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Observation of multicharged excitons and biexcitons in a single InGaAs quantum dot

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The effects of excess electron occupation on the optical properties of excitons (X) and biexcitons ($2X$) in a single self-assembled InGaAs quantum dot are investigated. The behavior of X and $2X$ differ strongly as the number of excess electrons is varied with the biexciton being much more weakly perturbed as a result of its filled *s*-shell ground state, a direct manifestation of shell-filling effects. Good correlation is found between charging thresholds observed from *s*-shell recombination perturbed by *p*-shell occupation, and direct observation of *p*-shell recombination.

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Over recent years, In(Ga)As-GaAs self-assembled quantum dots (QDs) have attracted considerable interest as a result of their discrete electronic spectrum, excellent optical quality and ease of incorporation into electro-optical devices.[1] Of particular interest from the fundamental physics perspective are the strong modifications of the optical properties which are predicted to arise from Coulomb interactions between particles (electrons and holes) localized within the dots.[2,3] For In(Ga)As QDs, the magnitudes of the Coulomb and quantization energies are comparable and the many-particle states are strongly sensitive to the exact number *and* configuration of electrons and holes (N_e,N_h) in the dot. Such effects were first investigated on large ensembles where the effects of electron occupation on the optical properties in emission[4] and absorption[5] were investigated. While these experiments clearly demonstrated shifts of the interband transitions and state blocking from electron charging, detailed interpretation was complicated by the large inhomogeneous broadening. Recently, these problems have been circumvented by performing single-dot photoluminescence (PL) spectroscopy for charge neutral ($N_e = N_h$) In(Ga)As QDs,[6,7] modulation doped ($N_e \geqslant N_h$) GaAs dots,[8] and charge tuneable InAs quantum rings.[9]

In the present work we investigate the effect of Coulomb interactions on the interband optical properties of a self-assembled InGaAs QD. Single-dot PL, performed on a gated, charge tunable structure allows the properties of both excitons (X) and biexcitons ($2X$) to be studied in both charge neutral and negatively-charged environments in the presence of up to three excess electrons. Markedly contrasting effects of excess charge on X and $2X$ are found and attributed to the stronger Coulomb perturbations on X as a result of its partially filled *s*-shell, as opposed to the filled *s*-shell of $2X$. Excited state *p*-shell recombination is also seen, and allows a coherent picture of the various charge configurations giving rise to the perturbed *s*-shell excitonic lines to be built up.

The sample consisted of the following layers grown by MBE on a semi-insulating [001] GaAs substrate: a 200 nm thick $n = 4\times10^{18}$ cm^{-3} GaAs contact layer followed by a 25 nm undoped (u.d.) GaAs spacer layer and the InGaAs quantum dots, formed by 6 ML of $In_{0.5}Ga_{0.5}As$. Atomic force microscopy performed on similar material revealed approximately lens shaped dots with lateral (vertical) dimensions of 23 ± 7 nm (2.5 ± 1 nm) and a density of $\sim5\times10^{10}$ cm^{-2}. The QD layer was capped with 15 nm u.d. GaAs, a 75 nm thick u.d. $Al_{0.33}Ga_{0.67}As$ blocking barrier and a 5 nm u.d. GaAs cap.

Ohmic contacts were established to the n^+ layer and an $\sim$70 nm thick titanium Schottky gate evaporated on the sample surface. Submicron apertures ranging from 100 to 500 nm were formed in the gate using electron beam lithography and dry etching. The samples were studied in a micro-PL system which enabled PL to be excited and collected through individual nanoapertures from single dots. Apertures exhibiting PL from only one dot were selected for detailed study. PL at T$\sim$10 K was excited using 632.8 nm radiation from a HeNe laser. The luminescence was dispersed by a 0.4 m single monochromator ($\sim$0.3 meV resolution) and detected with a cooled CCD detector.

