Band-gap renormalization in InP/$Ga_xIn_{1-x}P$ quantum dots

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A continuous and systematic red shift of the exciton emission energy in small InP/InGaP quantum dots is observed for increasing excitation energies and intensities. Superposed on this red shift, emission energy minima appear which show a one-to-one correspondence to emission intensity maxima as a function of the excitation energy. This band-gap renormalization is attributed to the hybridization of the quantum dot excited states with the wetting layer continuum. Polarization-resolved measurements reveal that the exciton fine structure splitting can be tuned up to 10% in the present case by changing the excitation energy. Possible implications of the present results on the development of entangled photon pair sources are discussed.

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I. INTRODUCTION

Many-body effects in the Coulomb interaction between carriers have been known for a long time to be relevant for the electronic structure and the optical properties of semiconductor systems. Probably the most ubiquitous many-body effect is the lowering of the fundamental energy gap on increasing the free-carrier density. This effect, known as band-gap renormalization (BGR) is due to the exchange and correlation contributions of the free carriers to the energy levels. BGR was originally described in bulk semiconductors,[1] but most of the later work has been done in two-dimensional (2D) and one-dimensional (1D) systems. Compared to bulk semiconductors, BGR in 2D systems (in effective Rydberg units) is reduced as a result of the reduced screening efficiency in 2D.[2–5] In 1D, different results have been reported. In most cases, no change in the exciton emission energy is observed, even at high carrier densities, due to the compensation of BGR with the increased electron-hole correlation in 1D.[6–8] However, a red shift in the emission of an electron-hole liquid in single InAs quantum wires has been reported at very high excitation intensities.[9] In 0D systems as quantum dots (QD), the full quantization of the energy levels results in discrete jumps and splittings of the emission lines upon addition of carriers to a single QD (charged excitons, biexcitons, etc.),[10,11] even for high QD occupancies.[12] Additionally, strong optical pumping of QDs also affect their performance as single photon emitters.[13] Strong BGR in the meV range has been reported in highly excited QD ensembles for nonresonant excitation.[14,15] For single QDs, coupling of the QD states to a nearby degenerate electron gas by tunneling or Coulomb interaction has been reported.[16,17] In this case, a continuous red shift of the single QD emission[17,18] as a function of the carrier density or the coupling strength is observed, which is reminiscent of BGR in higher dimensions.

In this work, we present photoluminescence (PL) and PL-excitation (PLE) measurements in small InP/InGaP single QDs, which reveal a continuous and systematic red shift of the exciton emission as the excitation energy or the excitation intensity increases. Additionally the exciton emission energy presents red-shift dips in a one-to-one correspondence with the PLE peaks, showing that the population of the QDs excited states determines this type of BGR in single quantum dots. This behavior, which is also observed (although weaker) in the biexciton emission, has been observed in 80% of the studied QD. The exciton red shift increases also monotonously as a function of the excitation intensity for any excitation energy. The origin of the observed BGR is attributed to the hybridization of the QD excited states to the wetting layer (WL) continuum,[19,20] although other possibilities are discussed. The excitonic emission as well as transitions involving excited states observed in PLE present a clear symmetry splitting. As a consequence, the red-shift dips of the fine-structure split exciton components occur at different excitation energies. This implies a modification (up to 10%) of the exciton fine-structure splitting (Δ_{FS}) by simply changing the excitation energy.

II. EXPERIMENT

The QD samples with an average dot density of 3×10^9 cm^{-2} have been grown by molecular-beam epitaxy on GaAs (001) substrates. Details of the growth procedure can be found in Ref. 21. The QD average diameter and height before capping are 35 and 6 nm, respectively. However, the height of QDs is well known to decrease during capping. Furthermore, the single QDs selected for this work are in the high-energy tail of the ensemble PL distribution, so that their height is lower. From the PL energies, we estimate the height of the studied QDs to be between 1 and 2 nm.[21,22] PL spectra of QDs were obtained through a 100 $\times$ microscope objective with a 1.0 μm spot size under variable excitation energy from a 4-dicyanomethylene-2-methyl-6-*p*-dimethylaminostyryl-4H-pyran (DCM) dye laser. Detection was done by a 0.85 m focal length double spectrometer with gratings of 1800 lines/mm, giving a resolution of 8 μeV, and a liquid nitrogen-cooled charge-coupled device detector. PLE spectra were recorded automatically using a computer-controlled feedback system to synchronize the dye laser and a prism fore-monochromator. This system has a resolution of 0.2 meV in the excitation energy. By looking into the 1.84–1.87 eV emission range, well above the average emission energy, single QDs were observed without the use of masks.

