Selective optical pumping of charged excitons in unintentionally doped InAs quantum dots

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Received 23 November 2007, in final form 6 February 2008
Published 5 March 2008
Online at stacks.iop.org/Nano/19/145711

Abstract
We have investigated the selective optical pumping of charged excitonic species in a sample containing quantum dots of different sizes and low areal density by photoluminescence and excitation of the photoluminescence microspectroscopy. We study the selective optical excitation of negatively charged excitons as an alternative to commonly used electrical methods. We demonstrate that under resonant excitation in impurity related bands, the selective pumping efficiency can be as high as 85% in small quantum dots having one electron shell and emitting at around 930 nm, and around 65% in big quantum dots having four electron shells and emitting at 1160 nm.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Nowadays, InAs/GaAs self-assembled quantum dots (QDs) are well known nanostructures with important applications in the fields of quantum computation and cryptography [1, 2]. In particular, the fine control of singly charged exciton states (negative or positive trions) has received much interest as a necessary step for single spin manipulation [3, 4]. The charge in QD states can be electrically controlled by tuning the gate voltage in field effect structures with embedded intrinsic QD layers [4–7]. However, this method can produce undesired effects like the reduction of the oscillator strength induced by the external field [8]. The charge state can also be controlled by optical injection, and different charging schemes have been proposed using either above or below barrier excitation [9–13].

In a previous study, we tentatively associated the prevalence of charged excitons in the emission spectra of single QDs to the presence of residual acceptor impurities [14]. In the present work, we report the complete electronic structure of these QDs and analyse carefully the charging mechanism by selective excitation at different photon energies. The optical and morphological characterization of the sample gives evidence of a bimodal distribution: small QDs (SQDs) emitting below 970 nm and large QDs (LQDs) emitting at ~1165 nm at 4 K and clear signatures of impurity related transitions. The SQD ensemble is characterized by a single electron shell (ground state), whereas the LQD one has four electron shells. In spite of this difference, we observe a common behaviour: the selective formation of charged exciton complexes in initially empty QDs that we associate with the presence of unintentional acceptor and donor impurities in the QD surroundings. This study opens the way to control the charge in QDs by optical pumping in the range of wavelengths where ionized acceptors absorb a portion of the incident light.
2. Sample growth and experimental details

The studied sample was grown by molecular beam epitaxy (MBE) on a GaAs substrate. The growth started with a 100 nm-thick GaAs buffer grown at a substrate temperature of 600 °C, followed by the InAs deposition at 505 °C with an equivalent coverage of 2.5 monolayers (ML) using a very low growth rate (0.009 ML s$^{-1}$) and ends with a 100 nm-thick GaAs cap grown by atomic layer MBE at 360 °C [15]. During the InAs deposition, the substrate was not azimuthally rotated, thus obtaining a continuous variation of the InAs coverage throughout the sample surface [16]. The combination of both conditions produces regions of the wafer with a very low density of InAs QDs, down to 1 μm$^{-2}$, suitable for optical investigation of isolated QDs and future use in quantum light sources. In particular, the coverage of the sample under consideration here has a density of about 16 QDs μm$^{-2}$, as estimated by atomic force microscopy (AFM) carried out on uncapped samples grown in the same conditions (inset in figure 1(a)). In the AFM images, we can also observe the bimodal character of the QD distribution with height/diameter pair values of 9/36 and 14/54 nm for the SQD and LQD ensembles, respectively. Such a bimodal size distribution and dimensions have been reported for samples grown under similar conditions [17, 18].

Conventional photoluminescence (PL) characterization was carried out with the sample held in the cold finger of a closed-cycle He cryostat. Single QD micro-PL and excitation of the micro-PL (micro-PLE) were performed by using an optical fibre based diffraction limited confocal microscope inserted in the He exchange gas chamber of an immersion He cryostat. Experiments at 77 K were carried out by inserting the microscope directly on a liquid nitrogen Dewar. The PL signal was excited by a tunable Ti:sapphire laser, dispersed by a 0.5 (0.3) m focal length grating spectrograph and detected with a cooled InGaAs photodiode array (back illuminated Si CCD) for wavelengths above (below) 1000 nm.

3. Results and discussion

3.1. Electronic structure

Figure 1(a) shows the macro-PL spectrum in its high energy range obtained upon optical pumping above the GaAs absorption band edge. The semilogarithmic representation allows the observation of the wetting layer (WL) emission at 1.425 eV, the recombination of GaAs acceptor bound excitons at 1.513 eV (C0X), the free-electron-acceptor/donor–acceptor transition at 1.493 eV (D0C0/C0/C0) and the corresponding LO phonon replica at 1.457 eV (e-C0) [19]. The unintentional incorporation of carbon acceptor impurities (C0) during the MBE growth, as well as with other growth techniques, is a well known effect. However, Hall measurements of similarly grown GaAs buffer layers reveal a residual n-type carrier concentration $n = N_D - N_A \sim 10^{15}$ cm$^{-3}$. This means that through the compensation effect a large number of acceptors are ionized and ready to enable efficient optical pumping of free electrons, as explained below.

