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Physica E 13 (2002) 114–118

PHYSICA E

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Spectroscopy of positively and negatively charged quantum dots: wave function extent of holes and electrons

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Abstract

We investigate semiconductor quantum dots by optically injecting a well 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 spectrally and temporally resolve the emission and show that it can be used to unambiguously determine the discrete charge states of the emitting quantum dot. In particular, we identify the emission from both negative and positive charge states of the same dot. 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 better confined wave functions of the holes. Due to their smaller volume, the energy associated with hole–hole repulsion is larger than the combined energy associated with electron–hole attraction and electron–electron repulsion. © 2002 Published by Elsevier Science B.V.

PACS: 78.66.Fd; 73.20.Dx; 71.35.Cc; 78.55.Cr

Keywords: Charged quantum dot; Exchange energy; Optical injection

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 from within a collective many body state of confined carrier complexes. It has recently been shown that the number of carriers which occupy a photoexcited QD greatly affect its photoluminescence (PL) spectrum [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 injecting optically

a controlled unequal number of electrons and holes into an isolated single dot. The injected carriers form charged complexes of carriers which are confined within the dot. In particular, complexes which contain charge of one type coupled to few charges of the other type are formed in this way. We report here on 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. In addition to previously reported PL spectra of negatively charged dots [3], we report here PL spectra of *both* negatively and positively charged states of the same dot and compare the observed PL spectra to those of a similarly prepared neutral sample.

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Optical excitation is a very convenient and efficient way to study confined many-carrier states in semiconductor quantum dots. It provides high spectral, spatial and temporal resolutions as well as a direct control of the average number of photogenerated carriers confined within a dot by varying the intensity of the optical excitation. In spite of its intrinsic charge neutrality, optical excitation can be used also to control 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 SAQDs within the wider GaAs quantum well. The second 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 employed 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 of the charge state of single QD including the transition from a negatively to positively charged dot.

The growth method of the semiconductor SAQDs for our studies were described elsewhere [7,8]. 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 [9]. 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 new electrons 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 [10]. In Figs. 2a and b, we

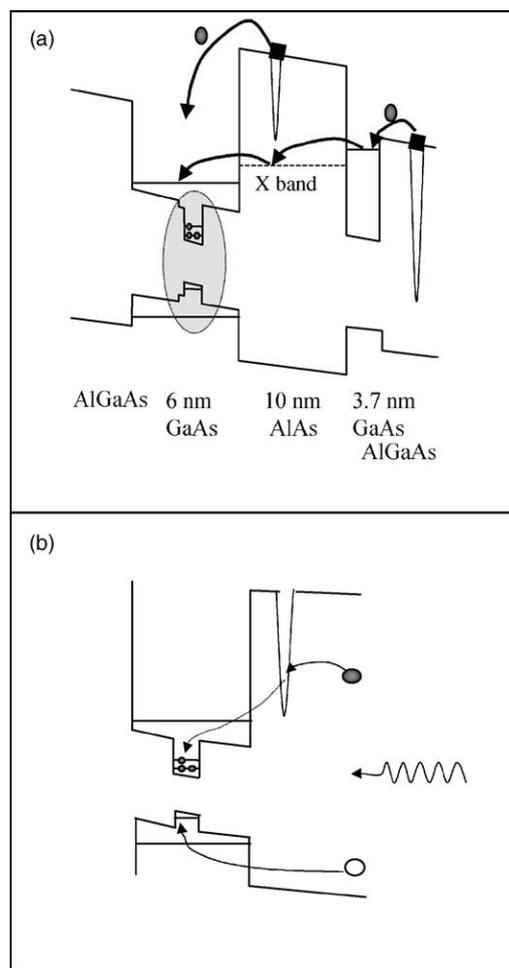


Fig. 1. The structure of the mixed type dot. (a) Initial (dark) electron capture from ionized donors. (b) e–h pair photogeneration. Note the faster hole capture which leads to photodepletion.

present the PL spectra from sample A(B) for various CW excitation powers at 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

