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Energy levels in self-assembled InAs/GaAs quantum dots above the pressure-induced Γ-*X* crossover

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Low-temperature photoluminescence (PL) studies of InAs self-assembled quantum dots (SAQD's) embedded in a GaAs matrix have been performed under hydrostatic pressure P up to 70 kbar. A strong blueshift of the PL line from the SAQD's with P up to 53 kbar changes to a relatively small redshift at higher P. This is the fingerprint of a Γ-X crossover. Above the crossover pressure, we find experimental evidence for type-II band alignment in the InAs SAQD/GaAs heterostructure system. This gives a reference point that allows us to determine independently the energies of the electron and hole levels in the QD. [S0163-1829(98)52132-7]

A large number of experimental studies of the electronic properties of In(Ga)As/Ga(Al)As self-assembled quantum dots[1,2] (QD's) grown by the Stranski-Krastanov mode have been performed in recent years. These include a wide range of optical,[1,3–10] capacitance,[3,11,7,12] and tunneling[13–16] spectroscopy measurements. As a result, extensive and, in some cases, conflicting information is now available on Γ-valley electron and hole states in these systems. On the other hand, L- and X-valley-related electron states in self-assembled QD's have not yet been studied experimentally, to our knowledge, and only recently theoretically.[17,18] X-valley states can be investigated by the application of a high hydrostatic pressure P. With increasing P, the conduction-band Γ-valley states move to higher energy and at some pressure cross X-valley states that move to lower energy, resulting in the so-called Γ-X crossover. The high-pressure investigations of self-assembled QD's reported to date have been performed in a liquid-clamp cell[10,19] that restricts the available pressure range to 10–15 kbar. Experiments in a diamond-anvil cell, which can cover the Γ-X-crossover pressure range, have been reported only for the related but distinct system of InAs quantum dots grown on a slightly misoriented (terraced) GaAs surface.[20]

A key question concerning the Γ-X crossover in a heterostructure system is the nature of the X-valley-related electron ground state. For InAs/GaAs QD's it might be either a size-quantized X state in the QD or the X-valley edge in the bulk GaAs matrix. In other words, is there a type-I or type-II alignment for X-valley states in self-assembled InAs/GaAs QD's? The latter case gives a reference point for independent determination of the energies of the electron and hole states in the QD. For the similar system described in Ref. 20, type-I band alignment was reported for pressures above the crossover, although the energy difference between bulk X states and the X level in the QD's was estimated to be only a few meV.

Here we report high-pressure photoluminescence (PL) investigations of self-assembled InAs/GaAs QD's at P up to 70 kbar that allow us to observe the Γ-X crossover. From the qualitative change observed in the PL spectra above the crossover, we conclude that there is type-II alignment for X-valley-related states, i.e., the crossover corresponds to an intersection of the energies of the size-quantized Γ states in the InAs QD's and X-valley free-electron states in the bulk GaAs matrix. We use this information to determine the energies of the of electron and hole states localized in the QD.

The sample was prepared by molecular beam epitaxy at 450 °C on a (100) GaAs substrate with a growth interrupt after deposition of 1.8 monolayers of InAs that formed the quantum dots. The dots were then capped by a GaAs layer grown at 600 °C. The sample ($\sim 100 \times 100\ \mu m^2$) was placed in a diamond-anvil cell with He used as a pressure-transmitting medium. Experiments were performed at 12 K in a continuous-flow ^4He cryostat. Photoluminescence was excited by an Ar^+ laser ($\lambda = 4880$ Å), dispersed by a Jobin Yvon T64000 triple spectrometer (1800 grooves grating) and detected by a nitrogen-cooled charge-coupled device array. The R1 fluorescence line from a ruby crystal was used to measure the pressure.

Figure 1 shows a representative series of PL spectra from our sample at various pressures. As expected for Γ-point transitions, the PL line exhibits a blueshift with increasing pressure up to $P \approx 53$ kbar. The pressure dependence of the energy of the maximum of the PL line recorded at low pumping densities (≈ 0.5 mW/cm^2) is shown in Fig. 2(a). We can see that at higher pressure the blueshift is replaced by a relatively small redshift with increasing P. This is accompanied by a strong decrease in the integrated line intensity, as shown in Fig. 2(b). Both these features are fingerprints of the Γ-X crossover.

