Charged Excitons in Self-Assembled Semiconductor Quantum Dots

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(Received 2 September 1997)

Interband excitations of an ensemble of InAs self-assembled quantum dots have been directly observed in transmission experiments. The dots are embedded in a field-effect structure allowing us to load the dots electrically. We establish an exact correspondence between Coulomb blockade in the device's vertical transport properties and Pauli blocking in the transmission spectra. We observe substantial shifts, up to 20 meV, in the energies of the higher excitations on occupation of the electron ground state. We argue that this is a consequence of an exciton-electron interaction. [S0031-9007(97)04868-0]

PACS numbers: 73.20.Dx, 71.35.–y, 73.40.Rw, 78.66.Fd

A self-assembled semiconductor quantum dot confines electrons and holes on length scales down to 10 nm in all three directions. Such a dot can therefore be thought of as an artificial atom as the density of states (DOS) consists of a series of very sharp peaks [1,2]. Furthermore, the dots can be made extremely uniform so that this DOS is preserved to some extent in the DOS of an ensemble of millions of dots [3,4]. These artificial atoms can be expected to have significantly different properties from real atoms as the dots can be filled with both electrons and holes, and the nature of the confinement is completely different. A notable example is the absence of strong many-electron effects in intraband spectroscopy due to the approximately parabolic confining potentials [5]. Interband optics does not in principle suffer from the same restriction, yet the available data on self-assembled dots show very little evidence of carrier-carrier interactions. There are theoretical predictions of such effects, particularly for charged excitons [6,7]. In fact, for highly charged dots a variety of splittings and rearrangements of oscillator strength have been calculated [8]. An important issue is the appropriate experimental technique with which to investigate these phenomena.

The standard techniques, photoluminescence (PL) and the related photoluminescence excitation (PLE), have quite clearly yielded significant data on semiconductor quantum dots. This includes state filling at only moderate laser powers and measurements of extremely sharp lines from single dots [1–4]. However, PL has the disadvantage that higher levels cannot be probed without filling all the lower-lying levels. This problem cannot be circumvented easily with PLE as the signals are convoluted with a strong energy dependence of the carrier relaxation rate which makes it difficult to determine the electronic structure unambiguously [9,10]. In both cases, it is extremely difficult to relate the signal strengths to microscopic matrix elements. An alternative is to attempt to measure the absorption directly as has been reported using a calorimetric technique [2]. We report here absorption measurements through small changes in the intensity of light transmitted through the sample.

The sample for the present study was grown using the Stranski-Krastanow growth mode as described elsewhere [11]. The InAs dots are about 20 nm in diameter with a height of about 7 nm. A field-effect structure has been developed so that the dots can be controllably charged with electrons [12]. The dots are separated from a highly doped GaAs layer, the back contact, by 25 nm of intrinsic GaAs which acts as a barrier for electron tunneling from the back contact into the dots. A 100 nm thick GaAs/AlAs superlattice between the dots and the sample surface acts as a blocking barrier, preventing electron tunneling to the surface. The electron occupation of the dots can be controlled by applying a voltage, V_g, between a gate electrode and back contact and monitored with the device's capacitance [5,12,13]. The sample we used for the optical experiments has a $C - V_g$ profile as shown in Fig. 1. The doublet structure around $V_g \sim -0.75$ V corresponds to charging of the first dot level, $|0\rangle$, split into two by Coulomb blockade. The broad feature at ~ 0.0 V corresponds to charging of the second level, $|1\rangle$. By integrating the capacitance over the first peak we estimate the dot density to be $(5 \pm 1) \times 10^9$ cm^{-2}.

We measure the transmission of the device at 4.2 K with a Fourier transform spectrometer, an unbiased Ge *p-i-n* diode as detector, and a commercial current-voltage preamplifier. Our setup gives exceptionally good signal: noise ratios, $\sim 10^5$ in a few hours of integration time. The spot diameter was typically ~ 1 mm corresponding to $\sim 4 \times 10^7$ dots. For each gate voltage of interest we recorded a reference spectrum at a large and positive gate voltage where the dots are completely filled with electrons and the interband transitions blocked. This procedure removes the spectral response of the setup.