Figure 1 (inset) shows a schematic band diagram for a large negative bias (V_g) on the gate, such that the quasi Fermi level (E_f) lies below the lowest state in the dot (s_1) and the dot is uncharged. As V_g is lowered, the electrostatic potential of the dot reduces[10] until s_1 becomes aligned with E_f and a *single* electron can tunnel into the dot from the n^+ contact. Subsequent charging events (s_2,p_1,p_2) occur at well separated biases due to the effects of quantum confinement and Coulomb blockade.[12]

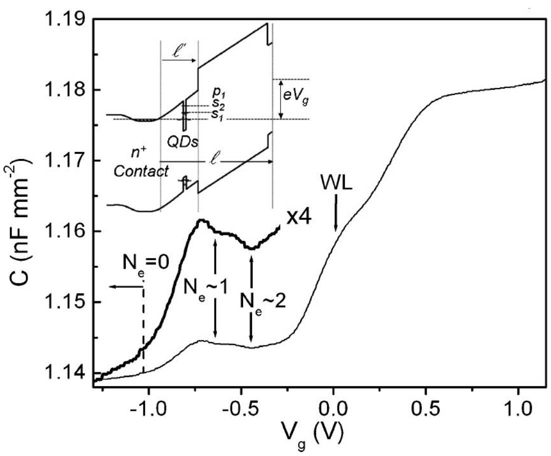

FIG. 1. Capacitance-voltage characteristics of gated device containing quantum dots (dotted curve). Features due to complete charging of the dot ensemble ground state with one and two electrons are observed ($N_e \sim 1,2$, full curve), followed by charging of the wetting layer. The inset of the diagram shows a schematic band diagram under applied bias V_g.

The capacitance-voltage characteristics of a structure containing $\sim 6\times 10^7$ dots are presented in Fig. 1,[13] recorded under weak ($\sim 0.1\ \mathrm{W\,cm^{-2}}$) optical excitation tuned to $E \sim 1290$ meV, the peak of the QD ground-state emission. For $V_g \lesssim -1$ V the capacitance shows a smooth variation with V_g due to depletion of the n^+ contact region, with the dot uncharged. As V_g is increased (less negative), pronounced features due to charging of the QD ground states are seen, with a broad peak at $V_g \sim -0.75$ V and two minima, marked by arrows at $V_g = -0.63$ V and -0.48 V. These features are a clear fingerprint of Coulomb blockade, the minima corresponding to charging the QD ensemble with one ($N_e \sim 1$) and two ($N_e \sim 2$) electrons, respectively.[12] As V_g is increased further, a strong increase of the capacitance signal for $V_g \gtrsim -0.20$ V is observed arising from charging of QD *excited* states and the underlying 2D wetting layer.

The evolution of the PL spectrum from a single dot with gate bias ($-1.3\ \mathrm{V} \leqslant V_g \leqslant -0.2$ V) and hence N_e is summarized in gray-scale format in Fig. 2(a). The intensity of the optical excitation (nominal 0.1 W/cm^2) was chosen such that single exciton recombination (X) dominates the spectrum, although a weak biexciton feature ($2X$) is also present. For $V_g \leqslant -1.3$ V no PL is observed due to efficient tunnelling of carriers out of the dot in the internal field of $\geqslant 130\ \mathrm{kV\,cm^{-1}}$. At $V_g \sim -1.2$ V a sharp emission line (X^0) is observed, arising from charge neutral single exciton recombination. This assignment is supported by the capacitance measurements which indicate an uncharged ensemble for $V_g \leqslant -1$ V (Fig. 1) and the linear dependence of the intensity of X^0 on excitation power.[14] For $V_g \gtrsim -1.1$ V additional lines appear in two distinct energy ranges, 1250–1265 meV and 1275–1295 meV, attributed to ground state (s-shell) and excited state (p-shell) recombination, respectively. A number of distinct thresholds are observed, indicated by horizontal broken lines in Fig. 2(a), for which sudden changes are observed in both the s and p-shell emission energies. These correspond to charging events where an additional electron is added to the dot. Spectra of the s-shell emission corresponding to voltages spanning the first two main charging thresholds are presented in Figs. 2(b) and 2(c), respectively.

