Few-Particle Effects in Semiconductor Quantum Dots: Observation of Multicharged Excitons

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We investigate experimentally and theoretically few-particle effects in the optical spectra of single quantum dots (QDs). Photodepletion of the QD together with the slow hopping transport of impurity-bound electrons back to the QD are employed to efficiently control the number of electrons present in the QD. By investigating structurally identical QDs, we show that the spectral evolutions observed can be attributed to intrinsic, multi-particle-related effects, as opposed to extrinsic QD-impurity environment-related interactions. From our theoretical calculations we identify the distinct transitions related to excitons and excitons charged with up to five additional electrons, as well as neutral and charged biexcitons.

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Quantum confinement in low-dimensional semiconductors has been shown to profoundly affect Coulomb correlations among charge carriers. In two-dimensional (2D) quantum wells (QWs), enhanced electron-hole correlations yield stable excitons that dominate the optical absorption and emission spectra near the band edge [1]. In 1D quantum wires (QWRs), excitons play an even more important role due to the reduced Sommerfeld factor [2], and their dominance in optical spectra was observed across many interband transitions [3]. In quantum dot (QD) systems, the importance of Coulomb correlations varies considerably as a function of the dot size L due to the difference between the $1/L$ dependence of the Coulomb potential versus the $\sim 1/L^2$ dependence of the confinement energy. Many-particle states can dramatically change the electronic spectra of QDs compared to the simple-minded single particle picture of these fully confined states.

Experimentally, the role of Coulomb correlation and many-body effects in quantum nanostructures has been extensively studied using different techniques. Evidence for formation of few-electron states in QDs was provided by capacitance and by far-infrared spectroscopies [4]. Multiexciton states were observed in the luminescence spectra of QDs formed in QWs and QWRs due to interface disorder [5] and of QDs produced by Stranski-Krastanow island growth [6]. The formation of charged excitons in doped QWs was also reported [7]. In the present Letter, we report the observation of multicharged exciton states in the photoluminescence (PL) spectra of QDs with controlled structure and composition. The binding energies and PL fine structure of the multiparticle states incorporating up to six electrons are found to be in good agreement with a theoretical model.

Our QDs are fabricated by epitaxial growth on (111)B-oriented GaAs substrates patterned with an array of micron-sized tetrahedral recesses [8,9]. Deposition of AlGaAs/GaAs/AlGaAs QW layers results in the self-formation of a GaAs QD exactly at the sharp tip of each tetrahedral recess. Thus, each QD's position is precisely controlled by the placement of the recess patterns while its size is controlled by the growth parameters [10]. Based on atomic force microscopy (AFM) studies [11], we estimate the thickness and diameter of the approximately lens-shaped QDs discussed here to be 5 and 20 nm, respectively, which gives rise to an energy splitting of 45 meV between ground- and excited-state interband transitions. After growth, we remove the GaAs substrate from our samples and obtain upright-standing pyramids with the QD embedded within the pyramid tip [Fig. 1(a)]. For luminescence measurements, we use a standard microscopic PL (μPL) setup with a $\leq$1-μm-diameter Ar^+-ion laser spot, which can be easily centered on a single pyramidal structure, thus permitting the selection of a single QD.

In the present study, the QDs are modulation doped due to a uniform background doping of the AlGaAs

