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Optical Spectra of Single Quantum Dots: Influence of Impurities and Few-Particle Effects

A. HARTMANN¹⁾ (a), Y. DUCOMMUN (a), E. KAPON (a), U. HOHENESTER (b),
C. SIMSERIDES (b), and E. MOLINARI (b)

(a) *Department of Physics, Swiss Federal Institute of Technology Lausanne,
CH-1015 Lausanne, Switzerland*

(b) *Istituto Nazionale per la Fisica della Materia (INFM) and Dipartimento di Fisica,
Università di Modena e Reggio Emilia, Via Campi 213/A, I-41100 Modena, Italy*

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The evolution of photoluminescence (PL) spectra of single GaAs/AlGaAs quantum dots (QD) is studied as a function of laser excitation power and temperature. At very low powers, where multi-exciton occupation of the QD can be excluded, an unexpected and pronounced spectral evolution is observed (large energy shifts and appearance of multiple emission lines). A similar evolution is observed at low excitation powers with increasing temperature. A model, taking into account the influence of the shallow, residual impurities in the environment of each QD, explains the observed spectral evolutions in terms of photo-depletion of the QD and hopping of impurity-bound carriers back into the QD. Theoretical calculations of the PL due to N electrons + 1 hole ($Ne + 1h$) QD states allow us to attribute the ≈ 2 meV spaced lines in the experimental spectra to the different charge states $Ne + 1h$, $(N - 1)e + 1h$, ... of the QD.

Luminescence spectra of single quantum dots (QD) provide useful information about the electronic states of these zero-dimensional (0D) structures. Unlike free atoms, these 0D objects are embedded in a solid state matrix. Interactions of QD confined carriers with free or bound charges in this environment will therefore affect the internal level structure of the QD. Furthermore, donor or acceptor impurities present in the QD environment can result in an equilibrium occupation of electrons or holes of the QD. In the present paper, we address the complex evolution of single QD photoluminescence (PL) spectra as function of laser excitation power in the low excitation regime (time averaged exciton density in the QD environment $N_X \approx 0.0003$ to 0.2). We explain this evolution in terms of charge transfer from residual shallow impurities and photo-depletion of the QD by the exciting laser light. Theoretical calculations of the $Ne+1h$ multi-particle states in the QD allow us to identify in the experimental spectra characteristic transitions for each $Ne + 1h$ charge state of the QD. While residual impurities do not lead to observable changes in the optical spectra of 2D quantum wells (QW), here, due to the small size and small number of states of the QD, the impurity environment seriously affects the QD spectrum.

The QD structures studied in the present paper have been produced by the technique of self-limited QD growth in pyramidal recess substrate patterns on (111)B GaAs

¹⁾ Corresponding author; Tel.: +41 21 693 5492; Fax: +41 21 693 5480;
e-mail: hartmann@dpmail.epfl.ch

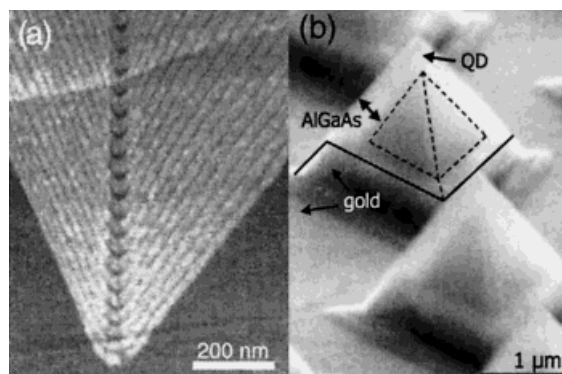


Fig. 1. a) x-AFM image of AlGaAs-barrier (light gray) and GaAs QW (dark gray) layers deposited in pyramidal recess, showing a vertical stack of QDs at the center. b) Scanning electron micrograph of pyramidal structures after back-etching

