlAs layers of 8 and 5 Å. The curves have been displaced vertically for clarity.

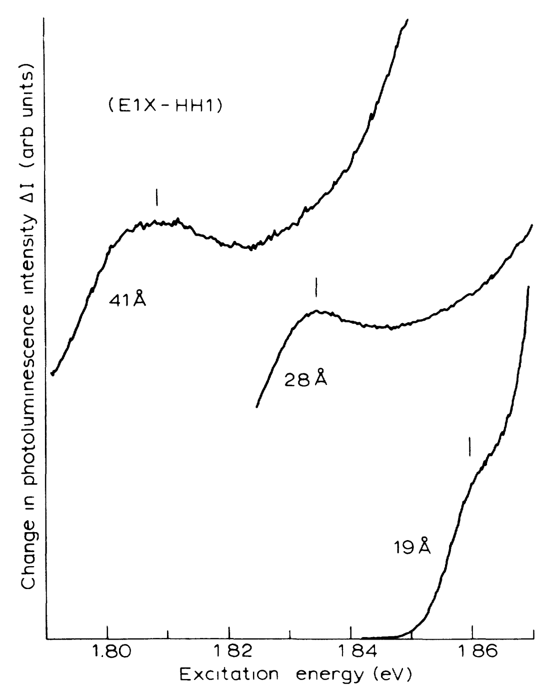

FIG. 3. Low-temperature (6 K) PLE spectra showing the type-II free-exciton peak ($E1X$-HH1) associated with the samples with AlAs layers of 41, 28, and 19 Å. The curves have been displaced vertically for clarity.

exciton peak, observed in the excitation spectrum, moves to lower energy by a few meV within the range 4–40 K. For example, for the sample with 28 Å AlAs, the energy difference between the type-II PL and PLE peaks at 4 K is 16 meV. Between 4 and 40 K we observe the emission peak moves to higher energy by 7 meV while the excitation peak moves by 3 meV to lower energy. Therefore at 40 K the energy difference between the type-II emission and excitation features is only 6 meV. The significance of this result will be explained in the discussion section.

Consistent with our identification of the emission process in samples with AlAs layers 41, 28, and 19 Å as type-II recombination, we note the continuous shift to higher energy of the type-II PL and PLE peaks with decreasing AlAs thickness. This reflects the increase in the electron confinement at the X minimum in the AlAs. We can follow the position of the Γ-related direct gap as a function of AlAs thickness from the energy of the type-I peaks in the PLE spectra as shown in Fig. 2. Initially, as we reduce the AlAs thickness the type-I exciton transitions are virtually constant in energy, as we would expect for isolated quantum wells with approximately the same GaAs thickness. However, when the AlAs thickness is reduced to 19 Å we observe a shift of the type-I transitions to lower energy and also a decrease in the splitting of the heavy- and light-hole exciton peaks. We believe this perturbation of the Γ confinement energies is a result of electronically coupling adjacent GaAs layers through thin AlAs layers. This reduces the energy of all the confined particle states and thus decreases the Γ transition energies. Since the effect is greater on the particles of smaller effective mass, i.e., the electrons and light holes, the $n=1$ light-hole subband moves closer to the heavy-hole subband and as a result, the splitting between the lowest Γ-related exciton peaks is reduced.

When the AlAs thickness is reduced still further to 8 and 5 Å the Γ states become extensively coupled and we observe a dramatic shift of the PL to lower energy. In these samples the nature of the emission has changed. We assign the PL peak to be type-I exciton recombination of GaAs Γ-state electrons and holes. This is a result of the continued lowering of the GaAs Γ-point subband minima such that the GaAs $n=1$ electron states now represent the lowest-energy electron states of the superlattice.[11] In both samples this assignment is confirmed by the coincidence of the $E1\Gamma$-HH1 exciton peaks in the PLE spectra (Fig. 2) with the energy of the emission lines. Turning our attention to the details of the PLE spectra in Fig. 2 of the samples with AlAs layers only 8 and 5 Å thick, we note a dramatic modification of their spectral shape. There is a well-defined peak representing the lowest exciton state of the system $E1\Gamma$-HH1; however, to higher energy there appears only to be very weak absorption in the continuum region. We will outline a possible explanation for these observations in the discussion section.