The PL spectrum of our sample is completed in figure 1(b) on the low energy side. Two emission bands are observed at 1.06 and 1.38 eV, corresponding to the LQD and SQD families identified on AFM images. The intensity ratio between these bands reflects the lower density of LQDs compared to SQDs (inset of figure 1(a)). The LQD ensemble exhibits excited state filling effects when increasing excitation power (B and C lines), as usually observed in QDs emitting at this energy [20, 21], whereas no saturation effect can be clearly detected on the SQD ensemble PL in the same excitation power range (only the ground state band A and a shoulder on its low energy side are observed). These data reinforce the bimodal interpretation of the AFM results and reflect the different electronic structure of LQD and SQD families.

Figure 2 gives further evidence of the previous peak assignment for the LQD and SQD families. The upper panels in figure 2 show the multi-Gaussian deconvolution of the ensemble emission spectrum at high laser powers. The lower panels contain the micro-PL spectra obtained at 77 K using different excitation powers. It is clear that structures labelled as α–γ in the micro-PL of LQDs are correlated one to one in energy with the bands labelled A–C in the corresponding ensemble spectrum. The observed resonances are associated with optical transitions between different shells of a single LQD with ground state transition at 1.075 eV [20, 21]. Similarly, the extra transition labelled as δ can be due to an optical transition involving the F shell,
although its contribution is merged with the SQD band in the ensemble spectrum. The four optical transitions included in the $\beta$-group appear at energies of 51, 59, 67 and 74 meV above the ground state transition, $\alpha$, the three transitions in the $\gamma$-group are at 110, 121 and 132 meV, while the $\delta$ one occurs at around 180 meV. These multipeak structures can be interpreted in the framework of the most recent atomistic calculations made by Narvaez and Zunger, for example [22]. They calculated optical transitions in two- and three-shell In(Ga)As lens-shaped QDs and reported four resolved 1Phh–1Pe transitions with similar oscillator strengths, just as observed in our LQDs. Above the P shell transitions, one intense 1Dhh–1De and two (very close in energy) 2Shh–2Se optical transitions can be correlated with the two most intense $\gamma$-lines in figure 2(a). Other lines in this energy window could be attributed to nominally forbidden transitions among unpaired shells [7, 22].

The emission of the SQD family does not show the same trend as observed in figure 2(b). We often observe structures like those labelled as i, ii and iii, at 1.297, 1.333 and 1.351 eV, respectively. Yet, their intensities do not scale with the excitation power as expected from the excited state shell filling. Hence, these structures are attributed to the emission from different SQDs within the illumination area. The lines observed in group ii (that under exact focus), for example, can be related to neutral (X$^0$), charged exciton (X$^-$, X$^+$) and biexciton (XX) optical transitions, as indicated in the inset of figure 2(b). In the next section we will discuss in more detail how this assignation can be made based on more accurate results obtained by micro-PL at 4 K.

### 3.2. Ground state optical transitions

The results of the preceding section allowed us to determine the best energy range and experimental conditions appropriate for study of the ground state transitions in single dots belonging to LQD and SQD families at 4 K. Figure 3 shows the micro-PL spectra of an individual QD of each family (LQD (a) and SQD (b)) recorded at three different excitation energies. Excitation at 1.53 eV always gives characteristic ‘spectral line sets’ like the ones shown in figure 3. Neutral exciton and biexciton features are easily identified by the slope of their integrated intensity dependence on the excitation power ($I_{XX} \sim I^2$), as shown in figures 3(c) and (d). The additional spectral lines observed on both sides of the neutral exciton show a predominant linear behaviour with power and are attributed to either negatively charged (X$^{-n}$, $n = 1, 2$) or positively charged (X$^+$) excitons [7, 13, 25].

In principle, the residual n-type doping of the sample should favour the capture of additional electrons by the QDs. However, at low temperatures this effect competes with the trapping of the same electrons by ionized donors. This equilibrium can be disrupted, and the population of free electrons can be increased, by resonantly pumping the optical transitions related to ionized acceptors, like (C$^-$–D$^+$) and, mostly, (C$^-$–e), at around 1.49 eV (their difference is of the order of 4 meV). Under these excitation conditions, we observe in figures 3(a) and (b) that the negative trion peaks are enhanced over the neutral exciton lines in both the LQD and SQD spectrum. This observation reinforces our assignation of the micro-PL lines for the negative trions, X$^-$ (and X$^{-2}$ for LQD), whose binding energies are 7.5 and 3.7 (5.0) meV for the SQDs and LQDs, respectively, values not far from those reported in the literature for similar nanostructures [7, 23–25]. The fact that we cannot observe X$^{-2}$ trions in the SQD micro-PL spectra is consistent with the absence of an excited state in these QDs, as discussed above. Finally, when optical pumping is resonant with the WL absorption edge (1.43 eV) we recover again the intensity ratios of above barrier excitation, as observed in figures 3(a) and (b).

