PHYSICAL REVIEW B, VOLUME 65, 121314(R)

Few-particle effects in single CdTe quantum dots

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(Received 21 July 2001; revised manuscript received 14 November 2001; published 14 March 2002)

Optical emission from individual, *n*-type modulation-doped CdTe quantum dots (QD's) is presented. Magnetomicrophotoluminescence and power-excitation-dependent measurements allows one to identify the neutral exciton, the negatively charged exciton, and the biexciton. All these few-particle species are exposed to randomly fluctuating electric fields attributed to charges trapped in the vicinity of the QD. The resulting quantum confined Stark effect, characteristic for each quantum dot, is analyzed in detail. The correlations between the emission energies of the neutral and charged exciton as well as between their integrated intensities confirm the identification of the charged species. The binding energies of the biexciton and charged exciton decrease sharply with the magnitude of the local electric field.

DOI: 10.1103/PhysRevB.65.121314 PACS number(s): 78.67.Hc, 78.55.Et, 73.21.La

The discrete atomiclike density of states of semiconductor quantum dots (QD's) is of considerable interest for ultimate nanoelectronics or optoelectronics devices. For example, QD's are expected to become the active region in single-electron memories or single-photon sources. But the small number of carriers involved in the operation of such devices will make them very sensitive to local fluctuations in the solid-state environment. For instance, fluctuation with time of electric fields created by localized carriers will lead to broadened emission lines even for individual QD's.[1] And impurities in the neighborhood of a dot can provide a source of doping as well as changing the discrete energy levels via additional Coulomb interaction.[2]

In this paper we report a study of charged- and neutral-exciton complexes in the microphotoluminescence (μPL) spectra of single CdTe QD's. The charged exciton, whose recombination emission appears between the emission lines of the exciton and of the biexciton, is identified by magneto-μPL measurements. The excitation power dependences of the exciton, the biexciton, and the charged exciton are measured and analyzed. Randomly fluctuating Stark shifts of the emission lines are recorded and are attributed to the electric field of carriers trapped near the QD's. The perfect synchronization in the Stark shifts of the three excitonic peaks in the spectrum enable us to assign them to the same QD. We find a perfect anticorrelation of the charged exciton and exciton intensities under fluctuating electric field. Analysis of the energy difference between the QD's emission lines reveals a significant electric-field dependence of the Coulomb correlation in the excitonic complexes. The binding energy of the biexciton and of the charged exciton both decrease with increase of the local electric field. This has a particularly pronounced effect on the charged-exciton transition, which is blueshifted by the electric field.

The samples for the present study consist of a CdTe layer 6.5-ML-thick embedded in ZnTe barriers and grown by atomic-layer epitaxy on a ZnTe substrate. The QD structure is formed by CdTe-rich regions of about 10 nm size in the ZnTe matrix, as revealed by compositional analysis of transmission electron microscopy (TEM) images.[3] To introduce excess electrons in the CdTe layer, a plane of aluminum donors with nominal concentration $N_{\mathrm{Al}}=4\times10^{11}$ cm^{-2} is grown after a 300-Å spacer. Due to compensation effects in the ZnTe barriers, only a fraction of donor electrons transfer into the QD's in the CdTe layer. Once electrical equilibrium is reached, the carriers in the CdTe layer are submitted to an average electric field created by the ionized donors in the doping plane.

Single dots are isolated for investigation by fabricating submicron apertures in an opaque aluminum mask using electron-beam lithography and wet etching. The sample is excited nonresonantly in the ZnTe barriers by the 488-nm line of an Ar^+ laser. The PL collected from the submicron apertures through a microscope objective is dispersed by a 1-m monochromator (0.07-meV resolution) and detected by a cooled charged coupled device camera.

Figure 1 shows typical μPL spectra of a single QD measured at 4 K through a 0.25-μm-diameter aperture. At low excitation density ($P_{ex}\approx5$ W cm^{-2}), the emission consists of three major lines labeled X, X_d, and X^-, and an additional weak line (X_2) on the low-energy side of the spectrum.

Measurements of the laser power dependence (inset of Fig. 1) allow clear assignment of peak X and peak X_2 to the optically active exciton and to the biexciton, respectively. With increasing excitation density, peak X gains intensity linearly at first, reaches a maximum, and then falls sharply for higher excitation. Peak X_2, which emerges 13.1 meV below X, gains intensity quadratically at low excitation density and saturates as X disappears. Similar behavior has now been observed in various QD systems[4–7] and is regarded as the fingerprint of exciton and biexciton emissions.