We can briefly summarize the results described above. We have observed that uncoupled GaAs/AlAs quantum wells with GaAs layers of ~25 Å have a type-II band alignment. However, as we reduce the thickness of the AlAs layer the system reverts to a type-I alignment when there is sufficient coupling between the GaAs layers to pull the lowest GaAs Γ electron state below the X minimum in the AlAs. Although the coupling between the GaAs layers for very thin AlAs layers provides the more interesting physics, the X minimum is also rising with reduced AlAs thickness as its energy levels are pushed up in the squeezed square well. We estimate that for these structures this type-II—type-I crossover occurs between 10–15 Å of AlAs.

DISCUSSION

First we turn to what is the subject of some controversy in the study of type-II GaAs/AlAs quantum wells. As describe in the Introduction, there is considerable disagreement on whether the lowest-lying conduction-band state is at the X_z minimum as predicted by envelope function calculations[10,11] or the X_{xy} minima as concluded by Ihm.[8] The theoretical results of Ruden and coworkers[10] and Duggan and Ralph[11] are based on similar effective-mass approaches where the relevant effective masses for the AlAs X electron states[16] at X_z and X_{xy} were taken to be $1.1m_0$ and $0.19m_0$, respectively. Thus consideration of the confinement effects on electrons with these effective masses clearly predicts that the X_z state will always be at a lower confinement energy than the X_{xy} states in any unstrained GaAs/AlAs quantum-well or superlattice system. It has been demonstrated that even when the effects of X_x-Γ and X_x-X_y mixing are taken into account[17] a lowering of the X_{xy} state only occurs if the AlAs thickness is an odd number of monolayers and would not predict a reversal of X_z and X_{xy} for the samples discussed here. All these treatments have ignored the effect of the small but finite lattice mismatch between AlAs and GaAs which results in the AlAs being under biaxial compression when deposited on a GaAs substrate. This lifts the degeneracy of the X minima and X_{xy} is then predicted to be the lowest-lying electron state[18] in bulk AlAs. However, the strain splitting is only a few meV so that in a quantum-well system confinement effects dominate and X_z is still predicted to be the lowest conduction-band minimum in AlAs.

As previously noted[4] we can gain some information about the assignment of the electron state involved in the absorption process by considering the shape of the type-II features in the PLE spectra. If the transition involves X_z electrons, then because the X_z minimum is mixed with Γ by the superlattice and has momentum allowed transitions, a peaked structure would be observed in absorption. Conversely since the unmixed X_{xy} minima still strictly maintain their indirect character, transitions are made allowed by random scattering and include all wave vectors. In this case a stepped feature following the change in the density of states would be observed in an absorption measurement. The type-II excitation feature observed experimentally is clearly a peaked structure, supporting the assignment of the excitonic absorption as involving X_z electrons. This is in agreement with our earlier publication[5] and also with the interpretation of other workers.[4]

We can now address the problem of assigning the electron state involved in the emission process. In all the type-II samples we have studied the PL line appears at lower energy than the type-II exciton peak. Finkman and co-workers assign the emission as indirect recombination of electrons at the X_{xy} minima and claim that in the samples they have studied the X_{xy} minima lie at lower energy than the X_z minimum. Envelope function calculations[10,11] in which the X_z state is always at a lower confinement energy than X_{xy}, predict that the splitting between the X_z and X_{xy} subband edges is expected to be a strong function of the AlAs thickness. For the samples we have studied the X_z-X_{xy} splitting is calculated to increase from 40 to 66 meV as the AlAs thickness is reduced from 41 to 19 Å. From our data, the difference in energy between the emission line and the type-II exciton peak in the PLE spectra is remarkably constant at 15±2 meV. This argues strongly against the interpretation of Finkman and co-workers and supports our argument that the emission and absorption processes involve a common electron state.