substrates using low-pressure organo-metallic chemical vapor deposition (LP-OMCVD) of AlGaAs/GaAs heterostructures. Here, the position of each QD is precisely controlled by the pyramidal recess substrate pattern, which can be arranged in dense 2D arrays (10^{10} pyramids/cm³ have recently been realized by e-beam lithography [1]) to achieve high QD densities. Deep QD potential wells (>200 meV) have been achieved by this method [2]. Finally, the QD interfaces and dimensions are defined by epitaxial growth leading to high crystal quality and good size homogeneity across the sample (low temperature photoluminescence (PL) spectra show an inhomogeneous linewidth (FWHM) of ≈ 10 to 15 meV [3]). Single QD PL spectra of structurally “identical” QDs can thus be compared.

Cross sectional atomic force microscopy (x-AFM) has been successfully used to study the growth evolution inside the pyramidal recess patterns, and reveals the formation of a complex system of connected nanostructures [3] (see Fig. 1a). Thin GaAs layers deposited on such patterns result in the formation of GaAs QWs on the pyramid sidewalls connected to GaAs QWRs along the pyramid corners, which finally meet at pyramid tip, where a QD is formed. x-AFM and microscopic PL (μ PL) studies indicate thickness ratios of 1:3:6 between GaAs QW, QWR, and QD [3]. These lateral GaAs nanostructures are also connected to vertical Ga-rich AlGaAs nanostructures, consisting of QWs along the pyramid corners and a QWR along the pyramid tip, all of which are formed during the self-limited AlGaAs growth.

Recently, we developed a back-etching process for the pyramidal QDs in which the sample is glued up side down onto a support and the GaAs substrate is removed, so only the epitaxial layers are left. In this way, the QD is situated at the tip of an upright standing pyramid [2] (see Fig. 1b). These back-etched pyramids show a luminescence enhancement of the QD line by a factor of 10^4 as compared to untreated inverted pyramids, due to the different conditions of optical refraction and total internal reflection for the two geometries [2]. This enhancement enables us to study the μ PL of single QDs at extremely low excitation conditions (here: $N_X \approx 0.0003$).

Fig. 2a shows a typical evolution of low temperature (10 K) single QD μ PL spectra as the exciting Ar⁺-ion laser power is increased (from 30 pW up to 10 μ W focused to a 0.7 μ m diameter spot on a single pyramid). The spectral intensities have been normalized to the QD ground state transition for better visibility. N_X denotes the exciton density at the QD approximated using geometrical factors and assuming an excitonic lifetime of 500 ps. The spectral evolution can roughly be divided into two regimes. In the high excitation