An enhancement of the negative trion intensity upon light excitation below the GaAs barrier was also reported in [11, 12] for QDs emitting around 1.3 eV. The authors considered the
partial ionization of neutral acceptors by the surface electric field to enable the resonant pumping of electrons into the conduction band. In our case, electron transfer towards QDs is warranted by the residual n-type doping of the sample. It implies a reservoir of \( N_A \) completely ionized acceptors at low temperatures ready to absorb light and promote their extra electrons towards the GaAs conduction band. This also explains why the slope of the power dependence of exciton and biexciton transitions can be smaller than 1 and 2, respectively, as shown in figures 3(c) and (d). The filling of the QD levels does not always occur as correlated e–h pairs. The QD can be filled with e–h pairs (up to two in the S shell), but can also be filled with single carriers coming from ionized acceptor impurity levels, or from the different mobility of electrons and holes undergoing above barrier excitation [26]. When radiative recombination takes place in the ground state, an e–h pair disappears and, depending on the initial state of the QD, it leaves behind four possible situations: empty dot, singly charged dot (with electron or hole), or another e–h pair. In this situation, we have recently demonstrated with the use of a master equation microstate (MEM) model that the excitation power dependence of the different excitonic species can show non-integer exponents even under symmetrical optical pumping [27]. Adding extra electrons to this MEM system and keeping the capture times constant, we obtain the predominance of negative trions over neutral excitons, as observed here when ionized impurities absorb photons at around 1.49 eV.

3.3. Selective optical pumping

To get a better insight into the different optical pumping schemes, we have recorded the excitation spectrum (micro-PLE) of neutral and charged emission peaks in individual LQDs and SQDs. Firstly, in figures 4(a) and (b), we represent the integrated micro-PLE spectrum obtained by adding up the intensity of all micro-PL lines as a function of the excitation energy for LQDs and SQDs, respectively. Such a spectrum reveals the contribution of intrinsic optical transitions associated with the WL, like the 2D heavy and light hole excitonic absorption, namely \( H_{\text{WL}} \) and \( L_{\text{WL}} \), at 1.435 and 1.477 eV, respectively [28]. These transitions are obscured in the micro-PLE spectrum of the individual peaks shown in figures 4(c) and (d) which are dominated by extrinsic or impurity related effects.

In both families, the carrier dynamics are strongly affected in the excitation region near 1.495 eV as explained above. The micro-PLE spectra for X\(^{−}\) and X\(^{2−}\) reaches a maximum in the region where ionized acceptor impurities absorb, as indicated in figures 4(c) and (d) by line patterned rectangles. On the contrary, the neutral and positive trion micro-PLE spectra exhibit an intensity minimum in the same energy region. This behaviour clearly confirms our assumption about the role played by the acceptor impurities in lifting extra electrons to the QD.

Finally, we can quantify the effect of the selective optical excitation proposed here defining a ‘selective pumping
Figure 5. Selective pumping efficiency of the differently charged exciton complexes for LQDs (a) and SQDs (b).

efficiency’ for the different charged exciton complexes:

\[ \eta = \frac{X^0 - X^n}{X^0 + X^n} \]

which is represented in figure 5. This parameter does not vary significantly when changing the excitation power, provided we do not reach the saturation level. According to this definition we measure a very high efficiency of negative trion formation, \( \eta \sim 65 \) and 85% for LQDs and SQDs, respectively, under optical pumping in the energy region 1.48–1.50 eV where the generation of free electrons is expected through resonant excitation of ionized acceptors. It should be noted that in both SQD and LQD families, the negative trions are largely depleted (negative values for \( \eta \)) near the WL and GaAs excitonic absorption edges, and the micro-PL spectrum is dominated by neutral and positive trion recombination, as shown in figure 5(a). At the band edges, the local density of states is very large and excitons are photocreated with nearly zero kinetic energy. In this situation a portion of the electrons could be trapped on the ionized donors instead of relaxing into the dots, diminishing the prevalence of negative trions with respect to the population of neutral and positive ones. This is a reasonable hypothesis given the larger concentration and shallower binding energy of donors in our case.

4. Conclusions

We have studied a sample containing a bimodal and low density distribution of quantum dots by using excitation wavelengths below and above the GaAs absorption band edge. Four electron shells have been identified for the larger quantum dots emitting at \( \sim 1.06 \) eV at 4 K, whereas only the S shell has been identified for the smaller quantum dots emitting at 1.36 eV. Despite these differences, by tuning the optical excitation above impurity related transitions we have demonstrated that the selective optical pumping of negative trions can be realized with an efficiency of 65 and 85% for the larger QDs and smaller QDs, respectively. Our findings are relevant for future all-optical schemes pursuing the preparation of single electrons inside quantum dots, of great importance for quantum information applications.

Acknowledgments

The authors gratefully acknowledge financial support from the Generaliat Valenciana (ACOMP07-120), the Spanish MEC through projects TEC 2005-05781-C03-03, NAN 2004-09109-C04-04 and the Consolider-Ingenio 2010 CSD2006-0019, from the Italian MIUR through the FIRB project ‘Nanotecnologie e Nanodispositivi per la Società dell’Informazione’ and from the European Commission through SANDIE Network of Excellence (NMP4-CT-2004-500101).

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