Excited states and selection rules in self-assembled InAs/GaAs quantum dots

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High-pumping-intensity photoluminescence (PL) studies of InAs self-assembled quantum dots (SAQD) have been performed under high pressure P up to 70 kbar. The origin of the higher-energy PL lines that appear in the spectra with increasing pumping intensity is determined by using the Γ-X crossover effect in the conduction band. With increasing P, these lines are sequentially quenched at particular values of P. From this we unambiguously conclude that the lines correspond to the transitions from different excited conduction electron states in the SAQD. This indicates the existence of strong selection rules for the electron-hole recombination in the SAQD. [S0163-1829(99)51428-8]

Structures of reduced dimensionality are currently a topic of considerable interest in the physics of semiconductors. Zero-dimensional nanostructures, i.e., quantum dots, provide a system with a fully quantized, discrete energy spectrum for both electron and holes. A variety of methods may be used to achieve zero-dimensional confinement. InAs/GaAs self-assembled quantum dots (SAQD) grown by Stranski-Krastanov techniques[1,2] have been studied in much detail in the last few years.[3,4] They show clear evidence for zero dimensionality in their optical and transport properties. Their small size (about 10 nm across and a few nm high) results in a large energy separation between size-quantized levels, making them ideal for studying zero-dimensional excitons, for example. The low emission energy (1.1–1.3 eV), together with their strong quantum confinement and high optical efficiency, makes the SAQD attractive for technological applications.[5,4]

Despite a variety of experimental[6–15] and theoretical[16–24] studies, the energy level structure of electrons and holes in InAs/GaAs SAQD has not yet been clarified. In particular, the existence and number of excited electron states, and the nature of the optical transitions, are still a matter of controversy. A few years ago higher-energy emission lines, which arise with increasing pumping intensity, were observed in the photoluminescence (PL) spectra from SAQD.[7,9] Different groups have interpreted these lines as arising from transitions either between the ground electron state in the dots and excited hole levels,[7,8,14] or between excited electron and excited hole states with the same quantum number.[9,12] The former interpretation was consistent with the theoretical prediction that there is only one confined electron state in the dots;[17] the latter took into account the results of capacitance measurements[6,9,10,12] that demonstrated the existence of an excited electron level in the SAQD.[15] However, in principle both interpretations are possible; moreover, it is also possible that some transitions involve the same, and other transitions different electron states.

Theoretical investigations of various degrees of complexity have also been reported, with effective-mass,[16,17,22] multiband $\mathbf{k}\cdot\mathbf{p}$,[19–21,23] and pseudopotential[24] approaches used. They predict different numbers of electron states localized in the dots, from one[17] to five,[22,24] the number increasing in general with the sophistication of the model employed. As far as the optical transitions are concerned, most of the theories predict transitions of significant strength between states of differing quantum numbers,[3,17,20,21,24] although for dots of small aspect ratio, dominant transitions between states of the same quantum number have also been predicted.[20]

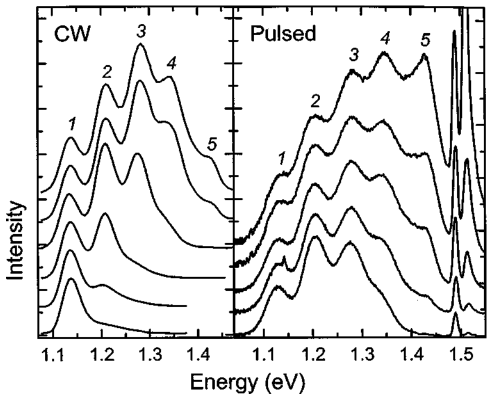

FIG. 1. PL spectra from the SAQD at 2 K at ambient pressure for different CW (left) and pulsed (right) excitation densities W that are CW—10 (bottom) and 100 W/cm^2, 1, 10, 20, and 40 (top) kW/cm^2; pulsed—10 (bottom), 20, 50, 100, and 200 (top) kW/cm^2. Numbers are to identify the peaks. Spectra are shifted and normalized for clarity.

