Dominance of charged excitons in single-quantum-dot photoluminescence spectra

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Single $In_xGa_{1-x}As/GaAs$ quantum dot photoluminescence spectra, obtained by low-temperature near-field scanning optical microscopy, are compared with theoretically derived optical spectra. The spectra show shell filling as well as few-particle fine structure associated with neutral and charged multiexcitons, in good agreement with the many-body calculations. There appears to be a greater tendency to charged-exciton formation, which is discussed in terms of the high diffusivity of photogenerated electrons.

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The optical properties of single $In_xGa_{1-x}As$ self-organized quantum dots (QDs), have been intensively investigated in recent years.[1] Atomiclike features and narrow lines have been observed in the power-dependent spectra, reflecting the shell-like electronic structure of the dots and the progressive filling of the confined single-particle states.[2] Besides, multipeaked structures arise from the carrier-carrier Coulomb interactions and related effects.[3]

While the photogenerated electron-hole complexes are intrinsically neutral, different mechanisms have been exploited in order to induce a tunable electrical charging of the dot, resulting in strong renormalizations of the optical spectra.[4–8] Among these, the spatial separation of the electron-hole pairs in coupled quantum wells,[9] the capture of photogenerated electrons by ionized donors,[10] the tuning of the ratio between the electron and hole capture rates by modifying T and the excitation wavelength.[11]

In this work we present a detailed study of the optical spectra of a single $In_xGa_{1-x}As/GaAs$ QD performed by low-temperature (35 K) near-field scanning optical microscopy (NSOM). These spectra are compared with a theoretical investigation of the few-particle states and of the optical properties of the QD. Both the experimental and theoretical luminescence spectra are shown to evolve, with increasing carrier population, from a single sharp line, to richly structured features, which we attribute to the formation of neutral and charged multiparticle complexes. The overall spectrum is found to include several exciton and multiexciton lines which increase linearly with the excitation intensity together with the charged-complexes emission which exhibits a superlinear behavior.

Indium gallium arsenide quantum dots were grown by metal organic chemical vapor disposition on n^+ GaAs(001) substrates. Following the growth of a 200 nm GaAs buffer layer, at a temperature of 580 °C and that of a 5 nm GaAs buffer layer at a slower growth rate, five monolayers of $In_xGa_{1-x}As$ were deposited, to form a layer of quantum dots. These were capped by an undoped 35 nm layer of GaAs. From atomic force microscopy measurements of a corresponding uncapped sample we estimate a dot density of $\approx(3-4)\times10^{10}$ cm^{-2}. In order to isolate single QDs, mesa structures of 100 nm diameter were fabricated by a combination of electron beam lithography and chemical wet-etching.

For the photoluminescence (PL) measurements we used an in-house built NSOM, based on an aperture-NSOM standalone head employing a tuning fork system to detect the tip-sample distance. The sample was mounted on a copper holder which is thermally connected to the cold finger of a He gas flux cryostat by an ultrapure (99.999 %) copper wire bundle. The system was immobilized by a suitably designed thermal insulating basement, which reduces the vibrations of the flux cryostat to a level complying with the vertical resolution of the distance control of NSOM (about 1 nm). The sample temperature during the measurements was 35 K.

The single-dot luminescence was excited in the near-field condition by the continuous wave 514.5 nm line of an Argon ion laser coupled to a tapered fiber with a nominal aperture of 50 nm (Nanonics Ltd). It was collected in far-field and dispersed by a 0.3 m focal length spectrograph equipped with a cooled low-noise charge coupled device detector (Andor Technologies). The spatial and spectral resolutions were approximately 200 nm and 0.4 meV in all the experiments. Integrations times of the order of 5-10 min were used in most measurements.