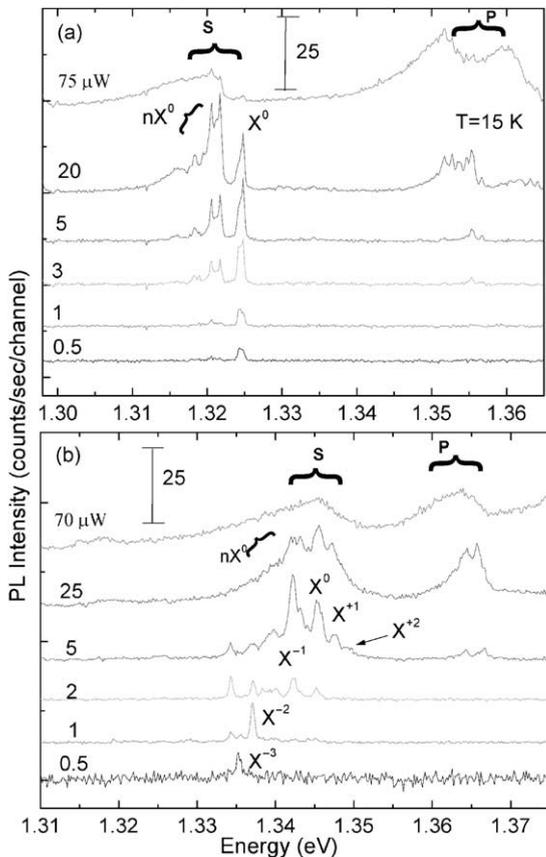


Fig. 2. (a) CW emission spectra of the neutral dot (sample A), for various excitation power at 15 K. X^0 denotes the neutral single exciton. (b) CW emission spectra of the mixed type dot (sample B) for increasing excitation power values at 15 K. $X^{\pm i}$ denote the various charged exciton states.

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 low CW excitation power, where the dot is singly occupied. We emphasize that no doping related PL lines were observed in sample A. 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 (multiexciton lines). 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 effectively reduce the band gap of the QD, when a number of spectator e–h pairs is present during the radiative recombination [11].

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 [9]. The above identification is also corroborated by following the evolution of the spectral lines under pulse excitation (not shown here, see Refs. [9,10] for more details).

In sample B, as explained above, the SAQDs are initially charged with electrons. The line marked X^{-3} (sample B, Fig. 2b) is identified as the radiative recombination of e–h pair in the presence of three extra electrons (and no other e–h pairs) in the dot. With the increase in the excitation power 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 the negative recharging is slow, thus at high enough excitation power the dot is positively charged [7,8]. The lines marked X^{+1} , X^{+2} are due to one and two, respectively, extra positive charges. Note that the PL lines from negatively charged QD is lower in energy, and those from a positively charged QD is 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 wave functions of the confined electrons and holes in the QDs are not equal. First, consider the case of equal confining potentials for the electron and hole wave functions. Addition of excess charge to the exciton lowers the emission energy because of carrier–carrier exchange energy and

wave function modification (which is responsible for trion binding in bulk semiconductors). Both effects are not sensitive to the sign of the excess charge. In a more realistic picture, the heavier holes are better confined by the QD potential and the spatial extent of their wave function is somewhat smaller than that of the electrons. As a result, 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 $C_{eh} - C_{ee}$ for each excess electron, in addition to wave function modification and electron–electron exchange interaction effects. For excess positive charge, the difference $C_{eh} - C_{hh}$ is negative, thus increasing the emission energy with respect to the case of equal confinement of electrons and holes.

