Effect of random field fluctuations on excitonic transitions of individual CdSe quantum dots

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(Received 20 August 1999; revised manuscript received 2 November 1999)

The quantum confined Stark effect is observed for quantum dots (QD's) exposed to randomly fluctuating electric fields in epitaxial structures. These fields, attributed to charges localized at defects in the vicinity of the QD's, lead to a jitter in the emission energies of individual QD's. This jitter has typical frequencies of below about 1 Hz and is characteristic for each QD thus providing a unique means to unambiguously identify the emission spectra of single QD's. Up to eight lines are identified for individual QD's and attributed to excitonic, biexcitonic, and LO-phonon-assisted transitions. The intensity of the LO-phonon replica is surprisingly large corresponding to Huang-Rhys factors of about one.

I. INTRODUCTION

Since the quantum confined Stark effect[1] (QCSE) has first been demonstrated in quantum wells, much work has been dedicated to the investigation of the interplay of the electronic states of quantum structures and external electric fields. Studies of the QCSE of quantum dots[2] (QD's) were done using CdS and CdSSe QD's in amorphous matrices.[3,4] These early investigations were focussing on the effect of electric fields on a large QD ensemble. The very recent progress in spatially resolved spectroscopy however made it possible to systematically investigate the QCSE of single QD's (Refs. 5–8) in *external* electric fields. Internal fields like those of defects, impurities, or localized charges in the vicinity of a QD will strongly influence its electronic structure as well. Discrete and bistable effects such as random-telegraph-noise-like blinking and quenching[9] of the luminescence, were reported for colloidal CdSe QD's[10,11] and for InP QD's in a GaInP matrix.[12]

This paper reports on the effect of randomly fluctuating local electric fields on the electronic states of QD's in epitaxially grown II-VI structures. For such II-VI structures high background doping together with self-compensation effects leads to a density of charged defects that is several orders of magnitude larger than in comparable III-V structures. Optically excited charge carriers will randomly neutralize the defects leading to random fluctuations of the electric fields which the QD's are exposed to. The resulting QCSE leads to a jitter of the emission energies of the QD's, which can be observed in a series of cathodoluminescence (CL) spectra taken in rapid succession. The jitter is characteristic for each QD and allows to identify surprisingly rich emission spectra for single QD's.

II. EXPERIMENT

The investigated sample was grown by low-pressure metalorganic chemical vapor deposition (MOCVD) on a (001) GaAs substrate at 350 °C. Initially, a 10 nm-thick ZnSe layer was grown followed by a 500 nm-thick $ZnS_{0.06}Se_{0.94}$ buffer lattice matched to GaAs. Subsequently, nominally 1.7 monolayers (ML) of CdSe were deposited followed by a 20 nm $ZnS_{0.06}Se_{0.94}$ cap. Under the given growth conditions the deposited CdSe forms Cd-rich nanoscale islands in the Volmer-Weber growth mode.[13] Structural characterization of samples grown under identical conditions identifies islands with a lateral extension of about 5 nm and a height of about 4 ML (1.2 nm) and a Cd content between 60% and 70%.[14] The latter is attributed to interdiffusion during the ZnSSe cap growth.

The growth having been completed, shadow masks were fabricated on the surface of the sample using electron beam lithography and a standard lift-off process. The masks consist of square shaped fields with lateral extensions of 8 μm$\times$8 μm of 10 nm Ti and 70 nm Pt. In the center of each field a small area is left uncovered creating apertures with a diameter as small as 100 nm. The metal film is transparent for the exciting electron beam but almost opaque for light (transmission $<10^{-4}$ at $h\nu=2.75$ eV). Only luminescence from QD's situated directly below the aperture is detected.

The measurements were carried out using a JEOL JSM 840 scanning electron microscope. The sample was mounted on the cooling finger of a He-flux cryostat. The luminescence light was collected by an elliptical mirror and dispersed by an 0.3 m spectrometer equipped with a 2400 mm^{-1} grating. A 1024$\times$256 pixel liquid nitrogen-cooled charge-coupled device was used as detector. The spectral resolution of the setup was $\approx$200 μeV. All measuring was done at a temperature of 7 K using an acceleration voltage of 7 kV.