In Fig. 1(a) we show the excitation-intensity dependence of the single dot PL spectra. The main features of these spectra are (i) at very low excitation intensity (0.26 μW) (Ref. 12) a single line [labeled X in Fig. 1(a)], of full width half maximum (FWHM) 1.5 meV, appears at 1.223 eV; (ii) around 1 μW the spectra become more structured. In particular a line B_0 first appears and grows to $\approx$1.5 meV below the X line, followed by a dominant emission line X_1, which grows superlinearly 4.5 meV below X; additional lines (X_2, X_3, X_4) appear in the energy range 10 meV below X: all these features are related to the s shell of the QD; (iii) above 1.3 μW two p-shell bands rise at 1.258 eV, and split by approximately 3 meV. Above 2.9 μW the s shell progres-

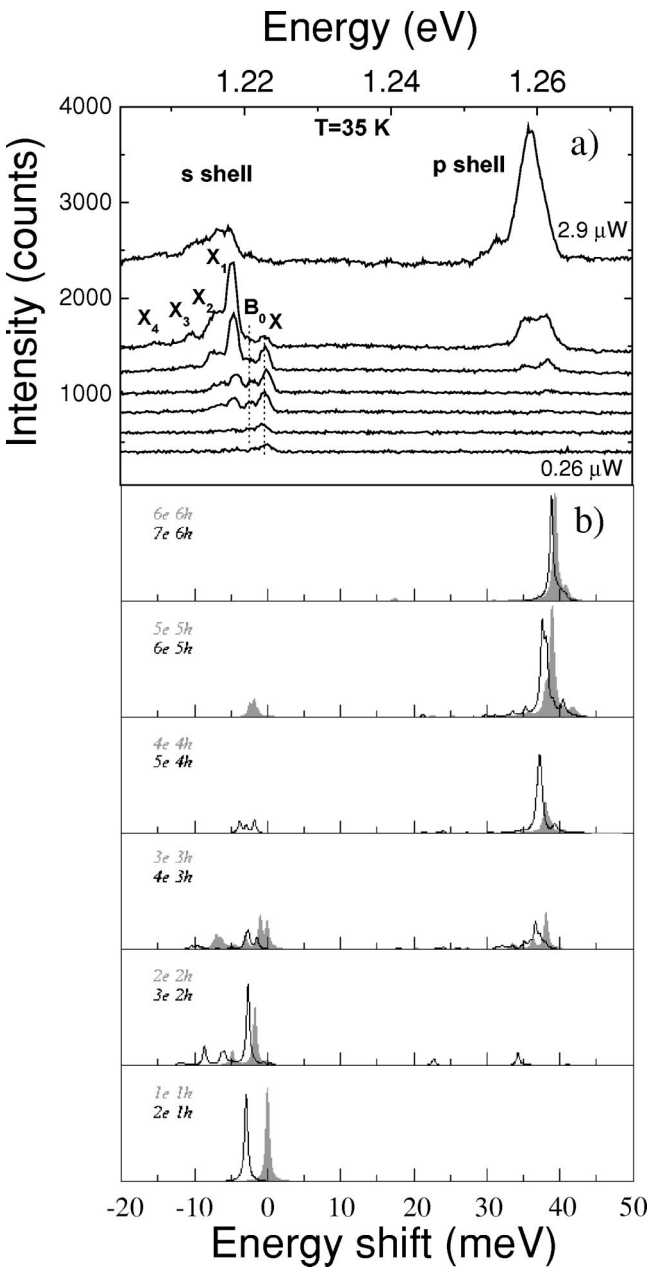

FIG. 1. (a) Photoluminescence spectra of a single $In_xGa_{1-x}As$ quantum dot, excited by a 514.5 nm line of an Argon laser at a sample temperature of 35 K, as a function of the excitation intensity; (b) calculated luminescence spectra for the recombination of neutral (gray filled lines) and negatively charged (black lines) multiexciton complexes.

sively saturates and disappears, and the *p* shell becomes more structured, with a shoulder in the low-energy tail of the high intensity feature at 1.258 eV.

In order to interpret the observed optical spectra we have investigated the few-particle states by means of detailed theoretical calculations. We started by computing the single-particle (SP) eigenstates and eigenvalues within the envelope-function and effective-mass approximations.[13] As a further step, the few-particle states are provided by a configuration-interaction calculation,[14] which fully accounts for the Coulomb-induced correlation effects. We expand the few-particle Hamiltonian, including all the carrier-carrier interaction terms, within the basis of the six bound SP electron states and of the ten energetically lowest hole states. We truncate the resulting Hilbert space by keeping only the configurations of lowest SP energy and finally obtain the few-particle states by directly diagonalizing the Hamiltonian matrix.[15]

