

Observation of Charged Few-Particle States in the Optical Spectra of Single Semiconductor Quantum Dots

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A detailed discussion of the optical properties of single n-type modulation-doped semiconductor quantum dots is presented. We use the photo-depletion/back-hopping mechanism to optically control the number of surplus electrons in the dot. Comparison of the experimental data with calculated luminescence spectra, obtained within a direct-diagonalization approach for calculating electron–hole states, allows the identification of luminescence from the decay of up to fivefold charged excitons. Finally, we study the influence of fluctuating local electric fields, produced by ionized impurities in the surrounding of the dots, on the optical selection rules and on the linewidth of the emission peaks.

Introduction The discrete and atomic-like density of states of quantum dots (QDs) is of considerable interest for applications in future optoelectronic devices [1–3]. However, coupling between QD carriers and their solid state environment is expected to have a noticeable influence on the optical properties. For instance, temporal fluctuations in the environment can lead to broadened emission peaks even for QDs with perfect size uniformity [4–6]. As another example, shallow impurities in the dot surrounding can provide a source of remote doping of equilibrium carrier populations, which, in turn, lead to renormalized energies because of additional Coulomb interactions [7–9].

In this paper, we analyze the optical properties of single n-type modulation-doped QDs. First, we discuss how above-barrier laser excitation in conjunction with the photo-depletion/back-hopping mechanism can be exploited for optical control of the number of surplus electrons in the QD. Using a general solution scheme for electron–hole QD states and comparing the calculated optical spectra with the measured ones, we unambiguously identify recombination from up to fivefold charged excitons. Finally, we discuss the effects of fluctuating local electric fields produced by ionized impurities in the surrounding of the QDs. Optical selection rules, as well as the linewidth of the QD emission peaks are shown to be strongly affected.

Experiment The QDs under study are fabricated by epitaxial growth on GaAs {111}B substrates patterned with an array of micron-sized inverted pyramids [10, 11]. Deposi-

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tion of barrier ($\text{Al}_{0.45}\text{Ga}_{0.55}\text{As}$) and well (GaAs) materials results in the self-formation of a GaAs QD at the tip of each inverted pyramid [11]. The position of the QD is accurately controlled by the placement of the inverted pyramid, while its size can be varied by appropriately choosing the growth time. The tunability of the inter-dot distance renders our structures ideal for the study of single QDs using conventional spectroscopic techniques. In order to optimally prepare our samples for optical measurements, a post-growth substrate removal method has been developed [11]. The resulting upright standing pyramidal structures are individually probed using a microscopic photoluminescence (μPL) set-up. Intense PL from the QD at the pyramid tip, as well as from other low-dimensional self-formed nanostructures inside the pyramid, has been successfully identified in previous studies [11]. Recently, in the very low excitation power regime of n-type modulation-doped single QDs we reported the observation of multi-charged exciton states [9].

Samples with an estimated donor concentration of $n \sim 10^{17} \text{ cm}^{-3}$ were grown. In the optical spectroscopy of single dots we use above-barrier excitation (514 nm line of an Ar^+ -ion laser), and the laser spot is focused on a single pyramid by means of a microscope objective. The PL light is collected by the same objective and dispersed by a single spectrometer. The spectrum is registered by a liquid N_2 -cooled 2000×800 pixels charge coupled device (CCD) chip. A spectral resolution of this μPL set-up of about 140 μeV is achieved.