Figure 1 shows a transmission spectrum for $V_g = -1.4$ V, i.e., for electrically neutral dots. At energies

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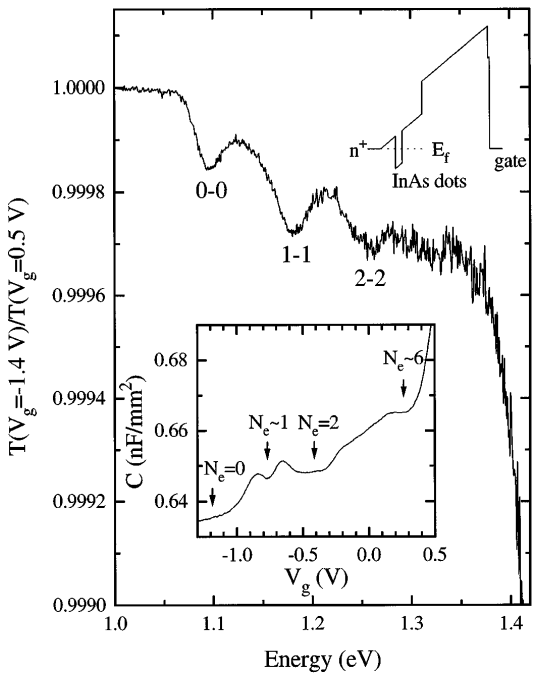

FIG. 1. The inset shows the conduction band profile of the device in the growth direction with Fermi energy, E_f. The capacitance, C, of the device at 4.2 K against gate voltage, V_g, is shown. Charging of the electron levels in the dots corresponds to peaks in the capacitance enabling the electron occupancy per dot, N_e, to be determined. The main figure shows the ratio of the transmission spectrum at $V_g = -1.4$ V to the spectrum at 0.5 V, also at 4.2 K.

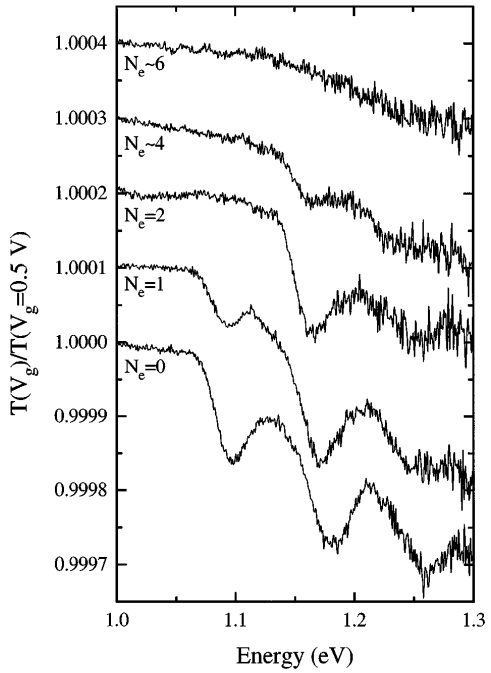

FIG. 2. Interband transmission spectra of the dot ensemble taken at $V_g = -1.2, -0.75, -0.4$, 0.0, and 0.2 V, all referenced to the spectrum at 0.5 V. The curves are labeled with the electron occupation, $N_e = 0$, 1, 2, 4, and 6, respectively, and are offset from 1 for clarity.

$\sim 1.1-1.3$ eV we observe three absorptions which we interpret as excitonic transitions between the states introduced by the lateral confinement of the dot. We denote the transitions as 0-0, 1-1, and 2-2. At higher energy a much larger absorption process sets in, probably caused by absorption in the wetting layer. The behavior on increasing V_g is shown in Fig. 2 where the curves are labeled with the electron occupation per dot, N_e, as determined from the capacitance. The 0-0 transition loses half its intensity at $N_e = 1$, and at $N_e = 2$ disappears altogether. The interpretation is that the Pauli exclusion principle forbids the 0-0 transition once the $|0\rangle$ level is fully occupied. At higher V_g, the 1-1 transition weakens and then disappears at $N_e \simeq 6$. The 2-2 line is more complicated: it persists to $N_e \simeq 4$ but at $N_e \simeq 6$ it is hard to say if the residual absorption comes from a broad 2-2 transition or from the background response. (The 2-2 could disappear if the $|2\rangle$ state is no longer bound at high N_e.) These observations establish the correlation between the dots' charge and Pauli blocking in the optical properties. Additionally, it can be seen that the spectra in Fig. 2 exhibit N_e-dependent shifts.

