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Competition in the carrier capture between InGaAs/AlGaAs quantum dots and deep point defects

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Abstract. The presence of an extrinsic photoluminescence (PL) band peaked at 1.356 eV at low temperature is observed, on a large number of self-assembled InAs and $\mathrm{In_{0.5}Ga_{0.5}As}$ quantum dot (QD) structures, when exciting just below the GaAs absorption edge. A detailed optical characterization allows us to attribute the 1.356 eV PL band to the radiative transition between the conduction band and the doubly ionized $\mathrm{Cu_{Ga}}$ acceptor in GaAs. A striking common feature is observed in all investigated samples, namely a resonant quenching of the QD-PL when exciting on the excited level of this deep defect. Moreover, the photoluminescence excitation (PLE) spectrum of the 1.356 eV emission turns out to be almost specular to the QD PLE. This correlation between the PL efficiency of the QDs and the Cu centers evidences a competition in the carrier capture arising from a resonant coupling between the excited level of the defect and the electronic states of the wetting layer on which the QDs nucleate. The estimated Cu concentration is compatible with a contamination during the epitaxial growth.

PACS. 78.67.Hc Quantum dots – 71.55.Eq III-V semiconductors

1 Introduction

The subject of semiconductor quantum dot (QD) structures has attracted increasing attention during the last decade. These zero-dimensional structures, being systems with an atomic-like density of states, are attractive for research in fundamental physics [1] and are expected to be promising for technological applications [2]. Peculiar quantum mechanical effects have been predicted and observed, such as Coulomb blockade [3], random telegraph [4], photon bunching [5], and so on. Nevertheless, the driving force in this research field is related to the development of new or more efficient devices. Applications to non linear optics devices [6], optical data storage [7], quantum computers [8] and in particular lasers [2] have been exploited or realized. The most successful QD heterostructures for microelectronics and electro-optics devices are fabricated using Stranski- Krastanov growth mode which is based on self-organization phenomena in strong lattice mismatched systems. The two most relevant advantages of this growth technique are the possibility of integrating the QD layers in a p-i-n junction allowing electrical carrier injection and the strong reduction of defect contamination of the QDs, which show high radiative efficiency. Indeed the growth of defect free semiconductor QDs is a very important technological achievement in order to optimize the luminescence efficiency at room temperature in view of laser applications. So far many experimental and theoretical studies have addressed the problem of photoluminescence (PL) thermal quenching and of the characterization of non-radiative channels [9,10]. Much less is known about the presence of deep point defects and their influence on the carrier kinetics in QDs. Only recently the characterization of electron trap states in or near the QD has been addressed [11,12]. Effects on the QDs carrier emission due to the Coulomb interaction between carrier localized in the QDs and in deep point defects have been reported [13].

In this paper we demonstrate that in the studied epitaxial structures deep levels are present which introduce carrier capture channels in competition with the photoexcited carrier capture by QDs. Our study concerns a detailed characterization of a QD PL quenching channel in resonance with the wetting layer (WL) states, in a large set of InAs and $\mathrm{In_{0.5}Ga_{0.5}As}$ QD structures grown on GaAs substrates. We found a strong reduction of the QD PL yield when exciting in a narrow spectral region just below the GaAs absorption edge. This phenomenology, observed in all the investigated samples, is also recognizable in the QD PLE spectra reported in the literature [14,15]. In correspondence of the QD PL yield quenching we observed the insurgence of an extrinsic PL band peaked at

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1.356 eV. An extensive optical characterization leads us to attribute the 1.356 eV PL band to the radiative transition between the conduction band and the doubly ionized Cu_{Ga} acceptor in GaAs. Evidence of a competition in the carrier capture between the Cu related defects and the QDs is given by the almost specularity between the QD and the 1.356 eV PLE spectra. The presence of an efficient recombination channel competitive with the WL-to-QD thermalization process is originated by a resonant coupling between the excited level of the defect and the electronic states of the WL on which the QDs nucleate.