The line labeled X_d on the low-energy side of the excitonic emission is observed in most of the investigated QD's but only for very low excitation density. We have attributed it to the emission of the dark-exciton states $J_z=\pm2$, by doing magneto-optical measurements.[8,10] The energy difference $\delta_0=0.95$ meV between these two lines X and X_d corresponds to the electron-hole exchange energy that is enhanced from the bulk CdTe value[9] ($\delta_0\approx0.07$ meV) by the quantum confinement.

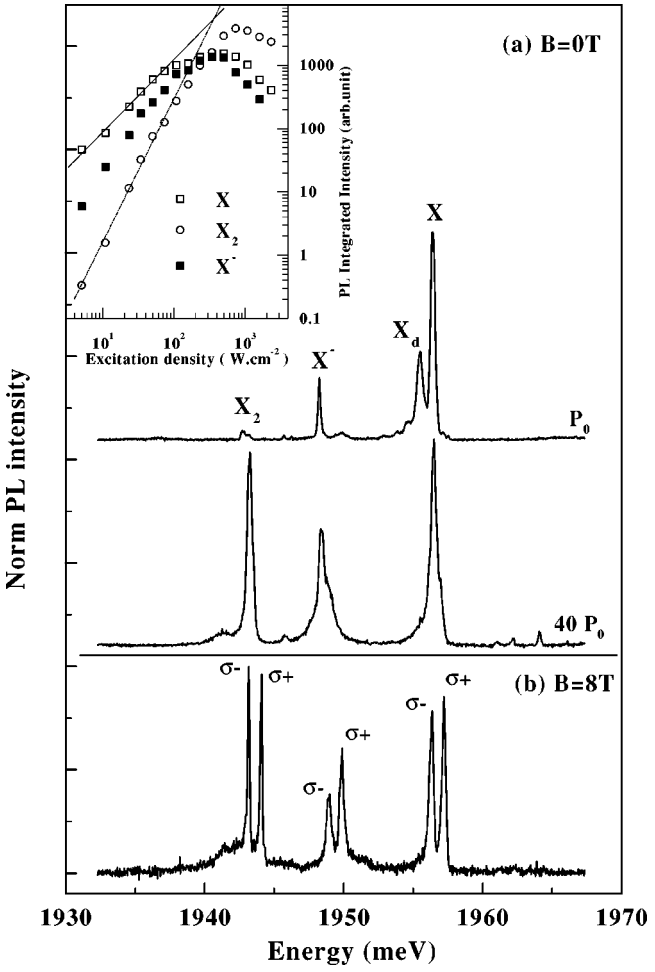

FIG. 1. (a) Photoluminescence spectra of a single QD taken under two different excitation densities P_0 and $40P_0$ ($P_0 \approx 5$ W cm^{-2}) at 4 K and at zero magnetic field. (b) Nonpolarized spectrum obtained under a magnetic field $B=8$ T applied along the growth direction [001]. The inset shows the integrated intensity of the emission lines of the exciton X, of the biexciton X_2, and of the charged exciton X^- plotted as a function of the excitation density.

We now consider the central line X^-, situated 8.0 meV below the excitonic transition X. The intensity of X^- increases faster than linearly at low-excitation density (inset of Fig. 1) but the slope of the logarithmic plot is clearly lower than two, indicating that this line does not correspond to a multiexciton complex. Moreover, X and X^- reach a maximum intensity simultaneously at $P_{ex} \approx 400$ W cm^{-2} and decrease for higher excitation density suggesting that X^- corresponds to a single-exciton species.

Under a magnetic field applied along the growth direction [001], the exciton states $J_z = \pm 1$ are split by the Zeeman energy and give purely circularly polarized lines in the luminescence spectra.[10] Since the biexciton is a spin-singlet state, the splitting and polarization properties of its recombination emission are governed by the exciton remaining in the final state of the optical transition. The biexciton emission then reproduces the spectral pattern of the exciton emission.[7,8,11,12]

