Electron accumulation in single InP quantum dots observed by photoluminescence

Dan Hessman, Jonas Persson, Mats-Erik Pistol, Craig Pryor, and Lars Samuelson
Solid State Physics/Nanometer Structure Consortium, Lund University, P. O. Box 118, 221 00 Lund, Sweden

(Received 24 August 2001; published 15 November 2001)

Single quantum-dot spectroscopy has revealed characteristic but so far unexplained differences in the optical spectra from different quantum-dot systems. We propose a size-dependent accumulation of carriers as the dominant mechanism behind these differences. We support our hypothesis with photoluminescence spectroscopy on single InP/GaInP quantum dots positioned below a transparent Schottky gate. We show that without external bias, the dots are filled with 15–20 electrons. By applying a reverse bias, we are able to reduce the electron accumulation while monitoring the evolution of the emission spectrum. We find that the emission peaks disappear one by one until, at a sufficiently low number of electrons in the dot, the remaining broad peaks are replaced by numerous very sharp peaks.

DOI: 10.1103/PhysRevB.64.233308 PACS number(s): 78.66.Fd, 78.55.Cr, 73.21.La

It has recently become possible to investigate the photoluminescence (PL) from individual semiconductor quantum dots (QDs).[1–4] These investigations have shown that there are two different types of emission spectra. In the first type, typical for InAs and InGaAs dots in GaAs, only a few sharp lines appear in the spectra. In the second type, typical for InP dots in GaInP, several broad lines appear in the spectra. In this paper, we propose a simple mechanism explaining these differences and present PL data in support of our model.

As a model system, we are using self-assembled InP QDs embedded in $Ga_{0.51}In_{0.49}P$ lattice matched to GaAs. The samples are grown using metal-organic vapor-phase epitaxy, with growth conditions optimized to give a dot density low enough to allow single QD spectroscopy. Details of the growth are given elsewhere.[5] This is an interesting dot system since the same sample can contain dots of both characters simultaneously. The reason for this is a bimodal size distribution of the InP QDs. One subset of the dots are truncated pyramids with a height of about 15 nm and a slightly elongated base of about 40 by 50 nm. The other dots are similar in lateral extension but only about 5 nm in height. We call the larger dots fully developed dots and the smaller ones partially developed dots, since they can be seen as prestages of the fully formed dots. The two types of quantum dots are spectroscopically easily distinguishable, as can be seen in Fig. 1. The PL spectrum from a single partially developed dot consists of a few sharp lines with linewidths smaller than our spectral resolution; the number of peaks and their relative intensities vary in a strongly nonlinear fashion with excitation power density. The partially developed dots are thus similar to self-assembled InAs quantum dots in GaAs, a system in which it has been shown that the different lines originate from different multiexcitonic states.[3,4]

The fully developed quantum dots behave quite differently: The PL spectrum from a single fully developed dot consists of several broad (>1 meV) emission lines, distributed over a range of approximately 50 meV.[2] In a typical spectrum, there are 3–5 distinct peaks and about the same number of weak peaks or shoulders. The shape of the PL spectrum is constant for excitation power densities below a threshold of about 10 W/cm^2 down to the lowest-possible excitation power density at which we can measure. Several models have been suggested to explain this unexpected PL spectrum. These include hot luminescence due to reduced relaxation among the electron and hole states.[2] A recent paper[6] suggests electron-phonon interaction as the main mechanism. The apparently constant peak separation could then be explained by a recently discovered disorder-activated longitudinal acoustic phonon[7] of 20 meV. We will present here experimental data that conclusively show that the origin of the multiple, broad peaks in the PL spectrum is none of the above. Instead, the emission spectrum is dominated by the presence of multiple electrons in the dot, occupying different (single particle) energy levels. It has previously been established that energy shifts due to few-particle effects are small in this system.[2] Each of these electrons can recombine with optically generated holes, giving rise to multiple PL peaks with a splitting corresponding to the energy splitting of the electron levels. The number of electrons, and thus the number of peaks, is controlled by the energy at which the Fermi-level crosses the QD potential. The different intensi-

