Direct-to-indirect energy-gap transition in strained $Ga_xIn_{1-x}As/InP$ quantum wells

P. Michler, A. Hangleiter, A. Moritz, G. Fuchs, V. Härle, and F. Scholz
4. Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, D-7000 Stuttgart 80, Germany
(Received 26 March 1993)

We present direct experimental evidence that in $Ga_xIn_{1-x}As/InP$ quantum wells the band structure undergoes a direct-to-indirect gap transition in k space above a critical value of x. We observe a drastic increase of the measured radiative exciton lifetimes for samples where $x > x_c$, with x_c depending on well width. Using a six-band $\mathbf{k} \cdot \mathbf{p}$ calculation of the valence subbands, we show that for $x > x_c$ the valence band maximum is at $\mathbf{k} \neq \mathbf{0}$, i.e., the band structure becomes indirect.

Strained-layer quantum wells have recently been subject to considerable interest both from a fundamental point of view and for state-of-the-art applications such as semiconductor lasers.[1–4] The strain introduced by the lattice mismatch primarily leads to a splitting and/or a mixing of the light and heavy hole valence bands and makes the valence subbands in quantum wells much more complex. However, this introduces a degree of freedom for the valence subbands and makes the effective mass of the valence bands an adjustable parameter.[5]

The strained-layer $Ga_xIn_{1-x}As/InP$ material system is particularly interesting since it allows for a variation of strain over a wide range. The strain in the $Ga_xIn_{1-x}As$ can be easily controlled for this system as the layer composition is changed from $x = 0$ (InAs) to $x = 1$ (GaAs). For gallium contents $x < 0.47$ the strain is compressive whereas for $x > 0.47$ it is tensile. Compressive strain effectively decouples the light and heavy hole subbands and moves the heavy hole subband to the top of the valence band. Tensile strain, on the other hand, moves the light hole subbands up in energy and makes them the highest valence bands. At the same time, this leads to strong band mixing effects and nonparabolicities.

We present direct evidence that strain-induced band-mixing effects in $Ga_xIn_{1-x}As/InP$ quantum wells lead to an indirect band structure in k space in a certain range of compositions and well widths. From a drastic increase of the measured radiative exciton lifetime at certain values of the Ga content and from the results of our six-band $\mathbf{k} \cdot \mathbf{p}$ band structure calculation we conclude that the valence band maximum in these structures is at $k \neq 0$. To our knowledge this is the first time that experimental evidence for such indirect valence bands is reported.

We performed composition and well width dependent time resolved experiments on $Ga_xIn_{1-x}As/InP$ quantum wells to investigate the influence of strain on the band structure. All of our samples are nominally undoped $Ga_xIn_{1-x}As/InP$ multiple quantum wells (MQW's) ($0.45 \leq x \leq 0.70$) grown on semi-insulating (100) InP:Fe substrate in a horizontal metalorganic vapor phase epitaxy technique (MOVPE) reactor using growth interruptions at all interfaces. The well widths and the well compositions are adjusted by the use of MOVPE growth parameters and are cross-checked by high resolution x-ray diffraction. The MQW's with 4.5- and 6-nm well widths consist of ten periods of $Ga_xIn_{1-x}As$ wells. All wells are separated by 20-nm InP barriers to avoid coupling between the wells. The values of the well widths were kept below the critical layer thickness which is a function of well width and composition.[6,7]

The time resolved measurements were performed using a photoluminescence setup, where the samples were excited by 5-ps infrared pulses in the 1.2–1.6-μm region. The infrared pulses are generated by mixing a 1.064-μm Nd:YAG (where YAG denotes yttrium aluminum garnet) laser pulse and a visible pulse from a cavity-dumped, synchronously pumped dye laser. The photon energy was low enough to generate carriers only in the $Ga_xIn_{1-x}As$ wells. The carrier density was estimated from the excitation power density and the absorption coefficient of $Ga_xIn_{1-x}As$ to be about 8×10^9 cm^{-2} in the wells. In this density region and at low temperature ($T < 50$ K) exciton recombination is the main decay channel.[8] The luminescence was detected with a Ge avalanche photodiode in a photon counting mode.[9] Continuous-wave PL measurements have been performed at 2 K using an Ar-ion laser operating at 514.5 nm.

