OPTICAL SPECTROSCOPY OF AlGaInP BASED WIDE BAND GAP QUANTUM WELLS

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An optical spectroscopic study of wide band gap AlGaInP based quantum wells is reported. GaInP quantum wells with AlGaInP barriers of two different Al compositions are studied. Type-II behaviour for narrow quantum wells with AlInP barriers is demonstrated. The onset of this behaviour allows limits to be placed on the size of the valence band offset. The first three orders of LO-phonon satellites are observed in quantum well PL spectra and their relative intensities are compared with theoretical predictions.

As the largest band gap, GaAs-latticed matched heterojunction system, Ga(Al)InP based quantum wells are of considerable importance for efficient visible electro-optical devices. A typical structure consists of GaInP quantum wells with $(Al_xGa_{1-x})_{0.52}In_{0.48}P$ barriers, where, by altering the Al composition, the size of the confinement potential can be continuously varied. For compositions above $x_c \approx 0.5$, AlGaInP has an indirect band gap [1]. Although the direct band gap continues to increase with increasing x the influence of the indirect gap results in reduced electron confinement, which can have important consequences for device performance. In this paper we report an optical investigation of these effects and, in addition, a study of the form of LO-phonon satellites of the photoluminescence from GaInP quantum wells.

Two GaInP-Al(Ga)InP quantum well structures, grown by solid source molecular beam epitaxy on [100] GaAs substrates, were studied. Each consisted of 1000Å-GaAs and 2000Å-Al(Ga)InP buffer layers followed by five single GaInP quantum wells, of nominal widths 100, 70, 40, 20 and 12Å, with 250Å Al(Ga)InP barriers. The first sample had a barrier Al content x=0.58, a composition close to that ($x_c \approx 0.5$) at which the lowest band gap becomes indirect [1]. The second sample had x=1.0 (AlInP) which represents the largest possible barrier direct band gap. PL was excited with the 4575Å line of an Ar^+ laser and dispersed and detected by a double grating spectrometer and photomultiplier. Photoluminescence excitation (PLE) was excited with a lamp and monochromator system.

Figure 1 shows 4.2K PL spectra of the two samples. Their excellent structural quality is demonstrated by the intense PL and associated narrow linewidths. PL linewidths of 11, 11, 13, 17 and 22meV (AlGaInP barriers) and 11, 11, 15, 32 and 43meV (AlInP barriers) are obtained for well widths 100, 70, 40, 20 and 12Å respectively. The quality of the first grown well (100Å) appears to degraded slightly, possibly by the presence of the underlying thick AlGaInP or AlInP buffer layer. An AlGaInP barrier sample with the quaternary buffer layer replaced with GaInP gave an improved PL linewidth for the first grown well (8.6meV for an 80Å well). The quality of the present samples, as indicated by their PL linewidths, are comparable with the best reported literature values [2-4].

Whereas all five wells with AlGaInP barriers show sharp intense PL, the PL from the two narrowest wells with AlInP barriers is weak and broad. For these wells the PL transition is type-II (indirect in both real and k-space) between the barrier conduction band X-minimum and well valence band Γ-maximum. This occurs because the strong electron confinement for these wells lifts the well Γ-state above the barrier X-state. The latter state is now lower in energy and electrons thermalise rapidly to this barrier state

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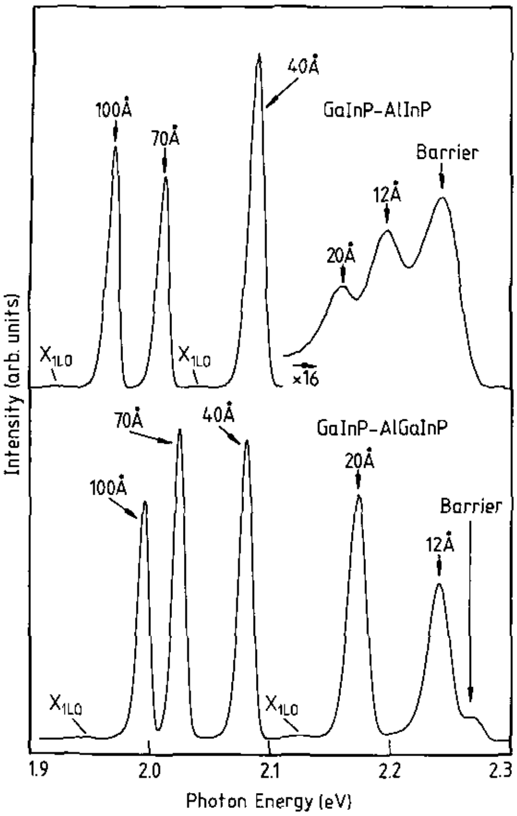

Fig. 1. Low temperature PL spectra of the five single GaInP quantum well samples with either AlInP or AlGaInP barriers.