III. RESULTS AND DISCUSSION

The integral CL spectrum taken from an area of about 40×60 μm^2 shows two peaks [see inset in Fig. 1(a)]. The high-energy peak at 2.835 eV originates from the $ZnS_{0.06}Se_{0.94}$ matrix while the low-energy peak at 2.61 eV with a full width at half maximum of 60 meV stems from the inhomogeneously broadened emission of the QD's. A high-resolution CL spectrum taken on a 120 nm$\times$120 nm aper-

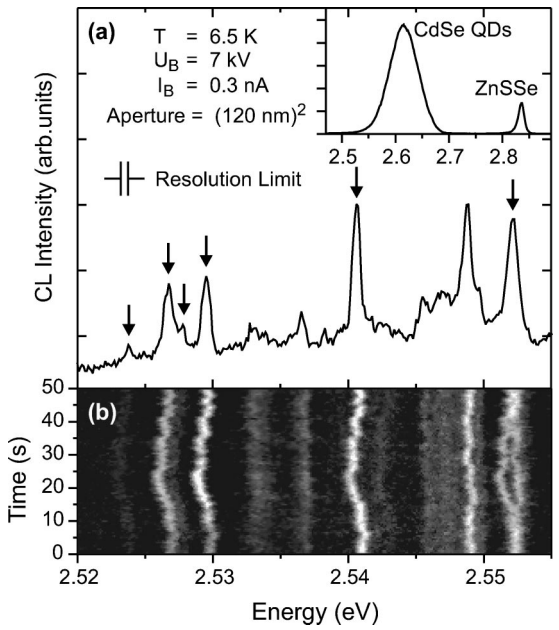

FIG. 1. (a) Section of a CL spectrum taken on a $(120\ \mathrm{nm})^2$ aperture showing single sharp luminescence lines of excitonic transitions of a few quantum dots. The inset shows an integral CL spectrum of the same sample. (b) The time evolution (0.5 s steps) of the above spectrum shows the characteristic jitter and drift of the emission lines. A synchronous group of six lines exhibiting identical jitter is indicated by arrows in panel (a). In panel (b) the rightmost line of the group is partially superposed by another emission line.

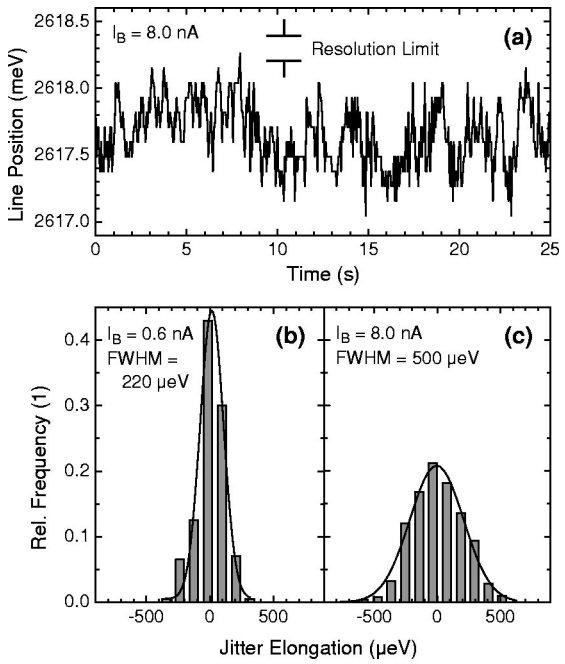

FIG. 2. (a) Time evolution of the position of a QD-exciton line. The line positions were derived from a series of 500 spectra taken in intervals of 100 ms. (b) and (c) show histograms of the line positions relative to the time averaged position measured for excitation beam currents of 0.6 nA and 8 nA, respectively. The histograms look like a normal-distribution (full line) whose variance increases with the excitation density.

ture shows that the smooth QD luminescence peak actually decomposes into about 80 lines of which about 15 fall into the energy range displayed in Fig. 1(a). Surprisingly the energies of these lines show a pronounced time-dependent jitter. The sequence of 100 spectra shown in Fig. 1(b) reveals this effect which to our knowledge was not reported before for epitaxially grown QD structures. Each emission line shows a jitter with an amplitude of up to 1 meV [see Fig. 2(a)]. The energy distribution of each line can be approximated by a Gaussian [see Figs. 2(b) and 2(c)] and the amplitude of the jitter increases with increasing beam current I_B and thus excitation density. A Fourier analysis of the jitter based on a series of 1000 spectra taken in intervals of 50 ms yields a white noise background and a significant contribution from frequencies between 0.1 Hz and 1.5 Hz. Beside the jitter some lines exhibit a slow energy drift on a timescale of several seconds up to tens of seconds.

The sequence of spectra in Fig. 1(b) reveals synchronous groups of lines which show exactly the same jitter pattern. The lines of one group are marked by arrows in Fig. 1(a). Groups of up to eight lines distributed over a range of about 50 meV can be identified (see, e.g., Fig. 3) the energy separations for them remaining constant within the experimental resolution.

