phys. stat. sol. (b) **235**, No. 2, 412–416 (2003) / **DOI** 10.1002/pssb.200301593

High-pressure photoluminescence study of the electronic structure of InP/GaP quantum dots

C. Kristukat[1], **A. R. Goñi**[*,1], **F. Hatami**[2], **S. Dreßler**[2], **W. T. Masselink**[2], and **C. Thomsen**[1]

[1] Institut für Festkörperphysik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany
[2] Department of Physics, Humboldt-Universität zu Berlin, Invalidenstr. 110, 10115 Berlin, Germany

Received 5 August 2002, revised 30 August 2002, accepted 30 August 2002
Published online 4 February 2003

PACS 62.50.+p, 78.55.Cr, 78.67.Hc, 81.07.Ta

The electronic subband structure of self-assembled InP/GaP quantum dots (QDs) has been investigated by means of photoluminescence (PL) measurements as a function of hydrostatic pressure up to 8 GPa and temperature. At ambient pressure the PL emission of the sample arises from *direct* optical transitions between the lowest electron and hole Γ-point states confined in the QDs. At a very low pressure of about 0.15 GPa, the Γ–X conduction band crossover occurs, after which the PL emission of the dots becomes roughly 20 times weaker in intensity and its energy exhibits the slight redshift typical of indirect recombination processes from the conduction band X valleys. Our results indicate a type-I band alignment for the strained InP/GaP dot structure at low pressure and yield a value of 300 ± 30 meV for the valence-band offset.

1. Introduction Semiconductor nanotechnology has experienced a recent breakthrough exploiting the self-organized growth of quantum dot (QD) structures which exhibit large quantum efficiencies for light emission and zero-dimensional density of states, among other important properties [1]. Whereas the InAs/GaAs system is subject of extensive study, optical emission from InP dots embedded in GaP has been demonstrated only recently [2]. The use of GaP as substrate has potential advantages taking benefit of the well established light-emitting diode technology and also because of the larger band gap, which leads to stronger carrier confinement and easier light extraction in vertical-cavity lasers, for instance. Due to the 7.7% lattice mismatch between InP and GaP, self-assembled QD formation is achieved with these materials by the Stranski–Krastanov mechanism under proper growth conditions [3]. For structures using $In_{0.48}Ga_{0.52}P$ as barrier material, which is lattice matched to a GaAs substrate, intense luminescence from the InP islands has been reported at photon energies between 1.6 and 1.85 eV [4]. In the case of having pure GaP as matrix, the larger built-in strain of the InP dots is expected to shift the energy of the fundamental optical transition close to that of the indirect Γ–X band gap. This would eventually result in a less efficient radiative recombination if the optical transition is indirect in reciprocal space or/and it would even lead to a type-II carrier confinement with electrons and holes spatially separated. In fact, this is the case for ultrathin InP/GaP quantum wells [5]. In this respect, the application of high hydrostatic pressure has proved to be very useful for the determination of QD band structure parameters and for gaining insight into the electronic and optical properties [6–8].

[*] Corresponding author: e-mail: goni@physik.tu-berlin.de, Phone: +49 30 314 24442, Fax: +49 30 314 27705

© 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 0370-1972/03/23502-0412 $ 17.50+.50/0

Here we report the dependence on pressure of the photoluminescence (PL) emission of InP dots in a GaP matrix as a function of temperature and laser excitation power. The results indicate that at ambient pressure conditions the band alignment is of type-I and that the intense emission arises from direct optical transitions between confined states of the QDs. With increasing pressure the dot structure undergoes successively a conduction band Γ–X crossover and a type-I–type-II transition at about 0.15 and 1.2 GPa, respectively, as determined from the behavior of the PL peak energies and intensities under pressure. Furthermore, our data allow us to obtain an estimation for the valence band offset in the strained InP/GaP system.