The luminescence spectrum in Fig. 1(b), recorded at 8 T without a circular analyzer, gives the degree of circular polarization of the QD's emission. The exciton and biexciton transitions do not present any significant circular polarization at 8 T. On the other hand, the central line X^- is clearly polarized $\sigma+$ (high-energy component of X^- doublet). This circular polarization of the peak labeled X^- indicates that it indeed corresponds to the recombination of a negatively charged exciton.[13] In its lower-energy state, a singlet state of the negatively charged exciton has the spin of the hole. Thus, if the holes are thermalized,[14] the degree of polarization of charged-exciton *emission* under magnetic field is governed by the hole g factor g_h. The measured degree of circular polarization ($P \approx 17\%$) corresponds to $g_h \approx 0.1$ given by $P = \tanh(g_h \mu_B B / k_B T)$. This small value of g_h is consistent with magneto-optical measurements from which we deduce a hole g factor approaching zero in all the investigated QD's.[8,10] This degree of polarization leads us to assign the central line X^- to the negatively charged exciton. The attribution to a negatively charged exciton in the same QD that gives lines X and X_2 will be confirmed by the time fluctuations of the emission lines, described now.

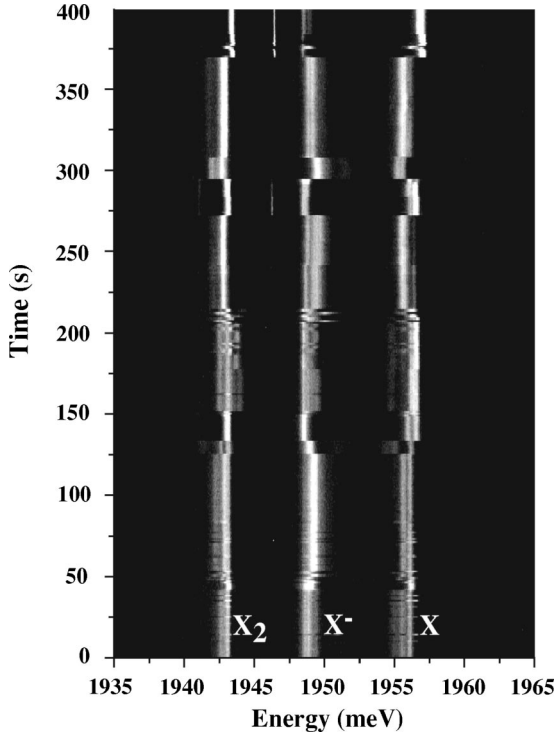

FIG. 2. Time evolution of the emission lines of an individual QD. This contour plot consists of 400 sequentially recorded spectra with an integration time of 1 s. The three emission lines exhibit synchronized energy fluctuations.

Figure 2 shows μPL spectra recorded sequentially with individual integration times of 1 s. Fluctuations of the positions of the three QD emission lines are clearly observed, with abrupt reversible energy shifts of about 1 meV at a time scale less than 1 s. Such behavior has recently been observed in other materials systems[16,17] and is attributed to fluctuating Stark shifts. In our modulation-doped structure, the QD's in the CdTe layer are submitted to an average electric field induced by the plane of ionized donors. The exciton lines are

then redshifted by the quantum confined Stark effect. Optically excited carriers trapped in the vicinity of the dot randomly screen the local electric field leading to random fluctuations of the emission line.[17] Due to the random distribution of traps, each QD is submitted to a different local electric field and so it exhibits its own sequence of Stark shifts. The synchronized fluctuations observed for the three emission lines X, X^-, and X_2 confirm that they arise from the same single QD.

Both the neutral and charged exciton line are observed in the emission spectra because a QD may contain one electron or no electron during the integration time. Coexistence of the two lines has also been reported over a certain bias range in μPL studies of $In_xGa_{1-x}As$ QD structures where a tuneable electrical bias is used to load the QD's with electrons.[18–20] As in the bias-controlled structures, the QD's in our CdTe layer are submitted to an average electric field, caused in our case by the plane of ionized donors. When the integration time is short enough, random Stark shifts of the sharp emission lines due to local fluctuations of this average field can be recorded.

The correlated fluctuations are also observed in the integrated intensities. In Fig. 3 the integrated intensities of the X and X^- lines recorded over a period of 250 s are compared with the energy shifts. First, there is a perfect correlation between the spectral shift and the intensity of the exciton line: a redshift of the X line is accompanied by a reduction of its intensity. A reduction of about 50% is obtained for a maximum redshift of 1.5 meV. This large decrease of the intensity cannot be explained simply by an electrical-field-induced reduction of the oscillator strength. Rather, these intensity fluctuations are correlated with those observed for the negatively charged exciton X^-, or more exactly an anticorrelation is found: when the intensity of the exciton decreases the intensity of the X^- line increases by about the same amount.