The shape of the potential accounting for the confinement of the carriers in the dot and the values of the composition-dependent physical parameters are required for the computation. The resulting eigenfunctions reflect the cylinder symmetry of the system: as discussed below, this implies selection rules with respect to the optical transitions, which are expected to simplify the optical spectra. The SP shell structure is reminiscent of that determined by a two-dimensional (2D) parabolic confinement potential.[13] We enumerate the shells by $n=0,1,2,\ldots$: each of them is composed by $n+1$ levels, with z components of the angular momenta $m=-n,-n+2,\ldots,n-2,n$. All the eigenvalues corresponding to $m\neq 0$ are doubly degenerate: $\epsilon(n,m)=\epsilon(n,-m)$. The energy-level splitting between the shells is of the order of 35 meV for electrons and 7 meV for holes. This is consistent with the overall splitting of the *s* and *p* shells (~ 40 meV) reported in Fig. 1(a).

Figure 1(b) shows the computed contributions to the optical spectra due to different numbers of electrons (ne) and holes (nh) in the dot. We assume that the few-particle complexes relax before a radiative recombination occurs: the initial state is thus a statistical mixture of the few-particle eigenstates associated to each system ($ne-nh$), the weight of each eigenstate being determined by the corresponding Boltzmann factor.[13] Let us first examine the complexes with *equal* numbers of electrons and holes ($ne-nh$ gray filled peaks). Starting from the single-exciton case [Fig. 1(b)], $1e-1h$. A single peak (X) is obtained, due to the recombination of the lowest exciton state, that can be identified with the configuration where the carriers occupy the respective *s* shells. Transitions from higher exciton states are either dipole-forbidden, due to the selection rules arising from the cylindrical symmetry of the system, or suppressed by the Boltzmann factors. With increasing photoexcitation intensities recombination from the multiexciton states appear in the optical spectra. The main peak (B_0) in 1(b) corresponds to the transition between the biexciton and the exciton lowest states. The line is redshifted by 1.5 meV with respect to X: this *biexciton binding energy* mainly arises from the Coulomb correlation between carriers.[16]

A transition to a higher exciton state appears on the low-energy side, with a smaller oscillator strength. As the number of carriers is further increased [see Fig. 1(b), $3e-3h$ to $7e-6h$ lines] the *p* shell is progressively filled: recombination of electron-hole pairs can thus occur both from the *s* and the *p* shells, with a splitting in agreement with the calculated value. The transitions in the *p* shell are all degenerate or quasidegenerate and thus give rise to a single broad peak.

Due to the continuous wave nature of the optical excitation in the experimental results described here, a steady state condition in the creation-recombination mechanisms of electron hole pairs in the dot is achieved. It is therefore reason-

able to expect that both neutral and charged multiexciton complexes are continuously created in the dot. The measured optical spectra are temporally averaged and thus encompass contributions due to transitions involving different numbers of carriers captured in the QD. In Fig. 1(b) (black curves) we show the emission of negatively charged complexes $(n+1)e-nh$: the presence of an additional electron produces a strong redshift of the exciton peak [lowest panel in Fig. 1(b)] and smaller redshifts of the multiexciton lines (upper panels).

The prevailing trend in the spectra is the greater tendency to form charged-exciton complexes instead of neutral multiexciton complexes. With increasing excitation intensity, the prevalence of charged-complexes formation is observed to increase. The main peak in both the *s*-shell (X_1) and the *p*-shell fine structure at high density can be attributed to charged single- and bi-excitonic transitions, whereas the lines X_2, X_3, X_4 mostly arise from transitions involving charged and neutral biexciton and triexciton complexes, as inferred by the comparison with the $3e-2h$ and $3e-3h$ curves in Fig. 1(b).

The very fact that optical excitation results in the formation of negatively charged excitons is counter-intuitive since optical excitation is intrinsically neutral through the photogeneration of electron-hole pairs. Due to the photon energy of the excitation (2.5 eV) in these experiments, the electron-hole pairs are generated in the GaAs barrier region and are then captured in the QD. The relaxation of the photogenerated electron-hole pairs occurs most probably by scattering events with longitudinal optical and acoustical phonons.[17] The smaller effective mass of the free electrons in the GaAs lattice results in a higher diffusivity of the electrons and therefore facilitates the capture in the QD.