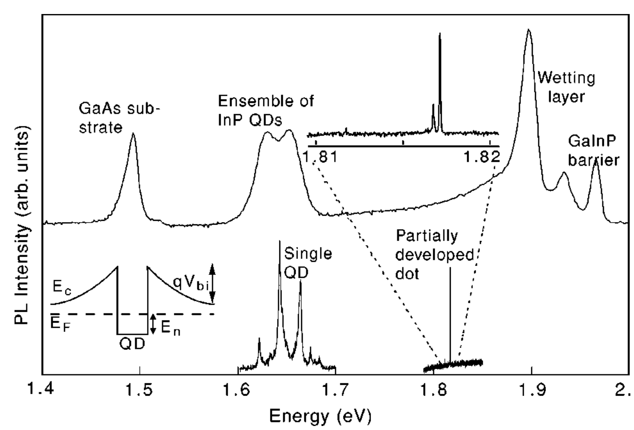

FIG. 1. Comparison of single QD PL spectra for a low-density sample and the ensemble averaging spectrum for a high-density sample. The fully developed QDs give rise to a well-defined peak in the ensemble average, implying a fairly homogeneous distribution in size and shape. The partially developed dots have a wider distribution, resulting in a broad emission tail extending from the QW-like wetting-layer peak. Note the completely different character of the single-dot spectra from the two types of QDs.

ties of the peaks is attributed to different optical transition matrix elements between the hole state and the various electron states, as is predicted by theoretical calculations.[8]

The nominally undoped GaInP barrier material is *n* type with a net donor concentration of about 10^{16} cm^{-3}. Even this low doping concentration will, at cryogenic temperatures, pull the Fermi level almost all the way up to the GaInP conduction band edge, implying that the InP quantum dot is filled with electrons. However, the charging of the quantum dot, as well as the depletion of the surrounding GaInP, will introduce band bending, lifting the bottom of the InP potential well until the highest-occupied electron state lines up with the Fermi level. This is shown schematically in the inset of Fig. 1. At equilibrium, the number of electrons in the QD can be estimated by requiring the band bending $qV_{\rm bi}$ and the energy of the highest occupied state E_n to sum up to the depth of the potential well. Calculating $qV_{\rm bi}$ using Poisson's equation and taking the depth of the potential well to be 250 meV,[8,9] this approach gives an estimate of about 20 electrons with an energy spread of 60 meV for a fully developed InP QD.

A PL spectrum with several peaks over a 50 meV range is thus not at all unexpected, although it has not been understood and demonstrated until now. Due to the band bending, an optically generated hole will be captured very efficiently into the QD where it will recombine with one of the electrons. At low-enough excitation density, each hole recombines before the next one enters and thus the PL spectrum scales linearly with the excitation density. If there are more than one positively charged hole in the QD, however, additional electrons will be allowed, resulting in new PL peaks at higher energy. This, indeed, explains the state filling reported for InP QDs in GaInP.[10]

A sample with a high QD density has previously been studied using space-charge techniques.[9] It was then estimated that the QDs were filled with 6–7 electrons. This value should be compared with the 20 electrons estimated above. The main uncertainty in the space charge measurement is in the determination of the island density, which was obtained by atomic force microscopy on uncapped samples. As a consequence, the measured electron filling could be off by at least a factor of two. Our estimated value of 20 electrons on the other hand is based on a very simple model and is, therefore, qualitative rather than quantitative. However, the number of states in a given volume that are below a certain energy is fairly independent of the details of the model. A different approach is to use the fact that PL spectra from single QDs are very similar and that the range of emission is always approximately 50 meV. Assuming that the observed PL emission range is equal to the energy spread of the electrons, E_n (Fig. 1), the number of electrons can be obtained by integrating the bulk InP density of states over this range and multiplying with the QD volume. By using 50 meV and a volume equivalent to a sphere with 15 nm radius, this method yields 13 electrons.