2. Experiment The sample consists of five periods of InP dots embedded in GaP grown on GaP(100) substrates by gas-source molecular beam epitaxy at a temperature of 490 °C in the Stranski–Krastanow mode. The nominal thickness of each InP layer is 2.3 monolayers (MLs) and the separation between dot layers is about 10 nm. Structural analysis indicates that the dots are approximately 20×20 nm^2 in lateral dimensions and about 3–5 nm in height [9]. The dot density scaling with the amount of InP deposited is in the range of $2{-}6 \times 10^8$ cm^{-2}. Further details of the growth and structure of the QD samples are given elsewhere [2]. A platelet-shape crystal 100×100 μm^2 in lateral size and 30 μm thick was fitted into a diamond anvil cell for high-pressure experiments. Photoluminescence measurements were performed at different temperatures in a helium-bath cryostat. Helium was used as pressure medium and the change of pressure was always performed above the He melting temperature in order to avoid non-hydrostatic conditions. The ruby luminescence method was used for pressure calibration [10, 11] with temperature correction according to Ref. [12]. The 441 nm line of a He-Cd laser was used for excitation of the sample luminescence. The emitted light was analysed by a 1 m single-grating spectrometer equipped with a photomultiplier detector.

3. Results and discussion Figure 1 displays low-temperature PL spectra of the InP/GaP QD sample taken with 5 kW/cm^2 laser power density for different pressures in the range up to 1.2 GPa. The prominent peak in the PL spectra corresponds to the emission from the QDs. A much weaker feature centered at 2.2 eV at low pressure is also apparent in the PL spectra and is assigned to optical transitions between states of the wetting layer (WL). At ambient pressure the main emission of the sample peaks at 1.92 eV and its width is about 70 meV exhibiting an asymmetric double-peak structure [2]. Based on the results presented below, we interpret the PL spectrum at zero pressure as due to direct optical transitions between Brillouin zone-center states of the dots. At the laser powers of the experiment and for the low dot density of our sample we expect saturation of the dot emission to be achieved, thus the two peaks apparent from the

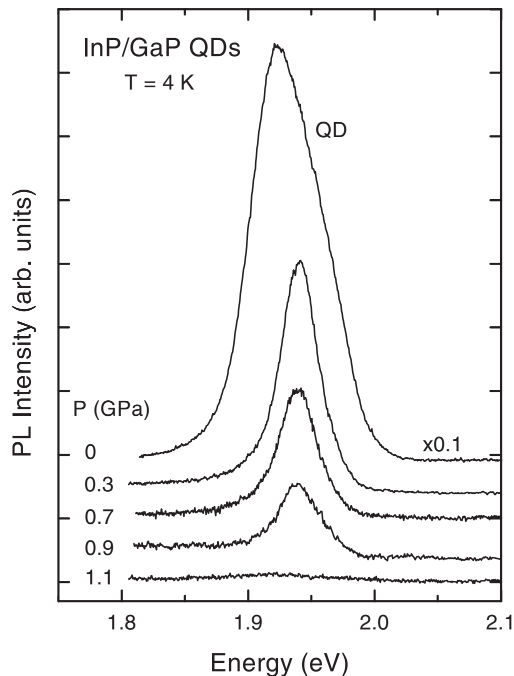

Fig. 1 Photoluminescence spectra of the InP/GaP QD sample for different pressures at 4 K and at high excitation density. QD stands for the PL emission from the dots. Spectra have been shifted by a constant offset for clarity.

0 GPa spectrum are attributed to recombination processes between the electron and hole ground states and the first excited ones of the dots, respectively. We note that this implies type-I band alignment.

At finite pressure a sudden blueshift of the PL peak maximum by about 20 meV occurs together with a reduction of the intensity by a factor 16 and the narrowing of the band width. With increasing pressure the position of the QD peak shifts slightly to lower energies, as it is the case for $\Gamma-X$ indirect transitions [7]. Further evidence for the indirectness of the optical transition at finite pressure is obtained from a lineshape analysis of the QD emission band, which shows a slight asymmetry of the peak towards lower energies due to a weaker line shifted down in energy by about 40 meV (the energy of zone-edge phonons in InP [13]). The main peak thus corresponds to the zero-phonon line activated in quantum dots due to the breakdown of translational invariance and the weaker feature at lower energies is attributed to the one-phonon replica of the indirect emission.

