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Abstract

InP quantum dots grown on GaInP by the Stranski–Krastanow technique are less well studied than InAs quantum dots grown on GaAs. We here give a review of the main experimental evidence for the InP dots being charged when grown in between n-type barriers.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The study of quantum dots grown by the Stranski–Krastanow technique is by now a fairly mature field. Most studies have been concentrated on InAs or InGaAs quantum dots in GaAs. We will here review the understanding of the less studied, but equally interesting, system of InP quantum dots in GaInP. We will only briefly touch on the fabrication aspects and instead concentrate on the physics of these quantum dots. Initial studies of the growth of InP dots were done by Petroff *et al* [1] and Carlsson *et al* [2] using metal–organic vapour phase epitaxy (MOVPE).

2. General photoluminescence results

It was found early on that the InP dots gave strong photoluminescence (PL), which in fact dominated the spectrum from the samples. In figure 1 we show the evolution of the spectra as a function of the thickness of the deposited InP layer and as a function of the growth interrupt time after depositing InP. The spectra consist of emission at an energy of about 1.96 eV which is due to the GaInP barrier. There is also emission at 1.5 eV which is due to the GaAs substrate. When only a thin layer of InP is grown there is emission around 1.85–1.95 eV which is due to recombination of excitons in a thin quantum well. The thickness of this quantum well is only between one and three monolayers. The calculated emission energies are indicated in the figure. However, when the amount of InP deposited is sufficient to give a quantum well of about four monolayers a drastic change occurs in the spectra and a new emission peak occurs

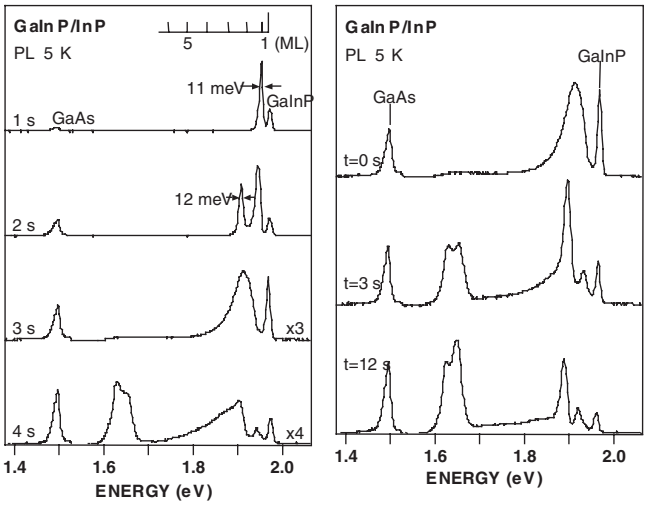

Figure 1. The left panel shows the evolution of PL spectra of samples with different amounts of InP being deposited. The peak around 1.65 eV is due to InP quantum dots. At an energy of 1.9 eV there is emission from thin quantum wells of InP. The right panel shows the evolution of PL spectra of samples having different interrupt times at the upper interface. About 1.5–2 monolayers of InP and a growth interrupt of about 12 s produces a strong signal from the dots.

at an energy of 1.65 eV. There is also a new emission between 1.65 and 1.9 eV. These new emission features are due to quantum dots of InP. It is necessary to perform a growth interrupt of several seconds to give the system enough time to form the dots and this is illustrated in the right panel of figure 1. Note that it is possible to have emission from both an InP quantum well and InP quantum dots. This is due to the Stranski–Krastanow growth mechanism where the dots grown at 580 °C form in equilibrium with a remaining wetting layer. It can be seen from the figure that a growth interrupt of three seconds is enough to form the dots.

3. Structure of the dots

The dots are about 15 nm in height which means that the growth rate of the dots is about 5 nm s^{-1}. The growth of InP dots is bimodal, and in addition to the fully developed dots, which have clear, low-index facets, there is also a set of smaller dots. These smaller dots have a lateral extension of about 50 nm and a height of a few nanometres. The fully developed dots are responsible for the emission at an energy of 1.65 eV and the smaller dots for the emission between 1.65 and 1.95 eV, shown in figure 1. The growth rate of the dots is about ten times higher than that of the quantum well (which is about 0.5 nm s^{-1}). Figure 2 shows an AFM image in top view of a sample containing both types of dots. Figure 3 shows an AFM image of one fully developed quantum dot [3] and figure 4 shows TEM images taken in cross-section of InP dots [4]. The AFM image shows that the dot has clear facets bounded by low-index planes. In particular, the top is not pointed. InAs dots on GaAs tend often to be lens shaped without clear facets [5]. The TEM images confirm the shape of the dots and also show that the interface between the dot and the barrier is coherent without any misfit dislocations. A careful inspection of the TEM images also shows that the lattice planes are slightly curved due to the presence of strain in the dots (and substrate). The dots are slightly elongated in the [110]-direction. The base is 45 nm by 60 nm and the height is 15 nm. Our dots have