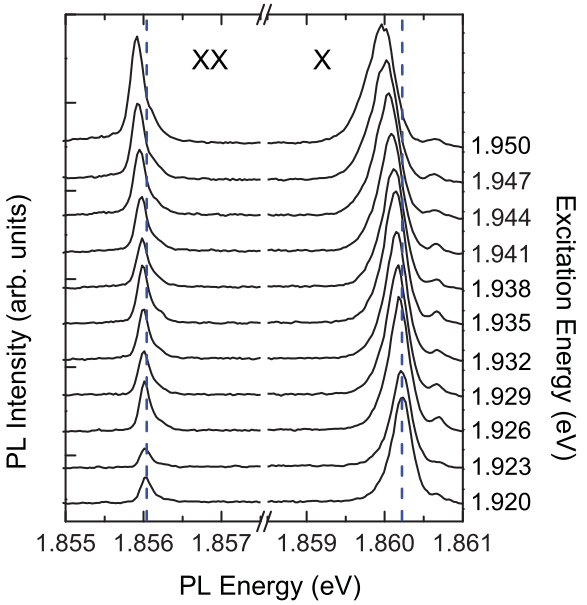

FIG. 1. (Color online) PL spectra of a single QD measured at 8 K with 23 kW/cm^2 excitation power. The spectra are plotted for several excitation energies from the range between 1.92 and 1.95 eV. The spectra are vertically shifted for clarity. A red shift of X^0 and XX^0 lines is observed as the excitation energy increases.

These are rather flat QDs with strong confinement energies, resulting in few confined states.[21] All measurements were recorded at 8 K in a continuous flow He cryostat. The wetting layer emission is at 1.936 eV at this temperature.

III. RESULTS AND DISSCUSION

The PL spectra of a typical single QD are plotted in Fig. 1 for increasing excitation energy from 1.92 to 1.95 eV in 3.0 meV steps. Both the exciton X and the biexciton XX lines show a clear energy decrease for increasing excitation energy. The total energy decrease of the biexciton in this excitation range is approximately one-half of the exciton one. This emission-energy decrease is better observed in Fig. 2, where the exciton emission energies (gray dots), together with their emission intensities (black dots), are plotted versus the excitation energy. Again a continuous red shift of the exciton line is observed as the PLE signal increases, corresponding to increasing light absorption. For excitation energy above the WL absorption edge (marked by an arrow), the exciton red shift becomes more pronounced. This indicates that free carriers photocreated in the wetting layer play a role in the observed red shift. By moving the excitation energy closer to the emission, a similar plot (Fig. 3) displays sharp peaks in the PLE spectrum at energies between 20 and 40 meV above the emission energy, corresponding to absorption transitions involving excited states of the QD. Whether these excited states are pure electronic transitions (between p states) or phonon-assisted absorption peaks is not relevant for the present discussion. We will term them anyway as p states. The most remarkable fact in Fig. 3 is the systematic appearance of weak but clear dips in the exciton luminescence energy at the energies of the PLE peaks, i.e. whenever the population

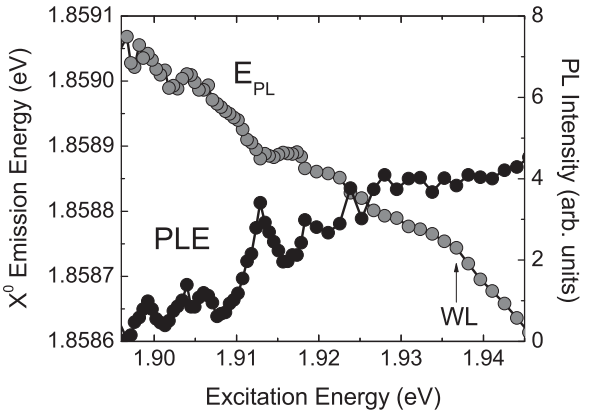

FIG. 2. PLE spectrum (black circles) and X^0 emission energy versus excitation energy (dark gray circles) of a single QD. The drop of X^0 energy with increasing excitation energy is subtle but systematic. Above the wetting layer the red shift is even more pronounced, indicating stronger band-gap renormalization.

probability of the QD excited states increases. These dips are also clearly visible in Fig. 2 below the WL absorption edge.

