phys. stat. sol. (a) **190**, No. 2, 491–497 (2002)

Spectroscopy of Single Semiconductor Quantum Dots at Negative, Neutral, and Positive Charge States

D.V. REGELMAN (a), D. GERSHONI[1]) (a), E. EHRENFREUND (a), W.V. SCHOENFELD (b), and P.M. PETROFF (b)

(a) Physics Department, Technion, Haifa 32000, Israel

(b) Materials Department, University of California, Santa Barbara, CA 93106, USA

(Received September 4, 2001; in revised form October 5, 2001; accepted October 12, 2001)

Subject classification: 71.35.Cc; 73.21.La; 78.55.Cr; 78.67.Hc; S7.12

We investigate semiconductor quantum dots by optically injecting a controlled unequal number of electrons and holes into an isolated single dot. The injected carriers form charged complexes of many carriers in the dot. Radiative electron–hole pair recombination takes place after the charged complex relaxes to its ground state. We resolve spectrally and temporally this emission and we show that while negative charging results in red shifted emission energy, compared with a neutral dot, positive charging results in blue shifted emission energy. We explain this observation in terms of the smaller volume of the hole wavefunctions compared with that of the electrons.

Optical studies of semiconductor quantum dots (QDs) have been a subject of very intensive recent investigations. It has been experimentally and theoretically established that light emission from an excited quantum dot originates from the recombination of an electron–hole pair within a collective many body state of confined carrier complexes [1]. In spite of its neutral nature, optical spectroscopy has recently proved to be a useful means for investigating and preparing charged QD systems [2–4]. Here, we investigate semiconductor quantum dots by optically injecting a controlled unequal number of electrons and holes into an isolated single dot. In particular, carrier complexes which contain charge of one type coupled to few charges of the other type can be formed. This is done by photoluminescence (PL) spectroscopy of single self-assembled QDs (SAQDs) embedded within a mixed type quantum well (QW) structure [5]. This specific design, which facilitates charge separation by optical means [6], is used here to tune the charge state of the QD under study. This design enables measurements of both negatively and positively charged states of the same dot and, at the same time, comparison with measurements obtained from a similarly prepared neutral sample.

Optical excitation is a very convenient and efficient way to study confined many-carrier states in semiconductor QDs. It provides high spectral, spatial, and temporal resolutions while controlling the average number of photogenerated carriers confined within a dot by the intensity of the optical excitation. In spite of its intrinsic charge neutrality, optical excitation can be used also for varying the charge state of the quantum dots. Two innovative methods have been recently invented for this purpose. The first utilizes spatial separation of photogenerated electron–hole pairs in coupled narrow and wide GaAs quantum wells, separated by a thin AlAs barrier layer [5, 6]. In this case, photogenerated holes remain in the narrow QW while the electrons accumulate in

[1]) Corresponding author; Phone: +97248293693; e-mail: dg@physics.technion.ac.il

 0031-8965/02/19004-0491 $ 17.50+.50/0

SAQDs within the wider GaAs quantum well. The second method utilizes photodepletion of electronically charged QDs together with slow hopping transport of impurity bound electrons back to the QD [3]. In this way, the intensity of the optical excitation can be efficiently used to control the number of electrons present in the QD when radiative recombination occurs. In this study, we combined these two methods to demonstrate optical control over the charge state of a single QD including the transition from a negatively to a positively charged dot.

The growth method of the semiconductor SAQDs for our studies were described elsewhere [5, 6]. Two samples were studied. Sample A, which is used here as a control, neutral sample, consists of a layer of low density In(Ga)As SAQDs embedded only within a thick layer of GaAs [7]. Sample B, which we used for optical charging, consists of a layer of similar SAQDs, embedded within the wider of two coupled GaAs QWs, separated by a thin AlAs barrier layer [5], as shown in Fig. 1a. Residual n-type impurities in the AlGaAs layer provide initial (dark) charging of the dot with electrons, due to the preferential efficient hopping transport of the electrons, Fig. 1a. We note that the maximal number of electrons in a given SAQD is limited by the electrostatic repulsion, which forces higher charge states to be unbound. We found experimentally and theoretically that this maximal number is three electrons.