For $P < 40$ kbar the pressure dependence of the PL line energy $\hbar\omega$ is clearly linear, with pressure coefficient

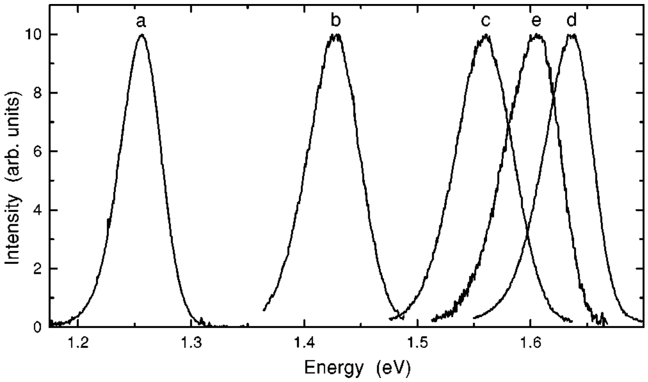

FIG. 1. A representative set of PL spectra at various pressures: (a) $P=1$ bar, (b) -20.7 kbar, (c) -37.2 kbar, (d) -58.8 kbar, and (e) -71.7 kbar. Peak heights are normalized.

$d\hbar\omega/dP=(8.0\pm0.2)$ meV/kbar, slightly smaller than that obtained for the pressure range below 10 kbar.[10] The observed pressure coefficient for the QD's is significantly smaller than that reported for bulk GaAs for $P<40$ kbar pressure range, 10.7 meV/kbar,[21,22] and bulk InAs, 10–12 meV/kbar.[23] This might in part be due to a decrease of electron size-quantization energy due to an increase of the electron effective mass with pressure,[24] and is consistent with a description of the QD states as Γ related within an effective mass approximation. As P approaches 50 kbar, $\hbar\omega$ increases less rapidly with P. We see no clear evidence for the interaction of the Γ- and X-electron states in the QD's, as reported in Ref. 20. This interaction has been recently predicted to be very small for quantum dots.[25] Above the crossover pressure, the line exhibits a steady redshift with increasing P, with $d\hbar\omega/dP\approx-(2.4\pm0.2)$ meV/kbar. This is consistent with the recombination of electrons from X-valley-related states.

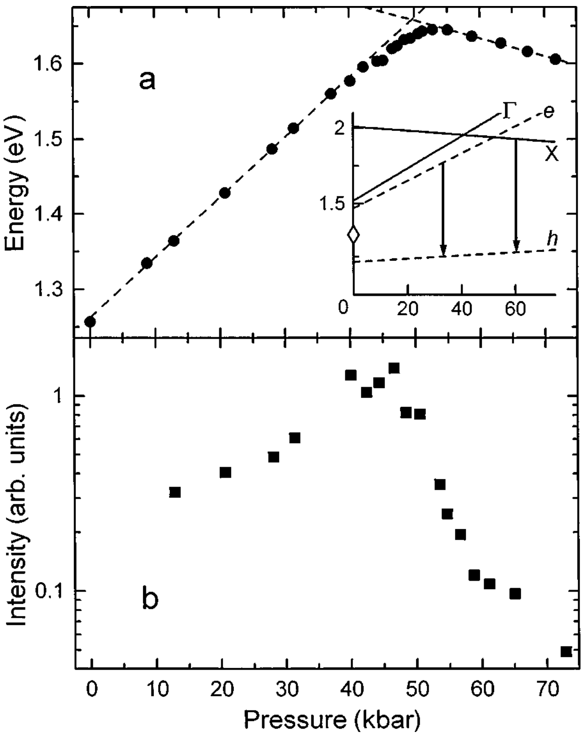

FIG. 2. Pressure dependence of (a) the energy position of the maximum of the QD PL line and (b) the integral intensity of the line in logarithmic scale. Inset to (a) shows a schematic diagram of the pressure dependence of the energies of the electron and hole ground states of the QD's (dashed lines) and of the Γ- and X-valley edges of bulk GaAs (solid lines). Both energies are relative to the GaAs valence-band edge. Arrows indicate optical transitions below and above the crossover.