2 Sample growth and experimental details

We investigated 15 different samples of InAs and $In_{0.5}Ga_{0.5}As$ grown by Atomic Layer Molecular Beam Epitaxy (ALMBE) [16]. Firstly, a 100 nm-thick GaAs buffer layer was grown by Molecular Beam Epitaxy (MBE) at 600 °C on (100) GaAs substrates. Then the substrate temperature was lowered to 460 °C and an InAs or $In_{0.5}Ga_{0.5}As$ layer of thickness larger than the critical thickness for the QD nucleation was deposited by ALMBE. Finally a GaAs cap layer was grown by ALMBE at a temperature (360 °C) lower than the QD growth temperature in order to reduce local In segregation [16]. The growth was interrupted for 210 s before and after the InAs (or $In_{0.5}Ga_{0.5}As$) deposition to stabilize the growth temperature of different layers. In few cases the QDs were embedded in thin (5 nm) $Al_yGa_{1-y}As$ layers. Either single QD layer or stacked QD layers were investigated. The PLE and PL spectra were resolved by a double grating monochromator and detected by a cooled Ge photodiode. The excitation source was a Ti-sapphire laser, pumped by a multiline Ar^+ laser. The measurements were performed between 2 and 300 K using a bath type cryostat.

3 Results and discussion

Figure 1 shows the PL spectra of InAs/AlGaAs/GaAs QD structure at $T = 80$ K in a semilogarithmic scale for two different excitation energies. The dotted line refers to an excitation energy above the GaAs absorption edge and shows the PL band from the QDs peaked at about 1.1 eV. Note that the PL high energy tail smoothly decays and no clear contributions are observed in the 1.3–1.4 eV region. The PL spectrum for the excitation energy of 1.493 eV is reported as solid line. A strong reduction of the QD PL intensity for this resonant excitation is observed (it will be discussed later). In addition, an intense PL band appears at 1.356 eV, which is not present for excitation above the GaAs band gap. This PL band, which also shows low energy shoulders that can be identified as the satellite LO phonon replicas, is observed in all the investigated samples and hereafter will be denoted as L1. The L1 band in QD samples has been recently observed in reference [17].

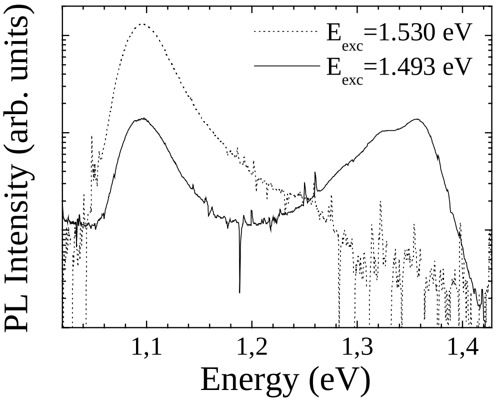

Fig. 1. PL spectra of InAs/AlGaAs/GaAs samples. The measurements have been performed at $T = 80$ K, exciting at 1.530 eV (dotted line) and at 1.493 eV (solid line).

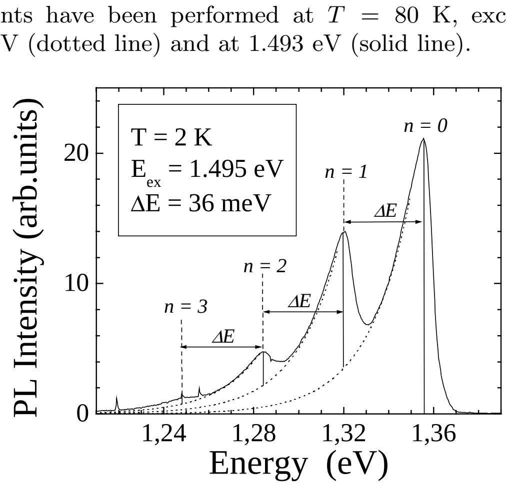

Fig. 2. PL spectrum of the L1 band at $T = 2$ K. The dashed lines are the exponential fits of the low energy tails of each replica; the bars show the intensity of the phonon replicas.

