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L-band recombination in $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{P/In}_{0.5}\mathrm{Al}_{0.5}\mathrm{P}$ multiple quantum wells

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We report the direct observation of recombination from the L_{1c} band in $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{P/In}_{0.5}\mathrm{Al}_{0.5}\mathrm{P}$ multiple quantum wells. The indirect L_{1c} transition is observed in unstrained structures with narrow wells and in tensile strained structures, using high-pressure photoluminescence measurements. L_{1c} recombination is characterized by a pressure coefficient of 60± 5 meV/GPa, considerably smaller than that of the direct gap Γ_{1c} states. In the same experiments we also identify heterostructure states associated with Γ_{1c} and X_{1c} from which we determine the separation among the conduction minima in unstrained bulk $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{P}$ for $x \leqslant 0.48$. [S0163-1829(96)06620-9]

$\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{P}$ is one of the most attractive materials for the development of semiconductor lasers emitting in the yellow-red region of the optical spectrum.[1] Current visible laser diode technology uses multiple quantum wells (MQW's), with $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{P}$ wells and $\mathrm{In}_{0.5}\mathrm{Al}_{0.5}\mathrm{P}$ or $\mathrm{In}_x(\mathrm{Al}_y\mathrm{Ga}_{1-y})_x\mathrm{P}$ barriers. This heterostructure combination coupled with the possibility of varying well width and composition offers large flexibility in the selection of the operating wavelength as well as for tailoring of the output characteristics. Successful design and optimization of advanced laser structures is based on a complete understanding of the band structure and band alignments of the heterostructure materials composing the laser. Normally knowledge of the direct energy band gap is sufficient for the selection of the operating wavelength. However, for specific requirements such as the reduction of the laser threshold current, it is necessary to know the separation among the conduction-band minima, so as to avoid any detrimental influences in the laser operation from the higher effective mass, indirect L_{1c} and X_{1c} valleys.

The band structure of bulk $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{P}$ has been investigated previously.[2–7] It is known that $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{P}$ is a direct-gap material for In compositions $x > 0.32$ and that it becomes indirect, with L_{1c} being the lowest conduction-band minima, for In compositions $x < 0.32$.[3,7] Decreasing the In composition further reveals the X_{1c} extrema that become the conduction-band minima for $x < 0.2$.[2,3,7] The proximity of the L_{1c} and X_{1c} transitions has made difficult the identification of L_{1c}. Previous optical studies in alloys with varying compositions did not show any evidence of the L_{1c} band.[2] The L-like behavior was also absent in optical measurements at high pressure conducted on In-rich alloys.[4–6] Evidence of L_{1c} was obtained from modulated piezoreflectance measurements[3] and high-pressure mobility measurements[7] from which the energy separation among the conduction-band extrema of $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{P}$ alloys was not obtained directly. The proximity of the Γ_{1c}, L_{1c}, and X_{1c} extrema for $x < 0.48$ places restrictions in the design of $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{P}$ MQW's, as indirect well structures can be obtained by tailoring the separation among the conduction-band states by means of varying the composition and the well width.

In this paper we report the observation of recombination from the L_{1c} states in $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{P/In}_{0.5}\mathrm{Al}_{0.5}\mathrm{P}$ MQW's. The L-like behavior of the conduction-band minima was identified in narrow lattice matched MQW's, and also confirmed on tensile strained MQW's, from pressure-dependent photoluminescence (PL) measurements at low temperature. Carrier recombination from L_{1c} was characterized by a reduced pressure coefficient compared to that measured for the lowest confined Γ_{1c} state. The identification of the MQW states associated with Γ_{1c} and X_{1c} in the same experiments made possible the calculation of the separation among the conduction-band extrema in $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{P}$ for compositions $x \leqslant 0.48$.

The combination of using hydrostatic pressure and MQW's with different well width and compositions was essential for the unique determination of the L_{1c} transition in $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{P/In}_{0.5}\mathrm{Al}_{0.5}\mathrm{P}$ MQW's. With hydrostatic pressure the relative position of the conduction-band extrema was modified and the indirect states were revealed as they became the lowest conduction-band minima. The Γ_{1c}, L_{1c}, and X_{1c} minima were distinctly identified as they shifted with pressure at rates of about 100, 60, and −20 meV/GPa, respectively, typical of other semiconductor materials.[8] Since both Γ_{1c} and L_{1c} have positive pressure coefficient, obtaining a band alignment in which L_{1c} becomes the conduction-band minimum at high pressures, requires the Γ_{1c}-L_{1c} separation to be considerably smaller than that of Γ_{1c}-X_{1c} at atmospheric pressure. This condition was achieved in the $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{P/In}_{0.5}\mathrm{Al}_{0.5}\mathrm{P}$ MQW's, by decreasing the well width and in a separate experiment by decreasing the In composition x.