There are two main reasons why the charge accumulation dominates the PL from QDs while it is usually negligible for QWs.[11,12] Due to conservation of the in-plane momentum in a QW, only majority carriers at the bottom of the subband will contribute to the PL. Charge accumulation in a QW will, therefore, primarily be seen as an increased Stokes shift, i.e., an increase in the energy difference between the PL peak and the corresponding absorption peak. For a QD, however, the translational symmetry is broken and all charge carriers may in principle contribute to the PL. Another difference between QDs and QWs is imposed by the different dimensionalities. Due to charge neutrality, the number of carriers in a QW is proportional to the width of the depletion layers on both sides of the well. The QD, however, will collect charge from a three-dimensional volume of the surrounding GaInP and the number of carriers will, therefore, increase as the cube of the depletion width. Combining this with Poissons equation in one and three dimensions, respectively, it can be found that the total band bending $qV_{\rm bi}$ is proportional to the square of the carrier concentration in a QW while it is approximately linear with the carrier concentration in a QD. A higher carrier concentration is, therefore, needed in the QD to introduce enough band bending that the last occupied state coincides with the Fermi level. Note that this effect is purely classical and not related to the differences in density of states between two- and zero-dimensional systems.

To test our interpretation of the multiple PL peaks, the evolution of the QD PL was studied while changing the electron accumulation. To do this, Schottky diodes were made by evaporating semitransparent gold squares, 600 μm wide and 5 nm thick, onto the top surface and alloying an ohmic contact on the substrate side. For PL measurements, the sample was mounted in a cold-finger cryostat at 10 K. As excitation source, either a frequency-doubled yttrium aluminum garnet laser operating at 532 nm (Fig. 1 and Fig. 2) or, for PL excitation (PLE) spectroscopy (Fig. 3), a tunable Ti:Sapphire laser was used. The excitation power density was typically 10 W/cm^2.

Illuminating the transparent Schottky diode under PL conditions resulted in an open-circuit voltage in the range 0.9–1 V. This is close to the estimated height of the Au/GaInP Schottky barrier. The QDs, being 90 nm below the surface will, therefore, be in a flat-band region, even though they are positioned in the depletion region when the sample is not illuminated. Simulating the Schottky structure using a commercial software package confirms that the QDs are in a flat-band region at the excitation densities needed to detect any PL signal. The luminescence was collected with a 0.4 NA (numerical aperture) microscope objective. Due to aberrations introduced by the cryostat window the spatial resolution is limited to approximately 1.5 μm. By choosing a region where the density of fully developed islands is below 10^6 cm^{-2}, individual QDs can easily be selected and their PL spectra recorded. The emitted light was detected using a liquid-nitrogen-cooled CCD camera.

We have measured the bias-dependent PL from several QDs and they all share the main characteristics described below. Figure 2 shows PL spectra from a single QD at different applied biases. The bottom trace is obtained when applying a voltage equal to the open-circuit voltage and is identical to the spectrum obtained when the diode is left unconnected. It is clear from the similarity between this spectrum and the spectrum of the (different) fully developed