In order to investigate the nature of the L1 band we have performed a detailed analysis of its temperature dependence. The PL spectra at 2 K with resonant excitation at 1.495 eV is reported in Figure 2. We clearly resolve up to 4 replicas spaced by the GaAs LO phonon energy of 36 meV. The different replica show the same PL lineshape. This is strongly asymmetric with a much more pronounced low energy tail. As a matter of fact a Gaussian analysis does not fit for the L1 band. In order to evaluate the PL intensity of each phonon replica we used a phenomenological procedure, based on the observation that each LO replica of the L1 band shows an almost exponential low energy tail (see the semilogarithmic plot in Fig. 3). We have fitted the replica low energy sides with exponential tails, which are shown as dashed lines in Figure 2. The difference between the PL peak intensity of the nth replica and the fit of the low energy tail of the $(n-1)$th replica (solid bars in Fig. 2) gives the intensity of each replica. These values, normalized to the peak intensity corresponding to $n = 0$, are reported in Table 1. They are compared to the Hopfield prediction

$$I_n = A\exp\{-S\}\frac{S^n}{n!} \tag{1}$$

for the intensity of the nth phonon replica, based on a configuration coordinate model [18], expressed in equation (1) and calculated with the Huang-Rhys factor $S = 0.5$. The

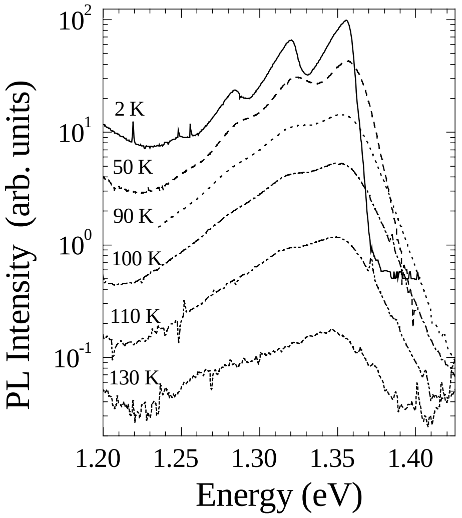

Fig. 3. PL spectra of the L1 band at various temperatures shown in a semilogarithmic plot.

Table 1. Peak intensity of phonon replicas deduced from the PL spectrum in Figure 3 ($I_{\rm PL}$) and from equation (1) ($I_{\rm TH}$). Data have been normalized to the value corresponding to $n = 0$.

	$n = 0$	$n = 1$	$n = 2$	$n = 3$
$I_{\rm PL}$	1	4.9×10^{-1}	1.20×10^{-1}	2.15×10^{-2}
$I_{\rm TH}$	1	5.0×10^{-1}	1.25×10^{-1}	2.08×10^{-2}

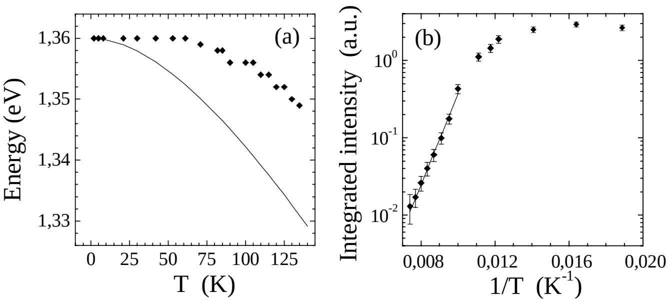

Fig. 4. (a) Energy position of the L1 band with increasing temperature (dots), compared to the thermal variation of GaAs energy gap (line). (b) Temperature dependence of the PL integrated intensity; the fit of high temperature data (full line) gives the activation energy $\Delta E = 120 \pm 15$ meV.

