Photoluminescence Up-Conversion in Single Self-Assembled InAs/GaAs Quantum Dots

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Microphotoluminescence measurements under cw excitation reveal the existence of a strong photoluminescence up-conversion from single InAs/GaAs self-assembled quantum dots and also from the InAs wetting layer. Excitation spectroscopy of the up-converted photoluminescence signal shows identical features from the wetting layer and the single quantum dots, i.e., a band tail coming from the deep states localized at the rough interfaces of the wetting layer quantum well. This observation of photoluminescence up-conversion demonstrates the influence on the quantum dot properties of the environment, and highlights the limitations of the artificial atom model for a semiconductor quantum dot.

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In recent years self-assembled semiconductor quantum dots (QDs) have become a popular field in nanostructure research [1]. One of the most studied systems consists in self-assembled InAs/GaAs QDs grown by molecular beam epitaxy in the so-called Stransky-Krastanov mode. The growth mode transition from layer-by-layer growth to three dimensional islanding occurs for an average InAs thickness of 1.7 ML and InAs dots with a lens-like shape (base $\sim$20 nm, height $\sim$2 nm) are obtained on top of an ultrathin rough InAs layer usually called wetting layer (WL) [2]. Because of the reduced size of the InAs dots, quantum carrier confinement occurs in all three spatial directions. This leads to atomiclike discrete electronic states so that QDs are often considered as artificial atoms. Apart from the investigation of these new physical aspects, it was suggested to use the properties of these artificial atoms for applications in high-performance devices such as low threshold lasers [3], novel single-electron devices [4], memories [5], detectors [6], single photon emitters [7] or, more prospectively, as parts of quantum information devices [8].

In most cases the picture of a semiconductor QD as an artificial macroatom might be oversimplified. As a matter of fact, contrarily to the atomic case, a QD can interact with many reservoirs through carrier-phonon, carrier-carrier interactions [9,10] involving one dot, or two dots, or a dot and the surrounding WL. Moreover, possible fluctuations of the electrostatic environment may occur [11]. In this context, the study of single QDs by means of space-resolved optical techniques may allow one to determine the unavoidable limitations of this isolated artificial atom scheme.

In this Letter, we show the existence of a new regime for shallow QDs where the discrete electronic states are coupled with a continuum of states corresponding to a band tail of the quasi-2D InAs WL. This coupling gives rise to striking features in the photoluminescence (PL) and photoluminescence excitation (PLE) spectra of single QDs. Surprisingly, at energies *higher* than the excitation energy, we observed a strong photoluminescence signal from carrier recombination in the WL and in the InAs/GaAs QDs. Thus laser excitation of the QD structure in its transparency region, i.e., for energies below 1.3 eV, allows efficient population of the QD electronic states. We performed photoluminescence excitation spectroscopy by detecting the photoluminescence of a given transition and exciting at higher energies (standard Stokes configuration) and also at lower energies (anti-Stokes configuration). Comparison between the photoluminescence excitation spectra obtained for the fundamental transition of a dot and the WL transition allows us to assign the continuum-like tail present in many excitation spectra of single dots [12,13] to band-tail states of the WL.

Our sample was grown on a GaAs substrate by molecular beam epitaxy. Rotation of the sample was interrupted during the InAs deposition step in order to obtain a variable concentration of InAs islands. The QDs layer is successively sandwiched between two 50 nm thick GaAs layers, two 14 nm $Ga_{0.75}Al_{0.25}As$ layers, and finally two 2 nm GaAs layers. This heterostructure is separated from the substrate by a 1 μm thick AlAs layer. In order to isolate single QDs and improve the collection efficiency of their emission, we have processed mesa structures on top of a gold mirror. To do this we have deposited a 200 nm gold coating on the top of the structure. The sample was then glued on a Si transfer substrate. The GaAs substrate and the AlAs layers were removed using two different liquid etchings. The mesa pattern was finally designed by e-beam lithography and reactive ion etching using $SiCl_4$. This etching procedure was interrupted at 10 nm from the gold mirror.

