Photoluminescence of charged InAs self-assembled quantum dots

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We have used capacitance and photoluminescence spectroscopy to study the optical properties of charged InAs self-assembled quantum dots. When the dots are loaded with electrons, the ground-state transition in the photoluminescence spectra shows a redshift of about 15 meV accompanied by a decrease in intensity and a broadening. In addition, an excited-state transition appears. All the observations mentioned above are attributed to many-body effects caused by charging of the quantum dots with electrons. The observed changes of the photoluminescence signal are also discussed in terms of field effects. [S0163-1829(98)06731-9]

The Stranski-Krastanow growth mode provides a simple technique to fabricate zero-dimensional (0D) quantum-dot systems with excellent optical and electronic properties.[1,2] One of the most intensively studied material system is the InAs/GaAs system.[3–5] Here, small coherently strained InAs islands form on top of a ≈1.5-(ML)-thick InAs wetting layer during the InAs deposition on (100) GaAs substrate. When covered by a wider band-gap material, these islands are transformed into quantum dots (QD's). Due to the small size of these coherently strained islands[6,7] and the absence of electronic traps, 0D quantum effects are clearly observable. The δ-functional line shape of the density of states,[3,4] the Coulomb blockade,[2,8] and hints for the phonon bottleneck[9–11]—characteristic features of a 0D system—have been already demonstrated in this system. However, little is known about the influence of Coulomb effects on the excitonic properties in charged InAs QD's.[12–16]

Combining photoluminescence (PL) and capacitance (C-V) spectroscopy we are able to study the optical properties of charged QD's in a metal-insulator-semiconductor field-effect-transistor (MISFET) device. In this structure the number of electrons in the QD's can be controlled by an external applied bias and detected by C-V spectroscopy. Thus, the PL signal measured under different bias conditions reflects directly the optical properties of excitons in a charged 0D system.

The sample under investigation has been grown in a Varian GEN II molecular-beam epitaxy system under an As pressure of 1×10^{-5} Torr. All material besides the InAs was deposited at 600 °C. In order to smooth the surface roughness of the (100) semi-insulating GaAs substrate, a thick GaAs buffer layer, a 160-nm-thick GaAs/AlAs (2 nm/2 nm) short-period superlattice (SPS) and 10 nm GaAs have been deposited. The back contact is formed by 20-nm Si-doped GaAs ($n_D=4\times10^{18}$ cm^{-3}). The InAs QD's are separated from the doped region by 20 nm of intrinsic GaAs. In order to achieve the formation of the InAs wetting layer (WL) and the QD's, 1.6 ML InAs have been deposited at a growth temperature of 530 °C and at a growth rate of 0.085 ML/s. The QD's have been capped with 5-nm GaAs before the temperature was ramped up again to 600 °C for further deposition of 25-nm GaAs. An additional 36-nm-thick GaAs/AlAs (2 nm/2 nm) SPS and a 4-nm-thick GaAs cap layer have been grown to reduce the leakage current and to prevent the sample from oxidation. A Ni-AuGe alloy annealed at 400 °C for 120 s gives contact to the n-doped region. The front contact is formed by 15 nm Cr followed by 10-nm Ni and 200-nm Au.

Due to the nontransparent front contact, the sample was pumped from the back side by a Ti sapphire laser with an energy of 1.3 eV. For this energy the GaAs substrate and the cladding layers of the InAs QD's are transparent and the electron-hole pairs are excited resonantly into higher QD levels. The focus and the position of the laser beam was checked by a charge-coupled device camera. The emitted light was collected from the back side of the sample and guided through a 0.8-m double spectrometer (resolution: 0.5 nm). The PL signal was detected by a liquid-nitrogen-cooled Ge detector.

In order to ensure that only the PL signal of QD's in the contact region contribute to the signal taken by the lock-in amplifier, we did not modulate the exciting laser beam but the bias (U) applied to the diode under investigation between a low level U_L and a high-level U_H. Thus, the PL signal from QD's excited by scattered laser light does not contribute to the detected signal. The measured signal directly reflects the bias-induced change of the PL signal originating from the QD's below the Schottky contact. The light from the unmodulated part of the sample was eliminated with this technique.