Multi-Charged Excitons In our experiments, the number of surplus QD electrons is optically controlled by means of the competition between negative photo-depletion of QD electrons (induced by the above-barrier excitation) and hopping of impurity-bound electrons to the QD [9]. At thermal equilibrium, donors around each QD are ionized and electrons are transferred to the dot. The number of electrons n in the QD is therefore equal to the number of ionized donors N_d in its surrounding. Under above-barrier photon illumination, electron-hole pairs are optically generated and separate. The hole is efficiently captured by the negatively charged dot, where it recombines with one of the doping electrons (negative photoconductivity [12]); the electron, on the other hand, neutralizes one of the ionized donors in the barrier. Its return to the dot is then governed by slow hopping events, which strongly depend on temperature and on the donor-dot distances. Hence, the stationary number of electrons n_{stat} in the QD depends on the balance between P_{depl} , which is controlled by the above-barrier excitation power, and on the back-hopping rates $r_{n,i}$ from donors $i \in \{1, \dots, N_d\}$ to the dot, which are determined by the specific donor distributions around each QD.

Figure 1 shows the power-dependent single-dot spectra for above-barrier excitation (experiments performed at 10 K). We kept the excitation power low enough to exclude multi-exciton occupations. Let us first concentrate on the spectral evolution of the low-energy peaks (photon energies $\sim 1.56 \text{ eV}$), which exhibit a pronounced blue-shift. With increasing excitation power peaks at lower energies become quenched, and additional peaks appear at higher energies. Comparing luminescence from a large number of QDs on the same sample, we always found similar spectral evolutions, thus reflecting a general behavior of luminescence from multi-charged complexes [9]. We ascribe this spectral evolution to the sequential photo-depletion of QD electrons due to photo-depletion and back-hopping of donor electrons. This explanation is in agreement with several

others experimental findings [9, 13, 14]: Increasing the sample temperature, the back-hopping rates $r_{n,i}$ of donor-bound electrons become significantly larger, and much higher QD electron occupation as compared to the same P_{exc} at lower temperature is observed; turning off photo-depletion by use of selective excitation of the GaAs material only, the spectral evolution is much less pronounced; finally, two-color time-resolved pump-and-probe measurements reveal time constants for the observed changes in the millisecond range, which exclude intrinsic QD mechanisms as the source of such spectral changes.

To gain insight into the nature of these luminescence peaks, a detailed theoretical analysis was performed. Electron-hole states are computed for an arbitrary 3D confinement potential, and the various electron-electron and electron-hole Coulomb interactions are accounted for within a full direct-diagonalization approach (for details see Refs. [9, 15]). For the QD confinement potential shown at the top of Fig. 2a, which we deduced from previous structural studies [16] (we assume additionally cylindrical sym-