Microphotoluminescence measurements were performed in the far field using a microscope objective (numerical aperture 0.5) in a confocal geometry. The excitation beam, provided by a tunable cw Ti:sapphire laser,

was focused on the sample with a spot size $\sim 1\ \mu$m, accurately positioned using X-Y piezoelectric stages moving the microscope objective with a precision $\pm 0.05\ \mu$m. The QDs sample was mounted on the cold finger of a continuous flow helium cryostat and the measurements were performed at 10 K. The photoluminescence signal (collected by the same microscope objective as for the excitation in our setup) was detected by a low noise Si-based photon counting module after spectral filtering by a 32 cm monochromator.

A typical photoluminescence spectrum is shown in Fig. 1(a). The excitation was performed at 1.428 eV with an incident power density $P_{ex} \sim 300$ W/cm^2. A broad line is observed at 1.42 eV. It corresponds to electron-hole recombination at the band edge of the quasi-2D InAs WL. Narrow lines are also observable at smaller energies. With a typical density of 10^8–10^9 QDs/cm^2 in our sample, a few dots are observable ($\sim$10 in this particular case) with emission lines between 1.3 and 1.4 eV. No evidence for the existence of excited states was found for these QDs.

When exciting the sample *below* the WL transition energy, a similar emission spectrum is recorded. Such a spectrum is shown in Fig. 1(b) for an excitation energy of 1.345 eV and an incident power density $P_{ex} \sim 10$ kW/cm^2. Great care has been taken to avoid any direct excitation due to possible high energy lines in the excitation laser spectrum. As a matter of fact, the PL spectrum displayed in Fig. 1(b) clearly shows an up conversion of the exciting photon energy. The vertical scales of Figs. 1(a) and 1(b) are the same but in the latter case the excitation power density was approximately 30 times larger than for the nonresonant excitation case, showing the high efficiency of the PL up-conversion.

Early observation of PL up-conversion in semiconductor structures has been reported in type II heterojunctions and the high efficiency of this nonlinear process under cw illumination has attracted much attention [14]. The existence of up-converted photoluminescence has also been found in QD structures. Paskov *et al.* have observed an up-converted photoluminescence arising from the GaAs substrate in a QDs sample [15]. PL up-converted signal from QDs levels has been observed in InP dots but in this case the dots were embedded in a biased heterojunction and electrons were flowing through the sample [16]. To the best of our knowledge, our measurements yield the first observation of an up-converted photoluminescence signal detected in InAs/GaAs QDs, without any electric current flowing in the sample.

As shown in Fig. 2 the excitation power dependence of the PL and up-converted PL signals is quite different. Among the several sharp lines observed in Fig. 1 we focused our attention on the quantum dot emission at 1.33 eV, which is the spectrally most isolated nanostructure with respect to the quasi-2D InAs WL. Nevertheless the results are qualitatively the same for other QDs. In Fig. 2 we have plotted the spectrally integrated intensities of the PL lines detected at 1.33 eV (single QD, triangles) and 1.42 eV (WL, circles) as a function of the excitation power density P_{ex}. In the Stokes configuration (full symbols) the excitation energy is 1.436 eV; in the anti-Stokes configuration (empty symbols) the excitation energy is 1.362 eV for the WL and 1.3 eV for the QD [17]. The excitation power density has been varied between 10 and 10^5 W/cm^2. For an excitation at 1.436 eV, the

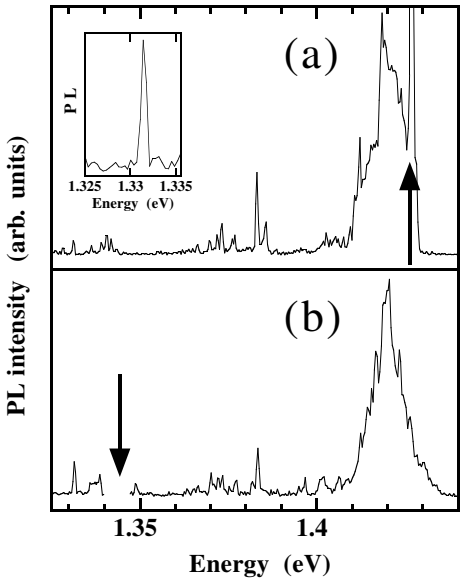

FIG. 1. MicroPL spectra recorded at 10 K under cw excitation at two different energies (indicated by the arrows). (a) Excitation at 1.428 eV with $P_{ex} \sim 300$ W/cm^2. (b) Excitation at 1.345 eV with $P_{ex} \sim 10$ kW/cm^2. The inset is an expanded view of the PL spectrum around 1.33 eV where a single QD line is observed.