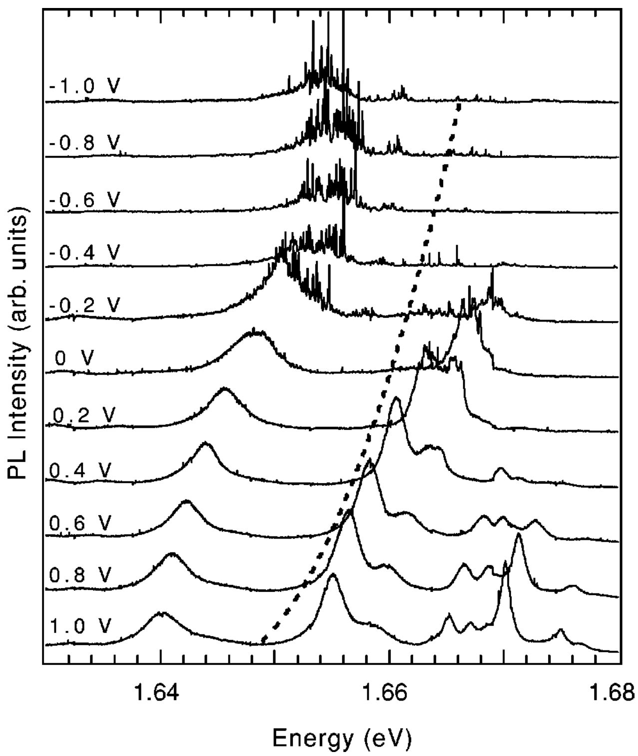

FIG. 2. Evolution of PL spectra of a fully developed QD with applied bias. With decreasing bias the number of broad lines is reduced and eventually the remaining broad lines are split into numerous sharp lines. The highest applied forward bias (1 V; the bottom trace) is equal to the open-circuit voltage generated by the laser illumination. The dashed line indicates the calculated Stark shift assuming an electric field of an ideal Schottky diode.

QD shown in Fig. 1 that the thin gold film itself does not induce any spectral changes. As the applied bias is decreased from its open circuit value, however, several things happen: First, the peaks disappear one by one, starting from the high-energy side. Second, the spectral features shift towards higher energy. Third, when only a few lines are left, the broad features are replaced by a multitude of very sharp peaks, each having a linewidth smaller than the spectral resolution. The PL is quenched for negative biases (relative to the Schottky metal) smaller than approximately -1 V.

The first observation, the disappearing high-energy peaks, strongly supports the assignment of these peaks as being due to excess electrons in the QD. As the bias is made more negative, the quasi-Fermi level is lowered relative to the conduction band, thereby depopulating the higher electron states. This makes it possible to control the number of electrons in the dot via the external potential.

A related experimental observation is the bleaching of PLE excitation processes when the excited electron states are occupied. It has previously been shown that there is a minor contribution to the PLE signal for excitation energies within the energy range where there is PL emission.[2] This observation is easily explained if the emission originates from occupied states, since there can be no absorption, and thus no PLE signal, unless the photon energy is high enough to excite an electron to an unoccupied state. However, if an occupied electron state can be depopulated by reverse biasing, that state should now show up as a new peak in the PLE spectrum. This is indeed also the case, as can be seen in Fig. 3. The PLE experiment is the final proof that the multiple PL lines are due to the presence of many electrons in the QD. A model based on electron-phonon interaction can not possibly explain the PLE results, even when including "sophisticated dynamical and nonadiabatic processes."[6] It can be seen in Fig. 3 that a PLE and a PL peak can coexist for certain biases. This is not particularly surprising considering that a partial population of the highest-occupied state, offering absorption as well as luminescence, is expected over this range of biases due to the thermal broadening of the Fermi distribution.

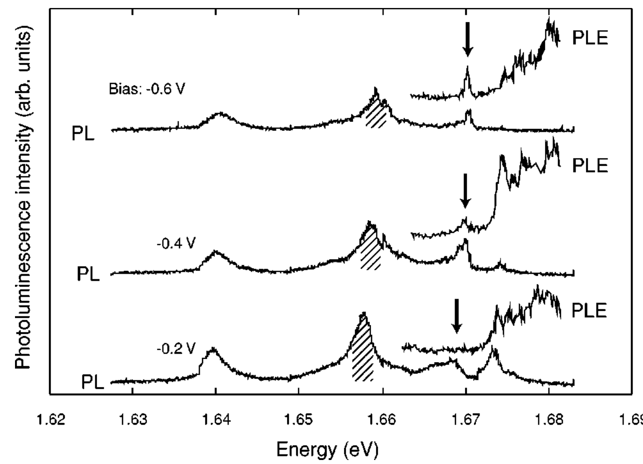

FIG. 3. PL and PLE spectra from a single QD for different bias. At a bias of -0.2 V there is no absorption at an energy of about 1.67 eV (indicated by an arrow), while at a bias of -0.6 V there is clear absorption at the same energy. This shows that the initially filled state is depopulated. The hatched area indicates the PLE detection energy.

