Electronic structure of self-assembled InP/GaP quantum dots from high-pressure photoluminescence

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The electronic structure of self-organized InP/GaP quantum dots (QDs) has been studied by means of photoluminescence (PL) measurements as a function of hydrostatic pressure up to 8 GPa, temperature, and laser excitation power. 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 QD's. 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. Upon further increase in pressure above 1.2 GPa we observe the quenching of the dot emission, which is taken as evidence for a type-I–type-II transition.

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I. INTRODUCTION

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, has had large impact on semiconductor nanotechnology.[1] Whereas the InAs/GaAs system is subject of extensive study, bright optical emission from InP dots embedded in GaP has been demonstrated only recently.[2] The use of GaP as substrate has potential advantages by taking benefit of the well-established light-emitting diode technology. The larger direct band gap of GaP as barrier and substrate material would also lead 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-Krastanow 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 and/or it would even lead to a type-II carrier confinement with electrons and holes spatially separated. In fact, this seems to be the case for ultrathin InP/GaP quantum wells.[5] The several phonon replicas apparent in PL spectra for submonolayer thicknesses of the InP layers and the very long carrier lifetimes of about 20 ns have been explained as resulting from spatially indirect recombination of electrons from the GaP *X* valleys with holes in InP.

Another issue of crucial importance for the performance of QD-based optoelectronic devices concerns the directness (in reciprocal space) of the optical transitions involved in the emission or absorption process, for it determines the light-conversion efficiency. Although InP is a direct band-gap material, the large built-in strain in the dots would split the *X* valleys by a couple of hundreds of meV, which eventually become the absolute conduction-band minimum. This would lead to a less intense indirect recombination within the dots. In fact, very basic information about band aligments in the strained InP/GaP system and a clear picture for the stress effects are still lacking. 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 their electronic and optical properties.[6–8] Key information like the direct-indirect character of the optical transitions can be readily obtained by tuning the energy levels with pressure through the Γ-*X* conduction-band crossover due to the very different dependences on pressure of the conduction-band minima at the Γ and *X* points of the Brillouin zone.[7] The valence-band offset can also be determined directly from photoluminescence (PL) data for pressures above the Γ-*X* crossing provided the type-I and type-II indirect emissions within the barrier and between barrier and dot, respectively, are simultaneously observed.[9–12]

Here we report the dependence on pressure of the PL emission of InP dots embedded 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 QD's. With increasing pressure the dot structure undergoes successively a Γ-*X* conduction-band 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 estimate for the valence-band offset in the strained InP/GaP system, which is in very good agreement with results of self-consistent band-structure calculations.[13]

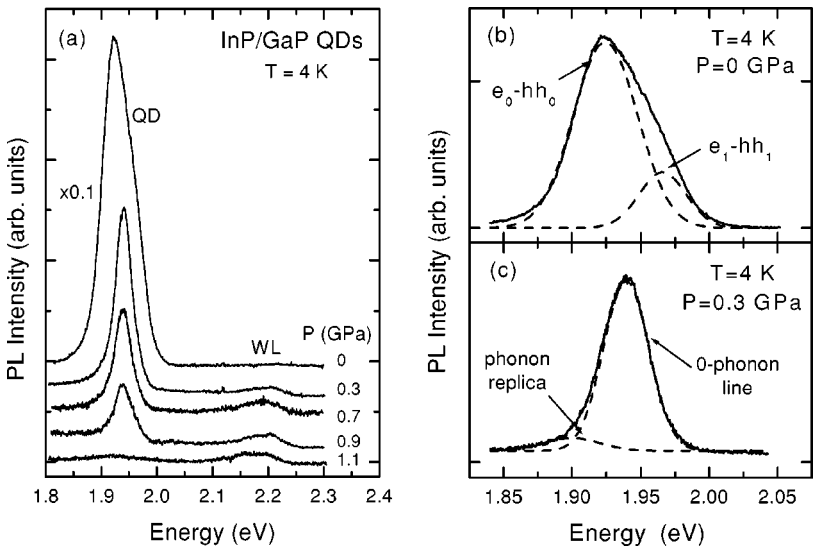

FIG. 1. (a) Photoluminescence spectra of the InP/GaP QD sample for different pressures at 4 K and at high excitation density. QD and WL stands for the PL emission from the dots and the wetting layer, respectively. Spectra have been shifted by a constant offset for clarity. (b) and (c) show an ambient pressure and a 0.3 GPa PL spectrum in the energy region of the QD emission, respectively. Dashed curves represent Gaussian line shapes fitted to the measured spectra. Their assignment is indicated.