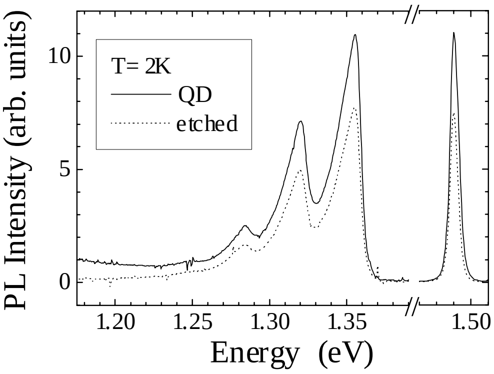

Fig. 5. Comparison of the PL from the virgin (solid line) and from the etched sample (dotted line), measured at 2 K. The spectrum on the left showing the L1 band is obtained exciting at 1.493 eV; the spectrum on the right showing the GaAs band-shallow acceptor band is obtained exciting at 1.589 eV.

good agreement between the experimental and the theoretical values (Tab. 1) leads us to conclude that the center responsible for the L1 emission is a deep defect associated with strong lattice distortion.

Further confirmations of this attribution arise from the temperature dependence of the L1 band. Figure 3 reports, in a semilogarithmic plot, the evolution of the L1 band for increasing temperature, between 2 and 130 K keeping the same scale factor in order to compare the relative intensities. A dramatic thermal broadening of the replicas is observed. For $T > 100$ K the phonon replicas cannot be anymore resolved despite the 36 meV splitting. This denotes a strong phonon coupling, in agreement with the presence of a lattice distortion around the defect. In addition the energy position of the L1 band shows a weak dependence on the temperature. Figure 4a shows the temperature dependence of the L1 peak energy. The experimental data are compared with the prediction of the Varshni law for the GaAs [19], scaled at 1.356 eV for low T. Clearly the shift of the extrinsic band does not follow the GaAs band gap variation, as expected for deep level transitions [19]. A strong quenching of the PL integrated intensity for increasing temperature is also found. The Arrhenius plot of the PL integrated intensity is reported in Figure 4b. An exponential fit of the high temperature data gives an activation energy of 120±15 meV, which agrees with the $\rm Cu_{Ga}$ activation energy of 140 meV obtained in reference [20] by means of electrical measurements. We attributed the PL thermal quenching to the thermal activation of carriers from the ground to the excited state of the defect. Indeed it is well known that the PL thermal quenching of the deep centers in semiconductor structures mainly occurs *via* the thermal population of the excited states [19].

The question arises whether this defect is a native defect of the GaAs layers or is a new interfacial defect introduced by the deposition of the strongly strained QD layers. In order to answer this question, we have chemically etched the QD layers and the surrounding barriers in one sample. In the left side of Figure 5 the comparison between the PL spectra at $T = 2$ K of the virgin and the etched samples for resonant excitation at 1.493 eV is shown. Note, in the PL spectrum of the etched sample, the lack of the low energy tail associated to the QD PL peaked at 1.1 eV. In the etched sample, the L1 band intensity turns out to be reduced as much as the GaAs band-shallow acceptor emission, shown in the right part of the Figure 5. Therefore in both cases the extrinsic band is present with similar PL efficiency. We conclude that the deep defect responsible of the L1 band is a native defect of the GaAs buffer layer, even if the possibility of accumulation of this defect at the QD layers cannot be completely ruled out. In fact, the accumulation of electron trap states at the InAs QDs layers has been recently reported [11,12].