Figure 1 shows the PL signal measured at different applied bias, i.e., different field and charging conditions. The PL spectra have been normalized to the QD ground-state transition. A schematic band structure of the investigated sample at zero applied bias is shown in the inset of Fig. 1.

At $U=0$ V, only the PL signal of the ground-state transition is clearly observable at $E\approx1.05$ eV. The Gaussian line

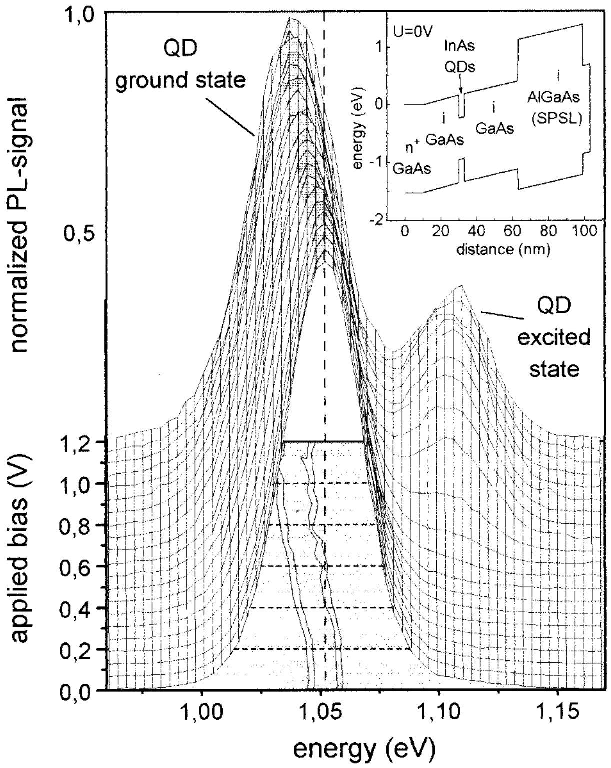

FIG. 1. Photoluminescence data measured at different applied bias U_H at $T=10$ K. The QD's were pumped resonantly with 20 mW of a Ti/sapphire laser at 1.3 eV ($U_L=-3$ V). The spectra are normalized to the QD ground-state transition. A constant offset is added for clarity. The contour lines are a projection of the energetic position of the QD ground-state transition into the energy plane. The inset shows a schematic of the band diagram of the investigated sample at $U=0$ V.

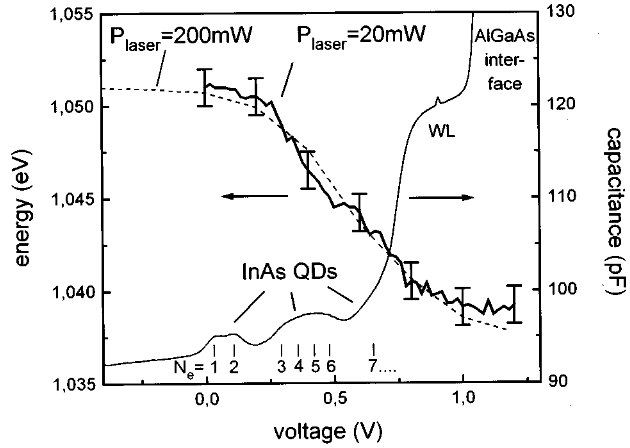

FIG. 2. Dark capacitance spectrum (thin solid line) measured at 4 K with a modulation amplitude of 5 mV and a modulation frequency of 500 Hz (right axis). N resembles the number of electrons in each QD. The thick solid line and the dashed line depict the energetic position of the ground-state QD transition at a pump intensity of 20 mW ($U_L=-3$ V) and 200 mW ($U_L=-1.2$ V), respectively versus applied bias U_H (left axis). Apart from the pump intensities and U_L the experimental conditions are the same as in Fig. 1.