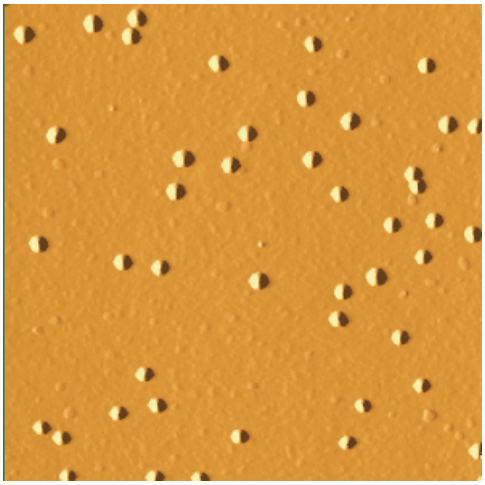

Figure 2. An AFM image in top view of a sample containing fully formed InP dots as well as small InP dots seen as a roughness of the wetting layer.

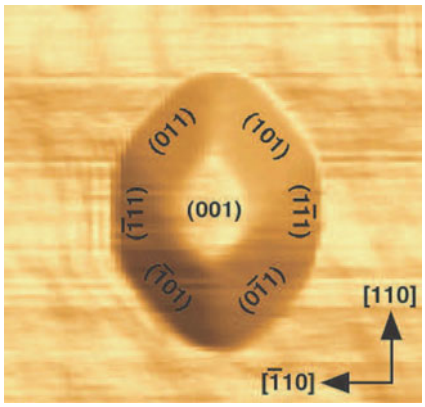

Figure 3. An atomic force migrograph of an InP quantum dot showing clear facets.

been grown at a temperature of 580 °C. It should be noted that InP dots on GaInP grown by gas-source molecular beam epitaxy have a different shape and in particular are only about 5–8 nm in height [6, 7]. The same situation has been found for InP dots grown by solid-source molecular beam epitaxy [8], with the height being down to 3 nm. The growth temperature in this case was 480 °C, and these experiments show the importance of the growth temperature in SK growth. MOCVD appears to give very stable dots with the majority of the dots having the shape shown in figures 2 and 3. The dots observed in MBE are quite similar to the small dots. We do note that by changing the phosphorus pressure during the growth interrupt it is possible also in MBE to obtain a bimodal population of dots [9] including a population of dots quite similar in size to the fully formed MOCVD-grown dots. It was found in [9] that a shape transition did occur to the fully formed dots and it was proposed that the fully formed dots are the more stable dots. The equilibrium shape of InP dots has been calculated and a faceted shape quite close to the shape shown in figures 3 and 4 was found [10].

4. Optical results

In this paper we will mainly concentrate on the fully formed dots. Theoretical calculations of the electronic structure can be expected to be quite accurate for these dots since the shape is so well defined. Investigations of MOCVD-grown capped dots have also found that the shape does not change during overgrowth [4]. There have also been extensive investigations of the initial overgrowth of InP dots by TEM, STM and luminescence [11]. In order to elucidate the electronic properties of the InP quantum dots a combined approach of experiment and theory has been used. Since the InP dots can be grown with a low surface density it is possible to use a simple microscope to select the emission from one quantum dot. Thus the problem with inhomogeneous broadening is avoided. This technique will be denoted micro-PL and is far easier to use than alternative techniques such as near-field scanning optical microscopy. In figure 5 we show the emission from one sample in top view. The emission has an energy of about 1.65 eV which corresponds to the fully developed dots. Individual dots can easily be resolved. In figure 6 we show the emission from one sample along with micro-PL spectra

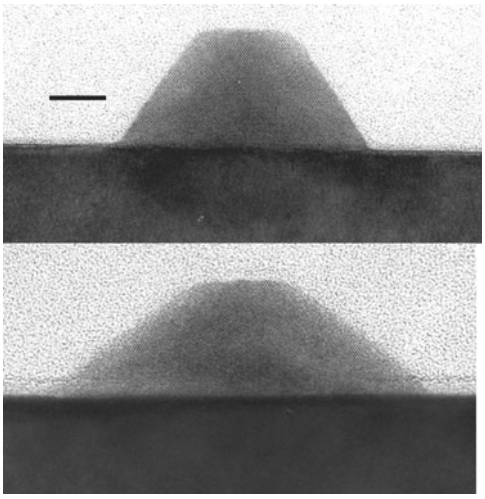

Figure 4. TEM images in cross-section of InP quantum dots along the [110]-direction (top image) and along the [$\underline{1}$10]-direction (lower image). The scale bar is 5 nm.