II. EXPERIMENTAL DETAILS

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 (ML's), 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. The dot density is about 5×10^9 cm^{-2}. Further details of the growth and structure of the QD samples are given elsewhere.[2] We point out that for high-pressure experiments the as-grown samples have been thinned down to a final thickness of 30 μm by wet chemical etching instead of polishing them mechanically. This is to avoid the introduction of defects or any other alteration of the highly strained original dots induced by tensions during the mechanical thinning procedure, as reported recently for the InAs/GaAs system.[14]

A platelet-shaped crystal 100×100 μm^2 in lateral size was fitted into a diamond anvil cell. 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 nonhydrostatic conditions. The ruby luminescence method was used for pressure calibration[15,16] with temperature correction according to Ref. 17. The 441-nm line of a He-Cd laser was used for excitation of the sample luminescence. The emitted light was analyzed by a 1-m single-grating spectrometer equipped with a photomultiplier detector. The photocurrent was then measured using a picoamperemeter.

III. RESULTS AND DISCUSSION

Figure 1(a) 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 QD's, whereas the much weaker feature centered at 2.2 eV at low pressure 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] as clearly seen in Fig. 1(b). 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. We note that this implies type-I band alignment. 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 0 GPa spectrum are attributed to recombination processes between the electron and hole ground states (e_0-hh$_0$) and the first excited ones of the dots (e_1-hh$_1$), respectively. In fact, the peak corresponding to the first-excited-state recombination becomes more pronounced with increasing laser power density due to the saturation of the population of photoexcited carriers in the ground state of the dots.

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 of 16 and the narrowing of the bandwidth. With increasing pressure the position of the QD peak shifts slightly to lower energies, as it is the case for Γ-X indirect transitions.[7] Further evidence for the indirectness of the optical transition at finite pressure is obtained from a line shape analysis of the QD emission band. A representative PL spectrum recorded at 0.3 GPa and at 4 K is shown in Fig. 1(c). The emission peak exhibits a slight asymmetry towards lower energies due to a weaker line shifted down in energy by about 40 meV [the energy of zone-edge phonons in InP (Ref. 18)]. 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, which speaks for these transitions being of Γ-X indirect character. This conclusion is further supported by the results of PL measurements performed on ultrathin InP/GaP layers.[5] Our WL emission line shape is

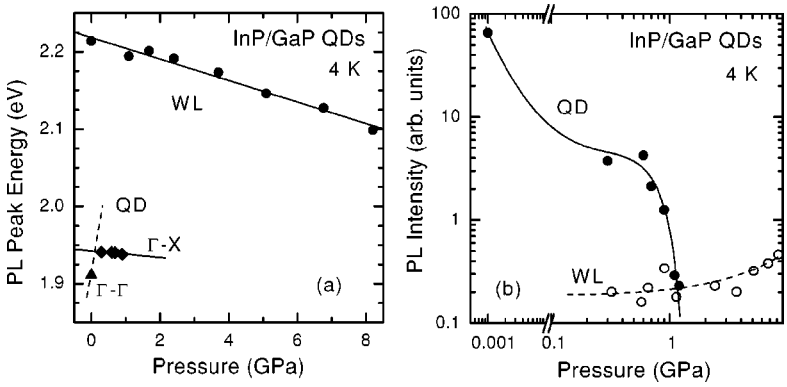

FIG. 2. (a) Energies of PL peaks of the InP/GaP QD sample as a function of pressure. The solid lines correspond to the results of least-squares fits. (b) Dependence on pressure of the PL peak intensities of quantum dots and wetting layer. Lines are a guide to the eye.

totally similar to the PL spectrum of a sample with 1.5-monolayer-thick InP layers, whose peaklike features were interpreted as different phonon replicas associated with the indirect optical transition.[5] The wetting layer represents a kind of δ-like potential well for carriers in the GaP matrix. This situation also holds for the conduction-band X minima since those of the InP WL are split by the built-in strain and pushed down in energy with respect to the X valleys in the GaP barrier. 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.[11] 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 energies of the PL peak maxima obtained from low-temperature spectra are plotted in Fig. 2(a) 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 Γ-X indirect gap of GaP,[19] the QD line displays a much smaller pressure coefficient of $-4.4(5)$ meV/GPa. The pressure dependence of the PL peak intensities of the dots and wetting layer is depicted in Fig. 2(b). The initial reduction in intensity in excess of one order of magnitude is also a clear indication of the occurrence of the Γ-X conduction-band crossover in the InP dots. Moreover, the quenching of the dot luminescence above 1.2 GPa is due to a type-I–type-II transition, at which the conduction-band X valleys in the wetting layer become lower in energy than the ones in the InP dots. In contrast, the intensity of the WL emission increases monotonically with increasing pressure.