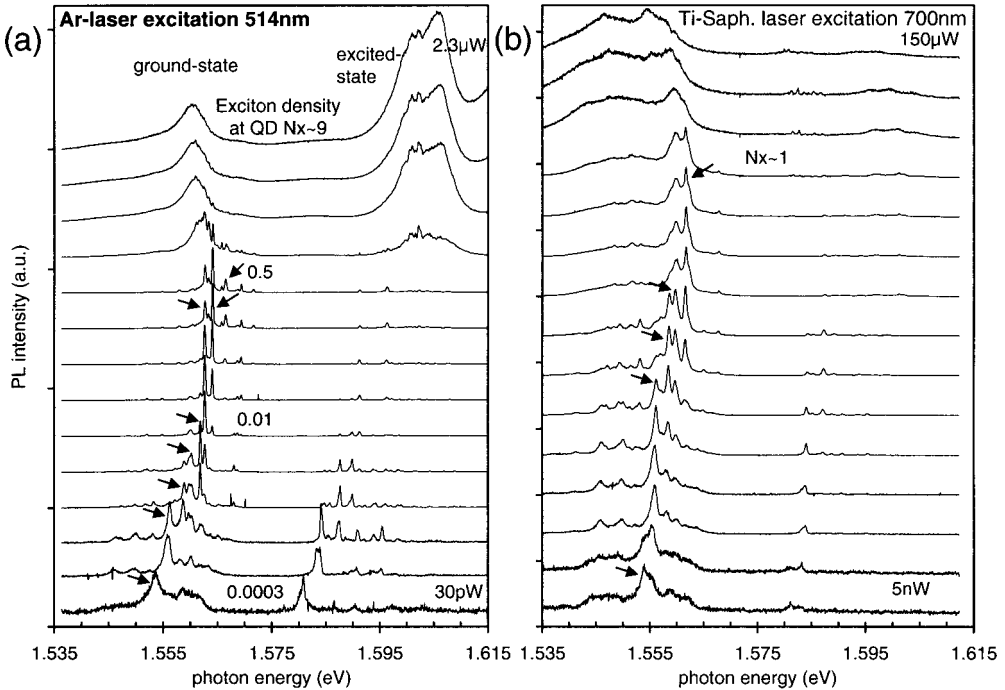


Fig. 2. Evolution of 10 K μ PL spectra of the same single QD as function of a) above barrier, Ar^+ laser and b) below barrier, Ti-sapphire laser excitation power (N_X : approximated time-averaged density of excitons at QD)

regime ($N_X = 0.5$ to 9), the QD ground state broadens, shifts to lower energy and strongly saturates. An excited QD state can be observed at ≈ 45 meV above the ground state, indicating multi-exciton occupation of the QD at these high excitation conditions. In the low excitation power regime ($N_X = 0.0003$ to 0.5), the dominating QD ground state is composed of a number of lines separated by 2 to 5 meV. Two trends are visible. With increasing power, lines at lower energy disappear and new lines at higher energy dominate the ground state transition, shifting the spectral weight by ≈ 10 meV to higher energy. At the same time, the originally 2 meV broad lines narrow down to 0.4 meV. A parallel evolution is observed for the QD excited state transitions, observed here at ≈ 25 meV higher energy, which, however, weaken considerably at higher excitation powers.

If the same single QD is not excited above (Fig. 2a, Ar^+ laser, 514 nm) but below (Fig. 2b, Ti-sapphire laser, 700 nm) the AlGaAs barrier, the spectral evolution looks surprisingly different. Even though, in the low excitation regime of Fig. 2b ($N_X < 1$), the general trend of new peaks at higher energy dominating over those at lower energy with increasing excitation is similar, the overall blue-shift (here ≈ 7 meV) and peak narrowing (down to 0.8 meV) are less pronounced.

Fig. 3 shows the evolution of μ PL spectra of another single QD at fixed excitation conditions as function of temperature. The evolution is similar to the excitation power evolution shown in Fig. 2a. From low to higher temperatures (or intermediate to low excitation powers in Fig. 2a) one observes additional peaks appearing at lower energies accompanied by a strong broadening of the individual lines.