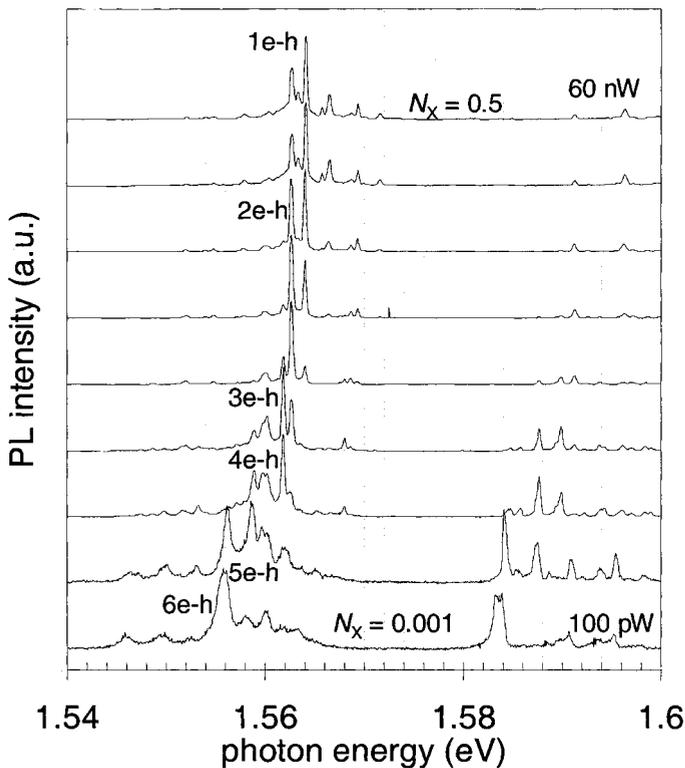


Fig. 1. 10 K μ PL spectra of a single QD at increasing above-barrier excitation power. We use $N_X = R_{\text{phot}} T a \sigma_{\text{QD}}$ as an upper estimate for the number of photo-excited excitons N_X in the QD, where R_{phot} is the number of incident laser photons per unit time, $T = 0.7$ the transmittance of the AlGaAs barrier, $a = 0.063$ the ratio of the integrated PL intensities of QD to the total pyramidal structure, and $\tau_{\text{QD}} = 0.5$ ns the estimated QD exciton lifetime. In the experiments the excitation power was kept sufficiently low throughout to exclude multi-excitonic occupations of the QD. Our assignment of charged-exciton states is indicated next to the corresponding emission peak

metry), we computed electron–hole states for an increasing number of surplus electrons. Figure 2a shows calculated emission spectra: the emission peaks of charged excitons monotonically red-shift as the number of electrons is increased, and for multi-charged complexes additional satellite peaks appear on the low-energy side. We emphasize the excellent agreement between experiment and theory, which allowed the unambiguous identification of recombination from up to fivefold charged excitons in the μ PL spectra of Fig. 1.

Influence of Impurity Fields In addition to doping, ionized impurities lead to fluctuating electric fields at the QD position, which have a noticeable influence on the optical properties. As can be inferred from Fig. 1, additional peaks appear at photon energies of ~ 1.585 eV, whose spectral evolution closely follows that of the ground-state emission peaks. We attribute these lines to the recombination of electrons in the first excited