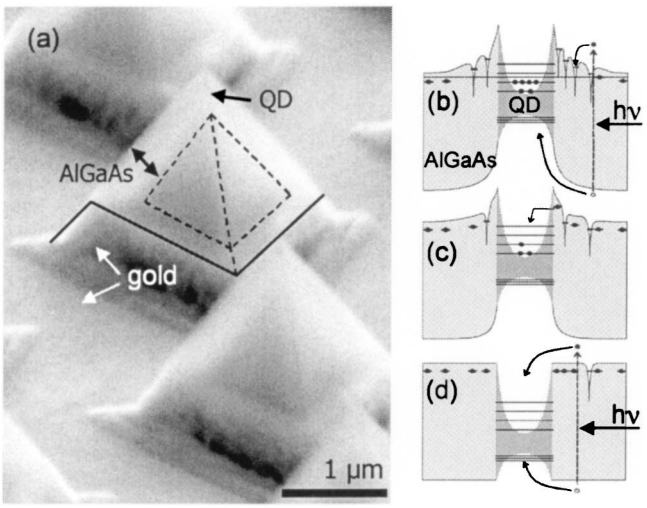

FIG. 1. (a) Scanning electron microscope image of pyramidal QD structures after the back-etching process. (b)–(d) Schematical illustrations of the mechanisms of (b) photodepletion, (c) back hopping of electrons, and (d) total depletion of the QD at high excitation power levels.

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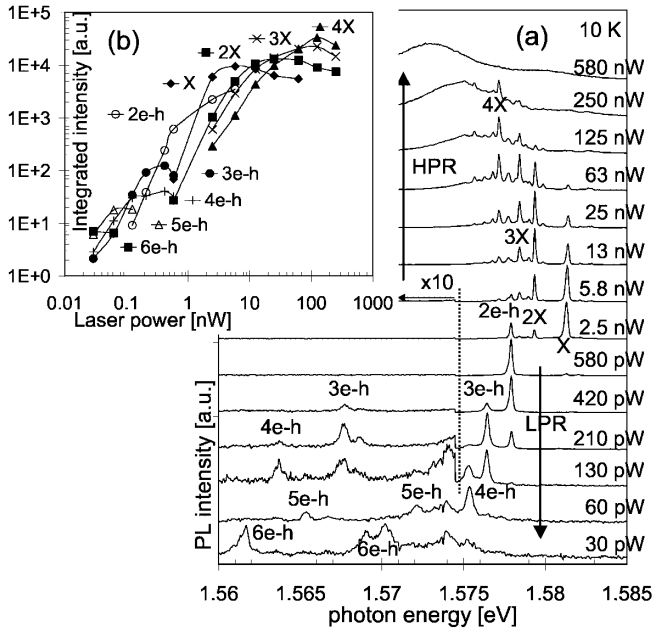

FIG. 2. (a) Excitation power dependent evolution of the PL spectrum of a single QD. A number of characteristic transitions for different multiparticle configurations in the QD are identified (see text). The intensities are normalized for better visibility. In order to underline the absence/presence of low energy satellite peaks for the $2e$-h/$3e$-h transitions, respectively, the intensities of the spectra left of the dashed, vertical line have been enhanced by a factor of 10. (b) Integrated PL intensity of the different characteristic transitions.

barrier ($x_{\mathrm{Al}} = 0.45$) obtained by organometallic chemical vapor deposition at the growth conditions used. The doping concentration is estimated from reference samples to be $n \approx 10^{16}$–10^{17} cm^{-3}. To control the number of electrons in the QDs, we rely on the photodepletion (or negative photoconductivity [12]) effect. Here, an electron-hole pair photocreated in the AlGaAs barrier separates due to the space charge field around the charged QD. The hole is attracted by the charged QD and subsequently recombines with a QD electron by emitting a photon, while the electron neutralizes one of the ionized donors in the AlGaAs barrier [Fig. 1(b)]. Thus, photodepletion removes electrons from the QD at a rate $r_{\mathrm{depl}} \sim P_{\mathrm{exc}}$ depending on the absorbed laser power P_{exc}. Second, in order to reestablish equilibrium, the electron bound at donors *hop back* into the QD with thermally activated rates $r_{\mathrm{hop}}(i)$ depending strongly on the distance of each donor i to the QD [Fig. 1(c)] [13]. Thus, for each excitation power P_{exc}, the competition between photodepletion r_{depl} and back hopping $r_{\mathrm{hop}}(i)$ will determine the stationary QD charge $n_{\mathrm{stat}}(P_{\mathrm{exc}})$. However, since the back-hopping rates $r_{\mathrm{hop}}(i)$ depend sensitively on the exact impurity configuration, $n_{\mathrm{stat}}(P_{\mathrm{exc}})$ will be unique for each QD. With increasing P_{exc} the QD will be continuously depleted until finally all charges are removed [Fig. 1(d)].