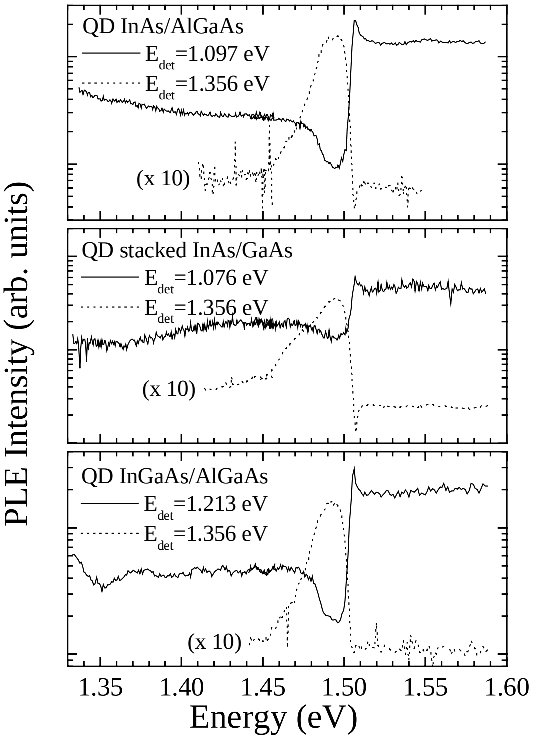

Fig. 6. PLE spectra at 80 K from various samples. The solid lines refer to a detection energy corresponding to the peak position of the QD band; the dotted lines refer to the detection energy of the L1 band.

On the basis of the present analysis and comparing with data reported in literature [21], we attribute the L1 band to the radiative transition between the conduction band or shallow donors and the 0.156 eV Cu acceptor in GaAs. Recently [20] the 0.156 eV level has been assigned to the $(-/2-)$ transition of the substitutional $\mathrm{Cu_{Ga}}$ defect, *i.e.*, the capture of the first hole by the doubly ionized acceptor.

Let us now go back to the most striking feature observed in our samples, that is the resonant quenching of the QD PL associated with the selective excitation of the L1 band. This is very clearly shown in Figure 6 where the QD-PLE (solid lines) are compared with the L1-PLE spectra (dotted lines) for three different structures at $T = 80$ K. Beside the GaAs excitonic peak at 1.505 eV, the PLE spectrum of the QDs shows a pronounced dip just below the GaAs absorption edge. This PLE dip, denoting a reduction of the PL efficiency from the QD, is found in all the investigated samples. The comparison with the PLE spectra of the L1 band helps us to understand the origin of the resonant quenching of the QD PL. A strong resonance is found in a narrow spectral region below the GaAs excitonic peak, in correspondence of the dip observed in the PLE spectrum of the QDs. Note that the energy separation between the L1 band and the resonance in the PLE spectrum of L1 band (of the order of 140 meV) nicely corresponds to the activation energy of the thermal quenching of the L1 band. We conclude that the PLE resonance for the L1 band is associated to the excited state of the defect.

Even more interesting is the fact that the PLE spectra of the L1 band are almost specular to the QD PLE (Fig. 6). Indeed a narrow dip in the L1 PLE spectra is found in correspondence of the GaAs excitonic peak present in the QD PLE spectra. These measurements clearly point out the competition in the carrier capture between the QDs and this new radiative center. The carriers photogenerated in the wetting layer can either relax into the excited state of the substitutional $\mathrm{Cu_{Ga}}$ defect or be captured by the QDs. Therefore the excited state of the deep defect, which also acts as an efficient quenching channel of the L1 band at high temperature, gives rise to a resonant quenching channel for the QD carrier population. The relevance of the $\mathrm{Cu_{Ga}}$ defects as efficient non radiative centers for Cu unintentionally contaminated GaAs epilayers, is reported in reference [22]. It is also worth stressing that the phenomenology observed in our samples seems to be quite general. As a matter of fact a similar dip just below the GaAs absorption edge has already been observed in the literature in the PLE spectra of either InAs QDs [14,15] and InGaAs quantum wells [23].

A comment is needed concerning the evaluation of the Cu contamination in our samples. In previous studies the L1 band in GaAs samples was easily observed using non resonant excitation with $\mathrm{Ar^+}$ laser even in case of very low copper concentration, typically below 10^{15} $\mathrm{cm^{-3}}$ [24,25]. In our QD sample the L1 band cannot be detected in the spectra excited above the GaAs band gap. This leads us to conclude that in our structures the density of $\mathrm{Cu_{Ga}}$ defects is small enough to be compatible with a unintentional contamination during the epitaxial growth. At the same time, as discussed before, the accumulation of defects at the InAs strained layers is possible [11,12]. When exciting resonantly on its excited level, the defect acts as an efficient recombination center, becoming competitive with QDs in the carrier capture. We believe that this competition arises from the resonance between this excited level and the electronic states of the wetting layer, which acts as an efficient reservoir of carriers for QDs.