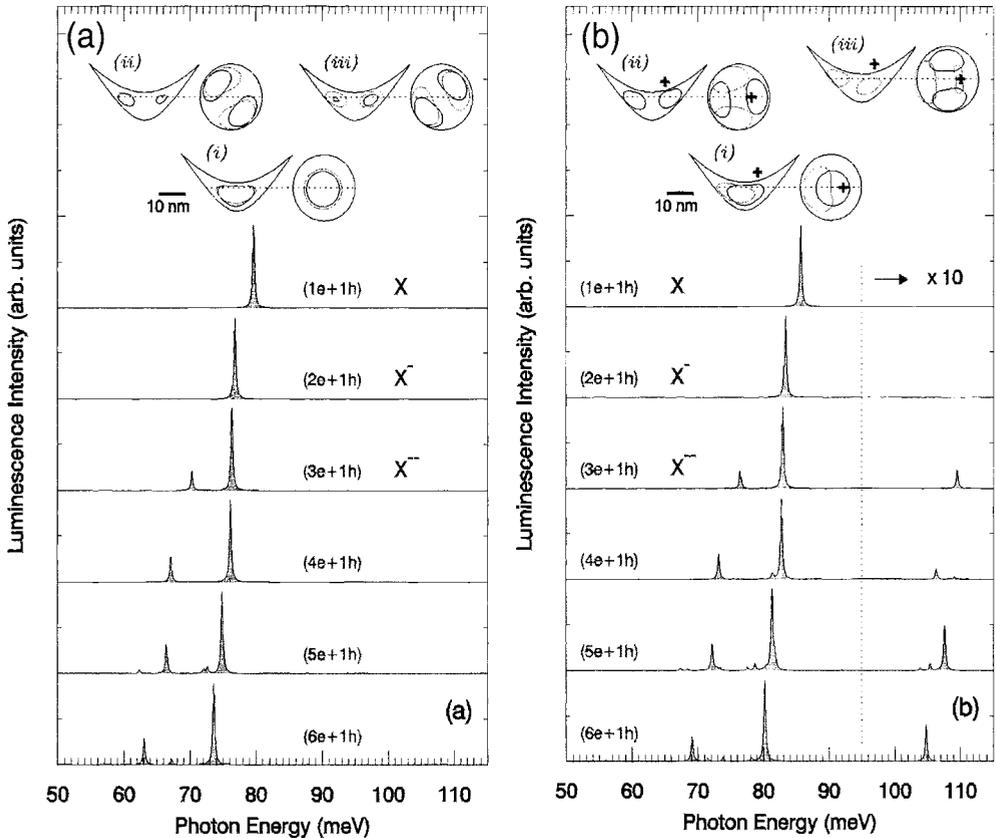


Fig. 2. Calculated luminescence spectra for a single QD and for an increasing number of surplus electrons (see expressions in parantheses; photon energy zero at the bandgap): a) without impurity field; b) with impurity field. The insets at the top sketch the single-particle eigenstates of lowest energy (black and gray lines for electrons and holes, respectively), and the confinement potential which we used in our calculations (dotted line at $z = 0$ and $y = 0$). In the presence of a positively charged impurity (position indicated by crosses) the optical selection rules for cylindrical confinement potentials break down, and new peaks appear in the optical spectra

state (“p-shell”) with holes in the ground state (“s-shell”). Several reasons support this assignment: First, the 25 meV energetic separation is in good agreement with our theoretical estimates; second, the decrease of the emission intensity with increasing P_{exc} is expected from the depopulation of excited-electron states. However, the calculations shown in Fig. 2a cannot reproduce the observed behavior, because the assumed cylindrical symmetry imposes optical selection rules where only transitions between electron and hole states with the same angular-momentum number are optically allowed. To explain the appearance of additional peaks, we have also considered the electric fields of ionized impurities in the surrounding of the QD. Figure 2b shows calculated emission spectra for the same QD as in Fig. 2a, but in presence of an ionized donor (indicated by a cross in the inset). Here, cylindrical symmetry is no longer present (see wavefunctions in inset) and the original optical selection rules do no longer apply. Optical recombination of electrons in the first excited state with holes in the ground state becomes possible, and new peaks appear on the high-energy side (~ 105 meV). Note the discrepancy between the heights of these additional peaks in the experimental and calculated spectra, which we attribute to uncertainties regarding the QD confinement potential and the impurity positions.

Temporal fluctuations of the impurities states, due to the random nature of the neutralization/ionization events, can also have an influence on the widths of the emission peaks. A strong decrease in the linewidth of the emission lines from ~ 5 meV at the lowest excitation power down to ~ 200 μeV at higher power can be observed. We attribute this spectral narrowing to the stabilization of the impurity charge states: at low excitation power, the QD is highly charged, meaning that a large number of impurities in its surroundings are ionized. However, after creation of electron–hole pairs in the barrier, impurities become neutralized and ionized again, thus leading to changing impurity state configurations. Such variations give rise to fluctuating Stark-shifted emission lines, and result in broadened PL peaks (since, in the experiment, we integrate over several seconds or minutes for each spectrum). The magnitude of the shifts is in the meV range, in agreement with our model calculations of ionized impurity fields. This phenomenon, known as spectral diffusion, has been observed recently in other zero-dimensional structures [4–6], and demonstrates the extreme sensitivity of QD energy levels to the details of their solid-state environment. As the excitation power is increased, more and more impurities remain neutral leading to a less fluctuating QD environment, in agreement with the observed reduction of spectral diffusion. However, the widths of the neutral exciton emission lines are still larger than our spectral resolution, thus indicating residual sources of broadening (e.g., interactions of QD carriers with other carriers in the neighboring environment).

Conclusion We have discussed optical properties of n-type modulation-doped semiconductor QDs. The pronounced spectral evolution observed at extremely low excitation power has been ascribed to photo-depletion of QD electrons due to above-barrier excitation. The resulting fluctuations of the charge-state configuration of impurities, leading to temporally fluctuating electric fields, have been shown to be a source of broadening and to break the optical selection rules. In order to fully benefit from the advantages of the three-dimensional QD confinement in future optoelectronic devices, the control of QD-environment couplings will be of crucial importance besides an improved size uniformity of QDs.

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