Definitive experimental results are required to clarify the nature of the optical transitions. In this paper we present an experimental technique that allows us to interpret unambiguously the higher-energy lines in the PL spectra as arising from different excited electron states in the SAQD. We also show the existence of strong selection rules for the optical transitions in SAQD. For this we employ the so-called Γ-X crossover effect under high pressure P. It is well known that the direct Γ-point band gap in bulk GaAs increases with pressure until, at P about 40 kbar, a crossing of the edges of the Γ and X valleys in the conduction band occurs,[25] termed the Γ-X crossover. This is followed by quenching of the Γ-point-related PL lines. In a sample containing SAQD, at higher P the X-valley edge intersects the Γ-related electron state(s) in the SAQD.[26] Therefore, if all optical transitions are from the same ground electron state in the SAQD, all PL lines should quench *simultaneously* at the same pressure. On the other hand, if the transitions involve different electron states in the dots, the lines should quench *sequentially* with increasing P.

We have performed high-pumping-intensity PL studies of InAs/GaAs SAQD under pressure up to 70 kbar. Samples were grown by molecular beam epitaxy on a (001) GaAs substrate at a temperature of 520 °C and consisted of a single layer of InAs SAQD (nominal thickness 2.4 ML) sandwiched between two GaAs layers. Transmission electron microscopy indicates that the dots have a square base of length ≈ 15 nm, height ≈ 3 nm, and areal density $\approx 5 \times 10^{10}$ cm^{-2}. The measurements were performed in a diamond-anvil cell at 2 K in an optical cryostat, with He used as the pressure-transmitting medium. The pressure was determined from the shift of the ruby R1 fluorescence line. To obtain the high pumping densities, we used both continuous-wave (CW) excitation from an Ar^+ laser (focused to 50 μm) and pulsed excitation from a Cu-vapor laser. The PL was dispersed by a single-grating monochromator and detected by a photomultiplier and photon-counting system.

Figure 1 shows a set of PL spectra at ambient pressure at various pumping densities W. At low W, the ground-state emission line is observed with maximum at 1.14 eV. When W is increased, up to four higher-energy lines arise in the spectra. The two sharp peaks at ≈ 1.5 eV are from bulk GaAs. Similar spectra from InAs SAQD, showing from three to five lines under high pumping, have been reported earlier.[7–9,11]

Figure 2 shows typical sets of spectra at different pressures recorded at different pumping intensities. For all pressures, the sequence of pumping densities is the same, from 10 W/cm^2 to 10 kW/cm^2 for CW, and from 20 kW/cm^2 to 200 kW/cm^2 for pulsed excitation. No qualitative change occurs in the spectra below 30–35 kbar, apart from a steady blueshift of all the PL lines. For example, at $P = 10.9$ kbar [Fig. 2(a)] the sequential emergence of the lines with pumping is similar to that at ambient pressure.

Qualitative changes in the spectra are observed at P from 35–40 kbar. At about 40 kbar the lines from bulk GaAs are quenched abruptly, the fingerprint of the Γ-X crossover. This is followed by successive quenching of the higher-energy lines from the SAQD when P is increased further. All dot lines disappear from the spectra *in sequence*, starting with the higher-energy lines; the higher the pressure, the greater the number of lines quenched. A remarkable feature is that at fixed P, when some higher-energy lines have been quenched, the lower-energy lines are not affected and develop with increasing W in the same way as at lower P. At $P = 38.8$ kbar [Fig. 2(b)] the spectra at $W \leqslant 10$ kW/cm^2 (i.e., for CW excitation) are very similar to the spectra at $P = 10.9$ kbar at the same W, apart from a blueshift of about 200 meV. For example, at $W = 10$ kW/cm^2 [the upper spectra in the left panels in Figs. 2(a) and 2(b)] three well resolved lines are clearly observed, as well as a shoulder corresponding to the onset of the fourth line. The qualitative difference is that the fifth line, which can be clearly seen at higher W at 10.9 kbar, is completely quenched at 38.8 kbar.