Figure 2(a) shows a typical excitation-power-dependent evolution of the ground state transition of a single QD. In this evolution, two complementary regimes are observed. The low power regime (LPR, $P_{\mathrm{exc}} \leq 2.5$ nW) is characterized by a global blueshift of the QD transitions, and the high power regime (HPR, $P_{\mathrm{exc}} > 2.5$ nW) by a redshift. An upper estimate of the average number of excitons in the QD as a function of excitation power is given by $N_X \approx 0.06 P_{\mathrm{exc}}$ excitons [14]. In the LPR, N_X is very small ($0.0017 \leq N_{X,\mathrm{LPR}} \leq 0.34$) and the integrated QD PL intensity I_{QD} increases almost linearly with the excitation power, $I_{\mathrm{QD}} \propto P_{\mathrm{exc}}$ [Fig. 2(b)]. We thus conclude that the strong spectral evolution in the LPR cannot be due to multiexcitonic effects. We tentatively ascribe the level shifts in the LPR to the change in the number of surplus electrons. In what follows, this interpretation will be confirmed by our detailed few-particle calculations, which show that the optical spectrum must change whenever an additional carrier is added to the dot because of the resulting additional Coulomb interactions. However, in the HPR multiexciton effects are believed to govern the spectral evolution since both N_X is rather high ($0.34 < N_{X,\mathrm{HPR}} \leq 33$) and I_{QD} saturates in this regime [Fig. 2(b)].

The following observations show that the LPR is indeed governed by the photodepletion/back-hopping mechanism. First, using a red Ti-sapphire laser, we could selectively excite only the GaAs material in our samples, virtually turning off the mechanism of photodepletion. In such power-dependent measurements, the pronounced spectral evolution in the LPR is absent (not shown here; see Ref. [14]). Thus, photodepletion is essential for the occurrence of this spectral evolution. Second, we performed two-color time-resolved pump and probe PL measurements revealing relaxation times in the ms range for the spectral changes observed in the LPR [15]. This is a clear indication for the importance of the slow back-hopping process. Finally, we mention the influence of temperature on the spectral evolution in the LPR. Figure 3(a) shows the 10-K spectral evolution obtained from another single QD of the same sample. Here, the blueshift observed in the LPR is much less pronounced than for the QD studied in Fig. 2(a), in spite of the larger range of excitation powers involved. Within the photodepletion/back-hopping model, this indicates a smaller change in $n_{\mathrm{stat}}(P_{\mathrm{exc}})$ and an almost complete depletion already at low P_{exc}. We therefore assume that for this specific dot the QD-donor distances are larger, leading to smaller back-hopping rates $r_{\mathrm{hop}}(i)$. Thus, increasing the temperature should enhance $r_{\mathrm{hop}}(i)$, giving rise to larger $n_{\mathrm{stat}}(P_{\mathrm{exc}})$ at low P_{exc} and consequently to a more pronounced blueshift with increasing P_{exc}. This is exactly what we observe in the 40-K spectra of Fig. 3(b). More quantitatively, we find similar spectra for $P_{\mathrm{exc}} = 3$ pW at 10 K and $P_{\mathrm{exc}} = 7$ nW at 40 K indicating a strong ($\sim$1000-fold) enhancement of the $r_{\mathrm{hop}}(i)$ with increasing temperature. To summarize this point, the dependence on excitation wavelength, the temporal evolution, and the influence of temperature all indicate that the model of photodepletion/back-hopping is appropriate for describing the observed LPR.