The wetting layer luminescence also shifts to lower energies with increasing pressure, indicating that these transitions are of $\Gamma-X$ indirect character. The wetting layer represents a kind of δ-like potential well for carriers in the GaP matrix. High-pressure experiments on an InAs monolayer in GaAs combined with tight-binding calculations have shown the existence of a bound state for electrons lying a few meV below the X conduction band edge of the barrier material [15]. Hence, we attribute the WL feature to optical transitions between states bound to the highly strained InP wetting layer, which are direct in space (type I) but indirect in reciprocal space (from the X to the Γ point). In fact, the WL emission is 50 meV lower in energy than the band gap of GaP and the luminescence of the barrier is completely absent in the spectra. The latter is an indication of an extremely efficient and fast capture of photoexcited carriers into the WL states.

The energies of the PL peak maxima obtained from low-temperature spectra are plotted in Fig. 2 as a function of pressure. Whereas the emission from the wetting layer shifts to lower energies at the rate of $-13.9(5)$ meV/GPa typical for the $\Gamma-X$ indirect gap of GaP [14], the QD line displays a much smaller pressure coefficient of $-4.4(5)$ meV/GPa. The pressure dependence of the PL peak intensity of the dots is depicted in the inset to Fig. 2. The initial reduction in intensity in excess of one order of magnitude is also a clear indication of the occurrence of the $\Gamma-X$ conduction-band crossover in the InP dots. The quenching of the dot luminescence above 1.2 GPa, in contrast, is due to a transition from type I to type II, at which the conduction band X valleys in the wetting layer become lower in energy than the ones in the InP dots.

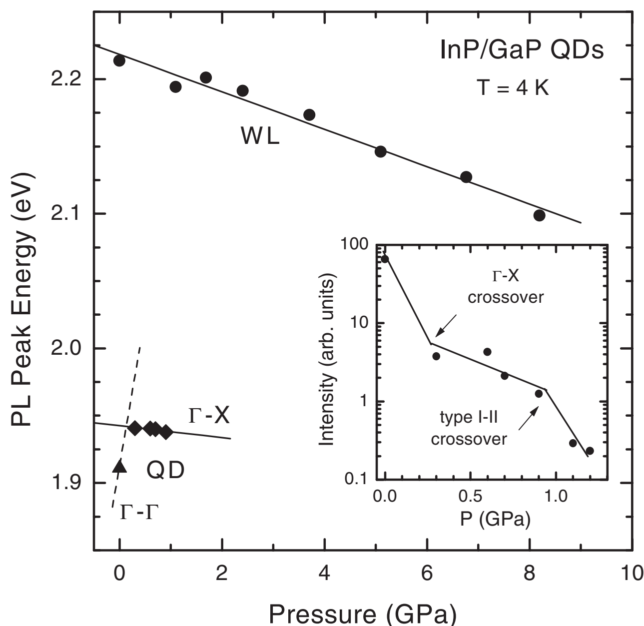

Fig. 2 Energies of PL peaks of the InP/GaP QD sample as a function of pressure. The solid lines correspond to the results of least-squares fits. The inset shows the dependence on pressure of the PL peak intensity. The lines are a guide to the eye.