The results of the PL decay time measurements at 5 K are summarized in Fig. 1. The composition dependence of the PL decay time of the samples with 6- and 4.5-nm well width is similar. At low Ga concentrations $x < x_c$ we find an almost composition independent lifetime of about 2–3 ns which is in good agreement with the radiative lifetime of an exciton in lattice matched

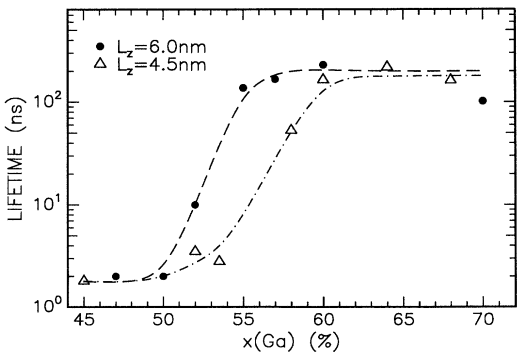

FIG. 1. PL lifetime vs gallium composition for the 4.5- and 6-nm MQW's at 5 K. Broken lines are only guides to the eye.

$Ga_{0.47}In_{0.53}As/InP$ quantum wells.[8] For gallium concentrations $x > x_c$ we observe drastically increased PL decay times by nearly two orders of magnitude. The transition takes place within a narrow region of about 4–5 % around the critical value x_c. The critical value x_c depends on the well width and is $x_c \approx 0.52$ for the samples with $L_z = 6$ nm and $x_c \approx 0.58$ for the samples with $L_z = 4.5$ nm.

By considering the strain dependent change of the valence band structure, the strong increase of the PL decay time can be well understood. We have performed band structure calculations using a six-band $\mathbf{k}\cdot\mathbf{p}$ theory based on a Luttinger-Kohn Hamiltonian.[10,11] Figure 2 shows the calculated valence band structures for a 4.5-nm quantum well with four different Ga compositions. With increasing tensile strain, the light-hole subband moves to the valence band ground state (see Fig. 2) which leads to a strong interaction between the light and heavy hole bands. As a consequence a second maximum at $\mathbf{k}\neq\mathbf{0}$ is induced in the highest hole band. For gallium compositions $x > x_c$ the second maximum has moved above the maximum at $k = 0$ and the band structure becomes indirect. This behavior was previously shown in theoretical studies by Houng and Chang[12] and Chu, Sanders, and Chang.[13] Our theoretically calculated values x_c for the transition from direct to indirect are $x_c = 0.53$ for a sample with $L_z = 6$ nm and $x_c = 0.59$ for a sample with $L_z = 4.5$ nm. This is in good agreement with our measured x_c values. The samples with Ga concentrations below x_c have a direct band structure and show PL decay times between 2 ns and 3 ns at low temperatures. The $x \approx x_c$ samples, situated close to the transition from direct to indirect band structure, display decay times between 10 ns and 100 ns. The samples $x > x_c$ situated clearly on the indirect gap side show time constants between 100 ns and 200 ns.

A direct-to-indirect gap transition of a different kind was found by Cebulla *et al.*[14] on GaSb/AlSb MQW's. In this material system, the small energetic difference between the L minimum and the Γ minimum of the GaSb conduction band and the different effective masses at these minima lead to a size induced direct-to-indirect crossover in the conduction band if the well width is reduced. They also measured a lifetime enhancement in the indirect samples of about two orders in magnitude.