We discuss now the possible origin of the observed red shift in Figs. 1–3 in terms of BGR due to the exchange and correlation effects of photocreated carriers in the excited QD states. The presence of extra carriers (together with the exciton) in the QD lowest state (s state) lead to the formation of the well-known charged excitons and neutral biexciton, producing discrete energy jumps (in both directions depending on the QD shape, strain, etc.) and splittings in the emission lines in the meV range.[23,24] If electron-hole pairs are present also in the excited states, the QD optical spectrum changes from a few discrete lines to a rich manifold.[10,13,25] In QD ensembles, a continuous red shift of the ground-state emission has been observed as the excitation intensity is increased and has been ascribed to the influence of the increasing occupation inside the QD.[14,15] In a single QD, this increase would produce discrete energy changes of a few meV in the emission spectrum,

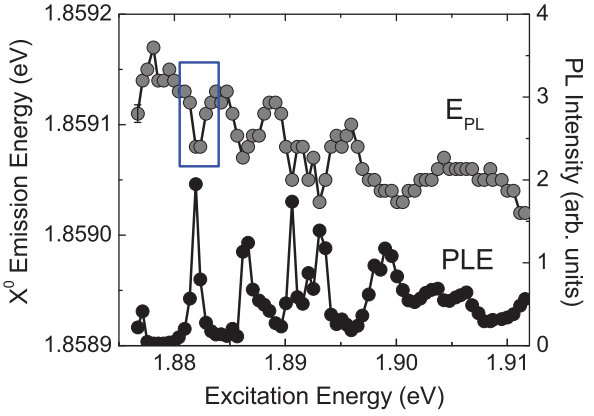

FIG. 3. (Color online) PLE spectrum and X^0 emission energy versus excitation energy for a single QD. The spectra were taken for energy between 20 and 40 meV above the X^0 energy. The PLE peaks corresponding to QD p states coincide with the E_{PL} red shift minima due to increased absorption and resulting band-gap renormalization. The resolution in the emission energy is indicated by error bars. The excitation energy has been measured with a resolution of 0.2 meV.

as stated above. In consequence the continuous red shift observed in single QDs is not likely to be due to the direct influence of excited carriers inside the QD. Another possibility is the existence of excited states of neighboring larger QDs in the same spectral region of the exciton emission, which could couple with the actual QD and alter its energy levels. However, the probability for this coupling to occur is low, as the average inter-QD distance in our low-density sample is 0.2 μm. Finally, we consider hybridization of the QD excited states with the wetting-layer continuum as the more likely origin of the observed BGR. Being hybridized, the QD excited states would have a partially extended nature so that the observed BGR in these QDs would have a similar origin as in higher-dimensional systems. Such hybridization has been reported in QDs[19] and invoked to explain the strong emission by cavity modes in QD-microcavity systems even for large QD-cavity energy detuning.[20] From our experimental results, we cannot determine which coupling mechanism originates the hybridization between the QDs and the wetting layer. However, we can guess that dipole-dipole coupling is the more likely one. Coupling of QD states by tunneling to a distant (∼20 nm) two-dimensional electron gas has been discussed in Ref. 19. In our case, due to short distance (∼1 nm) between the QD center and the WL states, the dipole-dipole interaction is likely to be very strong, while tunneling coupling would be comparatively more effective at higher distances. Moreover, the strong confinement of our small QDs brings the excited states (especially the hole ones) close in energy to the wetting layer, thus enabling coupling.[26] As the spin of the biexciton is compensated, one expects less hybridization with the wetting layer, as is reflected in its smaller red shift (Fig. 1). We have tried to check if this type of BGR occurs also in QDs with different composition. To the best of our knowledge, it has not been reported in the most common InAs/GaAs QD system. In fact, we do observe a similar but weaker effect in InAs quantum rings with GaAs barriers described in detail in Ref. 27 (not shown). Our conclusion is that BGR should occur in most of the QD systems grown by the Stransky–Krastanov method (i.e. having a wetting layer), although in cases of poor QD-WL hybridization, it might be too weak to be detected.