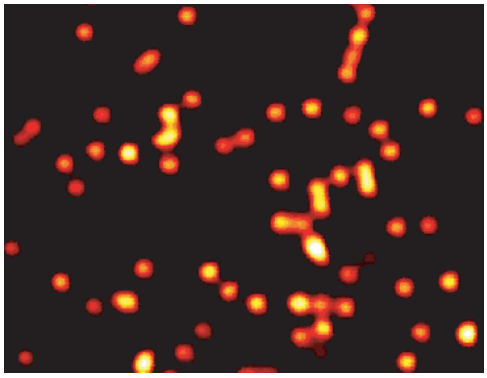

Figure 5. Top view image of the luminescence from a sample containing a low surface density of InP dots. The emission from the dots, having an energy of 1.65 eV, was monitored.

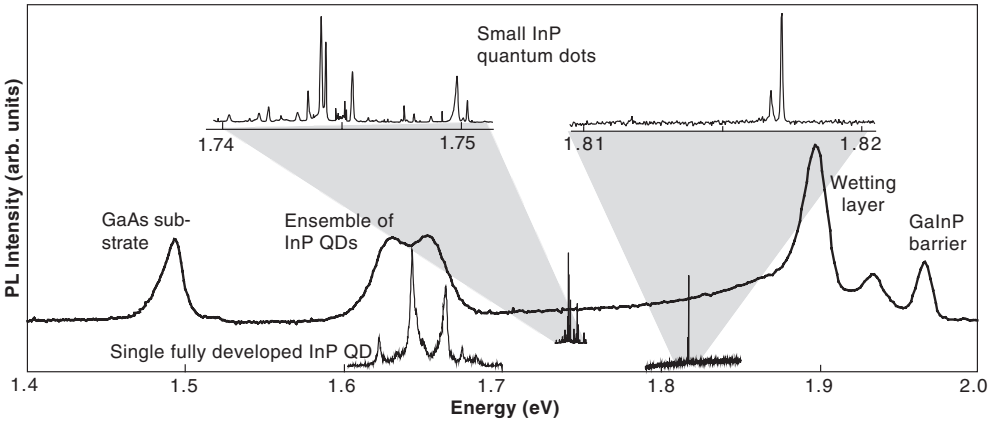

Figure 6. A macro-PL spectrum of a sample showing emission from the GaAs substrate, the InP dots, the wetting layer and the GaInP barrier. Also shown are micro-PL spectra of individual dots at different energies. At 1.65 eV the dot has several quite broad emission lines. At 1.75 eV the dots have many sharp lines and at 1.82 eV the dots has only two sharp lines. The reason is explained in the text.

taken at different energies [12]. It can be seen that the fully developed dots have several rather broad emission lines, whereas the small dots have a few narrow emission lines. In this respect the small dots behave like InAs dots in GaAs which also have a few sharp lines in PL [13, 14]. Figure 7 shows the emission spectrum of one fully developed dot in more detail along with photoluminescence excitation (PLE) spectra [15]. Each emission line in PL is about 2 meV broad and there are three main peaks and a few weaker peaks discernible. By detecting the emission from one of the main emission peaks and scanning the exciting laser it is possible to get information on excited states associated with this emission peak. One of these is denoted D in the figure and is common to all the PLE spectra. This proves that the different emission

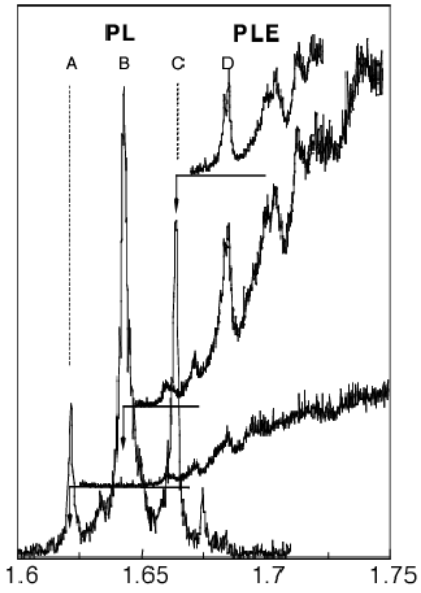

Figure 7. PL and PLE (photoluminescence excitation spectra) of a fully developed dots. The detection energy for each PLE spectrum is shown. The PLE spectra share excited states showing that only one dot is being monitored. A continuum is seen in the PLE spectra as well. No absorption corresponding to the emission peaks is seen.