The $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{P/In}_{0.5}\mathrm{Al}_{0.5}\mathrm{P}$ MQW samples used in these studies were grown by gas-source molecular beam epitaxy on (100) GaAs substrates with nominally lattice matched composition for the barrier material. The growth of the $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{P/In}_{0.5}\mathrm{Al}_{0.5}\mathrm{P}$ MQW's was carried out at 530 °C at 1.0 μm/h, conditions that produced a disordered, random alloy in bulk samples as previously determined by photoluminescence, photoluminescence excitation (PLE), and transmission electron diffraction measurements.[9] Each sample contained a buffer layer of GaAs of 0.5-μm thickness, followed by an $\mathrm{In}_{0.5}\mathrm{Al}_{0.5}\mathrm{P}$ buffer layer 0.035 μm thick, the MQW region and an $\mathrm{In}_{0.5}\mathrm{Al}_{0.5}\mathrm{P}$ cap layer 0.1 μm thick. All layers were unintentionally doped. The MQW's consisted of 50 periods of 50-Å wells and 150-Å barriers. The well composition x was selected equal to 0.48, 0.41, and 0.37 corre-

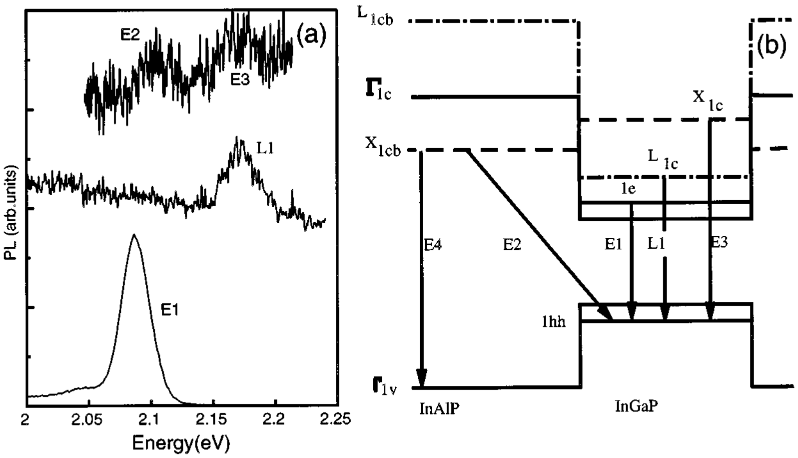

FIG. 1. (a) PL spectra from the −0.57% tensile strain MQW, corresponding to transitions associated with Γ_{1c}, L_{1c}, and X_{1c}. (b) Schematic diagram of the band structure of $In_xGa_{1-x}P/In_{0.5}Al_{0.5}P$ MQW's showing the various photoluminescence transitions observed in the experiments.

sponding to 0, −0.57%, and −0.87% tensile strain. For the unstrained composition a second structure consisting of 50 periods of 30-Å wells and 150-Å barriers was also grown. The high-pressure photoluminescence measurements were conducted at 50 K. Details of these experiments have already been described in Ref. 10.

Typical PL spectra originating from well states associated with Γ_{1c}, L_{1c}, and X_{1c} are shown in Fig. 1(a). The full width at half maximum of the PL signal corresponding to the direct transition was measured to be ~17 meV. The PL signals of the indirect transitions were broader and weaker compared to the direct transition. We notice that since the L_{1c} states are confined in the well, their PL is more intense and narrower than that of X_{1c}. As shown next, the identification of the PL transitions was made strictly on their pressure rate of change. Their labeling is shown in the band diagram of Fig. 1(b) and is consistent with our previous work on this material system.[10]

Figure 2 shows the pressure dependence of the PL transitions measured in the unstrained $In_{0.48}Ga_{0.52}P/In_{0.5}Al_{0.5}P$ MQW's investigated. The pressure behavior of both the 50-Å and the 30-Å MQW's is qualitatively similar. Four PL transitions were identified, one with a positive pressure coefficient (dE/dp) and three PL transitions with negative slope, characteristic of an X band. Among the three X-like transitions, two were observed over the whole pressure range of the experiments. These PL transitions, labeled $E3$ and $E4$, correspond to the indirect recombination of photoexcited carriers from the X_{1c} minima in the well (X_{1c}- 1hh) and in the barrier, respectively ($X_{1\text{cb}}$-Γ_{1v}). The third indirect transition ($E2$) was only observed at high pressures after the lowest confined conduction-band state becomes resonant with the barrier $X_{1\text{cb}}$ states. $E2$ corresponds to the indirect, in real and k space, ($X_{1\text{cb}}$-1hh) recombination. As expected, the onset of $E2$ occurred at lower pressures in the 30-Å MQW's as the separation between the lowest confined Γ_{1c} state ($1e$) and $X_{1\text{cb}}$ is reduced with increased carrier confinement.