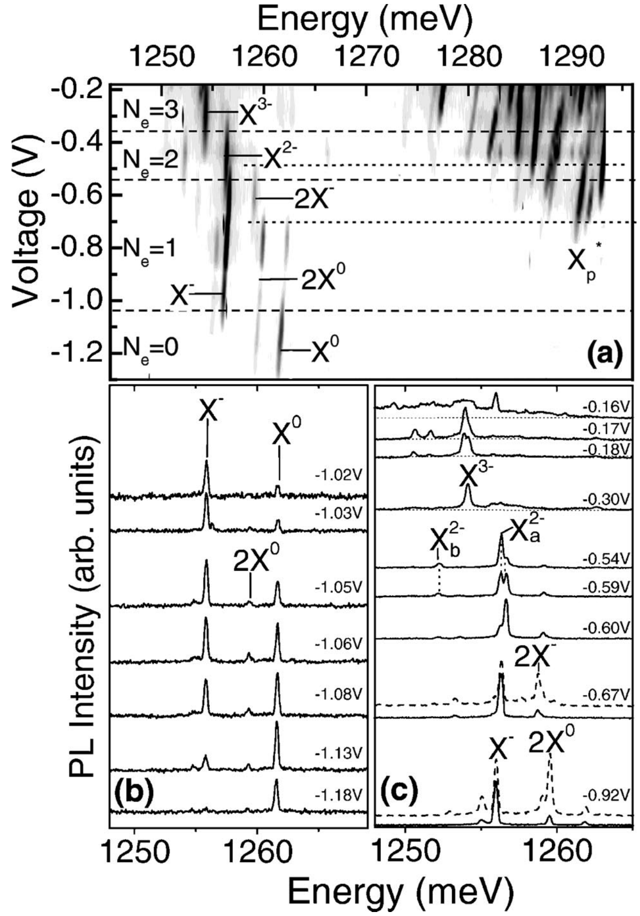

FIG. 2. (a) Gray scale plot of PL peaks as a function of bias. Ground state s-shell neutral (X) and charged single excitons (X^{n-}), neutral and charged biexcitons ($2X$,$2X^-$) and p-shell X_p^* emission lines are observed. The horizontal lines indicate charging thresholds. (b) s-shell spectra in the bias range -1.18 to -1.02 V, (c) in the bias range -0.73 V to -0.54 V. The dashed spectra in Fig. 2(c) are taken with a factor of three higher laser power.

At $V_g \sim -1.1$ V, X^0 disappears and a new line (X^-, Fig. 2) appears 5.8 meV to lower energy. This feature arises from recombination of a negatively-charged single exciton [Fig. 3(a)], the large energy shift between X^0 and X^- being a direct measure of the relative energy of three ($X^- \equiv 2e + 1h$) and two ($X^0 \equiv 1e + 1h$) particle configurations in the dot. The observation of X^- below X^0 demonstrates that electron-hole *attraction* dominates over electron-electron *repulsion* in the three particle ($2e+1h$) configuration. This arises as a consequence of the differing lateral spatial extent of the electron (l_e) and hole (l_h) wave functions, the sign of the energy shift indicating that $l_h < l_e$,[15] the holes being more strongly localized than the electrons. The $X^- - X^0$ separation of 5.8 meV is very close to that (6 meV) found in Ref. 9 in quantum rings, at first sight rather surprising in view of the significantly greater lateral size of the rings (100 nm) compared to the present dots (~ 20 nm).[16] However,

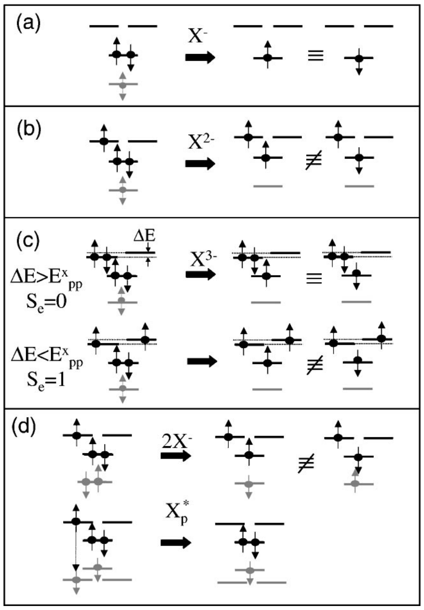

FIG. 3. Schematic diagrams of occupations of electron and hole initial and final states for X^-,X^{2-},X^{3-},$2X^-$ and X_p^* recombination. Hole states with two arrowheads on the same line indicate that the hole participating in the recombination may have up or down spin.