As a final remark, we comment on the role of the insurgency of L1 band in the study of the QD optical properties obtained with resonant photoluminescence excitation (RPL). Examples of RPL spectra are reported in Figure 7 for different excitation energies and also for different structures corresponding to different QD emission energies. For non resonant excitation ($E_{exc} = 1.589$ eV) the PL spectrum reflects the inhomogeneous QD size distribution. Multiple structures, showing a sizeable spectral narrowing with respect to the non resonantly excited PL spectra, appear in the QD RPL (upper spectra in Fig. 7). This occurs whenever the excitation energy matches an excited level of a certain QD inside the inhomogeneously broadened QD band, leading to a selective excitation of a small subensemble of QDs. The use of RPL has indeed recently attracted increasing interest due to the possibility of determining the energy position of the excited levels, thus addressing the single particle density of states of semiconductor QDs [15]. However our data clearly show that in addition to the multiple PL structure related to the

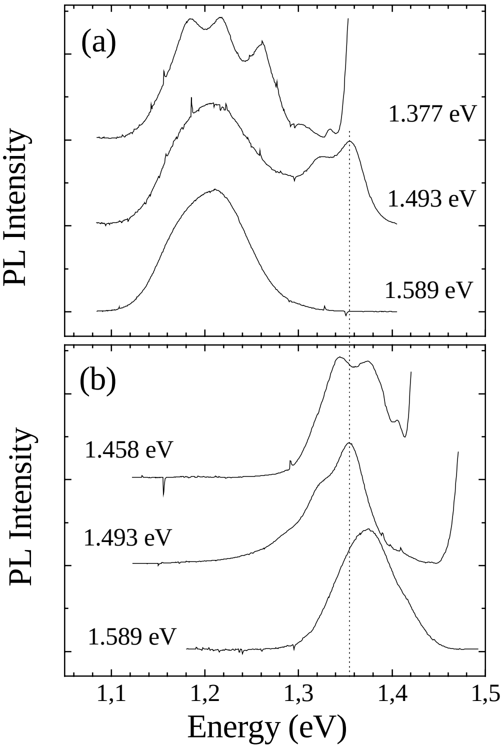

Fig. 7. RPL spectra of InGaAs/AlGaAs QD, performed at 80 K. Each spectrum is normalized to its maximum. The spectra are vertically shifted for clarity. The exciting energy is reported beside the corresponding spectrum. The L1 emission energy is marked by the dotted line. Panel (a) refers to $In_{0.5}Ga_{0.5}As$ QD with thin $Al_{0.15}Ga_{0.85}As$ barriers. Panel (b) refers to $In_{0.5}Ga_{0.5}As$ QD with thin $Al_{0.28}Ga_{0.72}As$ barriers.

selective excitation of the QDs the L1 band appears for resonant excitation at 1.493 eV. The L1 band can strongly warp the QD emission obtained with RPL leading to possible misunderstanding of the QD optical properties. This is particularly true for InGaAs QDs with thin $Al_{0.3}Ga_{0.7}As$ barriers (Fig.7b) where the fundamental emission energy is almost resonant with the L1 band.

4 Conclusions

In conclusion a large set of different QD samples have been studied by PL, PLE and RPL. Evidence of a resonant quenching of the QD-PL when exciting on the wetting layer states resonantly with the excited level of the Cu_{Ga} defect in GaAs is found. The presence of this point defect is demonstrated by the presence of the L1 PL band whenever exciting just below the GaAs absorption edge. The L1 band PLE spectrum is almost specular to the QD PLE. This correlation between the PL efficiency of the QDs and of the Cu_{Ga} centers denotes a competition in the carrier capture arising from a resonant coupling between the excited level of the defect and the electronic states of the wetting layer on which the QDs nucleate. In addition the L1 band may overlap with the QD PL producing a warping of the QD PL lineshape, eventually leading to a misunderstanding of the optical properties of the QDs in RPL measurements.

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