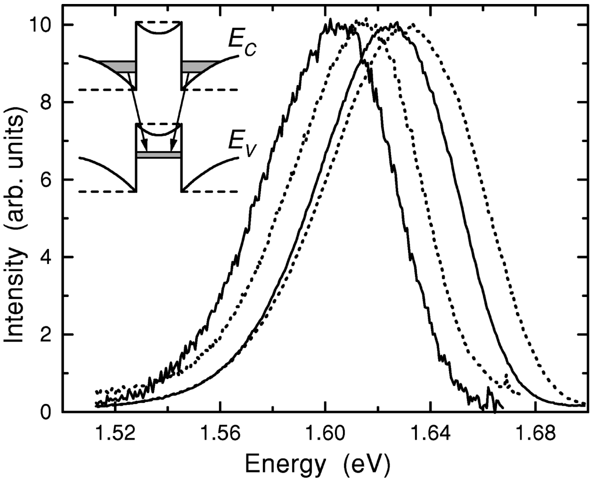

FIG. 3. Evolution of the QD PL at $P=71.7$ kbar with increase of pumping intensity W. Spectra (left to right) correspond to $W=0.5$, 5, 50, and 200 W/cm^2. Inset: Schematic band profile for QD's for type-II alignment without (dashed line) and with (solid line) band bending due to accumulation of spatially separated carriers.

Our spectra provide at least two pieces of experimental evidence that the X-valley states are those in the bulk-GaAs matrix. First, above the crossover the PL line energy becomes very sensitive to the pumping intensity. A strong (up to 25 meV) shift of the line is observed at pressures above crossover when the pumping density is increased from 20 mW/cm^2 to 200 W/cm^2. A representative series of spectra at $P=71.7$ kbar is shown in Fig. 3. A characteristic feature is that the energy shift is not accompanied by any noticeable change in the asymmetric line shape except for a small homogeneous broadening at the highest pumping intensities.

This behavior is typical of a type-II heterostructure system. In this case the recombination involves electrons from a quantum shell surrounding the positively charged InAs region. Due to the spatial separation of the photoexcited electrons and holes, their accumulation with increased pumping is accompanied by strong band bending (see inset to Fig. 3). Therefore an additional carrier quantization energy contributes to the energy of the PL transition. This effect is well known for type-II quantum wells.[26,27] It has been recently reported for InSb, GaSb, and AlSb self-assembled QD's that have type-II band alignment at ambient pressure.[27–29] In our case the effect is not as strong as that for quantum wells, due to the smaller quantization energy for the heavy X electrons in the GaAs.

We note that a small blueshift of the QD PL line with pumping can be also observed in our sample for pressures below crossover, i.e., for Γ-Γ transitions. However, it may be easily distinguished from that above crossover; it is smaller ($\leqslant 10$ meV), it saturates rapidly with pumping, and it is ac-

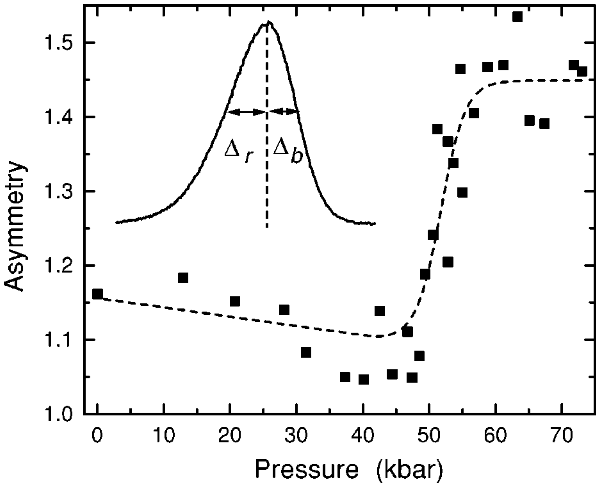

FIG. 4. Asymmetry (defined as Δ_r/Δ_b) of the QD PL line recorded at low excitation power at various pressures. The line is a guide for the eye. Inset: PL line at $P=63.3$ kbar showing clear asymmetry.

companied by a strong change in the line shape. A similar observation of the effect of pumping on the PL spectra has been reported recently for self-assembled InAs/GaAs QD's at ambient pressure[30] and was attributed to additional structure within the PL line.