from a survey of seven dots with ground state PL in the range 1260–1350 meV, we find $X^- - X^0$ separations ranging from 4.9–5.8 meV, showing the weak dependence of $X^- - X^0$ on detailed dot parameters. This weak dependence is supported by our calculations based on exact diagonalization of the electron-hole Hamiltonian with harmonic oscillator confinement in the vertical and lateral directions. These calculations yield $X^0 \rightarrow X^-$ shifts in the range 3–5 meV using a wide range of l_e values from 5–10 nm, consistent with the expected lateral size of our QDs, and l_e/l_h ratios between 2 and 4.[11]

The second main charging threshold arises for V_g close to -0.57 V [Fig. 2(b)]. The negatively-charged exciton (X^-) abruptly disappears between -0.6 V and -0.5 V and is replaced by a strong feature (X_a^{2-}) 0.4 ± 0.05 meV to lower energy and, in addition, a weaker peak (X_b^{2-}) 4.2 ± 0.05 meV below X_a^{2-}. As discussed by Warburton *et al.*,[9] the doublet structure results from the two different (triplet or singlet) final state configurations for X^{2-}, in which the two electrons have parallel (X_a^{2-}) or anti-parallel (X_b^{2-}) spins[15,17] [see Fig. 3(b)], the $X_a^{2-} - X_b^{2-}$ splitting being equal to twice the *s*-*p* electron exchange energy. The small energy shift between X^- $(2e+1h)$ and X_a^{2-} $(3e+1h)$ arises because the attractive *s*-*p* electron exchange interaction is present in the X_a^{2-} states before and after photon emission. As shown by a perturbation theory treatment, this results in a partial compensation of the Coulomb repulsion for X_a^{2-} and leads to the small energy shift between X^- and X_a^{2-}.[3] In contrast, for X_b^{2-}, the exchange interaction is absent in the final state [Fig. 3(b)] and the Coulomb repulsion between the *s* and *p*-shell electrons leads to a larger redshift, in agreement with theoretical predictions.[15,3]

The third charging threshold occurs at $V_g \sim -0.4$ V and is marked by a sudden reduction in the intensity of X_a^{2-} and X_b^{2-} and the emergence of a new line (X^{3-}) approximately midway between them [Figs. 2(a) and 2(c)]. The appearance of a single dominant emission line for the triply-charged exciton is somewhat surprising as two, energetically distinct, multiparticle configurations have been predicted theoretically for systems which possess perfect cylindrical symmetry.[3] However, reduction in the dot symmetry, for example due to inequivalent in-plane dimensions or the microscopic inequivalence of the [110] and [1$\bar{1}$0] crystallographic directions,[1] may result in a splitting of the *p*-states (ΔE) as depicted schematically in Fig. 3(c). In this case, the initial state for the triply-charged state depends upon the comparative magnitude of ΔE and the *s*-*p* electron exchange energy (E_{sp}^X) which is estimated for the present dot to be $\sim$2 meV from the discussion of X^{2-} above. If $\Delta E > E_{sp}^X$, the five particle $(4e+1h)$ system adopts a configuration in which the two *p*-shell electrons occupy the same *p*-orbital and have antiparallel spin [Fig. 3(c)]. In this case, the system posesses zero-net electron spin in the initial state [$S_e=0$–Fig. 3(c)], the two possible final states are energetically equivalent and a single emission line should be observed. In contrast, if $\Delta E < E_{sp}^X$ the system would tend to favor an initial state in which the two *p*-electrons have parallel spins ($S_e=1$),[3] occupying different *p*-orbitals [Fig. 3(c)]. In this case, photon emission leaves the system in one of two energetically distinct final states, as for X^{2-} discussed above, which would generate an emission doublet in PL [Fig. 3(c)]. We therefore identify X^{3-} as arising from the five particle $S_e=0$ configuration as depicted schematically in Fig. 3(c).

For further reductions of the gate potential below $V_g \sim -0.2$ V, additional discrete shifts of the *s*-shell emission are observed [Figs. 2(a) and 2(c)] as additional electrons are added to the dot. At $V_g \sim -0.16$ V a strong PL background [Fig. 2(c)] appears,[9] accompanied by broadening of the sharp emission lines, probably due to the occurrence of strong Auger processes and shortening of the quasiparticle lifetime as the wetting layer becomes occupied. This explanation is supported by the $C-V$ characteristics in Fig. 1 which show a strong increase in the capacitance signal for $V_g \gtrsim -0.2$ V as the wetting layer is filled.