The main result is that the 1-1 transition shifts to lower energy on going from $N_e = 0$ to $N_e = 2$. At $N_e = 0$ and $N_e = 2$ the dot occupations are unambiguous. In the first case, all the dots are neutral. In the second case, the features in the capacitance corresponding to tunneling into the $|0\rangle$ and $|1\rangle$ states are very well resolved implying that to all intents and purposes every dot is loaded with two electrons at $V_g = -0.4$ V. It might be thought that the energy shift arises from the different vertical electric field applied in the two cases. We can rule this out from the absence of an appreciable V_g dependence at large and negative V_g where we change only the vertical field, not the occupation (Fig. 3). We therefore argue that the energy shift of the 1-1 transition arises from an interaction between the exciton and the two electrons in the electron ground state.

The lateral potential of the dots is very close to parabolic for both electrons and holes [14]. Spectroscopy in the far infrared has measured the electron single-particle separation to be $\hbar\omega_e = 49$ meV [5]. Taking the electron effective mass to be $m_e^* = 0.07m_0$ we have an effective length $L_e = \sqrt{\hbar/m_e^* m_0 \omega_e} = 4.7$ nm. This is much smaller than the excitonic Bohr radius and means that excitons in the InAs dots are "strongly confined"; i.e., the single-particle energies dominate over the Coulomb energies. We therefore attempt to account for the energy shifts by treating the Coulomb interactions as perturbations to the single-particle structure.

When a 1-1 exciton is excited in an occupied dot, there are additional contributions to the energy as compared to excitation in an empty dot. There is a positive Coulomb energy due to repulsion between the $|1\rangle$ electron and the $|0\rangle$ electrons. We denote this (direct) Coulomb

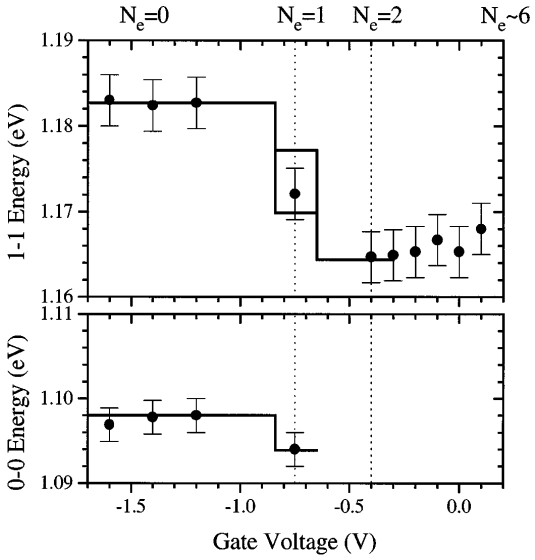

FIG. 3. The 0-0 and 1-1 transition energies against gate voltage. The solid lines are the perturbation theory results for a single dot.

interaction as E_c^{01}. This energy is reduced to some extent by the exchange interaction, E_x^{01}, between the $|1\rangle$ electron and one of the $|0\rangle$ electrons. Then there is a negative Coulomb energy from the interaction of the hole in the $|1\rangle_h$ state and the two $|0\rangle$ electrons, E_{eh}^{01}. Neglecting any exchange between the hole and the electrons, the shift in the 1-1 transition energy on twofold occupation of the $|0\rangle$ state is then $2E_c^{01} - E_x^{01} - 2E_{eh}^{01}$. Noting that the dots have a much smaller extent in the growth direction than in the lateral directions, the exciton and Coulomb energies can be calculated analytically by performing the appropriate integrals with the 2D harmonic oscillator wave functions. We give here the numerical results.