The second piece of evidence of type-II alignment is that the PL line shapes for below- and above-crossover pressures are very different. Above the crossover, the line becomes strongly asymmetric, with a relatively sharp blue edge. Figure 4 shows the line asymmetry at various pressures that is defined as the ratio Δ_r/Δ_b, where Δ_r (Δ_b) is the energy difference between the line maximum and the red (blue) edge of the line taken at half maximum (so $\Delta_r+\Delta_b$ is the line full width at half maximum, see inset to Fig. 4). The change in line asymmetry occurs at about-crossover pressure, 50–55 kbar.

The sharp blue edge of the PL line that occurs above the crossover is consistent with recombination from X-valley-related electron states of the GaAs matrix. The recombination time is long enough for these electrons to migrate between the quantum shells surrounding the QD's and reach a common equilibrium. Consequently, at low temperatures there is an abrupt edge between filled and empty electron states, which leads to the sharp blue edge of the PL line. If the electrons were recombining from X-valley states localized within the QD's, there would be no possibility of a common chemical potential and we would expect a symmetric line shape, as at lower pressures. A similarly asymmetric PL line has been observed in the spectra of type-II QD's at ambient pressure, see Figs. 1–3 from Ref. 29.

Due to the type-II alignment of X-like states, the Γ-X crossover gives a reference point for the determination of the energies of the electron and hole levels in the QD [see the inset to Fig. 2(a)]. The hydrostatic pressure dependence of the energies of the X-valley edge in GaAs has been reported as $E_X(P)=(2.010\pm 0.008)-(1.34\pm 0.04)\times 10^{-3}P$ [eV],[21] where P is in kbar. If we neglect the electron-hole Coulomb interaction energy, at the crossover [$P=53$ kbar, $\hbar\omega=(1.645\pm 0.005)$ eV] we immediately obtain $E_h=(290\pm 10)$ meV for the hole "binding energy," which is defined as the difference between the energy of the hole level in the QD and the Γ-point valence-band edge in bulk GaAs. To obtain the value of E_h at $P=0$, we need to extrapolate the linear dependence in the Fig. 2(a) of the line position above the crossover to the zero pressure. We believe that the linear extrapolation is valid both above and below the crossover, assuming that the difference between $d\hbar\omega/dP$ and dE_X/dP, which might be due to either the QD quantization energy or the InAs/GaAs band offsets changing with pressure,[18,31] is not affected by the crossover. At $P=0$ the extrapolation gives $\hbar\omega=(1.775\pm 0.01)$ eV for the X-state transition energy. With the band gap of bulk GaAs $E_\Gamma=1.519$ eV and the zero-pressure emission energy $\hbar\omega=(1.255\pm 0.005)$ eV, we obtain $E_h=(235\pm 15)$ meV for holes, and the remarkably small value of $E_e=(30\pm 15)$ meV for electrons localized in the QD.

If we take the electron-hole Coulomb interaction into account, we find that the above values of the binding energies are overestimated. For Γ electrons and holes in the QD, the Coulomb interaction energy has typically been estimated as $E_C^\Gamma\approx 15-20$ meV.[32] From reasonable estimates for X electrons that are outside the QD, the energy of interaction with holes in the QD E_C^X does not exceed 10 meV, and its effect on the transition energy is even smaller due to the band bending. Therefore, $E_C^X\approx 5-10$ meV is the degree of overestimation of the above "binding energy" of holes and $E_C^\Gamma-E_C^X$ is the degree of overestimation for electrons.

Another possible source of errors might be due to inhomogeneous strain in the GaAs matrix around a QD.[32,18] A uniaxial component of the strain might split strongly the X valleys in GaAs.[18] This lowers our reference point that is the energy of the lowest X-valley edge in bulk GaAs close to the QD. Recent calculations have estimated this correction δ_{loc} as 30–35 meV.[18] Our binding energy is overestimated for holes and underestimated for electrons by the value of δ_{loc}.

Finally these corrections give a more reasonable value of $E_e\approx 50$ meV. We therefore obtain $E_h\approx 215$ meV. The binding energy for electrons is still much smaller than that obtained both from calculations[32,18] and capacitance measurements on other samples.[7]

To conclude, we have investigated the low-temperature photoluminescence from self-assembled InAs quantum dots at high pressures up to 70 kbar, which allowed us to observe the Γ-X crossover for the QD's. The results of excitation-power-density studies provide experimental evidence for type-II alignment of X states in the InAs/GaAs self-assembled–quantum-dot heterostructure. The energy positions of the electron and hole levels in the QD have been estimated.

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