We believe that the emission appears at slightly lower energy than the free-exciton peak in the type-II PLE spectra because the excitons are localized, probably as a result of fluctuations in the layer thicknesses. In these samples the effect of well width fluctuations is quite dramatic, for example, changing the GaAs thickness by just one monolayer in 25Å changes the heavy-hole confinement energy by ~14 meV. This interpretation is confirmed by the temperature dependence of the energy of the type-II zero-phonon line. As already discussed, we observe that the emission shifts to higher energy with increasing temperature between 4–40 K and then follows the temperature dependence of the X gap for $T \gtrsim 40$ K. This upward energy shift is due to the progressive thermal delocalization of the excitons. Furthermore, the temperature dependence of the type-II PLE spectrum, which shows the expected decrease in exciton energy with increasing temperature, provides additional evidence to support our assignment of the excitation peak as the free exciton associated with the localized exciton observed in emission. Our lifetime measurements on these same samples,[15] show that at 4 K the emission has a slow and exponential decay which becomes faster when the temperature is increased. These observations can be correlated with the temperature dependence of the luminescence described above. At low temperatures we measure the radiative lifetime of the system, then as the excitons become free the probability of the exciton migrating to nonradiative centers increases and the decay becomes much faster.

In summary of these arguments, combining our observation of a Stokes shift, which is constant with varying AlAs thickness, with the temperature dependence of the PL and PLE, we believe that the emission and the absorption processes must be due to the same electron state. As already discussed, the peaked shape of the exciton feature in the PLE spectra can only be explained in terms of electron states with a well-defined k vector. Therefore we conclude that the features in both the PL and PLE are associated with type-II recombination arising from excitations involving electrons at the AlAs X_z minimum. Hence, while the electrons and holes are spatially separated, the type-II recombination is a pseudodirect transition. Furthermore, it follows that for the range of samples we have studied, X_z is always the lowest-energy state, as one would intuitively expect, and in accord with the simplest calculations.

The parameter which most strongly influences the size of the type-II energy gap is the value of the fractional valence-band offset Q_v. Using the energy of the type-II free exciton measured in a sample with AlAs layer ~70 Å, in which the X electron confinement effects are small, has allowed us to determine Q_v to lie in the range 0.33–0.34.[5] Assuming Q_v takes this value for all these samples, we can now make further comparisons between our experimental data and the simple models. Our investigations are summarized in Fig. 4 where we plot both the lowest direct Γ-related exciton energy ($E1\Gamma$-HH1) and the pseudodirect X_z-Γ exciton energy ($E1X$-HH1), measured from the PLE spectra, as a function of AlAs thickness. The AlAs thickness was determined by taking the total period, measured by x-ray diffraction, and subtracting the GaAs thickness derived by comparison of the Γ-Γ exciton peaks in the PLE spectra with effective-mass calculations. The theoretical curves, calculated within the envelope function approximation, represent the band-band transition energies associated with the lowest Γ-Γ, X_z-Γ, and X_{xy}-Γ band gaps. The calculations were made using a fractional valence-band offset of 0.33 and bulk longitudinal and transverse X-point masses of $1.3m_0$ and $0.19m_0$, respectively, for GaAs and $1.1m_0$ and $0.19m_0$ for AlAs. Other details of this calculation are described elsewhere.[11] To compare the calculated band-band transitions with our measurements of the free-exciton peak

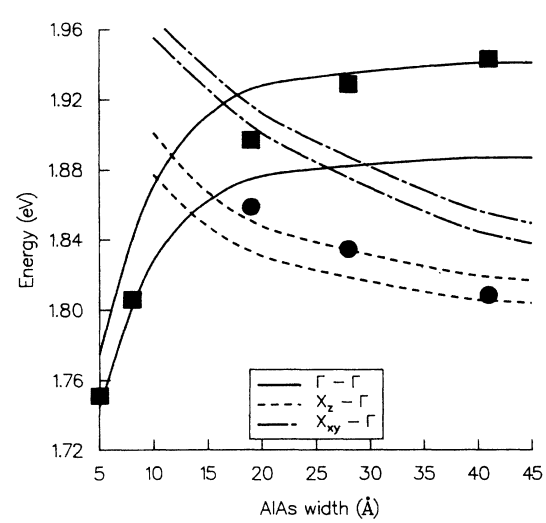

FIG. 4. Calculated band-band transition energies of GaAs/AlAs quantum-well structures. Each band gap is calculated for two fixed thicknesses of GaAs and plotted as a function of AlAs layer thickness. In each case the upper and lower curves represent GaAs thicknesses of 22.2 and 25 Å, respectively. The lowest-energy exciton peaks associated with the type-I (■) and the type-II (●) gaps are plotted, as measured in the PLE spectra.