The integrated intensity of the neutral or charged-exciton line is proportional to the probability of probing an empty or charged dot, respectively, during the integration time. The spectra show that the probability of probing a charged dot increases with the strength of the local electric field (redshift of the exciton). This is easily understood if we take the conjugated effect of ionized donors and trapped carriers into account. An electron trapped near the QD screens the electric field of the doping plane and increases the local potential seen by the electrons in the CdTe layer. This gives two effects: a decrease of the probability of finding an excess electron in the QD (decrease of X^- intensity and increase of X intensity) and a reduction of the Stark shift of the exciton. To some extent, these fluctuating intensities of the neutral exciton and the charged exciton recall the ''blinking'' effect in nanocrystals. However, in nanocrystals, the presence of an extra electron in the QD completely kills the luminescence (due to Auger effects[21]) while in self-assembled QD's it simply changes the emission energy. An intensity exchange between two excitonic states of a given dot has been also reported for InAs/GaAs QD's,[22] but no energy shifts were observed and no explanation was proposed.

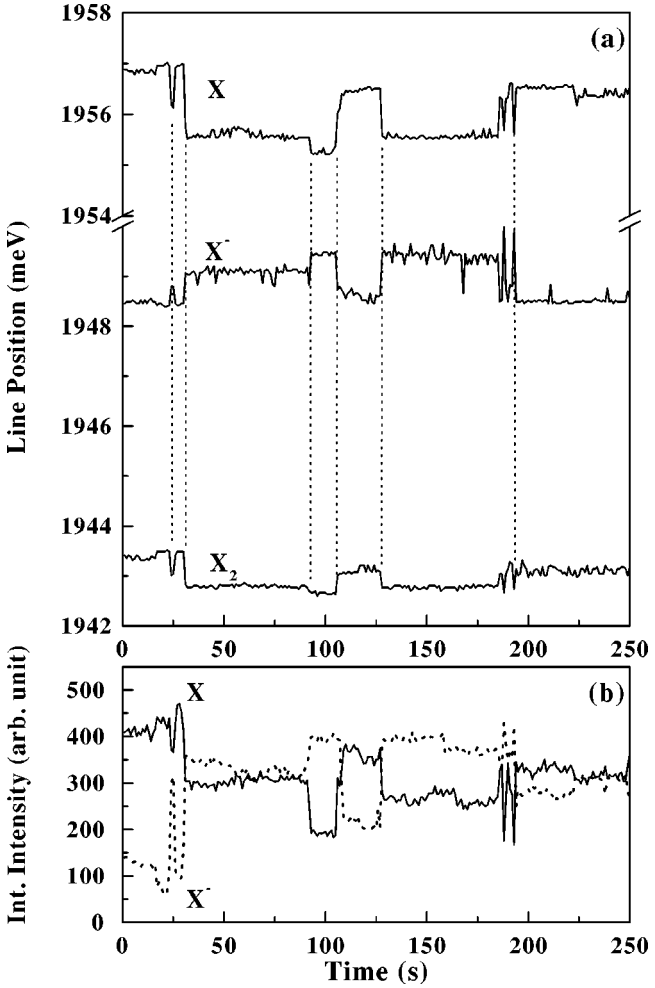

FIG. 3. (a) Energy shifts of the X, X^-, and X_2 lines as a function of time measured from 250 spectra recorded with an integration time of 1 s. (b) Synchronized evolution of the integrated intensities of the exciton X and charged exciton X^- lines.

Surprisingly, as observed in Fig. 3, the energy shifts of the X, X^-, and X_2 lines are not identical. When the exciton shifts to lower energy the shift of the biexciton is about a factor of 2 smaller. Even more striking is the behavior of the charged-exciton line: a redshift of the exciton correlated with a blueshift of line X^-. The redshift of the exciton gives a measurement of the increase of the local electric field. The reduction of the energy separation between the X and X^- lines and between the X and X_2 lines, respectively, can then be interpreted as a reduction of the charged-exciton and biexciton binding energies with increasing electric field.