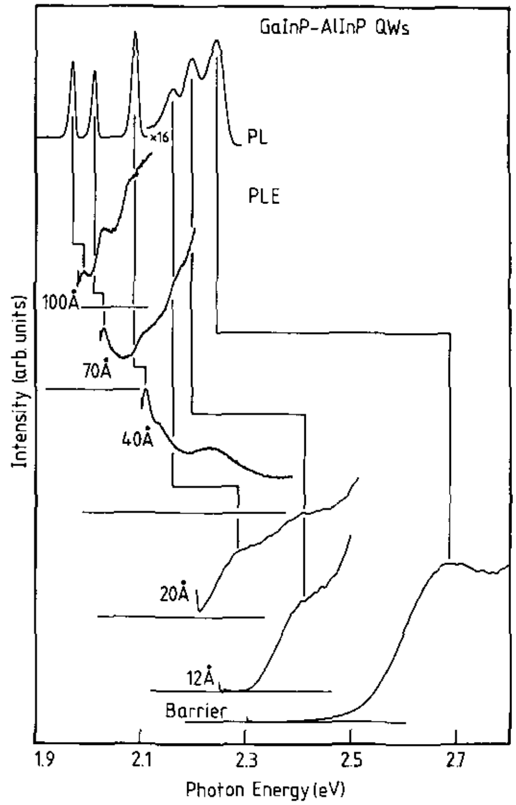

Fig. 2. PLE and PL spectra of the five well GaInP-AlInP structure.

before recombining with holes confined in the well. Because of the reduced spatial overlap of the electron and hole wave functions their radiative recombination time is increased and non-radiative recombination processes become relatively more important leading to the observed decrease in the PL intensity. This result indicates that for short wavelength electro-optical devices the optimum electron confinement is provided by barriers with an Al composition close to the cross over value $x_c \approx 0.5$.

Confirmation of this behaviour is provided in Figures 2 and 3. The former shows PLE spectra for the five quantum wells with AlInP barriers and, in addition, the PL and the barrier PLE. In Figure 3 the measured PL and PLE energies for the two systems are plotted against well width. Also included is data from samples with well widths of 80, 40, 20, 10 and 5Å. The data for each sample is adjusted for non-GaAs-lattice matched GaInP composition by shifting all the points rigidly to correspond to a bulk band gap of 1.980eV, the band gap determined for bulk unstrained GaInP [1]. All the quantum wells with AlGaInP barriers, and also the wider (≥40Å) wells with AlInP barriers, give PL and PLE of very similar energies, with only a small Stokes' shift (~20meV). However narrow (<40Å) wells with AlInP barriers show a large Stokes' shift between PL and PLE (141 and 223meV for 20 and 12Å well widths respectively). This behaviour occurs since the PLE and PL arise from the same transitions, associated with the same energy levels, in a type-I system but from transitions between different energy levels in a type-II system. In the latter PLE occurs between the higher energy direct band gap whilst, due to rapid electron thermalisation, PL occurs at the lower energy indirect real and k-space band gap. These two band gaps become increasingly separated in energy as the well width is decreased, in agreement with the behaviour observed in Figures 2 and 3. This results confirms that the GaInP-AlInP quantum well system changes from type-I to type-II as the well width is reduced from 40 to 20Å. Figure 2 also indicates a large Stokes' shift between the AlInP barrier PL and PLE, as expected for this indirect band gap material.