Similar quenching of all excited-state lines is observed when pressure is further increased. At $P = 49.5$ kbar [Fig. 2(c)] we can see that the fourth line is completely quenched, while the three lower-energy lines still appear with pumping in the same way as at lower pressures. At $P = 54.7$ kbar [Fig. 2(d)] the two lower-energy lines are still unaffected, but the third line is quenched almost completely. There is only a weak shoulder that which can still be seen at $W \geqslant 100$ kW/cm^2; at slightly higher pressure this line is fully quenched. At $P = 60.1$ kbar [Fig. 2(e)] we can see an intermediate situation, with the second line half-quenched; this line emerges only at higher W, and is much lower in intensity than at lower P. Finally, at $P = 65.1$ kbar [Fig. 2(f)] all higher-energy lines are quenched, and only a single ground-state transition is observed in the spectra.

Figure 3 shows the pressure dependence of the peak energies. The linear blueshift of the lines over a wide range of pressures is replaced by a small redshift over a small P range above the crossover pressure for a particular line, until the line is fully quenched. Each of the higher-energy transitions is quenched due to the crossing of the corresponding electron level in the dots with an X-valley-related state (either in the SAQD or in the GaAs matrix), as shown in the inset to Fig. 3 where a schematic diagram of the level structure under pressure in presented. For $P > 65$ kbar, the ground-state line is not quenched but becomes asymmetric in shape and starts to shift to lower energies. These are the fingerprints of the