Figure 4 shows the biexciton and the charged-exciton binding energies defined in this way as a function of the Stark shift of the exciton. This plot is composed of packets of points corresponding to the various discrete jumps of the energies of the spectral lines observed in Fig. 2. These discrete jumps arise from different stable charging configurations in the vicinity of the QD. Small fluctuations of the local electric field around these stable configurations contribute to the dispersion of the points. Since the Stark shift of the exciton is proportional to the square of the electric field, this

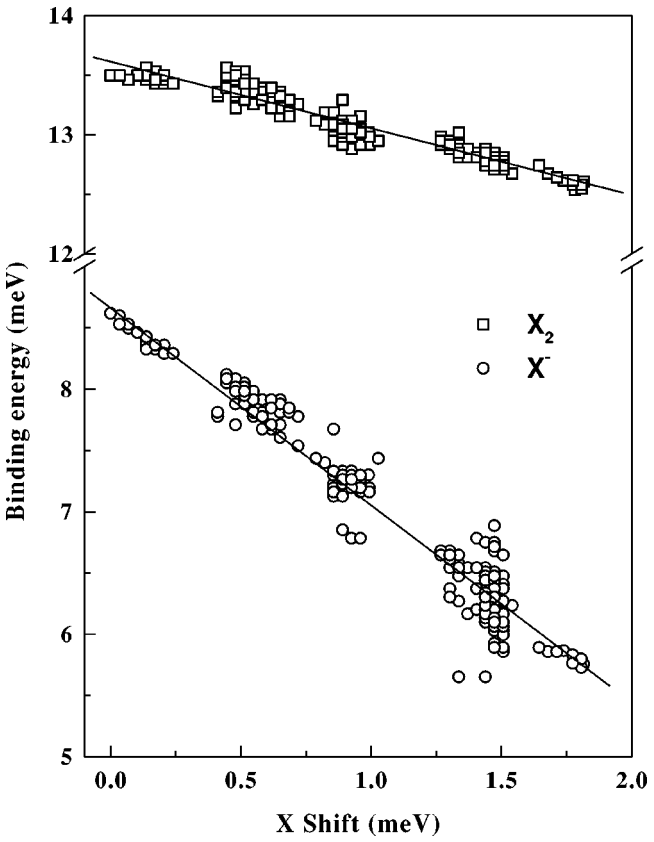

FIG. 4. Binding energy of the biexciton X_2 and charged exciton X^- plotted as a function of the energy shift of the exciton X deduced from the lines separation in the set of recorded spectra.

plot gives an estimate of the electric field dependence of the binding energy of these two excitonic complexes. A linear decrease of the binding energy as a function of the exciton's redshift is observed both for the biexciton and the negatively charged exciton. We deduce that the reduction of the binding energies is roughly proportional to the square of the electric field. The charged exciton's binding energy decreases about twice as fast as that of the biexciton. We note that a sharp reduction of the binding energy of the negatively charged exciton has been reported for $GaAs/Al_xGa_{1-x}As$ quantum wells, where an electric field of about 10 $kV\,cm^{-1}$ applied perpendicular to the quantum well nearly eliminates all binding of the excess electron.[23]

This reduction of the binding energies of the excitonic complexes can be explained by the polarization of the electron and hole wave functions along the direction of the electric field. Since the electrons and holes are polarized to opposite sides of the QD, the electric field increases the average electron-hole separation (i.e., reduces the electron and hole wave-function overlap) while having little effect upon the interelectron or interhole distance. The polarization of the wave functions weakens the attractive Coulomb terms but does not affect significantly the repulsive terms, inducing a reduction of the net binding energy of the excitonic complexes. The polarization of the wave function seems to be much more efficient for the charged species, giving a more pronounced decrease of the binding of the excess electron.

To summarize, we have identified the contribution from the exciton, the biexciton and the negatively charged-exciton in the emission spectra of single CdTe QD's. Correlated energy and intensity fluctuations of these three PL lines were observed. They have been discussed in terms of fluctuating local electric fields. Analysis of these random spectral shifts shows a sharp reduction of the binding energies of excitonic complexes with increasing strength of the local electric field. This reduction is particularly pronounced for the charged exciton, whose emission is blueshifted by the electric field.

The authors wish to thank R.T. Cox and Le Si Dang for informative discussions, and K. Sato from Nikko Materials Co. for providing the high quality ZnTe substrates. This work is part of the CNRS-CEA joint research program ''Nanophysique et Semiconducteurs.''

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