We spatially, spectrally, and temporally resolved the PL emission from single SAQDs in both samples using a variable temperature confocal microscope setup, described in detail elsewhere [8]. In Fig. 2a (2b) we present the PL spectra from sample A (B) for various cw excitation powers at a photon energy of 1.75 eV. By comparing the PL spectra of the neutral control sample with that of the charged one, we identified the various discrete spectral lines in the spectra. They are marked in Fig. 2 by the charge state of the SAQD from which they resulted. The groups of lines S and P result, respectively, from the first and second shells of confined single particle levels, which are split by the many-particle Coulomb interaction. The narrow lines in each group result from the radiative recombination of one e–h pair (exciton, marked as X in the figures) in the presence of other e–h pairs and/or unpaired positive and negative charges. The line marked X^0 is identified as the recombination of a single e–h pair when no other charges or pairs are confined in the dot. This is the only line appearing in the neutral control sample (A) at very low cw excitation power. The lines marked nX^0 are identified as the recombination of a single e–h pair when a total of n pairs, but no net charges, are confined in the dot. These lines appear experimentally at increasing excitation power, as the average number of pairs occupying the dot increases. They are red shifted with respect to the X^0 single exciton line due to the e–e and h–h exchange energies, which reduce the pair recombination energy when a number of spectator e–h pairs is present during the radiative process [9].

As the excitation power increases, the probability to find a higher number of e–h pairs within the QD increases. Consequently, the probability to find the QD with a small number of pairs rapidly decreases. As a result, all the observed discrete PL lines at their appearance order, undergo a cycle in which their PL intensity first increases, then reaches maximum and saturates, and eventually significantly weakens [7]. This was also directly demonstrated by time resolved spectroscopy [7, 8, 10].

In sample B, the SAQDs are initially charged with electrons. The line marked X^{-3} (sample B, Fig. 2b) is identified as the radiative recombination of an e–h pair in the presence of three extra electrons in the dot. With the increase in the excitation power,

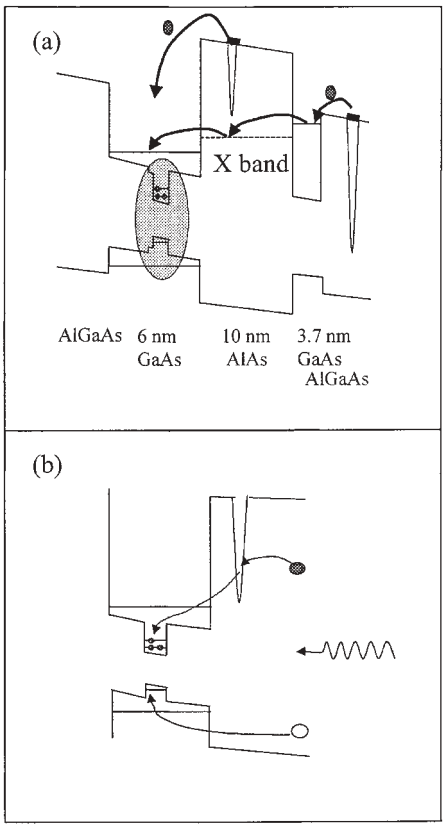

Fig. 1. Structure of the mixed type dot, a) initial (dark) electron capture from ionized donors and b) e–h pair photogeneration. Note the faster hole capture which leads to photodepletion

the SAQDs are first photodepleted, since positively charged donors in its vicinity efficiently capture photogenerated electrons while holes preferentially diffuse to the SAQDs [3], as schematically described in Fig. 1b. X^{-2} (X^{-1}) thus marks the e–h recombination when only two (one) extra electrons are present in the dot, and X^0 appears when all the three extra electrons originally present in the SAQD are eliminated by the photodepletion. The higher the excitation power is, the higher is the number of photogenerated holes which preferentially reach the SAQD. Note that negative recharging is slow, thus at high enough excitation power the dot is positively charged [11, 12]. The lines marked X^{+1} and X^{+2} are due to one and two, respectively, extra positive charges. The exact identification of the various spectral lines is based on the comparison between Figs. 2a and b and on similar power dependent spectra measured under pulsed excitation (not shown here [11, 12]). Note that the PL lines from a negatively charged QD are lower in energy and those from a positively charged QD are higher in energy than the respective PL lines from a neutral QD.