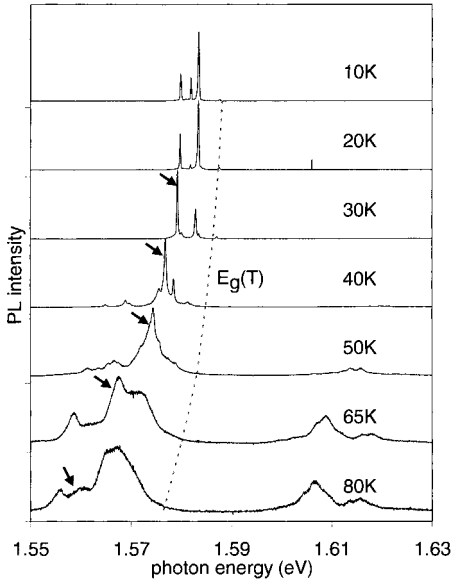


Fig. 3. Temperature dependent evolution of single QD μ PL spectra

The experimental results are explained within a model considering the influence of the QD environment on its spectrum. During OMCVD growth of the $\text{Al}_{0.45}\text{Ga}_{0.55}\text{As}$ barrier layers, the concentration of residual shallow impurities lies in the range 10^{16} to 10^{17} cm^{-3} , resulting in a modulation doping of the QD. The influence of these impurities on the QD spectrum is twofold. First, charged impurities give rise to an electric field at the QD, resulting in Stark-shifted QD PL lines. The $1/r^2$ decay of the impurity electric field with distance to the QD, together with the statistical placement of the impurities results in fields that are different for every QD and, in general, do not cancel out. Secondly, in equilibrium, a certain number of carriers are transferred from the impurities into the QD, resulting in multi-particle interaction related shifts (band-gap renormalization, BGR) of the PL transitions.

The behavior in the low excitation power regime observed in Fig. 2 is explained as follows. At low excitation powers, some charges (here electrons) are present in the QD due to the modulation doping by the impurities in the barrier (Fig. 4a). Electron-hole ($e-h$) pairs photo-excited in the space-charge region close to the QD will be dissociated. The holes are attracted by the negatively charged QD, and electrons by the positively charged ionized donors in the barrier. The photo-excited hole recombines with one of the QD electrons, depleting the QD of one electron,

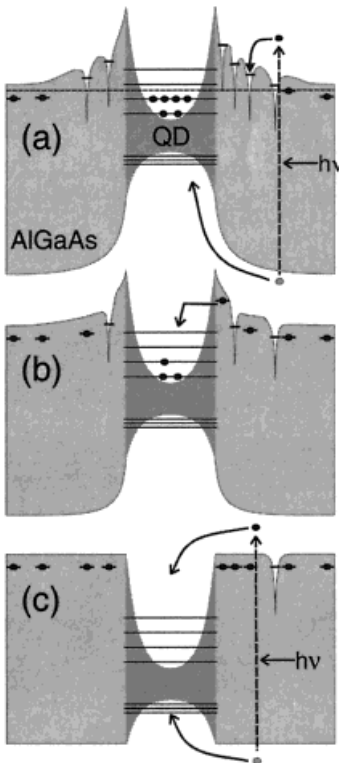


Fig. 4. Band diagram of QD showing a) reduction of charge in QD by photo-created $e-h$ pair; b) hopping of electron bound to impurity back into QD; c) flat-band conditions during high photo-excitation

while the photo-excited electron neutralizes one ionized impurity in the barrier (so called negative photo-conductivity effect or photo-depletion [4], Fig. 4a). In order to return to the original configuration the photo-excited electron has to return into the QD, which is only possible by slow hopping transport at these low temperatures (10 K, see Fig. 4b) [4]. As the excitation power is increased, the e–h pairs are created at a faster rate, leaving less time for the electron back-hopping into the QD. Thus, the spectral blue-shift observed is ascribed to the increasing rate of depletion of the QD from electrons, resulting in a reduced BGR. This depletion also explains the quenching of the QD excited state transition, which we ascribe to occupied excited electron states. At the same time, more and more impurities are neutralized. This results in a reduced electric field at the QD reducing the Stark-(red)-shift and therefore also contributing to the observed blue-shift. Since the exact occupational configuration of QD and environment fluctuates during the integration time of a PL measurement, multiple broadened PL lines appear, each one representing the probability for a certain configuration at the given excitation power. However, at intermediate powers, most of the impurities remain neutralized (flat-band conditions, Fig. 4c), resulting in less occupational disorder and therefore narrower and fewer QD lines, as observed experimentally.

For below-barrier excitation, the effect of photo-depletion is much less pronounced [5], resulting in smaller spectral changes as observed in Fig. 2b. Finally, also the temperature dependent evolution shown in Fig. 3 strongly supports this model. Increasing the temperature increases the hopping rate of electrons back into the QD (Fig. 4b) while at fixed excitation power, the rate of photo-depletion remains constant. Thus, the average QD occupation increases with temperature leading to an increased BGR and Stark-shift and therefore to a red-shift of the luminescence. The importance of impurities for the observed spectral evolution is also stressed by the long time-constants (ms range) of spectral changes observed in a two-color pump-and-probe measurement reported elsewhere [6].