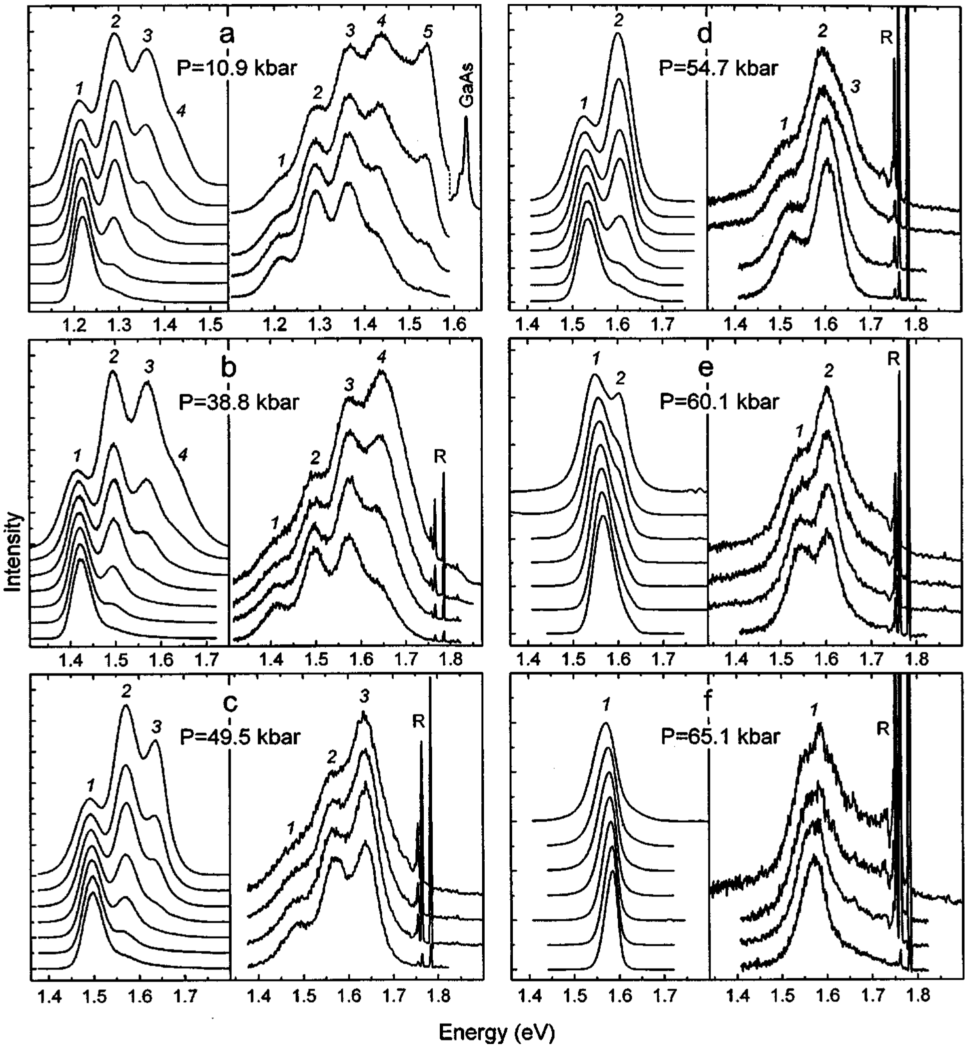

FIG. 2. PL spectra at different pumping densities and at different pressures (shown in kbar). For the sets of spectra at each pressure, the pumping densities are in the left panel—CW: 10 (bottom), 30, 100, and 300 W/cm^2, 1, 3, and 10 (top) kW/cm^2; right panel—pulsed: 20 (bottom), 50, 100, and 200 (top) kW/cm^2. Numbers in italics label the peaks. For $P > 30$ kbar the sharp features *R* at higher energies arise from the ruby crystal in the cell.

Γ-*X* crossover for the ground electron state in the dots.[26] The *sequential* quenching of all lines at different *P* indicates the *sequential* crossing of the electron levels with the *X* state. Therefore we conclude that each line is due to a transition from a *different* electron level in the dots. This proves the existence of four excited electron states localized in the SAQD. For the present $\approx 15\times 3$ nm dots this finding compares reasonably well with the prediction of Ref. 24 of three excited states for 11.3×2.7 nm dots.[27]

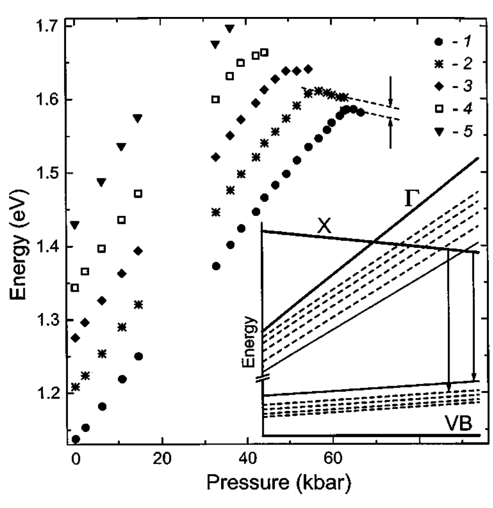

FIG. 3. Pressure dependence of the SAQD PL peak positions. Inset: schematic pressure dependence of the electron and hole level energies and optical transitions. Bold lines refer to the band edges of the GaAs matrix and dashed lines are the SAQD levels.

It has been widely assumed that the different dot-related lines in the PL spectra are due to transitions that involve different hole states,[7–9,11] although without direct experimental proof. Our data confirm this assumption. In Fig. 3 energy gaps are clearly seen between the lines above the crossover pressures; that between the two lowest-energy lines is marked by arrows. In the small *P* range above the crossover *for each line*, the transition occurs from the *same* *X*-valley-related electron state to the corresponding hole level. The gaps, therefore, indicate clearly that the transitions are to different hole states, and correspond to the energy differences between these states. Consequently, each transition below crossover corresponds to a particular pair of electron and hole states. This demonstrates the existence of strong selection rules that allow transitions between electron and hole states of the same symmetry, most likely having the same principal quantum number.[20]

Our results are consistent with the interpretation of the excited-state transitions in the optical spectra given in Ref. 9. However, it is conceivable that in quantum dots with a symmetry or confinement potential different from ours, the selection rules might be broken.[3,24] Under these circumstances, it may be possible to see PL transitions from a single electron ground state to excited hole states, as was proposed in Ref. 7, but in order to identify such transitions unambiguously, an experiment of the type described here is required.

To conclude, we have established unambiguously that higher-energy recombination lines that arise in the PL spectra from SAQD under high pumping conditions correspond to the transitions between different states of electrons and holes localized in the SAQD. This implies the existence of strong selection rules for the electron-hole recombination in the SAQD.

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