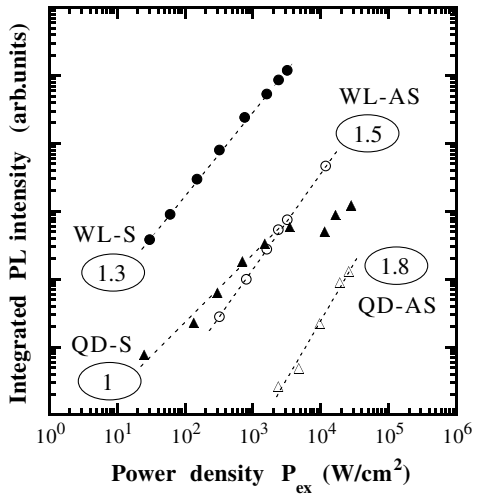

FIG. 2. Spectrally integrated PL intensities of the lines at 1.42 eV (wetting layer) and 1.33 eV (single QD) versus incident power density P_{ex} on a double logarithmic plot. Full (empty) circles for the WL and full (empty) triangles for the single QD in the Stokes (anti-Stokes) excitation configuration. The slope of each power density dependence is indicated.

double logarithmic plot indicates a linear variation of the QD emission for $P_{ex} \leq 2$ kW/cm^2 with a slope close to 1. Saturation of the dot emission is observed for higher power densities. For the QD up-converted emission the slope of the linear variation is close to 2 (slope $\sim$1.8). This nearly quadratic power dependence clearly reveals a second-order process for the PL up-conversion. As far as the WL emission is concerned, the slope of the linear variation is larger than 1 (slope $\sim$1.3) in the Stokes configuration. This slope could indicate the presence of efficient nonradiative channels for the WL emission. As shown in Ref. [18], even for excitonic recombination, slopes higher than 1 (and smaller than 2) can be measured when nonradiative channels are activated. If we examine now the anti-Stokes configuration, the nonlinear dependence on the excitation power density is less pronounced for the WL (slope $\sim$1.5) than for the QD (slope $\sim$1.8), indicating again an interplay between radiative and nonradiative channels in the WL. Still, and similarly to the single QD, a higher slope is measured in the anti-Stokes configuration where high-order processes are activated.

Because of the moderate excitation power densities used here (10^2–10^4 W/cm^2), direct two-photon absorption can be disregarded and Auger processes [14,19] or two step two-photon absorption [20–23] have been invoked to explain this nonlinear phenomenon. As our measurements were performed at 10 K we can also easily rule out a thermal excitation of carriers to the WL. On the contrary we cannot discriminate between Auger processes and two-step two-photon absorption which could both lead to a quadratic intensity dependence of the up-converted PL. If an Auger process is concerned, one electron-hole pair recombines while other carriers are promoted to higher energy levels by Coulomb interaction. For a two step two-photon mechanism, one electron-hole pair is created in a long-lived level by the first photon and then excited further by a second photon. The intermediate state could be the ground state of the QD or, as we will see in the following, a localized state related to the WL. In fact, whatever the mechanisms that up-convert the carriers, an intermediate state is needed which is resonant with the excitation and allows this efficient up-conversion.

To further elucidate the nature of these intermediate states we have performed excitation spectroscopy of the up-converted photoluminescence. In Fig. 3 we display photoluminescence excitation spectra recorded in this anti-Stokes configuration and in the usual Stokes configuration. In Fig. 3(a) the detection energy is set at the WL transition energy and the excitation laser is tuned in the range 1.28–1.43 eV, scanning therefore energies below the QD fundamental transitions up to the WL transition. The excitation power density P_{ex} is approximately 10 kW/cm^2. The up-converted PL signal increases continuously as the excitation energy approaches the WL energy. Furthermore, an important point is that no particular resonance occurs when the excitation is resonant with a QD transition. The