The Coulomb interaction $E_c^{00} = 29.2$ meV, in reasonable agreement with the value from $C - V_g$ [5,13]. The other direct Coulomb interaction $E_c^{01} = 21.9$ meV, less than E_c^{00} as the wave function overlap is reduced, and the exchange energy $E_x^{01} = 7.3$ meV. For the electron-hole interactions, we require the hole single-particle energy, $\hbar\omega_h$, and effective length, L_h, which we determine from the measured energy splittings between the neutral dot 0-0, 1-1, and 2-2 peaks. We find $\hbar\omega_h = 25$ meV and $L_h = 3.5$ nm, implying a hole mass of $0.25m_0$, and exciton energies $E_{eh}^{00} = 33.3$, $E_{eh}^{01} = 27.4$ and $E_{eh}^{11} = 22.3$ meV, which are very similar to the results of more sophisticated calculations [15,16]. We calculate an energy shift of -18.3 meV on complete occupation of the $|0\rangle$ state, in excellent agreement with the measured -18 ± 2 meV.

To investigate singly occupied dots we can apply $V_g = -0.75$ V where we can estimate from the $C - V_g$ that at least 80% of the dots are singly occupied ($\leq$10% have $N_e = 0$, and $\leq$10% have $N_e = 2$). The 0-0 energy is shifted by -4 ± 2 meV at $N_e = 1$ as compared to $N_e = 0$. A redshift has also been observed in photoluminescence on similar samples [17]. According to the perturbation theory, the energy shift is $E_c^{00} - E_{eh}^{00} = -4.1$ meV, in good agreement with the experiments. We note that the redshift implies that the X^- is bound (referenced to an exciton in one dot and a separate electron in an identical but well separated dot). This stems largely from the fact that $L_e > L_h$ in this system [6]. Further, the 1-1 transition is also shifted, by -10 ± 2 meV. The expected shift is $E_c^{01} - E_{eh}^{01}$ for $|0\rangle$ and $|1\rangle$ electrons of antiparallel spin, and $E_c^{01} - E_x^{01} - E_{eh}^{01}$ for electrons of parallel spin. We have neither spin polarization nor polarized light so we presumably see an average of the two energies, ~ -9 meV, again in good agreement with the experiment.

Figure 3 is a plot of the 0-0 and 1-1 transition energies and perturbation theory results against gate voltage. It can be seen how the 1-1 energy reduces at occupation 1 and then again at occupation 2, but is insensitive to further increases in electron occupation. This seems to reflect the shell structure of the dots. The possibility of studying highly charged exciton complexes is a particular advantage of self-assembled dots over quantum wells where the X^- is weakly bound [18] with a very limited number of excited states [19].

At voltages intermediate to those discussed so far we observe splittings and distorted line shapes [$V_g = -0.84$ and -0.65 V in Fig. 4(a)]. This can be understood as a consequence of the distribution of the dot occupancy. For instance, at $V_g = -0.84$ V we estimate that 50% of the dots are unoccupied and 50% singly occupied. The occupied dots have a down-shifted 1-1 resonance, causing the 1-1 line to split. The 0-0 line is distorted as the singly occupied dots absorb only half as strongly as the empty dots. Conversely, at $V_g = -0.65$ V, 50% of the dots are singly occupied and 50% doubly occupied, causing again a splitting in the 1-1 transition. At this voltage only the singly occupied dots can contribute to 0-0, the others being Pauli blocked, weighting the line in favor of the "high energy" dots.

The integrated absorption can be used to determine the oscillator strength per dot. For the 0-0 transition, the integrated absorption is $I_A = (5.2 \pm 0.2) \times 10^{-6}$ eV. In our geometry, $I_A = he^2Nf/2m_0\varepsilon_0 c(1 + \sqrt{\varepsilon_r})$ where the oscillator strength $f = 2|\langle p\rangle|^2/m_0E$. Any local field effects have been neglected. The density of absorbers, N, is twice the dot density for 0-0 so that the measurement translates into $f = 10.9$. The interband matrix element is dominated by the contribution from the Bloch parts of the wave function; in the strong confinement limit [20] one has $f = |\langle 0_h|0_e\rangle|^2E_p/2E$ where E_p is the Kane energy. Taking $E_p = 25.7$ eV, the GaAs value, and the wave functions as discussed above, we calculate $f = 10.7$, in excellent agreement with the experiment.