The PL transitions characterized by a positive dE/dp showed a distinct behavior. In the 50-Å MQW, this transition labeled $E1$ was characterized by $dE/dp=92\pm3$ meV/GPa, a value typical of a Γ-like behavior.[8] We associate $E1$ with the recombination between the conduction- and valence-band ground states ($1e$-1hh). By contrast, dE/dp in the 30-Å MQW's was measured to be 60 ± 5 meV/GPa. Although an ~6% reduction in the pressure coefficient of $E1$ is expected from the variation in the well width,[11] this effect cannot explain the almost 50% decrease measured in the narrow MQW's. The lower value of dE/dp indicates that in the 30-Å MQW's recombination takes place from a conduction-band state with an L-like behavior. L_{1c}-1hh recombination, labeled $L1$ in Fig. 1(b), is observed in the narrow well structures since $E1$ is shifted above L_{1c} due to the increased carrier confinement. The calculated pressure dependence of $E1$ in the 30-Å MQW is represented by the solid line in Fig. 2(b). In the 50-Å MQW the $L1$ transition was not observed, as it occurred at higher pressures where the indirect $E2$ transition becomes dominant. The $L1$ behavior in the 50-Å MQW, calculated assuming the same pressure coefficient

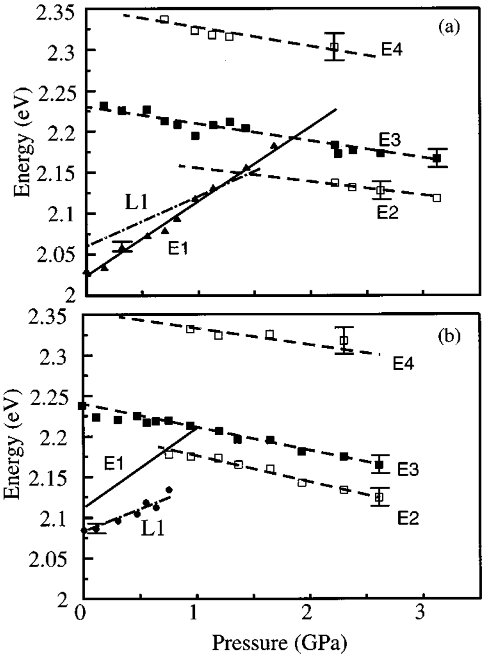

FIG. 2. Pressure dependence of the photoluminescence transitions of unstrained $In_{0.48}Ga_{0.52}P/In_{0.5}Al_{0.5}P$ multiple quantum wells of (a) 50-Å well width and (b) 30-Å well width. The pressure behavior of all transitions has been fitted using a least-square routine from which their pressure rate of change and the atmospheric pressure values are determined.

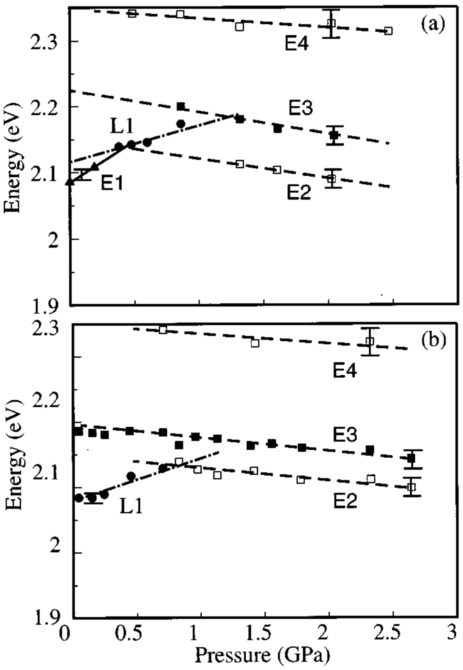

FIG. 3. Energy-pressure diagram for tensile strained MQW's with (a) -0.57% strain and (b) -0.87% strain.

as that measured in the 30-Å MQW, is shown by the dash-dotted line in Fig. 2(a).