The small negative linear pressure coefficient of the QDs and the change from type I to type II band alignment is a consequence of the reduction of the built-in strain of the InP dot layers with increasing hydrostatic pressure. This, in turn, is the result of a difference in bulk modulus between InP (71.1 GPa) and GaP (88.2 GPa) [13]. Since InP is more compressible than GaP, under pressure the lattice mismatch between both materials continuously reduces and so does the compressive stress upon the InP layers. This biaxial compression is at the origin of the splitting of the sixfold degenerate conduction-band X valleys into a X_{xy} quadruplet and a X_z doublet, the former being lower in energy. The X-valley splitting energy ΔE_X is given by [7, 16]

$$\Delta E_X = \Xi_u \frac{C_{11} + 2C_{12}}{C_{11}}\, \epsilon_{xx}\,, \tag{1}$$

where Ξ_u is the shear deformation potential [16], C_{ij} are the elastic constants [13], and ϵ_{xx} is the in-plane strain due to the lattice mismatch. For a 7.7% strain we obtain an initial splitting of ≈ 840 meV, corresponding to a downward (upward) energy shift of the $X_{xy}(X_z)$ levels by $-1/3\Delta E_X(2/3\Delta E_X)$. The pressure behavior of the X_{xy} states of the dots is essentially determined by two counteracting effects: the negative coefficient of the X states under hydrostatic compression and the pressure-induced reduction of the X-valley splitting, which tends to push the X_{xy} states up in energy. The energy separation between the X states in the QDs and the WL, thus, decreases with pressure at a rate of ≈ -10 meV/GPa, achieving degeneracy at about 1.2 GPa.

Further information about electronic states in the QD structure and relaxation processes between them can be gained from the temperature dependence of the luminescence at different pressures. Figure 3 shows the peak intensity of the PL lines corresponding to the dots and the wetting layer as a function of temperature at 0.7 GPa. The wetting layer emission decreases monotonically with increasing temperature showing thermal activated behavior. In contrast, the QD peak intensity goes through a maximum at around 30–40 K. Furthermore, the position of this maximum depends almost linearly on the pressure, decreasing from 70 K at ambient pressure to zero at around 1.2 GPa. This can be understood again in terms of the continuous reduction of the separation between conduction band X states of dots and wetting layer, as pressure increases. A striking result is the initial increase in intensity of the QD peak. We take this as evidence for an improvement of the carrier transfer from the wetting layer into the dots, which becomes more efficient with increasing temperature due to carrier delocalization.

In summary, at ambient pressure the band alignment in the InP/GaP QD structure is of type I and the QD emission is very intense arising from $\Gamma-\Gamma$ direct optical transitions between confined states of the dots. With increasing pressure this transition shifts up in energy very fast at a typical rate of about 100 meV/GPa [6, 14], such that at 0.2 GPa the absolute conduction-band minimum is at the X point and the QD recombination has become indirect in reciprocal space ($\Gamma-X_{xy}$ transition). The X_{xy} levels of the InP dots are initially approximately 10 meV below the X-bound state of the wetting layer. With increasing pressure, however, the energy separation between them

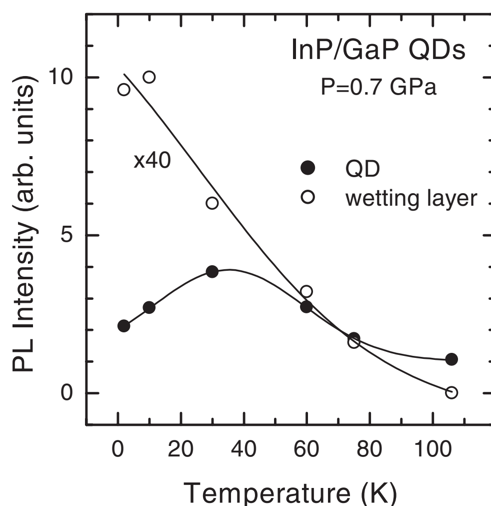

Fig. 3 Temperature dependence of the intensity of the PL emission from the InP dots (full symbols) and the wetting layer (open circles) measured at 0.7 GPa. The solid lines are a guide to the eye.

diminishes until at around 1.2 GPa they become degenerate and the quenching of the indirect QD emission is observed. Here we make use of this observation in order to extract the value of the valence-band offset ΔE_v of the strained InP/GaP heterostructure. The offset can be determined directly from the energy difference between the QD and WL emission lines for the pressure at which degeneracy of the X minima is attained, plus 40 meV corresponding to the localization energy of holes in the wetting layer measured from the top of the valence band of the GaP barrier. The latter has been estimated from the thermal activation energy of the WL luminescence. In this way, we obtain a value of $\Delta E_v = (300 \pm 30)$ meV, which is in very good agreement with the results of self-consistent tight-binding calculations [17] but almost half of the one measured in short-period InP/GaP superlattices [18]. We point out that in the latter case, the band offsets cannot be obtained directly from the experiment without the aid of empirical band-structure calculations.