We quantitatively account for this effect by numerically solving a many-body Hamiltonian using the configuration interaction method [12]. As argued previously [11], 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 QD confining potential. A $420 \times 380 \times 30 \text{ \AA}$ slab was best suited for calculating the electron single particle wave functions. In order to mimic the smaller extent of the hole envelope wave function, we artificially reduce the slab dimensions by a factor p (see Fig. 3 inset), and calculate the hole single particle wave functions for the smaller slab. Fig. 3 displays the calculated shift of recombination energies of charged excitons X^i , ($i = \pm 1, \pm 2, \pm 3$) with respect to the recombination of a neutral exciton X^0 , as a function of p . Note that for $p = 1$ (equal confinement for both electrons and holes) the emission energy for both X^{-1} and X^{+1} exciton recombination is lower compared to that of X^0 . As we decrease the volume ratio 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. Spectral lines of $X^{\pm i}$ ($i > 1$) excitons behave similarly to $X^{\pm 1}$ lines. However, it should be noticed that the relative intensities of various spectral lines vary with the volume factor, and some of the lines even disappear (like one of the X^{+2} lines) with the decrease of the vol-

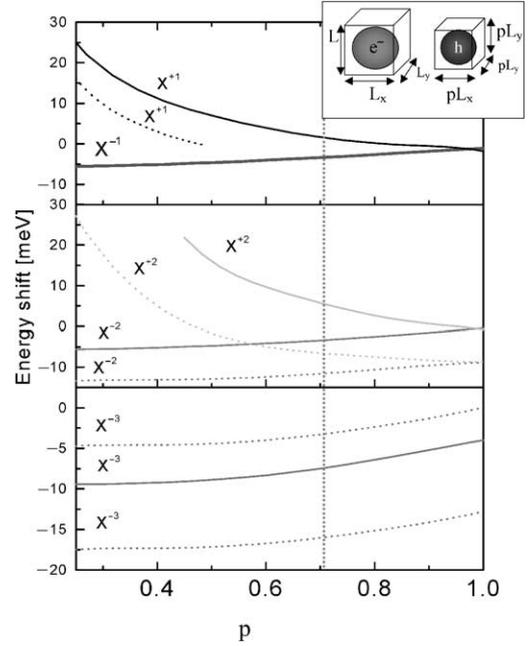


Fig. 3. The calculated PL energy shifts of charged excitons $X^{\pm i}$ ($i = 1, 2, 3$) relative to the X^0 line, as a function of the parameter p . Inset: schematic description of model slabs used for the calculation of the electrons (left) and holes (right) wave functions.

ume factor, while new lines appear, like in the case of X^{+1} recombination. Our experimental results for the charged excitons recombination energies are best fitted with the model for $p = 0.7$, leading to volume ratio of $\frac{1}{3}$ between the hole and electron confining potentials. 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 wave function. The discrepancies of 2–3 meV in the actual values of the spectral lines are due, probably, to the incompleteness of the model and the uncertainties in the exchange energies.

In conclusion, we have reported on the observation of PL from both positively and negatively charged single QD. Our experimental observations prove that in self-assembled quantum dots the extent of the hole wave functions is smaller than that of the confined electrons.

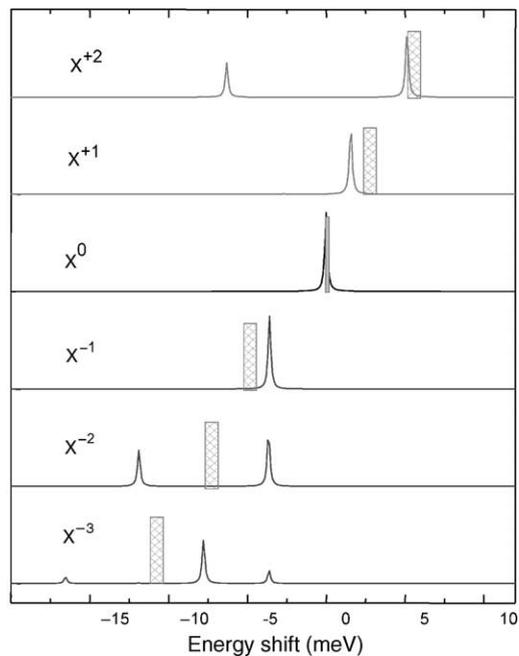


Fig. 4. The calculated emission spectra for the respective charge states for $p = 0.7$ (lines), compared with the experimentally measured data (bars).

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.

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