The phenomenon that negative charging leads to red shifted PL and positive charging leads to blue shifted PL results from the fact that the wavefunctions of the confined electrons and holes in the QDs are not equal.

First consider the case of equal wavefunctions. In this case, addition of excess charge to the exciton always lowers the emission energy because of the exchange and correlation energies. This is similar to the well known case of charged excitons (trions) in higher dimensionality semiconductors [13], which are bound for both charge signs. If, however, the holes are better confined by the QD potential and the spatial extent of their wavefunction is smaller than that of the electrons, then the energy associated with the repulsion between two holes C_{hh} is larger than the energy associated with the attraction between electron and hole C_{eh}, which is still larger than the repulsion energy between two electrons C_{ee}. In this case, addition of electrons lowers the PL emission energy approximately by the amount equal to the difference $C_{eh} - C_{ee}$ [14]. For excess positive charge, the difference $C_{eh} - C_{hh}$ is negative, thus it increases the emission energy if it is larger than the exchange and correlation terms.

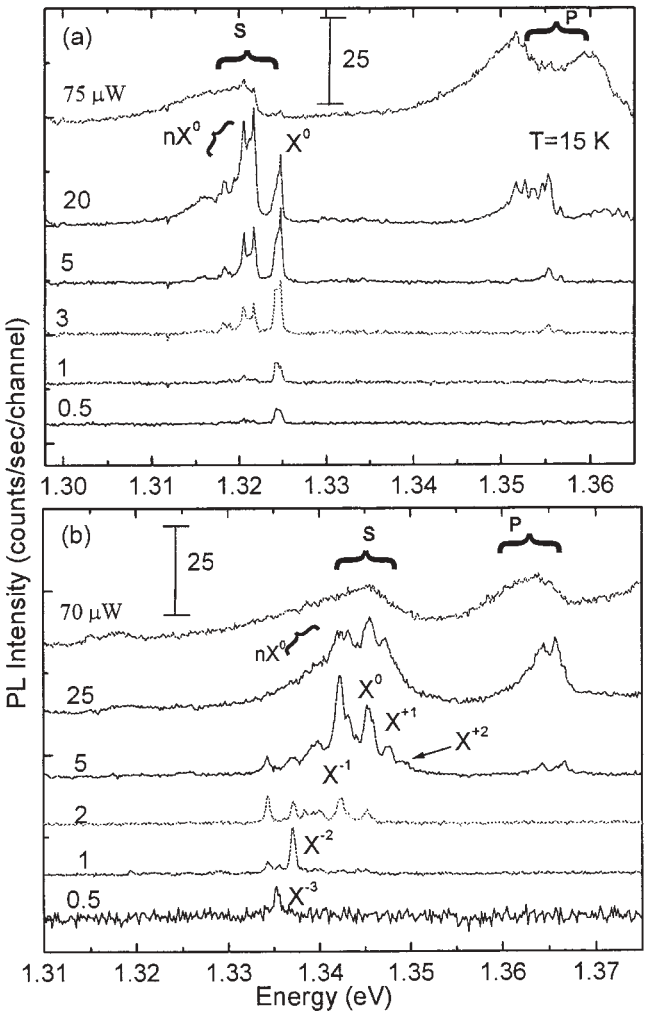

Fig. 2. The cw emission spectra of a) the neutral dot (sample A) and b) the mixed type dot (sample B), for increasing excitation power values at 15 K. X^0 denotes the neutral single exciton and $X^{\pm i}$ denote the various charged exciton states

We quantitatively account for this effect by numerically solving a many-body Hamiltonian using the configuration interaction method [15]. As argued previously [9], the exact shape of the confining potential does not alter in any significant way the derived values of the Coulomb and exchange energies. We have therefore chosen a rectangular slab as a model for the QD confining potential. A $420 \times 380 \times 30$ Å slab was best suited for calculating the electron single particle wavefunctions. In order to mimic the smaller extent of the hole envelope wave function, we artificially reduced the slab dimensions by a factor p (see inset of Fig. 3), and calculated the hole single particle wavefunctions for the smaller slab. Figure 3 displays the calculated shift of the recombination energies of charged excitons X^i ($i = \pm 1, \pm 2, \pm 3$) with respect to the recombination