It is notable from Fig. 2(a) that the voltage interval between the $N_e=1\rightarrow2$ and $2\rightarrow3$ charging thresholds is $\sim$3 times smaller than between $N_e=0\rightarrow1$ and $1\rightarrow2$. This arises since the former reflects both the *s*-*p* level spacing and Coulomb blockade effects while the latter is determined solely by the weaker Coulomb repulsion energy between the two *p*-shell electrons, further supporting the attribution of the charging thresholds above.

We now consider the biexciton recombination ($2X^0$) observed as a weak feature between X^0 and X^-, labeled $2X^0$ in Fig. 2. It is identified from the near quadratic dependence of its intensity on excitation power, as seen from the dashed spectra taken at three times higher laser power in Fig. 2(c). The energy of $2X^0$ is unaffected by the $N_e=0\rightarrow1$ charging threshold at $V_g=-1.06$ V, the first shift occurring at $V_g \sim -0.7$ V [dotted line–Fig. 2(a)]. This behavior is expected since, for $2X^0$, the *s*-shell is full and the first charging threshold arises for the V_g at which an electron can first be added to the *p*-shell [Fig. 3(d)]. This occurs at ~ -0.7 V and results in a sudden decrease of the amplitude of $2X^0$ with the negatively-charged biexciton ($2X^-$) emerging 0.9 meV to lower energy. The energy shift between $2X^0$ and $2X^-$ is much smaller than the 5.8 meV between X^0 and X^-; this arises since for $2X^-$ the interaction of the additional electron with the four particle system ($2e+2h$) in the dot is strongly reduced due to the completely filled *s*-shell. This observation is a direct manifestation of shell filling phenomena for quantum dots.

While both the $2X^0 \rightarrow 2X^-$ and $X^- \rightarrow X^{2-}$ charging thresholds involve electron charging of the *p*-level, the $X^- \rightarrow X^{2-}$ charging is expected to occur for higher V_g due to the stronger Coulomb repulsion effects for X^{2-} which contains *two* excess electrons. This prediction is in good agreement with experiment, the single and biexciton *p*-shell charging thresholds occurring at -0.57 V and -0.69 V, respectively in Fig. 2(a).

We now turn to the *p*-shell emission observed for energies $\geqslant 1275$ meV [Fig. 2(a)], and show that its behavior is fully consistent with the charging threshold for addition of *p*-shell electrons deduced above. Weak *p*-shell emission is first observed for $V_g \sim -0.7$ V with the appearance of a weak doublet centered at ~ 1292 meV [labeled X_p^* in Fig. 2(a)]. This bias corresponds very closely to the $2X^0 \rightarrow 2X^-$ charging threshold [dotted line in Fig. 2(a)], the lowest voltage and multiparticle configuration for which an electron can be added to the *p*-shell under the optical excitation conditions in Fig. 2. Further reduction of V_g results in a series of discrete changes in the *p*-shell emission, with groups of lines appearing sequentially to lower energy as V_g reduces. We note that for both the *s* and *p*-shells, the dominant trend with increasing N_e is a redshift of the center of gravity of the emission, analogous to the band-gap renormalization observed in higher dimensional systems. However, the magnitude of the observed shifts, particularly for the *p*-shell (~ 10 meV, for $N_e = 3$), is very large, reflecting the effects of zero-dimensional confinement in quantum dots.

Finally we note that in several bias regions, e.g., -1.1 V$\leqslant -0.9$ V for X^0, X^-, -0.9 V$\leqslant V_g \leqslant -0.6$ V for X^-, $2X^0$, X^0 emission lines from differing charge states are observed simultaneously. This probably arises from the statistical nature of photoexcited carrier capture into the dot which, when averaged over time, leads to spectra composed of transitions involving differing charge states and differing numbers of excitons.

In summary, we have investigated the effects of Coulomb interactions on the optical properties of excitons and biexcitons in a single In(Ga)As quantum dot. For single excitonic species, strong perturbations arising from electron charging are observed with large (several meV) shifts occurring as electrons are added sequentially. Weaker perturbations of the biexciton are observed as a consequence of the completely filled *s*-shell for $2X^-$. Electron charging of the dot results in large redshifts of the center of gravity of both *s* and *p*-shell emission with correlated shifts of both *s* and *p*-shell emission as electrons are added to the dot.

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