shape reflects the size distribution of the QD's.[17] Since higher excited-state transitions do not appear in the spectrum at $U=0$ V, carrier relaxation is faster than radiative recombination processes and saturation of the QD ground state is not achieved for the pump laser intensity of 20 mW in the investigated sample. With increasing forward bias a shift of the ground-state transition to lower energies is observed. This is in good agreement with the data presented in Ref. 15. In contrast to PL, the absorption technique used in Ref. 15 is an excellent tool to study the ground- and excited-state transitions of a neutral QD but it is not possible to observe the QD ground state for $N>1$ in such spectra (N is the number of charging electrons in the dot). With PL, however, the shift of the QD ground-state transition can be investigated also in a highly charged system. At high charging conditions the full width at half maximum of the QD ground-state transition increases from 33 to 38 meV (Fig. 1) accompanied by a decrease in intensity by a factor of 2. In addition to the QD ground state, a higher excited-state transition appears in Fig. 1 at $E\approx1.11$ eV for $U>0.55$ V, which gains in intensity with increasing forward bias.

In order to explain these effects we investigated the capacitance spectrum of our sample (Fig. 2). For $U<0$ V all QD levels are above the Fermi level and the C-V signal in Fig. 2 is determined by the geometry of the sample and the doping concentration in the back contact. At $U\approx0.03$ V the ground state of the QD's is shifted below the Fermi level and the first electron tunnels from the back contact into each QD. Since the QD's are now negatively charged with one electron, additional energy is necessary to get a second electron from the back contact into the dots. This process is described by the second peak in the C-V trace at $U\approx0.1$ V. Due to Coulomb blockade and confinement effects the tunneling of the third, fourth, fifth, and sixth electron into the QD's is reflected by the broad shoulder between $0.3\text{ V}<U<0.5$ V.[2] At $U>0.6$ V the d shell is gradually filled with electrons and finally at $U>0.8$ V tunneling into the 2D WL system occurs resulting in a strong increase of the C-V signal. For $U>1.4$ V a 2D electron gas is formed at the interface between the GaAs intrinsic region and the GaAs/AlAs front barrier.

Since the carrier relaxation times are a few hundred ps,[9,10] the lifetimes of QD excitons are ≈1 ns (Refs. 9 and 10) and tunneling times are of the order of ms, the optically excited carriers remain in the QD's and recombine for $U>0$ V.[18] This is confirmed by photocurrent measurements done on the same sample.[16] Consequently, there is no optically induced band bending and the C-V signal is barely affected by the illumination for $U>0$.[16] Thus, it is possible to determine the charge in a QD's in dependence of the applied bias even under illumination.

Besides the C-V spectrum, Fig. 2 depicts also the energetic position of the QD ground-state transition versus the applied bias determined for a pump intensity of 20 and 200 mW, respectively. As already mentioned in the discussion of Fig. 1, a redshift of the QD ground-state PL occurs with increasing forward bias. Since the voltage-induced shift of the QD ground state does not depend on the pump intensity, we assume that the experiments are done in a regime where the dynamics of the optically excited carriers and of the electrically injected electrons do not interfere. As can be seen from Fig. 2, a redshift of the PL ground-state transition of up to ≈15 meV is observed only when the QD's are charged with electrons from the back contact. For $U>0.8$ V and U

>1.1 V a 2D electron gas is formed in the wetting layer and at the $Al_xGa_{1-x}As$ front barrier interface, respectively. In this voltage regime, a change in the external bias barely affects the charging conditions of the QD's and the redshift of the ground-state transition saturates. Below $U=0$ V, the QD levels are above the Fermi level and no charging of the QD's from the back contact occurs. Again, the energetic position of the QD ground-state transition remains constant. Thus, the charging process in the voltage regime $0<U<0.8$ V seems to be responsible for the observed increase of the exciton binding energy in InAs QD's.