The solid lines in Figure 3 are the HH1-E1 energies calculated using a finite square well model and appropriate material parameters [2,3,5]. A conduction band offset of $\Delta E_C = 0.67\Delta E_G$ is used for both systems as deduced from hydrostatic pressure measurements [6]. Although the

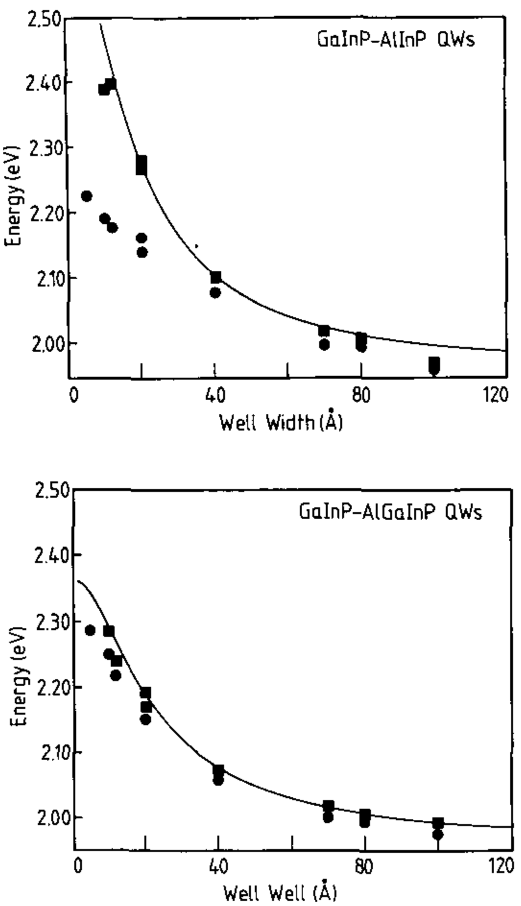

Fig. 3. PL and PLE energies of GaInP-Al(Ga)InP quantum wells plotted against well width. The solid lines show the results of a calculation of the E1-HH1 transition energy.

agreement between the calculated curve and the measured PLE values is good, it is found that this fit is relatively insensitive to the precise value of ΔE_C. Limits can be placed on the value of the valence band offset, ΔE_V, for the GaInP-AlInP system by observing the well width for which the onset of type-II behaviour occurs. Consideration of the band structure shows that for a well to be type-I the following inequality must hold

$$E^B_{G,INDIR} > E^W_{G,DIR} + \Delta E_V + E_1 \quad (1)$$

where $E^B_{G,INDIR}$ and $E^W_{G,DIR}$ are the barrier indirect and well direct band gaps respectively and E_1 is the confinement energy of the lowest well electron state. The opposite inequality holds for a type-II well. Figure 3 indicates that the type-I→type-II transition occurs for a well width between 20 and 40Å. Using these widths as the lower and upper limits for type-I and type-II behaviour respectively, the limits $0.25 \leq \Delta E_V \leq 0.40 \Delta E_G$, where ΔE_G is the total direct band gap discontinuity, can be found. In this calculation the bulk band gap energies are taken from work on bulk AlGaInP [1] and E_1 is calculated using a finite depth square well model with appropriate material parameters. These limits on ΔE_V for the GaInP-AlInP system are in agreement with the more precise value of $\Delta E_V = 0.30 \Delta E_G$ determined from hydrostatic pressure measurements [6].

In Figure 1 weak features (X_{1LO}) are visible between the much stronger main quantum well emissions. These are found to be separated by ≈47meV from quantum well no-phonon (X_{NP}) PL peaks and are attributed to LO-phonon satellites (X_{1LO}) of the quantum well PL. The dominant GaP-like LO phonon of GaInP has an energy of 47.6meV with the weaker InP-like LO mode at 45.2meV [7]. The 10meV PL linewidth of the sample precludes the observation of coupling to the latter mode. No evidence for coupling to the barrier LO-phonons (InP-like at 43.4meV and AlP-like at 55.8meV for AlGaInP with x=0.58 [8]) is observed [9]. The phonon satellites are visible more clearly in Fig. 4 which shows the PL of a 30 period GaInP-AlGaInP MQW, with 90Å well width, where, by making use of the increased sensitivity of a multichannel CCD detector, the first three orders of satellite (X_{nLO}, n=1,2,3) are observed. Similar spectra are obtained for a sample with AlInP barriers. It can be shown theoretically that the intensity, I_n, of the n^{th} phonon satellite is given by [9-11]