The jitter of the luminescence lines is attributed to the QCSE.[1] Defects in the vicinity of the QD's randomly change their charge state trapping or releasing carriers and thus generating fluctuating electric fields that can reach a strength of several ten kV/cm at the position of the QD's. Such fields modify the carrier confinement in the QD's leading to a shift of the luminescence energy. The jitter reflects the slow timescale of such charging processes, which typically occur in a range of milliseconds up to hundreds of milliseconds. The model is consistent with the observed excitation density dependence of the jitter amplitude: the increasing number of charge carriers available with increasing excitation density leads to a stronger screening of the local fields and larger charge fluctuations.

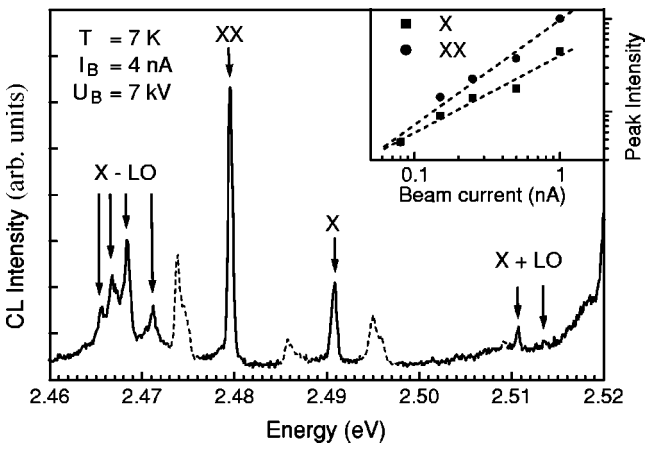

FIG. 3. Excitonic spectrum of an individual QD, the eight marked lines exhibit synchronous jitter. *X* denotes the excitonic groundstate recombination, *XX* the line from the biexciton decay, *X*-LO marks a set of LO-phonon replica of the exciton decay involving at least four different LO phonons. The origin of the two high energy lines is not yet clear, they might be attributed to LO enhanced decays. The dashed peaks belong to other QD's. The inset shows the excitation beam current dependence of the intensities of the exciton (X) and the biexciton (XX) line.

In flat GaAs/AlGaAs quantum islands Stark shifts of a few hundred μeV have been observed for externally applied electric fields of several 10 kV/cm.[5] Slightly larger shifts of 2 to 3 meV have been observed for self-organized InAlAs QD's in an AlGaAs matrix when external electric fields of up to 60 kV/cm were applied.[6]

To obtain an estimate of the QCSE induced energy downshift for the present system, model calculations were performed. The weak coupling of conduction and valence bands in the wide gap II-VI materials allowed the use of effective mass theory.[15] A flat cylindrical dot with a height of 1.2 nm, a diameter of 5.0 nm, and a Cd content of 65% was assumed. Strain effects were included as biaxial strain in the growth plane, and the exciton binding energy was calculated treating the Coulomb interaction as a first order perturbation to the confinement potential.[16]

The calculated transition energy of the exciton groundstate shows a parabolic dependence on the electric field. An electrostatic field of 100 kV/cm in the growth direction, i.e., perpendicular to the QD plane, leads to an energy downshift of the emission of 260 μeV. Due to the larger lateral extension of the QD's the same electric field directed parallel to the QD plane induces a downshift of 1.8 meV. Both values are of the same order of magnitude as the observed jitter. The exciton binding energy amounts to 90.2 meV and is slightly field dependent. Local electric fields reaching several 10 kV/cm can be generated by a few charged defects located very close to the QD. For example three elementary charges in 10 nm distance from the QD induce an average field of 45 kV/cm.

The random field fluctuations are liable to obey a narrow normal distribution around a nonvanishing average field strength. The observed near normal distribution of the emission energy [Figs. 2(b) and 2(c)] can occur only if the average field value is clearly larger than the standard deviation. Under such conditions the parabolic field dependence can be linearized.