The electric field of the ionized impurities alone does not explain the experimentally observed shifts of the luminescence peaks (≈ 10 meV). If we assume an electric field of ≈ 8 kV/cm (a typical value ≈ 10 nm away from an isolated impurity), from the analysis of semiconductor quantum wells [7, 8] the optical Stark shift is not expected to exceed a few meV. We have performed calculations for some model QD potentials modified by an ionized impurity in the surrounding, and confirm that the expected spectral shifts are definitely not sufficient to explain the present experimental findings. Although the situation is more complicated in the actual samples, due to the presence of several impurities randomly distributed around the QD, it is clear that an additional mechanism is needed to account for the observed shifts.

To address this issue and to explain the origin of the complex multiple-line patterns in our experimental spectra, we next turn to the theoretical analysis of the optical properties of (unintentionally) doped QDs. For simplicity, we only consider the case of n-type doping, and we assume that at low laser excitation power conditions the QD is initially populated by N electrons and one hole. Then, luminescence involves a process where one electron–hole pair is removed from the interacting many-particle system $Ne+1h$, and one photon with corresponding energy is created. More specifically, the luminescence spectrum $I(\omega)$ can be computed as [9]

$$I(\omega) \propto \text{Im} \sum_{\mu} \frac{|\langle \Psi_{\mu}^{(N-1)e} | \hat{p} | \Psi_G^{Ne+1h} \rangle|^2}{\Omega - E_G^{Ne+1h} + E_{\mu}^{(N-1)e} + i\Gamma}. \quad (1)$$

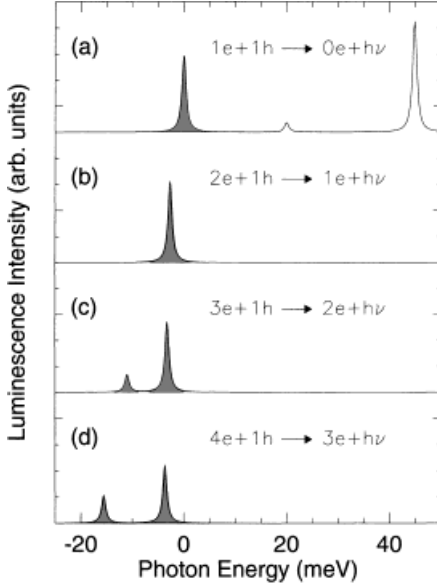


Fig. 5. Luminescence spectra for a QD populated by N electrons and one hole, as computed from eq. (1). a) The shaded area shows the single-exciton luminescence (energy of groundstate exciton taken as the origin of the energy scale); the other peaks correspond to the excited excitonic states; b) luminescence from the negatively charged exciton X^- ($2e + 1h$); c), d) luminescence from exciton complexes with two and three electrons, respectively

Here, $|\Psi_G^{N e+1h}\rangle$ is the groundstate of the interacting $N e + 1h$ system with energy $E_G^{N e+1h}$, $|\Psi_\mu^{(N-1)e}\rangle$ is the μ -th excited state of the interacting $(N-1)e$ system with energy $E_\mu^{(N-1)e}$, Γ is a phenomenological damping constant which accounts for the interaction with the QD environment (e.g., phonons or photogenerated carriers in the surrounding of the QD), and \hat{p} is the interband polarization operator describing the light-matter coupling within the usual dipole and rotating-wave approximations [10]. Note that in eq. (1) we have assumed that – before the photon emission – the interacting system $N e + 1h$ is in the lowest available state.