It is interesting to analyze the nature of the indirect transition, i.e., if it is phonon assisted or not. Further information was gained from Fig. 3, which displays two typical spectra for a sample with a direct band structure (part *a*) and an indirect band structure (part *b*). Both spectra were measured at 2 K using an excitation intensity of about 25 (mW/cm^{-2}). For all samples with a Ga content $x < x_c$ the PL spectra exhibit a single emission line. This emission line is attributed to excitonic luminescence, since in this density region and at low temperature (2 K) excitonic recombination dominates the radiative recombination in QW's.[8] In contrast, the spectra for the samples with $x > x_c$ are composed of two separate lines. The low-energy line is a phonon replica, which is due to LO phonons. The replica consists of InAs-type and GaAs-type LO phonons with energies of 30 meV and 35 meV. The interpretation of the low-energy line as a phonon replica is supported by the identical transient decay of the two lines.

For radiative transitions, the recombination in the indirect samples takes place via an indirect exciton, consisting of an electron in the Γ conduction band minimum and of a hole in the indirect valence band maximum at $\mathbf{k} \neq \mathbf{0}$. The intensity ratio of the original line to its LO phonon replica is 4:1. As a consequence, at low temperature the LO phonon assisted recombination processes have a smaller transition probability and therefore do not limit the observed lifetimes in the indirect samples. Making the hypothesis that the radiative recombination rate of the no-phonon line determines the lifetime for the

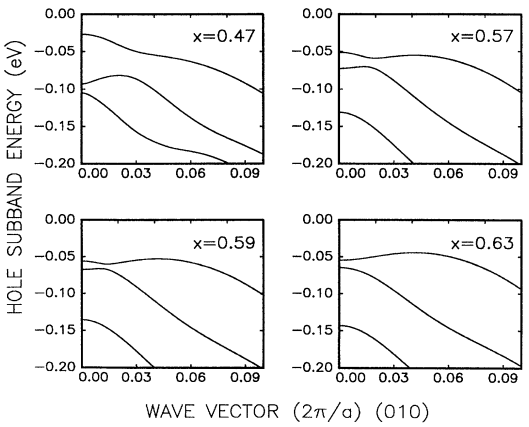

FIG. 2. Valence subband structures of 4.5-nm $Ga_xIn_{1-x}As/InP$ quantum wells with varying contents of gallium calculated by a six-band $\mathbf{k}\cdot\mathbf{p}$ theory.

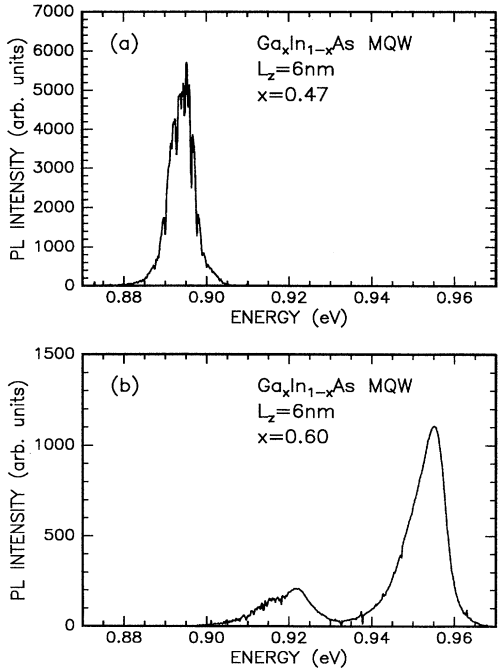

FIG. 3. Low-temperature (T = 2 K) photoluminescence spectra of 6-nm $Ga_xIn_{1-x}As/InP$ MQW's with gallium contents of (a) $x = 0.47$ and (b) $x = 0.60$.