Our experimental observations agree very well with the calculations published in Ref. 13 by Wojs and Hawrylak. In neutral QD's the PL energy $h\nu$ of the QD ground-state transition is given by $h\nu = E_{00} - E_X$. E_{00} is the transition energy between an electron and a hole (both in the QD ground state) in the single-particle model and E_X is the exciton binding energy. In negatively charged QD's however, the exciton interacts with the additional electrons injected from the back contact. The transition energy changes to $h\nu^* = h\nu + E_{ee} - E_{eh} + E_{\mathrm{exchange}}$. The Coulomb energy E_{ee} is caused by the repulsive interaction between the optically excited electron and the charging electrons. The attractive term E_{eh} reflects the Coulomb attraction between the photon generated hole and the additional electrons. In a first approximation E_{ee} and E_{eh} are similar and a charged-induced energy shift of the QD ground-state PL signal is mainly determined by the exchange energy term E_{exchange}.[13] According to Ref. 13 E_{exchange} is negative and a redshift is observed for negatively charged QD's. Also the theoretically predicted broadening of the ground-state PL signal and its decrease in intensity are reproduced well by our experiments.

However, not only the number of electrons in the dot but also the electric field in the QD region is changed with the applied bias. As it is already well known from the quantum confined Stark effect (QCSE), such a field change might also affect the energetic position of the QD PL signal. In quantum-well (QW) systems, a redshift of the PL signal occurs when the electric field is increased.[19] Assuming a lens shape effective QD potential,[20] a blueshift is expected from theory when the internal electric field is decreased in a QD system. However, we observe a redshift for $U>0$ V in our experiments (Figs. 1 and 2). Furthermore, a field-induced energy shift should be weak since the height of the QD's in field direction is only ≈3 nm. Due to the weak internal fields ($<1\times10^4$ V/cm) and the strong dependence of the QCSE on the dimension L of the quantum structure in field direction [$\sim L^4$ for QW's (Ref. 19)] field effects should be negligible in the investigated QD structures.

In order to confirm this interpretation, we have measured the intensity of the QD PL signal at three fixed detection energies in dependence of the applied bias (Fig. 3). Trace 1 has been taken at the low-energy side ($E_1=1.04$ eV), trace 2 at the maximum ($E_2=1.06$ eV), and trace 3 on the high-energy side ($E_3=1.07$ eV) of the Gaussian PL ground-state transition (see inset of Fig. 3 and Fig. 1, $U=0$ V). At high reverse bias ($U>-0.9$ V) most of the optically excited carriers are extracted from the QD's by the high internal electric field in the intrinsic region. The field is even strong enough that the holes can tunnel through the front barrier, which results in a strong photocurrent signal.[16] Consequently, the PL signal is weak and gradually decreases with increasing reverse bias (increasing internal field). More and more carriers leave the QD's at higher fields and are lost for radiative recombination processes. For $-0.9\,\mathrm{V}<U<0$ V electrons and holes are still able to leave the QD's but now the holes are blocked by the $Al_xGa_{1-x}As$ front barrier and form a 2D hole gas at the $GaAs/Al_xGa_{1-x}As$ interface. This hole accumulation results in a band bending and a reduction of the electric field in the QD region until steady state is reached. Additional optically induced electron hole pairs remain in the QD's and recombine. Thus, the PL signal increases. As soon as charging of the QD's takes place at $U>0$ V a change of the relative intensities between traces 1, 2, and 3 is observable in Fig. 3. Due to the redshift of the QD ground-state PL in this voltage regime, the PL intensity at 1.04 eV (trace 1) increases while the signal at 1.06 eV (trace 2) and 1.07 eV (trace 3) decreases. It is important to note that a shift of the QD ground-state PL is always related to a change of the relative intensities between traces 1, 2, and 3, respectively. If field effects similar to the QCSE were responsible for the observed redshift of the QD ground-state feature, they should be present in the whole field range and should be most pronounced at high fields. However, at high reverse bias the energetic position of the QD transition is constant since there is no relative change of the PL intensity between traces 1, 2, and 3 observable. Thus, *charging and not field effects* seem to be responsible for the observed decrease in the transition energy of the ground-state PL signal.