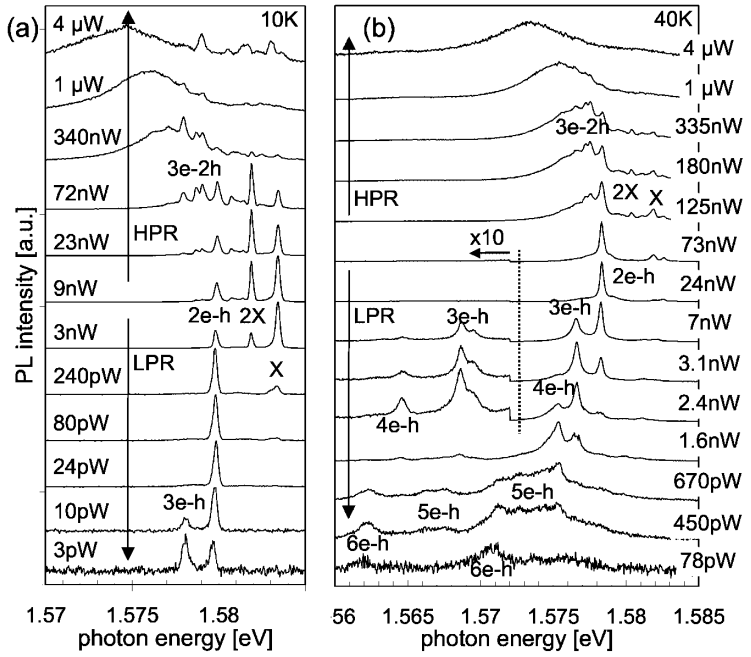

FIG. 3. (a) 10 K excitation power-dependent PL evolution of different single QD than shown in Fig. 2. (b) Same QD as in (a) measured at 40 K (see also caption of Fig. 2).

Next, we address the question whether the fine structure in the LPR is governed by *intrinsic* QD multiparticle interactions or by *extrinsic* QD-impurity interactions. Such extrinsic effects could be Stark shifts or modifications of the optical selection rules due to deformations of the QD-confined wave functions by electric fields of ionized impurities close to the QD. Since intrinsic factors depend only on the QD potential, they should be reproducible from QD to QD. Extrinsic factors, on the other hand, depend on the exact impurity configuration and are therefore not reproducible. Thus, we have compared the evolution of the LPR fine structure of many QDs grown on the same patterned substrate and present here as an example those of Figs. 2, 3(a), and 3(b). All QDs exhibit indeed remarkably similar evolutions in the LPR. We can identify in both samples of Figs. 2 and 3 a number of characteristic peaks or peak multiplets appearing at lower energies as the excitation power is reduced. The numbers and relative energetic positions of the individual peaks with respect to the highest energy transition X are identical (within 0.5–1 meV) for the two QDs presented in Figs. 2 and 3 as well as for the ten other QDs which we studied in detail. Hence, these peaks or peak multiplets are intrinsic to the QD and can therefore be attributed to specific multiparticle configurations. With increasing excitation power, electrons are sequentially removed from the QD via the photodepletion/back-hopping mechanism. We therefore attribute each peak or peak multiplet to a certain electron occupation of the QD.

To investigate the multiparticle states of single dots, we performed detailed theoretical calculations. We start from the single-particle states, which are derived by numerically solving the 3D single-particle Schrödinger equation within the envelope-function and effective-mass approximations. The QD confinement is assumed to have cylindrical symmetry, with the shape of the confining potential obtained from the experimental AFM data [11]; for the conduction- and valence-band offsets we use material parameters for GaAs/AlGaAs. Without further adjustment of parameters, we obtain an energy level splitting of approximately 30 meV for electrons and 10 meV for holes. Next, the many-particle Hamiltonian (containing all possible electron-electron, electron-hole, and hole-hole Coulomb matrix elements) is expanded within the basis of the ten energetically lowest single-particle states for electrons and holes, respectively. Keeping the ~100 Slater determinants of lowest single-particle energies for electrons and holes, respectively, we obtain the many-particle states by direct diagonalization of the Hamiltonian matrix. This approach is similar to those presented in Refs. [16,17] and will be discussed in detail elsewhere.