The interband transitions are inhomogeneously broadened. The dominant broadening arises from fluctuations in the dots' thickness which give rise to a Gaussian

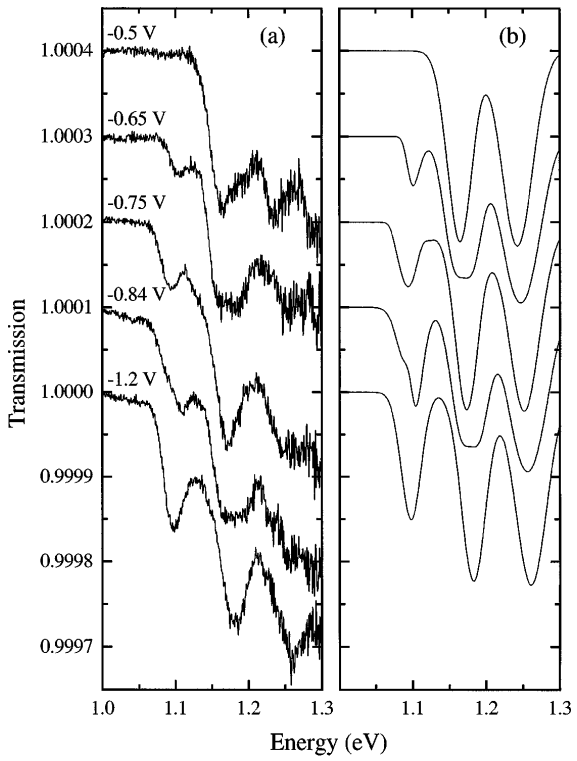

FIG. 4. Measured (a) and simulated (b) transmission spectra at several gate voltages. The curves are offset in multiples of 0.0001 for clarity.

distribution (width Γ_0) in the conduction band ground state energy, E_0, with respect to the Fermi energy. We determine Γ_0 from the $C - V_g$ trace. The thickness fluctuations broaden the interband spectra by $(1 + \alpha)\Gamma_0$, the contribution $\alpha\Gamma_0$ due to the holes. Furthermore, fluctuations in the lateral size of the dots also broaden the interband transitions. We postulate that for each E_0 the single-particle energy $\hbar\omega_e + \hbar\omega_h$ has a Gaussian distribution (width Γ_1). The interband transitions for empty dots then have widths $\sqrt{(1 + \alpha)^2\Gamma_0^2 + (i\Gamma_1)^2}$ with $i = 1, 2, 3$ for 0-0, 1-1, and 2-2, respectively. For occupied dots, the E_0 distribution can be divided into regions corresponding to different N_e. For each N_e we calculate the transmission from a convolution of the two Gaussian distributions (describing the vertical and lateral size fluctuations) including the N_e-dependent intensities and shifts. We take α and Γ_1 as fit parameters but otherwise use the results of the calculations for the overlap integrals and energy shifts. The results [Fig. 4(b)] can be seen to reproduce the measured spectra very well. The noticeable discrepancy is that the transmissions at the 1-1 and 2-2 resonance energies are much lower in the measurements than in the simulations. This probably comes from the tail of the absorption at higher energy.

In conclusion, we have demonstrated that interband absorption in self-assembled quantum dots can be observed directly in transmission experiments. We show how the Coulomb interaction between excitons and electrons in the dots can drastically alter the transition energies. The homogeneous widths of the interband transitions are typically ≤ 100 μeV [1,2], in which case we can predict large (several %) changes in transmission if the light is concentrated over a single dot. Furthermore, the many-particle shifts should completely dominate over the homogeneous widths. We hope therefore that our results will motivate transmission experiments on single dots.

We would like to thank A. O. Govorov for some very helpful comments and suggestions and S. Huant for critically reading the manuscript. The work was funded by the DFG (SFB 348), by QUEST, a National Science and Technology Center (Grant No. DMR 20007), and by the BMBF (Max Planck Research Award). J. P. K. would like to thank the staff at QUEST for their hospitality.

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