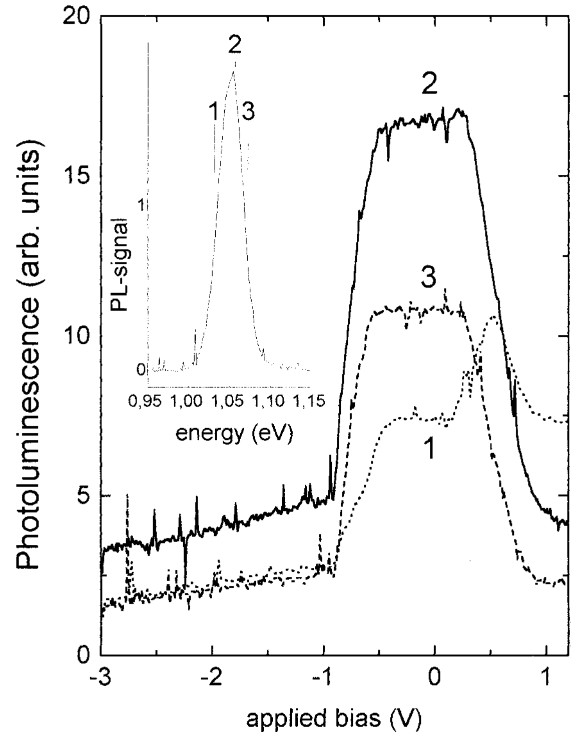

FIG. 3. Photoluminescence signal in dependence of the applied bias U_H measured at a fix detection energy of $E_{\mathrm{det}}=1.04$ eV (1), 1.06 eV (2), and 1.07 eV (3), respectively ($U_L=-4$ V). The sample was pumped with 200 mW under the same experimental conditions as described in Fig. 1. The inset shows the photoluminescence signal ($U_L=-3$ V, $U_H=0$ V) and the three different detection energies E_{det}.

Let us focus now on the excited-state transition that appears at high forward bias (see Fig. 1) at $E = 1.104$ eV. Up to an applied forward bias of $U \approx 0.5$ V only the PL ground-state transition is observable in Fig. 1. For such an applied voltage, however, the first excited electron level is already filled with electrons from the back contact (see Fig. 2). Since the intersubband relaxation process of the optically excited carriers is fast [tens of ps (Refs. 9 and 10)], holes are only available in the QD ground state (*s* character). Thus, the transition between the first excited electron state (*p* character) and the hole ground state (*s* character) seems to be forbidden, which is in good agreement with the model of a parabolic QD potential.[13,20] However, as soon as the electron *d* shell of the QD's is filled with electrons at $U > 0.6$ V a higher excited-state transition appears in Fig. 1. According to Ref. 13 we attribute this feature to a recombination process between an electron in the *d* shell (second excited quantum-dot state) with a hole in the *s* shell (ground state).

The magnetic momentum of the hole in the *s* shell is 0. Due to selection rules, only the recombination with an electron in the *s* shell is allowed in neutral QD with a parabolic QD potential. Since electrons in the *p* shell have a magnetic momentum of $m = \pm 1$, the recombination with the *s* hole ($m = 0$) is forbidden even in charged QD's. However, in the electron *d* shell there exists a level with $m = 0$ besides two other ones with $m = \pm 2$, respectively. Due to Coulomb interaction, the transition between the *s*-shell hole ($m = 0$) and an electron in the *d* shell ($m = 0$) becomes allowed in negatively charged QD's. This results in a peak at higher energy.[13] According to Ref. 13 the energetic distance between the QD ground-state transition and the s-d-shell transition should be about twice the energy splitting of the electron levels in the QD's ($\approx$90 meV). The experimentally observed value is smaller than the theoretically predicted one. However, it is possible that the parabolic potential used in the modeling is not adequate in this QD strained system.

In conclusion, we have studied the PL of charged InAs self-assembled QD's. A redshift of the QD ground-state PL of $\approx$15 meV is observed when the dots are loaded with electrons from the back contact. This redshift is attributed to many-body interaction between optically excited excitons and electronically injected electrons in the QD's. At the same time a decrease of the PL intensity appears that is attributed to a reduced oscillator strength of excitons in the charged system. Radiative recombination of electrons in the *p* shell with holes in the *s* shell seem to be weak since no PL above the ground-state PL appears when the *p* shell is filled with electrons from the back contact. Only when electrons tunnel into the *d* shell, an excited state transition appears at higher energies. Because of favorable selection rules, this transition becomes probable. More experiments and theoretical calculations are needed to confirm this interpretation.

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