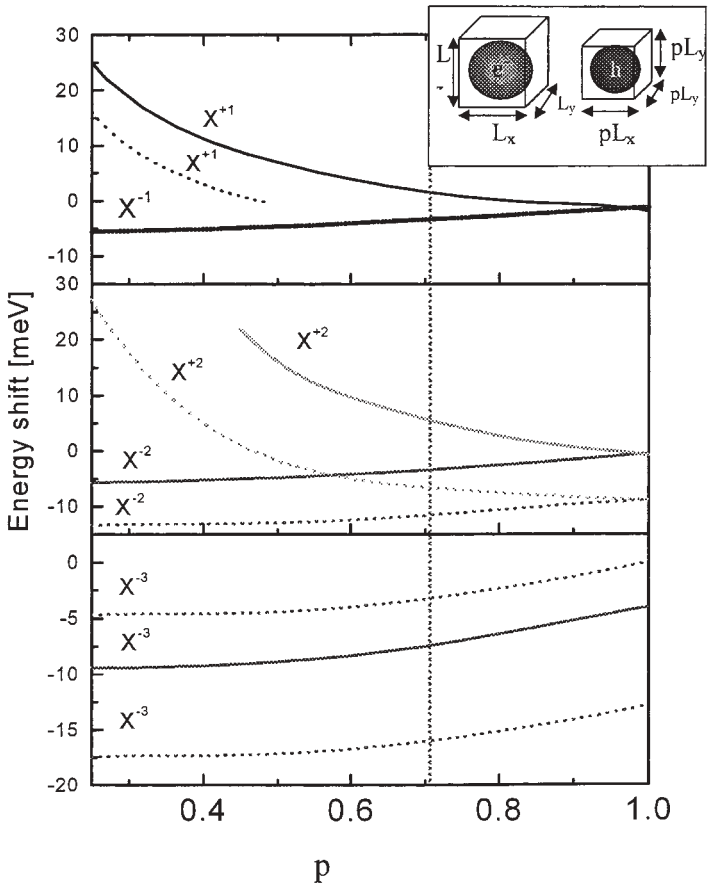

Fig. 3. Calculated PL energy shifts of charged excitons $X^{\pm i}$ ($i = 1, 2, 3$) relative to the X^0 line, as a function of the parameter p. Inset: schematic description of model slabs used for the calculation of electron (left) and hole (right) wavefunctions

of a neutral exciton X^0 as a function of p. Note that for $p = 1$ the emission energies for both X^{-1} and X^{+1} excitons is equally lower than that of X^0. As we decrease the factor p, the X^{-1} line shifts to lower energies, while the X^{+1} line shifts to higher energies, overlapping at $p \approx 0.8$ with the X^0 emission line. The spectral lines of $X^{\pm i}$ ($i > 1$) excitons behave similarly to $X^{\pm 1}$ lines. It should be noticed, however, that the relative intensities of various spectral lines vary with p. Some of the lines disappear, while new lines appear, upon varying p. Our experimental results for the charged excitons recombination energies are best fitted with the model for $p = 0.7$, leading to a volume ratio of $1/3$ between the hole and electron envelope wavefunction squared. The calculated emission spectra for various charge states (for $p = 0.7$) compared with the experimental data (shown by bars, indicating the variations between different dots) is presented in Fig. 4. It is seen that the blue and red shifts for the $X^{\pm i}$, respectively, are semiquantitatively explained by the smaller extent of the hole envelope wavefunction. The discrepancies of 2–3 meV in the actual values of the spectral lines are probably due to the incompleteness of the model and the uncertainties in the exchange energies.