Now we turn to the polarization properties of the BGR. The emission spectra of the QD exciton of Fig. 1 are shown in the left side of Fig. 4(a) for horizontal (H) and vertical (V) linear polarization. The corresponding exciton fine-structure splitting, due to QD anisotropy, either in shape or in piezoelectric field,[23,24] is 300 μeV. Similarly, the excited state at 1.882 eV in Fig. 3 has a polarization splitting (250 μeV), as shown at the right side of Fig. 4(a). Notice that Δ_{FS} has an opposite sign in the p state compared to the s state in this particular QD. A high resolution, polarization-resolved record of the BGR peak marked by the rectangle in Fig. 3 is shown in Fig. 4(b). The red shifts of the two polarization components of the exciton emission are shown as a function of the excitation energy. The solid lines are fits to inverted Gaussians, including the decreasing continuous background. In this case, the excitation light was linearly polarized at 45° from H and V to equally populate both split levels of the p state. One notices that the maximum red shift of both polarization components of the exciton emission occurs at different excitation energies. The energy separation of 250 μeV corresponds to the

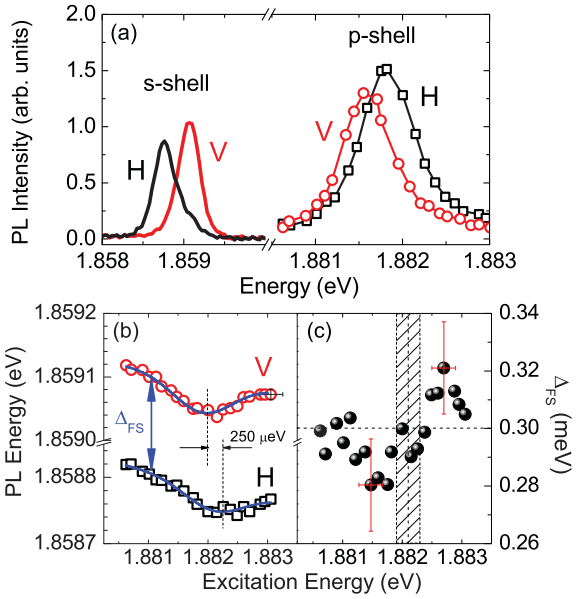

FIG. 4. (Color online) (a) PL and PLE spectra of a single QD taken at 8 K with 95 kW/cm^2 excitation power. The red (dark gray) and black plots represent vertical (V) and horizontal (H) polarization, respectively. Fine-structure splitting (Δ_{FS}) is observed for both s and p shell. Δ_{FS} is approximately 300 and 250 μeV for s and p state, respectively. (b) X^0 emission energies versus excitation energy. X^0 energy minima in V (circles) and H (squares) polarizations coincide with maxima in p shell, and they are independent from each other. The lines are fits to inverted Gaussians, including the decreasing continuous background. (c) Δ_{FS} of the s state versus excitation energy. The horizontal dashed line represents the splitting for excitation not resonant with the p shell. The vertical dashed line indicates the excitation energy value ($1.8821 \pm 2 \times 10^{-4}$ eV), where the separation between the theoretical fits from (b) is equal to the off-resonant Δ_{FS} value. The modulation around the nonresonant value is a consequence of the different positions of the X^0 energy minima in (b). The energy resolutions are indicated by error bars in (b) and (c).

difference of the respective PLE peaks. In this situation, the energy difference Δ_{FS} between the two polarization components, marked by the vertical arrow in Fig. 4(b), varies with the excitation energy. The expected behavior of Δ_{FS} for increasing excitation energy is: (a) to decrease first when the V exciton PL starts red-shifting; (b) to recover its original value for an excitation energy corresponding to the midpoint of the PLE polarization doublet (1.8821 eV); (c) to further increase beyond this point as the H exciton red-shifts and the V exciton blue-shifts back; and (d) to recover its original value (300 μeV) when both exciton components are nonresonantly excited. This variation is experimentally observed and presented in Fig. 4(c). A small but clear modulation of $\pm$ 20 μeV is observed in Δ_{FS}, in spite of the fact that it is close to the resolution limit of our experiment, as indicated by the error bars. It corresponds to 10% of the total fine-structure splitting for excitation not resonant with the p shell. The natural question at this point is whether this polarization-dependent BGR could be increased enough to become an alternative method to suppress Δ_{FS} for entangled photon pair production.[28,29] The obvious advantage over other methods of controlling Δ_{FS} (external magnetic