Figure 4 shows luminescence spectra as computed for different numbers of electrons and holes (see expressions on the right-hand side of each spectrum) [17]. For a single electron-hole pair confined in the QD [X, Fig. 4(c)], the luminescence originates solely from the decay of the ground-state exciton. Our calculations reveal an energy splitting between the (occupied) exciton ground state and the (unoccupied) first excited exciton state of 43 meV; this value matches well the experimentally observed features from higher shells and further supports our theoretical choice of the confining QD potential. In the HPR, we observe the appearance of a biexcitonic line [B, Fig. 4(b)] which is shifted by ~2 meV to lower photon energies; a further redshift is observed for the decay of the charged biexciton [$3e$-$2h$, Fig. 4(a)]. In the LPR [Figs. 4(d)–4(h)], the QD is populated by only one hole and multiple electrons.

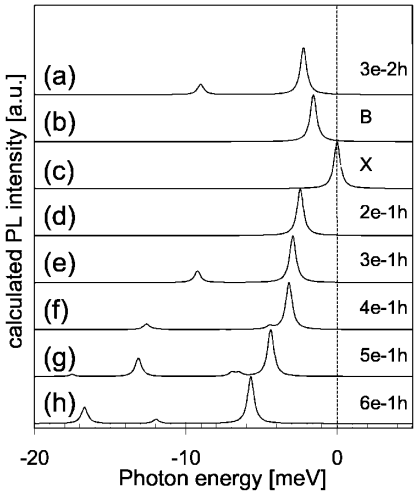

FIG. 4. (a)–(h) Calculated spectra for different multiparticle configurations in the QD; photon energy zero is given by the ground state exciton X. In the calculation of the luminescence spectra we assume that before photon emission the interacting electron-hole states are occupied according to a thermal distribution at temperature $T = 10$ K, and we introduce a small broadening of the emission peaks accounting for interactions with the dot environment (e.g., phonons, additional carriers in the surrounding).

When increasing the number of electrons, the main emission peaks in the optical spectra monotonically redshift as a consequence of the modified interactions [18,19], and additional peaks appear on their low-energy side.

We used the good agreement between the theoretical results (Fig. 4) and the experimental spectra to identify the transitions due to the different multiparticle states (as marked in Figs. 2 and 3). For example, in both the theoretical as well as in the experimental spectra, the excitonic line X is followed in the LPR by a strongly shifted, single line ascribed to the charged exciton $2e$-h. At still lower powers, a weaker shifted line $3e$-h with a weak satellite appears at lower energies, and so on. Charged exciton states with up to five electrons can thus be identified in the optical spectra. We attribute the minor differences regarding the peak positions in the experimental and theoretical spectra (Figs. 2, 3, and 4) to the uncertainties regarding the detailed shape of the QD confinement potential. Finally, to clarify the role of electric fields of ionized impurities on the few-particle states we have additionally performed model calculations for a dot potential modified by an impurity in the surrounding and have found only minor variations in the optical transition energies (e.g., less than 1 meV for a dot-impurity distance of 10 nm) [20].

In conclusion, we have presented an experimental and theoretical investigation of modulation-doped single QDs. We have demonstrated that the mechanism of photodepletion/back-hopping can be efficiently used to control the number of electrons in the QD. The evolution of single-QD PL spectra as a function of excitation power was shown to be governed by intrinsic QD-multiparticle effects. The comparison with theoretical spectra allowed us to identify the different characteristic transitions of each QD-multiparticle state. In particular, we have observed the formation of charged QD exciton states obtained by sequentially adding electrons to the QD.

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[20] Such small shifts of the optical transition energies allow us to explain the experimentally observed spectral narrowing of emission peaks in Fig. 2: With increasing P_{exc} more impurities in the vicinity of the QD remain neutralized or are screened by additional photoexcited carriers in the barrier, leading to smaller electric-field fluctuations at the QD.