positions from the PLE spectra, we should correct the experimental data by an amount corresponding to the exciton binding energy. This is of the order of 10 meV for both the type-I (Refs. 19 and 20) and type-II (Ref. 21) case.

All three band gaps have been calculated for two fixed thicknesses of GaAs, differing by a single monolayer, where the upper line of each pair is for 22.2 Å of GaAs and the lower line is for 25 Å of GaAs. Notice that although there is only a total thickness variation of one monolayer over the five samples, this can cause significant shifts in the Γ-electron confinement energies. This illustrates the high degree of sensitivity of the direct Γ-related transitions to the GaAs thickness and has allowed us to determine the values of d_1 given in Table I to ±0.5 Å. The X-Γ band gap is much less sensitive to the GaAs thickness but has a much greater dependence on the valence-band offset. Within the tolerance limits we have defined for the GaAs thickness, the experimentally determined peaks in the type-II PLE spectra of samples with AlAs layers of 41 and 28 Å are clearly well described by the calculation in terms of recombination associated with electrons at the X_z minimum. The type-II transition in the 19-Å sample falls marginally outside the bounds we have created. While this may represent a shortcoming of the simple model it should be noted that an error of only 1.5 Å in the determination of the superlattice period would bring the measurement into agreement with the calculation.

Finally, we return to the details of the PLE spectra of the samples with 8 and 5 Å of AlAs. Both these samples have a type-I band alignment and the peaks labeled as $E1\Gamma$-HH1 in Fig. 2 represent the lowest exciton state in each structure. However, the spectral shape to higher energy is quite startling since there appears to be virtually no absorption in the continuum region. We believe that we can offer a simple explanation for these observations in terms of the band structure which arises in samples where there is extensive coupling of the Γ states. Crucial to our explanation is the fact that the superlattice regions in our structures are only clad by layers of GaAs. Therefore the effective direct band gap of the superlattice is actually greater than the band gap of the surrounding material. When we perform an excitation measurement we create free electron-hole pairs which thermalize rapidly down to the lowest conduction-band and valence-band states, form excitons, and recombine. The weak continuum could be explained if we were losing free carriers via an alternative nonradiative path. In the case of the samples with 8 and 5 Å of AlAs we suggest that when we pump into the continuum region, the carriers tunnel easily through the AlAs layers to recombine in the GaAs, most probably nonradiatively at the free surface, before forming excitons. However, when we pump directly into the exciton state we create only excitons and therefore expect to lose fewer carriers to the GaAs, leading to an increase in luminescence efficiency at this energy.

CONCLUSIONS

Detailed spectroscopic investigations have provided evidence which confirms that the type-II exciton features observed in both emission and excitation measurements arise from the same transition and involve electrons at the AlAs X_z minimum. Therefore we conclude that in all the type-II structures we have studied, the emission is a pseudodirect transition and that the X_z minimum always lies at a lower energy than the X_{xy} minima.

We have made a systematic investigation of the effects of electronic coupling of the GaAs Γ states on the band alignment of GaAs/AlAs quantum-well structures. Combining the techniques of PL and PLE we have mapped out both the direct Γ-related band gap and the X_z-Γ band gap as a function of AlAs thickness. We have demonstrated that structures with GaAs layers ~25 Å and relatively thick AlAs layers have a type-II band alignment. Reducing the AlAs thickness allows the GaAs Γ states to become coupled and we have observed a significant lowering of the Γ subband energies when the AlAs thickness is decreased below ~25 Å. Eventually, for sufficiently thin AlAs layers, the lowest Γ-electron state is pulled below the rising X_z minimum and we have observed type-I recombination in samples with 8 and 5 Å of AlAs. Therefore we conclude that by introducing coupling of the GaAs Γ states we have forced a reversal of the band alignment. For a GaAs thickness ~25 Å this type-II–type-I crossover occurs between 10–15 Å AlAs.