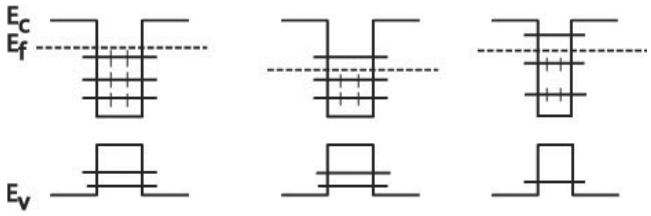

Figure 8. Schematic illustration of the influence of the Fermi level on the charging of quantum dots. If the Fermi level is above the ground state of the dot, the dot may be charged with electrons (left panel). By lowering the Fermi level (middle panel) or decreasing the size of the dot (right panel) it is possible to decrease the degree of charging. Each single particle level contains two electrons due to the Kramers degeneracy.

peaks, A, B, and C, belong to the same dot. It is puzzling that a broad continuum is seen in the PLE, since quantum dots are expected to have discrete energy levels. The decay time of the emission is about 1 ns which gives a line-broadening of 1 μeV. It is thus necessary to understand what mechanism broadens the lines. We will now clarify the reason for the occurrence of multiple lines in the emission spectrum. The samples are n-type with a donor concentration of about 10^{16} cm^{-3}. By evaporation by a transparent gold film acting as a Schottky gate it is possible to perturb the dots by an electric field and, more importantly, it is possible to change the position of the Fermi level in the vicinity of the dots [16]. This is schematically illustrated in figure 8 and the experimental results are displayed in figure 9 [16].

At an applied voltage of 1 V we have the situation as displayed in the left panel of figure 8; that is, the dots are filled with electrons. As the applied bias is changed to 1.0 V the Fermi level goes down in energy and the population of electrons in the dot is decreased, as shown in the right panel of figure 8. In the spectra (figure 9) we observe that the number of emission lines does decrease in the expected manner when the applied bias is changed. What is very puzzling is that when the dot becomes un-charged (or weakly charged) the broad line at an energy of 1.65 eV splits into a set of sharp lines (100 μeV). Naively one would expect emission

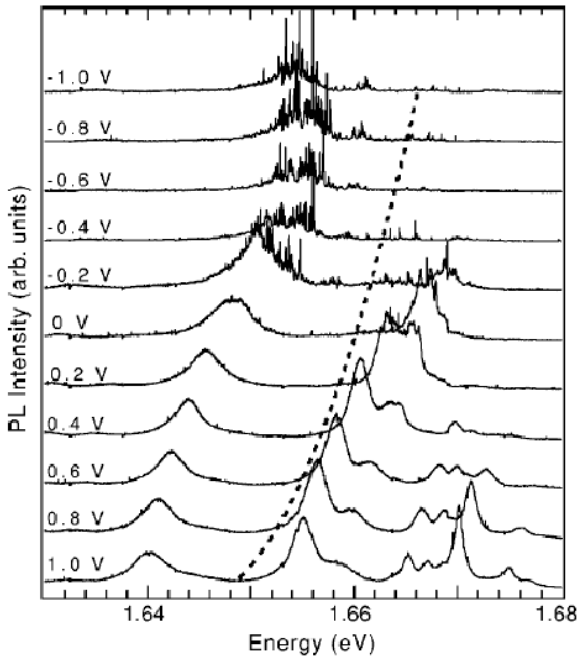

Figure 9. The evolution of the spectrum from one InP dot as a function of applied bias. A bias of 1.0 V corresponds to a dot filled with about 20 electrons which give rise to a set of emission peaks. As the bias is reduced the number of emission peaks becomes fewer due to a decrease of the charging. The lowest energy peak splits into a large number of narrow peaks at a bias of -0.4 V. The dotted curve shows the calculated energy shift.

from one neutral exciton at low power density, which would contribute with four lines (when few-particle interactions are included). This is not what is seen though and the reason is not understood. A possibility is that the holes do not relax easily and may recombine while in an excited state. One reason for the broadening that has been proposed is charge fluctuations in the neighbourhood of the defect. These conclusions were based on a dramatic narrowing of the lines at a temperature of 45 K [17]. In other samples, the lines are still broad up to room temperature, meaning that such charge fluctuations are strongly dependent on sample. If a state is filled with electrons then absorption is forbidden into this state. However, if the state is empty then there is a possibility of transitions into this state. Since absorption is very low in single quantum dots it is necessary to resort to PLE as a substitute experiment.