Positively charged complexes (not reported here) have also been considered in our calculations. The addition of an excess hole does not produce the redshifted peaks observed experimentally (for example, of the exciton and biexciton lines). This is due to the fact that the hole wave functions are more localized compared to those of the electron: the hole-hole repulsion exceeds the electron-hole attraction in the mean-field limit, thus compensating the negative contributions due to correlation and exchange interactions.[5]

Finally, we discuss the dependence of the integrated intensities of the lines X_i and B_0, which we determine by fitting the spectral peaks and fine structure by means of Lorenztian and Gaussian curves, on the power intensity (Fig. 2). Unlike the case of bulk and quantum well systems, we do not observe a quadratic dependence of the biexciton line B_0 with respect to the *X* line (close circles in Fig. 2). We attribute this

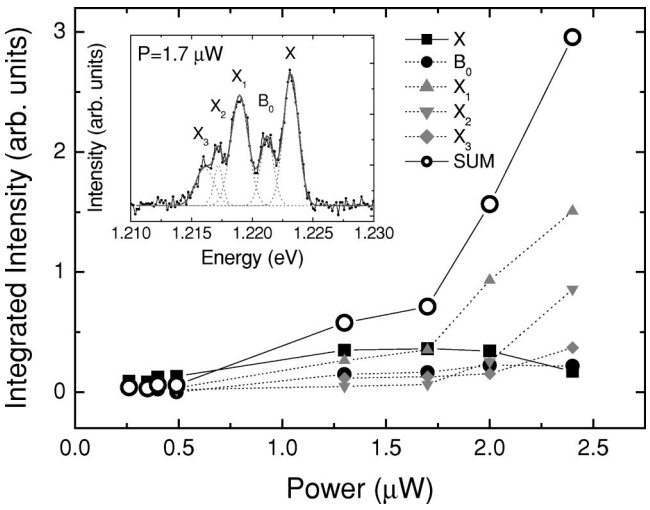

FIG. 2. Integrated intensity of peaks *X*, B_0, X_1, X_2, and X_3 from Fig. 1 as a function of the excitation power intensity. Gaussian fits to the PL spectrum used to determine the integrated intensities of the individual spectral components are shown in the inset.

to the simultaneous occurrence of several different neutral and ionized complex states, into which the total oscillator strength of the related states is distributed. Upon the injection of more than two excitons in the dots, neutral and charged excitons and biexcitons are indeed formed, resulting in a complex intensity dependence of the spectra. Note that the total intensity (open circles in Fig. 2), that is the sum of all the contributions except for *X*, is superlinear.

In conclusion we have measured the photoluminescence of a single $In_xGa_{1-x}As/GaAs$ quantum dot at low temperature by employing cryogenic scanning near-field optical microscopy. The physical origins and evolution of the spectral features have been compared with theoretical calculations. The clear power-intensity dependence of the PL spectra strongly suggests that few interacting excitons are populating the quantum dot. A greater tendency to form charged excitons rather than neutral multiparticle complexes has been observed, probably due to preferential electron trapping in the QD upon diffusion and scattering in the wetting layer.

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[1] For recent reviews, see R. Rinaldi, Int. J. Mod. Phys. B **12**, 471 (1998); A. Zrenner, J. Chem. Phys. **112**, 7790 (2000).

[2] J.-Y. Marzin, J.-M. Gerard, A. Izraël, D. Barrier, and G. Bastard, Phys. Rev. Lett. **73**, 716 (1994); D. Gammon, E.S. Snow, and D.S. Katzer, Appl. Phys. Lett. **67**, 2391 (1995); L. Landin, M.-E. Pistol, C. Pryor, M. Persson, L. Samuelson, and M. Miller, Phys. Rev. B **60**, 16 640 (1999); E. Dekel, D. Regelman, D. Gershoni, E. Ehrenfreund, W.V. Schoenfeld, and P.M. Petroff, *ibid.* **62**, 11 038 (2000); R.M. Thompson, R.M. Stevenson, A.J. Shields, I. Farrer, C.J. Lobo, D.A. Ritchie, M.L. Leadbeater, and M. Pepper, *ibid.* **64**, 201302 (2001); E. Dekel, D. Gershoni, E. Ehrenfreund, D. Spektor, J.M. Garcia, and P.M. Petroff, Phys. Rev. Lett. **80**, 4991 (1998); L. Landin, M.S. Miller, M.-E. Pistol, C.E. Pryor, and L. Samuelson, Science **280**, 262 (1998).