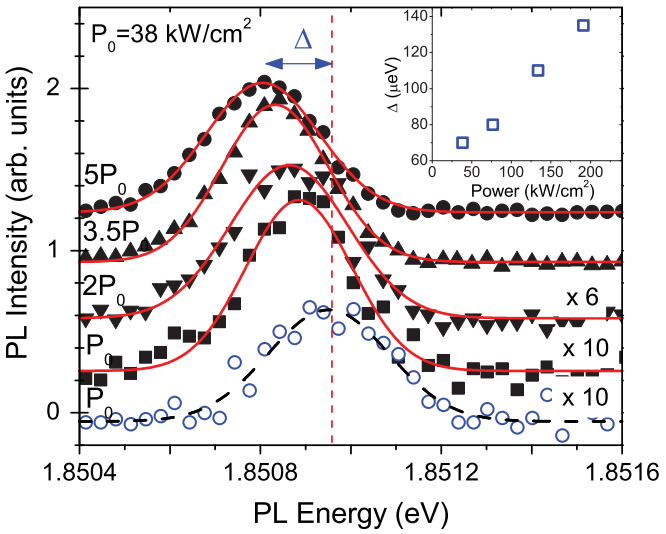

FIG. 5. (Color online) PL spectra for X^0 off-resonance (blue dots) and on-resonance (black symbols) measured for different excitation power values. The spectra are vertically offset for clarity. The red shift is observed for higher excitation powers. The inset graph shows the total displacement (Δ) of the PL peak from the off-resonant X^0 position.

or electric fields, elastic strain modulation, or postgrowth thermal annealing) is that polarization-dependent BGR is a reversible process requiring only optical access to the sample. However, it is not clear whether a total cancellation of Δ_{FS} is possible by this method. The required conditions for a total cancellation or even sign reversal of Δ_{FS} would be a large polarization splitting of the p state and a small one for the s state. This would correspond to bringing the two curves in Fig. 4(b) closer together in vertical direction while increasing the horizontal separation between their minima until they cross each other. Such a condition could eventually be fulfilled by QDs with adequate shape and strain.[23,24] A simple argument to support this possibility is the fact that p states are more extended laterally than s ones along the crystallographic axes, which in turn determines the polarization directions of the exciton fine-structure doublet. Consequently, p states should be more sensitive than the s states to the QD anisotropy. Actually, an increasing hole p-state splitting has been reported for pyramidal QDs with increasing lateral size due to the piezoelectric potential.[23]

Finally, we present PL measurements as a function of excitation power. Figure 5 displays the exciton emission line for excitation power densities ranging from 38 to 190 kW/cm^2 (filled symbols and solid fit lines) and excitation energy resonant at the p shell. A spectrum excited off resonance (open dots and dashed fit line) is presented for comparison. The spectra have been vertically offset and the lower ones magnified for a better display. Again, BGR is evident from the red-shift Δ observed, which varies almost linearly with the excitation power (see inset). As no significant variation of the linewidth or the intensity normalized to the excitation power are observed, we can safely exclude sample heating as the origin of the red shift. Instead, this result confirms our interpretation of the red shift as due to band-gap renormalization of the QD caused by hybridization of its excited state with the wetting layer.

In summary, a systematic red shift of the exciton emission with excitation energy has been observed in small InP/(Ga,In)P QDs. The coincidence of the X energy minima with PLE maxima indicates that the observed BGR increases with excited-state occupation probability. This effect is explained by hybridization of the QD excited states to the wetting-layer continuum. The polarization dependence of the X red shift allows a modulation up to 10% of the exciton fine-structure splitting by changing the excitation energy. A linear dependence of the red shift on the excitation power is also observed, confirming the hybridization as the origin of the BGR.

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