We attribute most of the observed energy shifts to the quantum-confined Stark effect. The dashed line in Fig. 2 indicates the calculated Stark shift, obtained by extending the 6-band $\mathbf{k}\cdot\mathbf{p}$ calculations of Pryor *et al.*[8] to include an electric field. The electric field for a given bias was estimated by assuming an ideal Schottky diode. For clarity, a constant energy term has been added to the calculated curve. In addition to the electric-field-induced shift, the changing number of carriers in the QD can induce a shift via Coulomb and exchange interactions.[13] It is interesting to note the blue shift of the PL with increasing electric field. This is in contrast to QWs where the PL is generally red shifted due to the electric-field-induced separation of the electrons and holes. In the case of the fully developed InP QD, the hole is confined by a strain-induced potential minimum at the base of the pyramid-shaped QD.[8] The direction of the electric field in the present configuration is such that also the electron will bepushed to the bottom of the pyramid. The main effect of the electric field is, therefore, an increase of the electron confine-ment, resulting in the observed blue shift. An asymmetric quantum-confined Stark shift has, however, previously been reported for InAlAs/AlGaAs[14] and InAs/GaAs QDs.[15]

The most surprising result of the bias-dependent PL is the sudden appearance of sharp lines. This occurs approximately at the bias when the last of the disappearing high-energy PL peaks is quenched. A recent paper[16] reports a similar transition from broad to sharp peaks for unbiased samples as the temperature is increased to about 40 K. Based on the simultaneous decrease of the wetting-layer luminescence, the authors suggest that the apparent broadening is caused by dynamic fluctuations in the charge configuration of the environment. For our samples, we do not observe sharp lines from the fully developed QDs at any temperature up to 300 K, unless we apply a reverse bias. Since the partially developed dots, present in the same sample, have sharp lines at all biases, we do not favor an explanation based on dynamic fluctuations in the environment. Instead, we propose that the large PL linewidth observed under unbiased conditions is due to a short dephasing time, T_2,[17] when multiple electrons occupy the dot. A reduction in T_2 is expected in such a case, due to Coulomb interaction between the electrons. This would explain the appearance of sharp lines as the dot is depleted at high reverse bias. A T_2 of the order of a few ps would result in a broadening of about 0.1 meV, approximately the spacing between the sharp lines, enough to smear a group of sharp lines into one broad peak. What we observe as a peak under unbiased conditions is thus the envelope of a group of broadened lines. Further experiments are, however, needed to conclusively show that the linewidth is determined by the dephasing time.

The large number of sharp lines is very intriguing. The typical spacing between the peaks agree rather well with the energy spacing of the confined hole states. Hence we may be observing multiple recombination events, each one involving a single hole, occupying one of several different hole levels, recombining with the single electron remaining in the dot under these conditions. To exclude the possibility of multiple holes in the dot, we have decreased the excitation power density as far as we can but we always observe a multitude of lines. The fact that the luminescence of the sharp lines is spread over about 3–4 meV, considerably more than the measured kT of 1 meV, would then indicate a nonthermal distribution of the holes.

In conclusion, we have shown that the multitude of broad lines in the emission spectra from large InP quantum dots originates from charges accumulated in the dot. The reason for this is the relatively large size of the dots and the fact that the host material is weakly *n* type. In addition, we have demonstrated the possibility to tune a quantum dot from a single-particle configuration, via few particles, to a multiparticle configuration by using an external bias.

We acknowledge the growth and processing of the samples by W. Seifert, N. Carlsson, and M. Graczyk. This work was supported by the Knut and Alice Wallenberg Foundation, the Swedish Natural Science Research Council, the Swedish Foundation for Strategic Research, and the Swedish Research Council for Engineering Sciences.

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