Figure 10 shows that when the bias is -0.2 V there is no absorption into the peak marked with an arrow. At higher bias, e.g. -0.6 V, there is a clear absorption into this peak, in agreement with expectations. Due to statistical fluctuations there is still emission from this peak in PL. The charging of the dots has also been seen in electrical measurements [18]. These experiments quite directly measure the charge in the dots via capacitance transients after the dots have been filled by an applied electrical bias pulse. Reflectivity measurements on samples containing InP dots have also shown the existence of charging close to the dots, which however was attributed to acceptors in the neighbourhood of the dots [19]. If the dots become small, they should have fewer and fewer levels below the Fermi level and the degree of charging should become less and finally the dots should be uncharged. This is actually seen in figure 1 where dots emitting at an energy of 1.75 eV have a set of very sharp emission lines and the

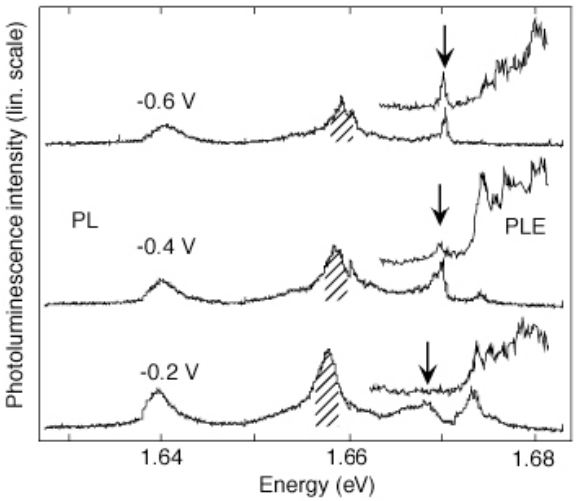

Figure 10. Photoluminescence excitation spectra of one InP dot along with PL spectra at different applied biases. The detection energy for the PLE is indicated by the shaded PL peak. One peak marked with an arrow becomes visible in PLE when the bias is decreased. This is due to the state becoming empty of electrons and thus becoming allowed in absorption. Due to the statistical nature of the measurement this peak can be simultaneously seen in emission and absorption.

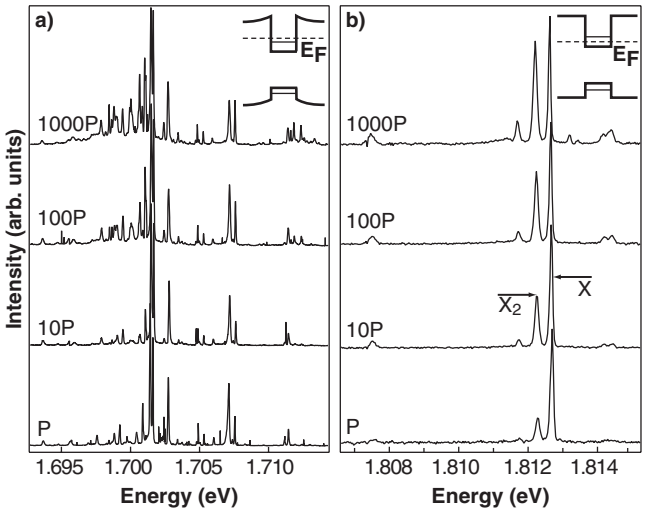

Figure 11. The left panel shows emission spectra from a small InP dot which is still charged. Many sharp emission lines are seen. The right panel shows emission spectra from a small InP dot which is not charged. The spectrum originates from the recombination of excitons, X, and bi-excitons, X_2. The bi-exciton spectrum becomes more dominant at higher excitation power densities.

dot emitting at an energy of 1.8 eV has only a few emission lines in similarity to InAs dots in GaAs. Figure 11 shows the situation in more detail. For weakly charged dots there is quite a large number of narrow emission lines and the number of lines agrees quite well with what is calculated [12]. For uncharged dots we have only a few lines corresponding to excitons and bi-excitons. The linewidth is about 100 μeV which is typical for other types of SK dots such as InAs in GaAs.