To confirm our assignment of L_{1c}, we examined the results of the tensile strained MQW's. The L-like behavior should also be apparent in these structures as the separation between L_{1c} and Γ_{1c} decreases with decreasing In composition.[3] Figure 3 shows the energy-pressure data of the $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{P/In}_{0.5}\mathrm{Al}_{0.5}\mathrm{P}$ MQW's with well compositions $x=0.41$ and 0.37, corresponding to -0.57% and -0.87% strain, respectively. Hereafter, we discuss the behavior of the transitions with positive dE/dp, as the indirect transitions are equivalent to those observed in the unstrained MQW's. In the -0.87% strain MQW's, dE/dp was measured to be 60 ± 5 meV/GPa, identical to that of $L1$ in the 30-Å unstrained MQW's. In the -0.57% strain MQW's the PL transition with positive dE/dp showed at first glance a distinct behavior. Below 0.5 GPa it shifted at a rate $dE/dp=110\pm5$ meV/GPa and above 0.5 GPa at a slower rate $dE/dP=60\pm5$ meV/GPa, as shown by the solid and dash-dotted lines of Fig. 3(a). This change in the slope indicates that a pressure-induced $E1$-$L1$ crossover takes place at 0.5 GPa. The low pressure at which this crossover occurred shows that $E1$ and $L1$ are separated approximately 35 meV at ambient conditions. With increased tensile strain, the $E1$-$L1$ separation was decreased and $L1$ became the lowest conduction-band state, as observed in the -0.87% strained MQW.

The identification of the MQW states associated with the Γ_{1c}, L_{1c}, and X_{1c} extrema in the $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{P}$ wells allowed the calculation of the energy separation among the conduction-band extrema in $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{P}$ for $x\leqslant 0.48$. In reference to Fig. 1(b), the Γ_{1c}-L_{1c} separation was calculated from the difference of $L1$ and $E1$ at atmospheric pressure and by adding the $1e$ confinement energy.[12] We neglected the $L1$ electron confinement energy since it is small due to the large effective mass of the L_{1c} band.[13] The Γ_{1c}-X_{1c} separation was determined from the difference between $E3$ and $E1$ at atmospheric pressure and by adding the $1e$ confinement energy[12] and the strain-induced splitting of X_{1c}, calculated using the model solid theory.[14] The values of $E1$ in the MQW's with composition $x=0.37$ and $x=0.48$ (30 Å well width), in which this transition was not observed, were determined from PLE measurements.[15]

In unstrained bulk $\mathrm{In}_{0.48}\mathrm{Ga}_{0.52}\mathrm{P}$, L_{1c} was calculated to be 0.1 ± 0.02 eV above Γ_{1c} and 0.18 ± 0.04 eV below X_{1c}. Decreasing the In composition x decreased the Γ_{1c}-L_{1c} separation to 0.08 ± 0.02 and 0.03 ± 0.02 eV for $x=0.41$ and 0.37, respectively. The L_{1c}-X_{1c} separation was detremined to be 0.21 ± 0.05 eV for $x=0.48$. For the lower In compositions its value was equal to 0.175 ± 0.05 eV. The insensitivity of our results for determining the separation of X_{1c} relative to the other conduction-band extrema arises from the uncertainties involved in calculating the strain-induced shift of X_{1c}. From the measured variation of the Γ_{1c}-L_{1c} energy separation with In composition and assuming a linear behavior in the range of compositions investigated, we determined that L_{1c} becomes the conduction-band minima at $x=0.3$. A similar value was predicted by Bugaski, Kontkiewicz, and Mariette[13] and also determined from Hall measurements at high pressure[7] and piezomodulated measurements.[3] Although the agreement in the Γ_{1c}-L_{1c} crossover composition with previous work[3,7] is very good, the values of the Γ_{1c} band gap used as reference in this work are found to be approximately 60 meV smaller than that reported by Merle *et al.*[3] While ~20 meV can be accounted for by the localization energy, the rest is likely to arise from differences in the growth conditions.[16]

In conclusion, we have identified the L_{1c} band in narrow unstrained and in tensile strained $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{P/In}_{0.5}\mathrm{Al}_{0.5}\mathrm{P}$ MQW's and determined from these results the separation of the conduction-band extrema in $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{P}$ for In compositions $x\leqslant 0.48$.

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[12] The electron and hole confinement were calculated at the finite well approximation using a value of $\Delta E_c/\Delta E_v=$ 70/30 for the band discontinuities of the unstrained system. Values of $\Delta E_c/\Delta E_v=$ 62/38 and 60/40 were used for the -0.57% and -0.87% strained structures, respectively. These band offset ratios were calculated from the measured valence-band discontinuity and using a value of 2.6 eV for the direct band gap of $\mathrm{In}_{0.5}\mathrm{Al}_{0.5}\mathrm{P}$ determined from absorption measurements in our samples. Changes of the effective masses with strain were calculated using the model solid theory.

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