$$I_n = \exp(-S_\nu)\frac{(S_\nu)^n}{n!} \quad (2)$$

where n=0 corresponds to the no-phonon line and S_ν is the Huang-Rhys factor for the phonon mode ν. From Eq.(2) the intensity ratio of successive satellites is given by

$$\frac{I_{n+1}}{I_n} = \frac{S_\nu}{n+1} \quad (3)$$

allowing S_ν to be determined from experimental measurements. For the present sample values for S_ν of (0.0051±0.0002), (0.050±0.002) and (0.046±0.007) are deduced using the integrated intensity ratios 0:1, 1:2 and 2:3 respectively. Although the latter two values are consistent within experimental errors the first value, determined from the intensity ratio of the first phonon satellite and the no-phonon line is an order of magnitude smaller. A similar behaviour was first observed, and explained, by Brener et al [12] in a GaAs-GaAlAs quantum well and was also observed, but not commented on, in a GaInP-AlGaInP quantum well by Dawson and Duggan [3].

The reason for this discrepancy is that only a fraction of the recombining excitons contribute strongly to the phonon satellites. The strength of S_ν depends upon the polarisation

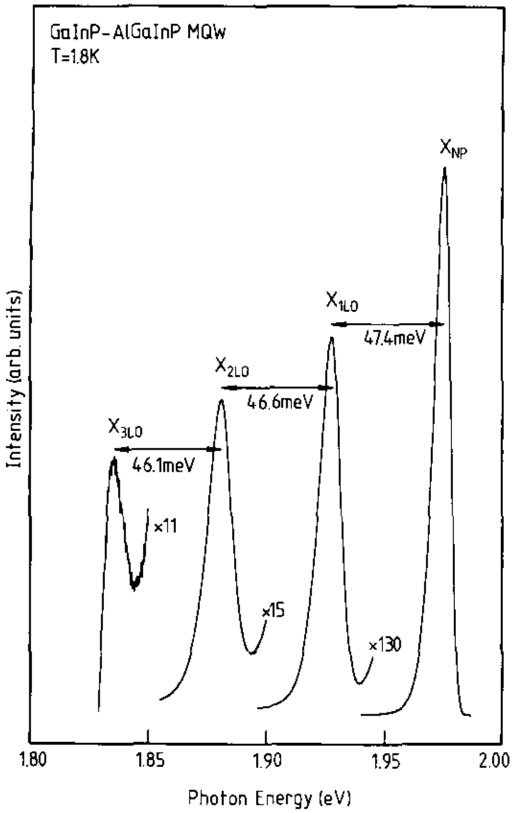

Fig. 4. PL spectrum of a 30 period GaInP-AlGaInP multiple quantum well showing the zero-phonon line (X_{NP}) and the first three orders of phonon satellites (X_{nLO} n=1,2,3).

of the lattice produced by a recombining exciton. Although small for a free exciton it may be considerably enhanced if the exciton is strongly localised [9-11]. Hence, although all recombining excitons contribute to the no-phonon line only the fraction which are strongly localised make a significant contribution to the phonon satellites. The value of S_v determined from the ratio of the first satellite to the no-phonon line will therefore be smaller than the true value determined from the ratios of successive satellites. This is exactly the behaviour observed experimentally. PLE measurements of the present sample show a 10meV Stokes' shift between the PL and free exciton observed in PLE, indicating that all the excitons contributing to the PL are localised. However, taken with the above results, we conclude that the majority (~90%) of these excitons are only weakly localised, on a length scale larger than the exciton diameter. Only a small minority (~10%) are localised on a length scale small enough to give a significant contribution to the LO-phonon satellites. The present results confirm the validity of Eq. (2) and also emphasise the importance of observing at least two orders of phonon satellite for a reliable determination of S_v.

To conclude, we have reported a detailed spectroscopic study of the electronic states in GaInP-Al(Ga)InP quantum wells. Clear evidence for type-II behaviour in thin wells with AlInP barriers is observed. Although AlInP barriers provide the largest possible direct band gap confinement, the influence of the indirect barrier band gap suggest that the optimum electron confinement is provided by samples with lower Al barrier composition (x≈0.5). In the PL of a GaInP-AlGaInP MQW the first three orders of the LO-phonon satellite are observed. Their relative intensities allow a reliable determination of the Huang-Rhys factor and provide information on the relative contributions to the PL emission of both strongly and weakly localised excitons.

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