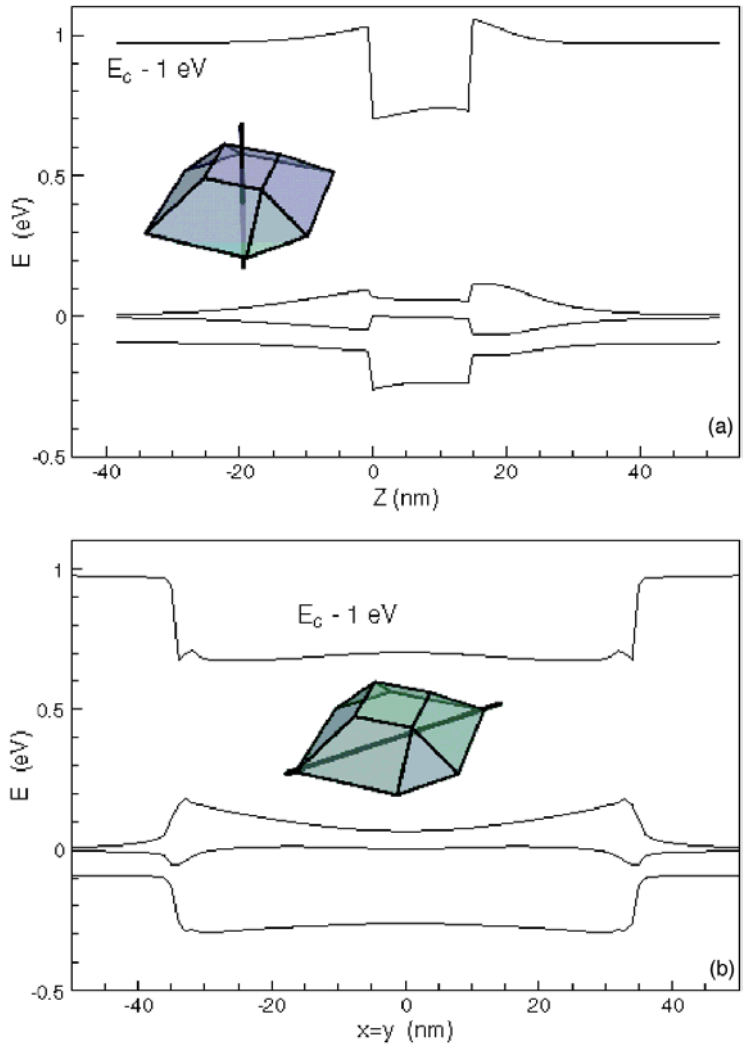

Figure 12. Potential energy diagrams through two different directions in an InP quantum dot. The conduction band well is much deeper than the valence band well. Thus the holes are less strongly bound than the electrons.

5. Theory and discussion

It is necessary to compare with theoretical calculations to more surely identify the origin of various peaks. In figure 12 we show the potential profile along two different directions in the dot. These calculations involve the determination of the strain throughout the dot followed by a determination of the energies of the band-edges using deformation potential theory [20]. It can be seen that the electrons are deeply bound whereas the holes are weakly bound. Figure 13 shows the calculated energy levels as a function of height of the dot. The energy splitting in the conduction band is typically about 10 meV, while the energy splitting in the valence band is about 1–2 meV. The conduction band splitting agrees well with the experimental splitting between the main peaks observed in figures 7 and 9. It is important to notice that