Acknowledgements This work is supported in part by the Deutsche Forschungsgemeinschaft in the framework of Sfb 296.

References

[1] Proceedings of the 25th Int. Conf. Phys. Semicond. Osaka (Japan) September 17–22 2000, edited by N. Miura and T. Ando (Springer, Berlin, 2001).
[2] F. Hatami, W. T. Masselink, and L. Schrottke, Appl. Phys. Lett. **78**, 2163 (2001).
[3] B. Junno, T. Junno, M. S. Miller, and L. Samuelson, Appl. Phys. Lett. **72**, 954 (1998).
[4] J. Ahopelto, A. A. Yamaguchi, K. Nishi, A. Usui, and H. Sakaki, Jpn. J. Appl. Phys. **32**, L32 (1993).
A. Kurtenbach, K. Eberl, and T. Shitara, Appl. Phys. Lett. **66**, 361 (1995).
F. Hatami et al., J. Cryst. Growth **216**, 26 (2000).
[5] F. Hatami, G. Mussler, M. Schmidbauer, W. T. Masselink, L. Schrottke, H.-Y. Hao, and H. T. Grahn, Appl. Phys. Lett. **79**, 2886 (2001).
[6] C. Ulrich, S. Ves, A. R. Goñi, A. Kurtenbach, K. Syassen, and K. Eberl, Phys. Rev. B **52**, 12212 (1995).
[7] A. R. Goñi and K. Syassen, Semicond. Semimet. **54**, 247 (1998).
[8] I. E. Itskevich, M. S. Skolnick, D. J. Mowbray, I. A. Trojan, S. G. Liapin, L. R. Wilson, M. J. Steer, M. Hopkinson, L. Eaves, and P. C. Main, Phys. Rev. B **60**, R2185 (1999);
phys. stat. sol. (b) **211**, 73 (1999).
[9] H. Kirmse, private communication.
[10] G. J. Piermarini, S. Block, J. D. Barnett, and R. A. Forman, J. Appl. Phys. **46**, 2774 (1975).
[11] H. K. Mao, J. Xu, and P. M. Bell, J. Geophys. Res. **91**, 4673 (1986).
[12] S. Buchsbaum, R. L. Mills, and D. Schiferl, J. Phys. Chem. **88**, 2522 (1984).
[13] Handbook Series on Semiconductor Parameters, Vol. 1/2, edited by M. Levinstein, S. Rumyantsev, and M. Shur (World Scientific, London, 1996, 1999).
[14] A. R. Goñi, K. Syassen, K. Strößner, and M. Cardona, Phys. Rev. B **39**, 3178 (1989).
[15] G. H. Li, A. R. Goñi, C. Abraham, K. Syassen, P. V. Santos, A. Cantarero, O. Brandt, and K. Ploog, Phys. Rev. B **50**, 1575 (1994).
A. R. Goñi, A. Cantarero, H. Scheel, S. Reich, C. Thomsen, P. V. Santos, F. Heinrichsdorff, and D. Bimberg, Solid State Commun. **116**, 121 (2000).
[16] I. Balslev, Phys. Rev. **143**, 143 (1966).
I. Balslev, Proc. 8th Int. Conf. Phys. Semicond., Kyoto, Japan, 1966, J. Phys. Soc. Japan **21**, Supplement, 101 (1966).
[17] Y. Foulon and C. Priester, Phys. Rev. B **45**, 6259 (1992).
[18] G. Armelles, M. C. Muñoz, and M. I. Alonso, Phys. Rev. B **47**, 16299 (1993).