Comparison of our experimental data with envelope function calculations has been made using a band offset ratio of 67:33. We have used the energy of the Γ transitions to fix the GaAs thickness for each sample, and the period, determined by x-ray diffraction, to fix the AlAs thickness in a self-consistent manner. The type-II process is then well described by the calculation in terms of X_z-Γ recombination in all but one sample where the agreement is marginally less good. In addition the calculation predicts a reversal of the band alignment in excellent agreement with our experimental observations.

ACKNOWLEDGMENTS

We acknowledge the help and support of many of our colleagues at Philips Research Laboratories. In particular we thank G. Duggan for theoretical contributions to all aspects of this work, P. F. Fewster and C. J. Curling for the x-ray diffraction measurements, and D. Hilton for assistance with the molecular-beam-epitaxy growth.

[1]G. Duggan, J. Vac. Sci. Technol. B 3, 1224 (1985).
[2]P. Dawson, B. A. Wilson, C. W. Tu, and R. C. Miller, Appl. Phys. Lett. **48**, 541 (1986).
[3]D. J. Wolford, T. F. Keuch, J. R. Bradley, M. A. Gell, D. Ninno, and M. Jaros, J. Vac. Sci. Technol. B **4**, 1043 (1986).
[4]E. Finkman, M. D. Sturge, and M. Tamargo, Appl. Phys. Lett. **49**, 1299 (1986).
[5]P. Dawson, K. J. Moore, and C. T. Foxon, Proc. SPIE **792**, 208

(1987).
[6]G. Danan, B. Etienne, F. Mollot, R. Planel, A. M. Jean-Louis, F. Alexandre, B. Jusserand, G. Le Roux, J. Y. Marzin, H. Savary, and B. Sermage, Phys. Rev. B **35**, 6207 (1987).
[7]K. J. Moore, P. Dawson, and C. T. Foxon, J. Phys. (Paris) Colloq. **48**, C5-525 (1987).
[8]J. Ihm, Appl. Phys. Lett. **50**, 1068 (1987).
[9]F. Minami, K. Hirata, K. Era, T. Yao, and Y. Masumoto, Phys. Rev. B **36**, 2875 (1987).
[10]P. P. Ruden, D. C. Englehardt, and J. K. Abrokwah, J. Appl. Phys. **61**, 294 (1987).
[11]G. Duggan and H. I. Ralph, Proc. SPIE **792**, 147 (1987).
[12]C. T. Foxon and J. J. Harris; Philips J. Res. **41**, 313 (1986).
[13]J. W. Orton, P. F. Fewster, J. P. Gowers, P. Dawson, K. J. Moore, P. J. Dobson, C. J. Curling, C. T. Foxon, K. Woodbridge, G. Duggan, and H. I. Ralph, Semicond. Sci. Technol. **2**, 597 (1987).
[14]B. Monemar, Phys. Rev. B **8**, 5711 (1973).
[15]P. Dawson, K. J. Moore, C. T. Foxon, and G. W. 't Hooft (unpublished).
[16]B. Rheinlander, H. Neumann, P. Fischer, and G. Kuhn, Phys. Status Solidi B **49**, K167 (1972).
[17]D. Z-Y. Ting and Yia-Chung Chang, Phys. Rev. B **36**, 4359 (1987).
[18]T. J. Drummond, E. D. Jones, H. P. Hjalmarson, and B. L. Doyle, Proc. SPIE **796**, 2 (1987).
[19]P. Dawson, K. J. Moore, G. Duggan, H. I. Ralph, and C. T. Foxon, Phys. Rev. B **34**, 6007 (1986).
[20]K. J. Moore, P. Dawson, and C. T. Foxon, Phys. Rev. B **34**, 6022 (1986).
[21]G. Duggan and H. I. Ralph, Phys. Rev. B **35**, 4152 (1987).