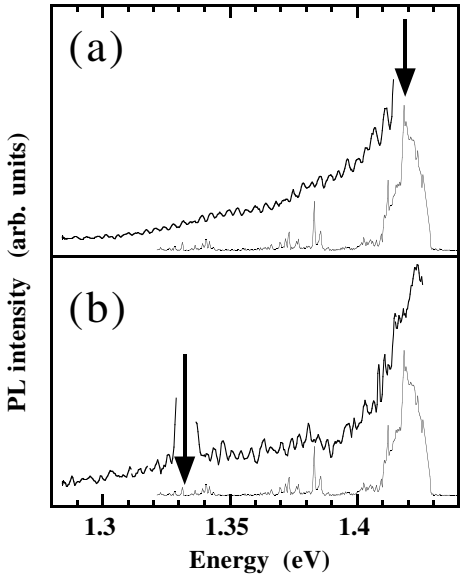

FIG. 3. MicroPLE spectra recorded at 10 K with $P_{ex} \sim$ 10 kW/cm^2 for two detection energies (indicated by the arrows). (a) Detection at 1.42 eV (wetting layer). (b) Detection at 1.33 eV (single QD). The bottom curve (thin line) in (a) and (b) shows on another scale the corresponding microPL spectrum under nonresonant excitation [Fig. 1(a)].

first conclusion we can draw is that the intermediate states responsible for the up-conversion process are related to the WL. Actually the WL is far from being an ideal two-dimensional layer and the unavoidable interface roughness gives rise to localized states with a high enough density to create a quasicontinuum band tail [24]. To get a picture of these states, one has to keep in mind that the formation of a QD induces a local depletion of the WL. Thus the WL thickness presents strong spatial fluctuations. For dilute QDs arrays, the WL shows a 1 ML thick region in the immediate surrounding of a QD and 1 or 2 ML thicker regions approximately 50 nm away [25]. Terraces separated by monolayer steps are created where carriers are confined in states with potentially very different localization degree and energy. In this picture the fact that we see these states in the PLE spectrum of Fig. 3(a) and not in the corresponding PL spectrum, suggests efficient nonradiative decay channels in the quasicontinuum band tail of the WL.

If we focus now [Fig. 3(b)] on the excitation spectrum of the QD, the fundamental transition of which is at 1.33 eV, we observe on the Stokes and anti-Stokes sides a slow increase of the PLE signal with the excitation energy. Except the experimental hole around 1.33 eV to avoid detector damage because of the resonant excitation of the QD transition, we clearly notice the continuity of the PLE signal between the low and high-energy sides. Finally we point out the striking similarity between the PLE spectra of the QD and WL [Figs. 3(a) and 3(b)]: we observe the same background which increases gradually up to the WL

absorption band edge, confirming the existence of a quasicontinuum of states.

The existence of such a quasicontinuum in the excitation spectroscopy of a single QD has already been reported in the literature but its origin could not be identified [12]. On the other hand an extremely different PLE spectrum was found in Ref. [26] where no quasicontinuum was observed. Our PL up-conversion data in single InAs/GaAs QDs give the missing link between these two studies and point out a key element for determining the validity of the artificial macroatom scheme. In fact our up-converted PL measurements allow us to identify the background in the PLE spectrum of a single QD as an intrinsic feature of the WL. Depending on the roughness of the WL the band tail of localized states penetrates more or less deeply in the quasi-OD spectral region where the sharp lines of QDs develop. Therefore we attribute the apparent contradiction between Refs. [12] and [26] to very different interface states of the WLs. Indeed the WL morphology is essential and extremely sample dependent as we observed on single QD PLE spectra of different samples. Additional proof of the validity of this description is given by similar measurements performed on a sample (without mesa structures and gold mirror) where the central energy of the QDs was lower (1.27 eV) and not overlapping with the quasicontinuum band tail of the WL [27]. We did not observe PL up-conversion for the QDs but still for the quasi-2D InAs layer with a comparable efficiency. Again we found a great similarity between the PLE spectra of the QDs and of the quasi-2D InAs layer. These measurements confirm clearly the role of the localized states of the WL as intermediate states for the up-conversion processes.