In our calculations for the QD, we start from the single-particle properties derived by solving the single-particle Schrödinger equation within the envelope function and effective-mass approximations, by means of a plane-wave expansion with periodic boundary conditions [11].²⁾ The total wavefunctions and energies of the interacting $N e + 1h$ and $(N-1)e$ system are obtained by direct diagonalization of the many-particle Hamiltonian [9]³⁾, accounting for carriers confined in the QD which mutually interact through the Coulomb potential. Following the scheme presented in Refs. [9, 12, 13], we only consider one- and two-electron excitations out of the single-particle ground state. In this way, we describe excitons, $1e + 1h$, and negatively charged excitons, $2e + 1h$, without further approximation, whereas carrier complexes consisting of more than two electrons are treated in the approximation of two electrons and one hole moving in the mean field of the rest.

²⁾ For the confinement potential, we assume a QW profile along z (5 nm width), and an in-plane parabolic potential with $a_0^e = 34$ meV for electrons and $a_0^h = 6$ meV for holes; with this choice, electron and hole wavefunctions have the same lateral extension. Material parameters for GaAs are used.

³⁾ A single-particle basis consisting of the ten energetically lowest electron and hole single-particle states is used.

Fig. 5a shows the optical spectrum for an undoped QD as computed from eq. (1). Here, the level splitting of ≈ 40 meV reflects the confinement potentials for electrons and holes (the small peak at ≈ 20 meV is due to a Coulomb coupling between an optically allowed and an optically forbidden single-particle transition). Fig. 1b shows the luminescence spectrum for a negatively charged exciton X^- . Our detailed calculation reveals a binding energy of X^- of approximately 2.5 meV. However, in QDs Coulomb correlations are not only responsible for energy renormalizations: The strong quantum confinement imposes the formation of carrier complexes; thus, in the optical spectra of QDs a strong enhancement of few-particle effects is expected as compared to semiconductor systems of higher dimensionality, where carrier complexes can break up into spatially separated constituents. Indeed, additional emission peaks appear in the optical spectra of higher charged excitons (Figs. 5c, d). To understand their origin, in the following we concentrate on the system $3e + 1h$ (Fig. 5c): To a good approximation, the ground state of this system consists of two electrons (with opposite spin orientation) populating the single-particle state of lowest energy, one electron in the first excited state, and the hole populating the single-particle hole state of lowest energy. Owing to wavefunction orthogonality [14], in a luminescence process the hole recombines with an electron in the lowest shell, leaving the $2e$ system in an excited state; here, the energy splitting of excited states, which is due to exchange and correlation effects [12, 13], is of the order of 10 meV. We note that a similar behavior has recently been observed in the optical spectra of exciton complexes in QDs (see Ref. [14] and references therein).

Following the theoretical results presented in Fig. 5, a reduction of the QD charge by one electron is seen in a PL spectrum as the replacement of one (predominant) peak at lower energy $Ne + 1h$ by a new peak at ≈ 2 meV higher energy $(N - 1)e + 1h$. This is what we observe in the excitation-power dependent spectra of Fig. 2. As the excitation power increases and the photo-depletion becomes more important, a series of such peak replacements from lower to higher energy is observed (arrows in Fig. 2), each one indicating that in the time average of the PL integration, one less electron is present in the QD. Similarly, as the temperature is raised in Fig. 3, each peak appearing at lower energy indicates that, again in the time average, one more electron is able to tunnel into the QD at the given excitation conditions.

In summary, we have experimentally studied the PL spectra of single QDs at high down to extremely low excitation conditions. At extremely low excitation and as function of temperature, an unexpected pronounced spectral evolution was observed. We proposed a model based on the interaction of the QD with the shallow impurities in the QD environment. The effect of photo-depletion depletes the QD of carriers during the PL measurement, leading to a different BGR of the QD and to different Stark-shifts of the QD transitions. A theoretical calculation of the multi-particle charged exciton states in the QD finally allows us to attribute individual lines in the fine structure of the observed spectral evolution to changes of the QD charge by one electron.

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