measured samples, the transition rate in the absence of phonons should be proportional to the square of the exciton wave function in k space at the Γ point ($k = 0$). The k value of the indirect maximum in the 6-nm MQW is $k \approx 0.027\ (2\pi/a)$, whereas the value of the 4.5-nm MQW is $k \approx 0.042\ (2\pi/a)$. Because of the larger k value of the 4.5-nm MQW's, one expects for the indirect radiative transition a much longer lifetime for the 4.5-nm MQW's, since the square of the exciton wave function at $k = 0$ is much smaller than in the case of the 6-nm wells. We have performed detailed calculations of the transition probability using the calculated band structure and the wave function of the ideal 2D exciton in k space. The results show that the lifetime in the 4.5-nm MQW's should be more than one order of magnitude larger than in the 6-nm MQW's. This disagrees with our experimental findings of nearly well width independent lifetimes of 100-200 ns for both the 6- and the 4.5-nm samples. Therefore we conclude that the maximum lifetime in indirect samples is limited by nonradiative recombination centers. This interpretation is supported by the results of integrated PL intensity measurements. The indirect samples show a reduced quantum efficiency by a factor of 4 in comparison to the direct samples, with a further reduction towards high temperatures. The results taken together clearly show that the observed recombination from the indirect maximum in the valence band is partly phonon assisted and the absolute value of the lifetime in the indirect samples is limited by nonradiative recombination centers.

In summary we have presented direct experimental evidence that in $Ga_xIn_{1-x}As/InP$ quantum wells the band structure undergoes a direct-to-indirect gap transition in k space above a critical value of x_c. The experimental results are supported by our six-band $\mathbf{k} \cdot \mathbf{p}$ calculations of the valence subbands which show that for $x > x_c$ the valence band maximum is at $\mathbf{k} \neq \mathbf{0}$, i.e., the band structure becomes indirect. We observed a drastic increase of the PL lifetime by two orders of magnitude (from 2 ns to 100–200 ns) for samples whose gallium content is above the critical value x_c, with x_c depending on well width. The value for x_c was determined to be $x_c \approx 0.52$ for the 6-nm well width samples and $x_c \approx 0.58$ for the 4.5-nm well width samples.

We thank M. H. Pilkuhn for stimulating discussions. The financial support of this work by the Deutsche Forschungsgemeinschaft under Contract No. Ha 1670/1 is gratefully acknowledged.

[1] T.Y. Wang and G.B. Stringfellow, J. Appl. Phys. **67**, 344 (1990).
[2] D. Gershoni, H. Temkin, J.M. Vandenberg, S.N.G. Chu, R.A. Hamm, and M.B. Panish, Phys. Rev. Lett. **60**, 448 (1988).
[3] D. Gershoni and H. Temkin, J. Lumin. **44**, 381 (1989).
[4] S. Murata, K. Naniwae, J. Shimizu, M. Nido, A. Tomita, and A. Suzuki, Electron. Lett. **28**, 1456 (1992).
[5] E.P. O'Reilly, Semicond. Sci. Technol. **4**, 121 (1989).
[6] R. People and J.C. Bean, Appl. Phys. Lett. **47**, 322 (1985).
[7] J.W. Matthews and A.E. Blakeslee, J. Cryst. Growth **27**, 118 (1974).
[8] P. Michler, A. Hangleiter, A. Moritz, V. Härle, and F. Scholz, Phys. Rev. B **15**, 1671 (1993).
[9] W. Häcker, O. Grözinger, and M.H. Pilkuhn, Appl. Phys. Lett. **19**, 113 (1971).
[10] J.M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955).
[11] U. Ekenberg, W. Batty, and E.P. O'Reilly, J. Phys. C **5**, 533 (1987).
[12] Mau-Phon Houng and Yia-Chung Chang, J. Appl. Phys. **65**, 3092 (1989).
[13] Hanyou Chu, G.D. Sanders, and Yia-Chung Chang, Phys. Rev. B **36**, 7955 (1987).
[14] U. Cebulla, A. Forchel, G. Tränkle, S. Subbana, G. Griffiths, and H. Kroemer, Phys. Scr. **35**, 517 (1987).