In conclusion, we report the first observation of a strong PL up-conversion in self-assembled InAs/GaAs QDs. Excitation spectroscopy of the up-converted PL signal allows us to identify the intermediate states for this nonlinear process as localized states of the rough WL. We bring thus a new insight into the absorption spectrum of a single QD by reconciling apparent contradictory results obtained by different groups on single QD excitation spectroscopy. This study on the coupling between a QD and its environment highlights the limitations of the isolated artificial atom picture of a semiconductor QD. Moreover, for future technological developments, this study opens prospects to circumvent these limitations. One may either use selective thermal desorption of In atoms to remove at least partially the WL [28] or deepen the QDs levels to get rid of the spectral overlap between the QDs states and the quasicontinuum band tail of the WL. We believe that future efforts in this direction could significantly improve the performances of semiconductor QD based devices, and especially quantum information devices where the suppression of decoherence channels is a fundamental requirement.

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[1] For a review, see, e.g., *Quantum Dot Heterostructures,* edited by D. Bimberg, M. Grundmann, and N. Ledentsov (Wiley, Chichester, 1998).
[2] J. Y. Marzin *et al.,* Phys. Rev. Lett. **73,** 716 (1994).
[3] P. G. Eliseev *et al.,* Appl. Phys. Lett. **77**, 262 (2000).
[4] H. Drexler *et al.,* Phys. Rev. Lett. **73**, 2252 (1994).
[5] G. Yusa and H. Sakaki, Appl. Phys. Lett. **70**, 345 (1997).
[6] S. Kim *et al.,* Appl. Phys. Lett. **73**, 963 (1998).
[7] P. Michler *et al.,* Science **290**, 2282 (2000).
[8] E. Biolatti *et al.,* Phys. Rev. Lett. **85**, 5647 (2000).
[9] S. Hameau *et al.,* Phys. Rev. Lett. **83**, 4152 (1999).
[10] R. Ferreira and G. Bastard, Appl. Phys. Lett. **74**, 2818 (1999).
[11] H. B. Robinson and B. B. Goldberg, Phys. Rev. B **61**, R5086 (2000).
[12] Y. Toda *et al.,* Phys. Rev. Lett. **82**, 4114 (1999).
[13] J. J. Finley *et al.,* Phys. Rev. B **63**, 073307 (2001).
[14] W. Seidel *et al.,* Phys. Rev. Lett. **73**, 2356 (1994).
[15] P. P. Paskov *et al.,* Appl. Phys. Lett. **77**, 812 (2000).
[16] I. V. Ignatiev *et al.,* Phys. Rev. B **60**, R14 001 (1999).
[17] With an excitation at 1.3 eV for both the WL and the QD, one may get a slightly different value for the slope of the WL (see Ref. [15] where the slope of the power dependence is studied as a function of the excitation energy). However, this does not affect the fact that a higher slope is measured in the anti-Stokes configuration.
[18] N. H. Ky *et al.,* Phys. Rev. B **46**, 6947 (1992).
[19] F. A. Driessen *et al.,* Phys. Rev. B **54**, R5263 (1996).
[20] R. Hellmann *et al.,* Phys. Rev. B **51**, 18 053 (1995).
[21] J. Zeman *et al.,* Phys. Rev. B **55**, R13 428 (1997).
[22] Y. H. Cho *et al.,* Phys. Rev. B **56**, R4375 (1997).
[23] T. Kita *et al.,* Phys. Rev. B **59**, 15358 (1999).
[24] Defects in the GaAs and AlGaAs barrier layers may also give rise to band tails below their absorption edge. However, these defect states play a minor role in the up-conversion process as shown in Ref. [15] where the up-converted PL signal of the GaAs substrate vanishes when the WL-QD layer is etched away.
[25] J. M. Gérard *et al.,* J. Cryst. Growth **150**, 351 (1995).
[26] P. Hawrylak *et al.,* Phys. Rev. Lett. **85**, 389 (2000).
[27] G. Cassabois, C. Kammerer, R. Sopracase, C. Voisin, C. Delalande, Ph. Roussignol, and J. M. Gérard (to be published).
[28] Z. R. Wasilewski, S. Fafard, and J. P. MacCaffrey, J. Cryst. Growth **201**, 1131 (1999).