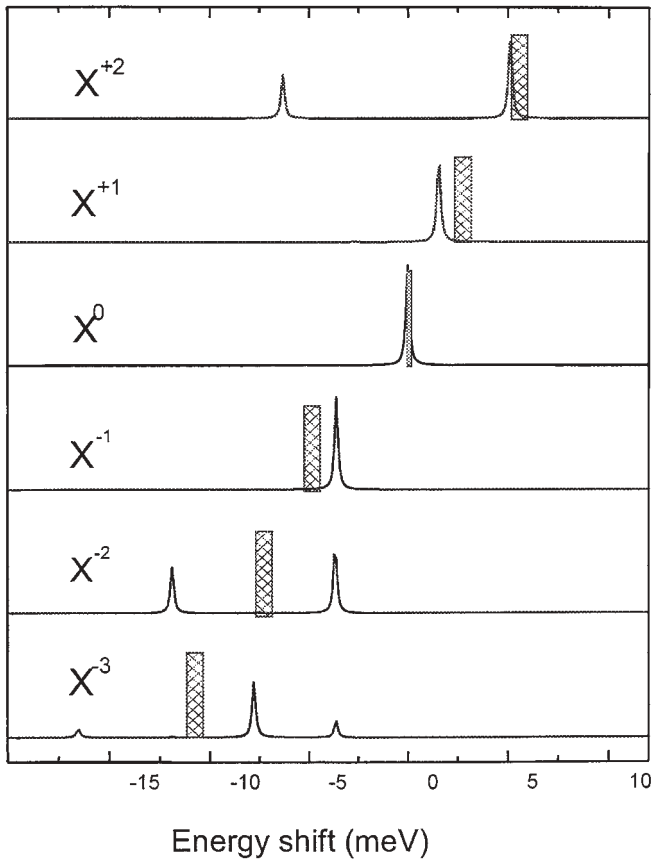

Fig. 4. Calculated emission spectra for the respective charge states for $p = 0.7$ (lines), compared to the experimentally measured data (bars)

Acknowledgements The work was supported by the US–Israel Binational Science Foundation (453/97), by the Israeli Science Foundation (335/99), and by the Fund for the Promotion of Research at the Technion.

References

[1] D. Gammon, Nature **405**, 899 (2000).
[2] R.J. Warburton, C. Schaflein, D. Haft, F. Bickel, A. Lorke, K. Karrai, J.M. Garcia, W.V. Schoenfeld, and P.M. Petroff, Nature **405**, 926 (2000).
[3] A. Hartmann, Y. Ducommon, E. Kapon, U. Hohenester, and E. Molinari, Phys. Rev. Lett. **84**, 5648 (2000).
[4] F. Findeis, M. Baier, A. Zrenner, M. Bichler, G. Abstreiter, U. Hohenester, and E. Molinari, Phys. Rev. B **63**, 121309 (2001).
[5] W.V. Schoenfeld, T. Lundstrom, P.M. Petroff, and D. Gershoni, Appl. Phys. Lett. **74**, 2194 (1999).
[6] T. Lundstrom, W.V. Schoenfeld, H. Lee, and P.M. Petroff, Science **286**, 2312 (1999).
[7] E. Dekel, D.V. Regelman, D. Gershoni, E. Ehrenfreund, W.V. Schoenfeld, and P.M. Petroff, Phys. Rev. B **62**, 11038 (2000).

[8] E. Dekel, D. Gershoni, E. Ehrenfreund, J.M. Garcia, and P.M. Petroff, Phys. Rev. B **61**, 11009 (2000).
[9] E. Dekel, D. Gershoni, E. Ehrenfreund, D. Spektor, J.M. Garcia, and P.M. Petroff, Phys. Rev. Lett. **80**, 4991 (1998).
[10] E. Dekel, D.V. Regelman, D. Gershoni, E. Ehrenfreund, W.V. Schoenfeld, and P.M. Petroff, Solid State Commun. **117**, 395 (2001).
[11] D.V. Regelman, E. Dekel, D. Gershoni, E. Ehrenfreund, W.V. Schoenfeld, and P.M. Petroff, Springer Proc. Phys. **87**, 1145 (2001). [cond-mat/0104142]
[12] D.V. Regelman, E. Dekel, D. Gershoni, E. Ehrenfreund, A.J. Williamson, J. Shumway, A. Zunger, W.V. Schoenfeld, and P.M. Petroff, Phys. Rev. B **64**, 165301 (2001).
[13] S. Glasberg, S. Finkelstein, H.G. Shtrikman, and I. Bar-Joseph, Phys. Rev. B **59**, R10425 (1999).
[14] Ph. Lelong and G. Bastard, Solid State Commun. **98**, 819 (1996).
[15] A. Barenco and M.A. Dupertuis, Phys. Rev. B **52**, 2766 (1995).