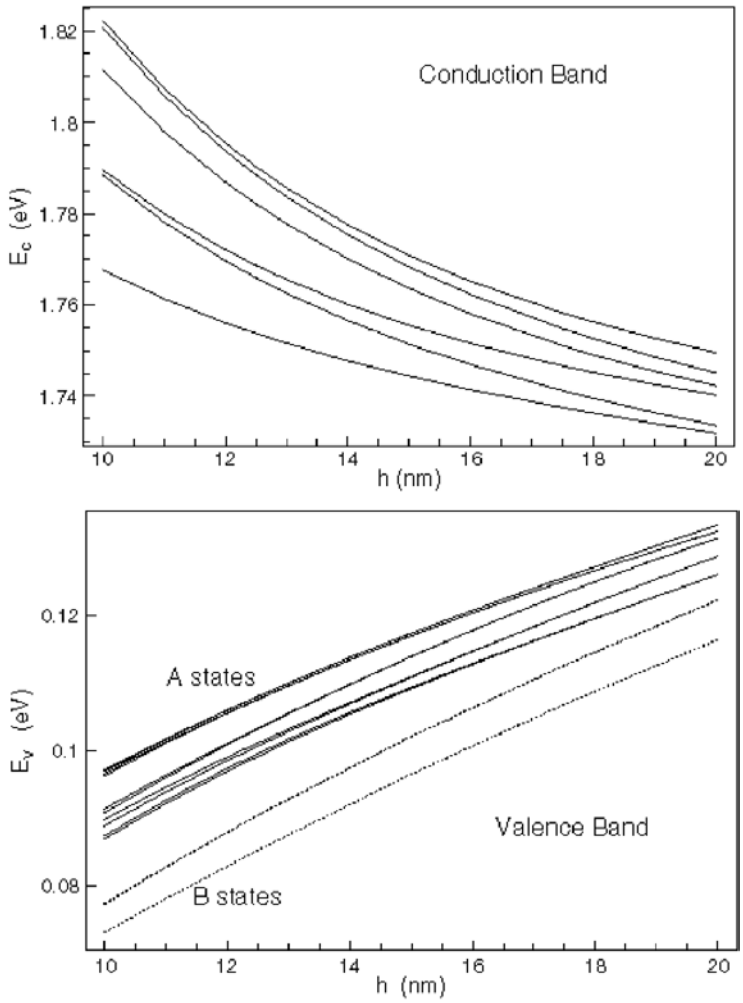

Figure 13. Calculated single-particle energies for electrons and holes as a function of dot height. Two sets of hole states, defined in figure 14, have been calculated.

the calculated splitting of the hole states is sufficiently large that it should be visible in the experimental spectra (given a linewidth of 0.1 meV or less). This conclusion is not changed even if excitonic interactions and splittings due to exchange are included. An inspection of the wavefunctions, plotted in figure 14, shows that the holes are localized at the interface of the InP and the GaInP at the bottom of the dot. The electrons are however localized in the centre of the dot. This gives a rather strong dipole moment of the exciton in comparison to the more commonly studied InAs dots in GaAs where both electrons and holes are localized within the centre of the dot [21, 22]. There are in fact two sets of hole states in InP dots, since at higher energy the holes may be localized at the top of the dot. These calculations have been performed using $\boldsymbol{k} \cdot \boldsymbol{p}$-theory within the envelope function approximation and include strain and the piezoelectic polarization, which is important close to the interfaces [21, 22]. Since the calculations are in three dimensions they are quite demanding. An added complication is that the exciton, or more generally multi-particle states, also experience effects from the Coulomb

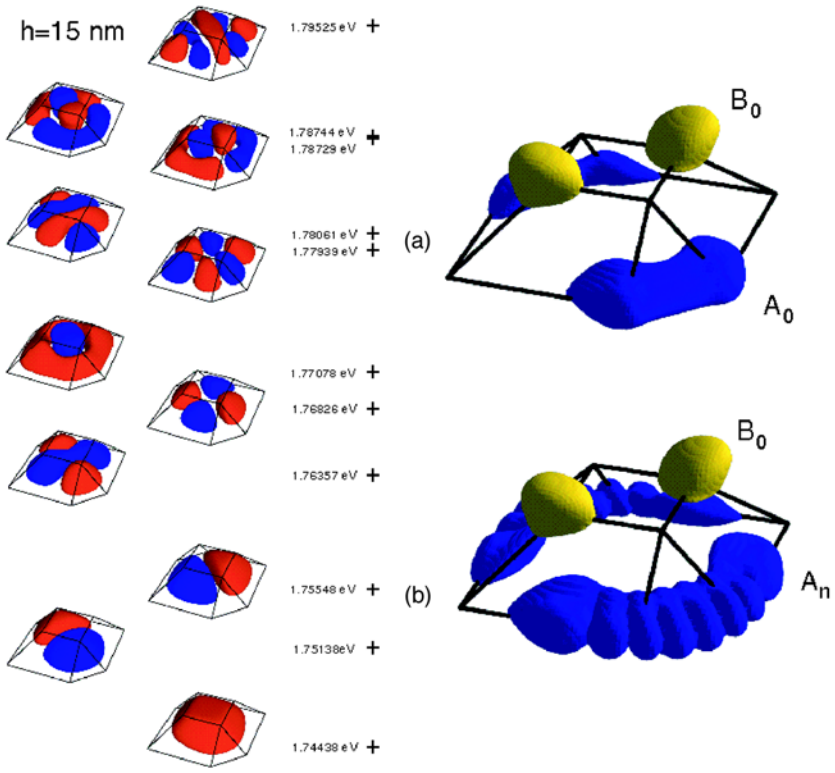

Figure 14. The left panel shows the electron wavefunctions and the right panel shows the hole wavefunctions. Two sets of holes are seen, A states, which are localized at the bottom of the dot, and B states, which are localized at the tip of the dot. The B states have a higher energy than the A states; see figure 13. The electrons are localized in the centre of the dot.