[3] R. Rinaldi, S. Antonaci, M. De Vittorio, R. Cingolani, U. Hohenester, E. Molinari, H. Lipsanen, and J. Tulkki, Phys. Rev. B **62**, 1592 (2000); M. Bayer, O. Stern, P. Hawrylak, S. Fafard, and A. Forchel, Nature (London) **405**, 923 (2000); A.J. Williamson, A. Franceschetti, and A. Zunger, Europhys. Lett. **53**, 59 (2001); R. Heitz, F. Guffarth, I. Mukhametzhanov, M. Grundmann, A. Madhukar, and D. Bimberg, Phys. Rev. B **62**, 16 881 (1998).

[4] J.J. Finley, P.W. Fry, A.D. Ashmore, A. Lemaitre, A.I. Tartakovskii, R. Oulton, D.J. Mowbray, M.S. Skolnick, M. Hopkinson, P.D. Buckle, and P.A. Maksym, Phys. Rev. B **63**, 161305 (2001); J.J. Finley, A.D. Ashmore, A. Lemaitre, D.J. Mowbray, M.S. Skolnick, I.E. Itskevich, P.A. Maksym, M. Hopkinson, and T.F. Krauss, *ibid.* **63**, 073307 (2001).

[5] D.V. Regelman, E. Dekel, D. Gershoni, E. Ehrenfreund, A.J. Williamson, J. Shumway, A. Zunger, W.V. Schoenfeld, and P.M. Petroff, Phys. Rev. B **64**, 165301 (2001).

[6] M. Baier, F. Findeis, A. Zrenner, M. Bichler, and G. Abstreiter, Phys. Rev. B **64**, 195326 (2001).

[7] F. Findeis, M. Baier, A. Zrenner, M. Bichler, G. Abstreiter, U. Hohenester, and E. Molinari, Phys. Rev. B **63**, 121309 (2001).

[8] K.F. Karlsson, E.S. Moskalenko, P.O. Holtz, B. Monemar, W.V. Schoenfeld, J.M. Garcia, and P.M. Petroff, Appl. Phys. Lett. **78**, 2952 (2001).

[9] W.V. Schoenfeld, T. Lundstrom, P.M. Petroff, and D. Gershoni, Appl. Phys. Lett. **74**, 2194 (1999); T. Lundstrom, W.V. Schoenfeld, H. Lee, and P.M. Petroff, Science **286**, 2312 (1999).

[10] A. Hartmann, Y. Ducommun, E. Kapon, U. Hohenester, and E. Molinari, Phys. Rev. Lett. **84**, 5648 (2000).

[11] E.S. Moskalenko, K.F. Karlsson, P.O. Holtz, B. Monemar, W.V. Schoenfeld, J.M. Garcia, and P.M. Petroff, Phys. Rev. B **64**, 085302 (2001).

[12] All measurements of the laser power intensity were made before the coupling with the optical fiber.

[13] L. Jacak, P. Hawrylak, and A. Wojs, *Quantum Dots* (Springer, Berlin, 1998); D. Bimberg, M. Grundmann, and N. Ledenstov, *Quantum Dot Heterostructures* (John Wiley, New York, 1998); U. Woggon, *Optical Properties of Semiconductor Quantum Dots* (Springer, Berlin, 1996).

[14] R. McWeeney, *Methods of Molecular Quantum Mechanics* (Academic, London, 1992).

[15] U. Hohenester and E. Molinari, Phys. Status Solidi B **221**, 19 (2000).

[16] J. Shumway, A. Franceschetti, and A. Zunger, Phys. Rev. B **63**, 155316 (2001).

[17] M. De. Giorgi, C. Lingk, G. von Plessen, J. Feldmann, S. De Rinaldis, A. Passaseo, M. De Vittorio, R. Cingolani, and M. Lomascolo, Appl. Phys. Lett. **79**, 3968 (2001); B. Ohnesorge, M. Albrecht, J. Oshinowo, A. Forchel, and Y. Arakawa, Phys. Rev. B **54**, 11 532 (1996).