Due to the random distribution and population of defects each QD is exposed to a different local electric field. Furthermore the strength of the QCSE depends strongly on the geometrical extent of the QD. Thus, each QD exhibits its own characteristic jitter and the observed groups of synchronous emission lines must each originate from the same single QD. The origin of the lines of the QD emission spectrum has been analyzed by excitation density-dependent measurements where the excitation beam current (I_B) was varied between 80 pA and 1.0 nA. Figure 3 shows the spectrum of a coherent group of lines and the inset shows the I_B dependence of the intensities of the lines denoted X and XX, respectively. The intensity of the line denoted X grows sublinearly with a slope of roughly 0.8. The line denoted XX shows a superlinear increase with a slope of about 1.2. Judging by the excitation density dependence it is reasonable to conclude that the line denoted X originates from radiative recombination of the excitonic groundstate and that the line denoted XX originates from biexcitonic decay. Remarkably the biexciton line can be observed, even at the smallest currents I_B, indicating that the excitation density is still in the nonlinear regime. The separation between the exciton and the biexciton line in Fig. 3 is 11.4 meV, which is smaller than values reported by others[17,18] for samples grown by molecular beam epitaxy. The deviation may be attributed to the different shape and composition of the QD's in the MOCVD grown samples. The decay of charged excitons (trions) as the origin of the line denoted XX is unlikely because such charged particles should react differently to electric fields and should thus exhibit at least a different jitter amplitude. The intensities of the four lines between 2.465 and 2.473 eV show the same excitation density dependence as the exciton line X, suggesting a set of four LO-phonon replica. The LO-phonon energies are 19.6, 22.5, 24.0, and 25.3 meV, respectively. For different QD's a variation of the LO-phonon energies by about ± 2 meV is observed, indicating that the LO-phonon energies are a specific property of each QD depending on its size, shape, strain, and composition. Broad bands attributed to QD specific LO phonons (called local phonon modes) have been observed in photoluminescence excitation studies, too.[18]

The energy separations between all lines of a group are constant in time and thus independent of the strength of the random electric fields. For LO-phonon replica such a behavior is naturally expected. The constant separation between the exciton (X) and the biexciton (XX) lines is attributed to the fact that the QCSE is much smaller than the biexciton binding energy.

The intensities of the LO-phonon replica in Fig. 3 are large, the strongest replica being of approximately the same intensity as the direct exciton groundstate emission. This points to strong exciton LO-phonon coupling. The coupling strength is usually described by the dimensionless Huang-Rhys factor S.[19] S is given by the ratio of the integral intensities of the phonon replica and the zero phonon line.[20] Using this model, $S \approx 1$ is obtained which is of the same order as values obtained for spherical II-VI QD's in a glass matrix,[21–23] but two orders of magnitude larger than for III-V QD's.[24] It has been proposed[25] that the large values of S observed in II-VI QD's in amorphous matrices are due to electric fields induced by charges located at the dot-matrix interface, which increase the nonvanishing part of the electron and hole polaron clouds in the exciton state. In the present epitaxially grown structures the QCSE jitter indicates the presence of a strong electric field and, at the same time, the Huang-Rhys factor is large. Both these observations support the assumed connection between the Huang-Rhys factor and local electric fields in the QD's. The absence of measurable LO-phonon replica of the biexciton line could then be explained by a similar polar character of the biexciton state.

Two additional lines are to be found at energies above the exciton groundstate (Fig. 3). The energy separations of 19.9 and 22.6 meV are consistent with two of the observed local LO-phonon energies.[26] This could indicate an interaction with hot phonons generated by the electron beam: In CL electron hole pairs are generated with an excess energy of about 2–3 eV and relaxation takes place mostly by LO-phonon emission. This could result in a non-equilibrium phonon distribution. For excited state transitions different jitter amplitudes would be expected, which are not observed. Further investigations to clarify the precise origin of the lines are in progress.

IV. CONCLUSION

The excitonic transitions of individual QD's in MOCVD-grown CdSe/Zn_xS_{1-x}Se structures show a jitter on a time-

scale between a few tenths of a second and a few seconds. The jitter is assigned to a QCSE induced by randomly fluctuating electrostatic fields induced by charges localized at defects in the vicinity of the QD's. The jitter amplitude depends on the excitation density and therefore on the density of generated charge carriers. Identical jitter patterns allow the unambiguous identification of the emission spectra of single QD's. The spectra have a remarkably rich structure with up to eight sharp lines. By means of excitation density dependent spectroscopy the lines are identified as exciton and biexciton recombinations and phonon replica of the exciton transition involving local LO-phonon modes of the QD. Large Huang-Rhys factors of up to $S \approx 1$ are observed.

ACKNOWLEDGMENTS

We would like to thank M. Grundmann and A. Hoffmann for helpful discussions. Further thanks are due to the group of J. Christen at the Otto-von-Guericke-University in Magdeburg for being permitted to use their CCD detector. Part of this work has been funded by Sonderforschungsbereich 296 of Deutsche Forschungsgemeinschaft.

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