interaction as well as from exchange. Using the single-particle states as a basis it is possible to include these effects in a direct diagonalization procedure [21]. Figure 15 shows the calculated results for an exciton, a charged exciton and a biexciton in an InP dot. The exciton has four levels which are grouped in two closely spaced pairs. The charged exciton has only one line since both the initial and final state consist of only one level. The bi-exciton consists of only one level, but decays to an exciton which has four levels. Consequently, four emission lines are expected with exactly the same spacing as the emission lines from an exciton. Transitions involving a spin-flip are highly forbidden and thus very hard to see in experiment. The same pattern is seen for InAs dots in GaAs [13], where the exciton is split by about 5 meV into two pairs of closely (0.1 meV) spaced levels. The notation in figure 15 is as follows: $(\mathrm{e2{:}h0})_{1/1}$ means two electrons in the lowest single-particle level (orbital) and no holes, which is called a configuration. The second number in the subscript indicates the number of levels in the configuration and the first number the state in the configuration (where the lowest energy level has number 1). A symbol such as $(\mathrm{e21{:}h1})_4$ means a configuration with two electrons in the lowest orbital, one electron in the first excited orbital and one hole in the lowest orbital. This configuration has four states. This labelling system identifies all levels unambiguously, is based on energy considerations and avoids the unnaturalness of standard atomic physics notation (which was initiated before quantum mechanics was known). It also avoids reference to non-existing symmetry of quantum dots, whereas notations such as s-shell, p-shell etc imply

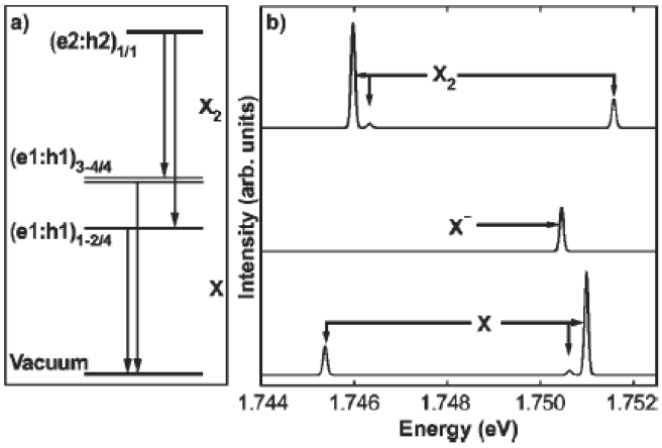

Figure 15. The left panel shows the energy levels of a bi-exciton, an exciton and the vacuum along with possible transitions. The bi-exciton and the vacuum consist of only one level whereas the exciton has four levels. The right panel shows the calculated transition energies for an exciton, X, a bi-exciton X_2, and a negatively charged exciton, X^-.

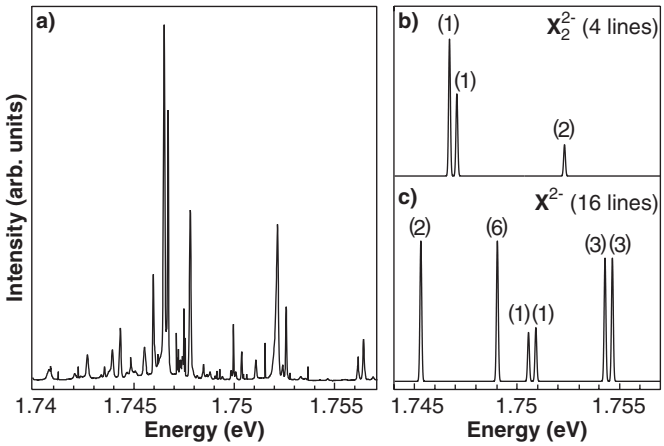

Figure 16. The left panel shows the emission spectrum of one small InP dot which is charged. The right panel shows the calculated spectra of a doubly charged exciton, X^{2-}, and a doubly charged bi-exciton, X_2^{2-}. The experimental spectra show about twice as many lines as expected (from a doubly charged exciton).

the existence of a spherical symmetry, as well as the z-component of spin being a good quantum number. The number of possible transitions can be large if the dot is charged. In figure 16 we show the calculated transitions for a doubly charged exciton decaying to a doubly charged dot, i.e. (e21:h1) $\rightarrow$ (e11:h1) which has 16 possible transitions. A highly symmetric dot, such as an InP dot, has a large degree of degeneracy among the levels responsible for these transitions. A doubly charged bi-exciton, i.e. (e22:h2), is expected to have four emission lines. In summary, we can say that if sufficiently large InP quantum dots are grown in n-type GaInP they will be charged with electrons. There are several emission lines which are fairly broad. Also for smaller quantum dots we observe charging but the emission lines are in this case narrow. Only the smallest dots are neutral and the emission is then dominated by excitons and by bi-excitons.

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