The small negative linear pressure coefficient of the QDs and the change from type-I to type-II band alignment are 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).[18] 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[20,7]

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

$$E(X_{xy}) = E_X^{hydr} - \frac{1}{3}\Delta E_X, \tag{2}$$

$$E(X_z) = E_X^{hydr} + \frac{2}{3}\Delta E_X, \tag{3}$$

where Ξ_u is the shear deformation potential,[20] C_{ij} are the elastic constants,[18] and ϵ_{xx} is the in-plane strain due to the lattice mismatch. Using literature data we obtain for a 7.7% strain an initial splitting of $\approx$840 meV, which corresponds to

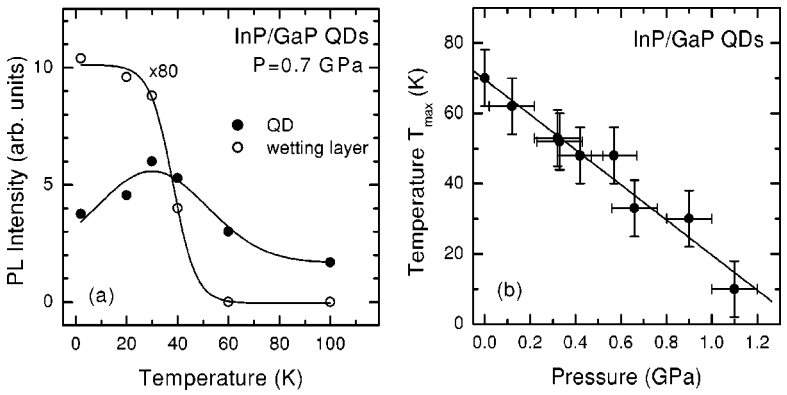

FIG. 3. (a) Temperature dependence of the intensity of the PL emission from the InP dots (solid symbols) and the wetting layer (open circles) measured at 0.7 GPa. The solid lines are a guide to the eye. (b) Dependence on pressure of the temperature of maximum in the PL intensity of the QDs. The solid line represents a linear fit to the data points.

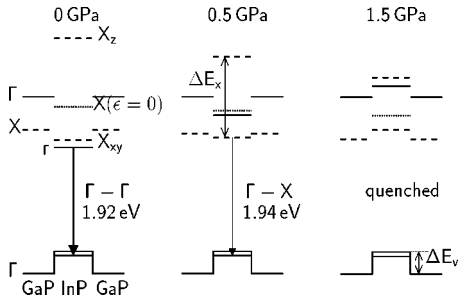

FIG. 4. Sketch of the Γ- and *X*-point conduction-band and Γ-point valence-band profiles of the InP dots for three different pressure situations. Arrows indicate the assignment of the observed optical transitions. ΔE_v stands for the valence-band offset.

a downward (upward) energy shift of the X_{xy} (X_z) levels with respect to the centroid energy E_X^{hydr}, the latter being affected only by the hydrostatic part of the compressive strain and the external pressure. 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. From the difference in linear pressure coefficients we infer that the energy separation between the *X* states in the QD's and the WL decreases with pressure at a rate of ≈ -10 meV/GPa. Because degeneracy of conduction-band minima is achieved at about 1.2 GPa, as indicated by the quenching of the dot luminescence, we can estimate the energy position of the X_{xy} states in the QD's at ambient pressure being about 10 meV below the *X* level bound to the wetting layer.

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(a) shows the peak intensity of the PL lines corresponding to the dots and wetting layer as a function of temperature at 0.7 GPa. The wetting layer emission decreases monotonically with increasing temperature, showing thermally activated behavior. In contrast, the QD peak intensity goes through a maximum at around 30 K. As depicted in Fig. 3(b), the position of this maximum depends almost linearly on 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. In other words, the activation energy for thermally induced carrier escape out of the dots decreases with pressure, resulting in the quenching of the dot emission, when the energy barrier vanishes. 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. Measurements at different laser excitation powers show a similar effect: at low temperatures the intensity of the QD peak increases superlinearly with laser power, showing saturation only above 70 K. In order to unravel the origin of this behavior, time-resolved PL experiments under pressure are being considered.

We summarize our results for the electronic structure of the InP/GaP QD sample with a series of level schemes for three different pressures, as illustrated by the diagrams of Fig. 4. 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 Γ-Γ 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,[6,19] 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 (Γ-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 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[13] but almost half of the one measured in short-period InP/GaP superlattices.[21] 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. This might be the reason for the large discrepancy between the value of the valence-band offset determined here and that using monolayer-thick multiple quantum wells.

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