Effects of post-growth annealing on the optical properties of self-assembled GaAs/AlGaAs quantum dots

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Abstract

Photoluminescence spectroscopy is used to analyze the effects of post-growth thermal annealing on the electronic properties and capture processes of self-assembled GaAs/AlGaAs quantum dots grown by modified droplet epitaxy. Post-growth annealing induces deep changes in the electronic structure of the quantum dots material, modifying both capture processes and photoluminescence quenching channels. The optical data, together with theoretical models, are used to quantify such structural and electronic modifications in the annealed materials. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The semiconductor artificial atoms, or quantum dots (QD), are becoming essential materials for fabricating novel and strongly improved photonic and electronic devices [1]. Recently, self-assembling of high quality, nanometer scale, QDs have been obtained by modified molecular beam epitaxy (MBE) methods [2] or via strained epilayer epitaxy in the Stranski–Krastanov (SK) growth mode [1,3]. The availability of self-assembled QD materials, obtained with epitaxial techniques, has triggered an in-depth research of the physical phenomena related to the QD growth.

Self-assembling of high quality, defect free, QDs with the SK method has its major drawback in the necessary presence of strain for triggering the island formation in the epitaxial layer. Strain deeply modifies the electronic structure of the materials composing the QD system.
Orthorhombic deformation potentials induce up-shift of the band edge of the QD. Because of the breaking of two-dimensional symmetry caused by the three-dimensional growth, the strain field is not uniform and not limited to the epilayer. Strong strain gradients, both in the QDs and in the barrier, change the electronic wave function localization and affect capture mechanisms and thermalization processes of the carriers. Moreover, shear strain components, present on the QD facets and edges, give rise to piezoelectric fields affecting the electronic wave functions and enhancing the electron phonon interaction in QDs [4]. The comprehension of the intrinsic wave function localization effects and of the interplay of strain and localization on the electronic properties and the capture and thermalization processes in III–V self-assembled QD materials, calls for strain free, high quality, QDs.

Lately, we reported a modified droplet epitaxy (MDE) method for self-assembling high density, strain free and defect free QDs [5] which is based on the droplet epitaxy method [2,6,7]. The MDE growth method permits the growth of QDs whose composition, because of the lack of the lattice mismatch constraint as in the SK method, is completely uncorrelated with that of the growth substrate. The QD samples grown with this methodology (GaAs/AlGaAs and InGaAs/GaAs) show a good emission yield, even at room temperature [5,8]. In addition to the possibility of tuning the strain of the structure, the complete uncoupling of QD from the substrate allows the growth of QDs on a wetting layer (WL) of variable thickness. Eventually, the WL can be suppressed [9]. Moreover, by modification of the surface reconstruction and of the adatom mobility it is possible to obtain QD samples with a surface density ranging as low as \( \approx 6 \times 10^8 \text{cm}^{-2} \). Such peculiar characteristics make the MDE growth a promising candidate for obtaining ad-hoc QD materials for the investigating fundamental aspects of the physics of the 0D confined heterostructures, getting rid of strain, WL and, eventually, permitting the study of single, isolated QD. In addition, the large set of degrees of freedom left free by the MDE growth technique should allow the design of QD heterostructures devices, like medium infrared light detectors and semiconductor optical amplifiers, with improved performances.

However, the MDE growth is performed at low substrate temperature (around 180°C), where the quality of the as-grown materials is, in general, poor. Post-growth annealing is the typical procedure used to recover material quality. Because of the highly non-equilibrium growth procedure of the MDE growth, the modifications induced by the annealing process are expected to be marked and to involve both the morphological and electronic aspects of the QD material. The aim of this paper is to present and discuss the effects of post-growth annealing procedure on the electronic properties of the MDE–QDs. We will devote particular attention to the possible changes in the QD carrier capture processes and to the QD PL emission modifications that the post-growth annealing process induces on these non-equilibrium grown materials.

We used in a combined manner PL and time resolved PL in order to quantify the structural modification that these QDs undergo, and characterize the change in their optical properties as a function of the annealing temperature. From the ground and excited states transition energies we gain information on the potential profile that carriers within the QD are subjected to. QD PL temperature dependence gives us additional information on the evolution of the electronic structure of the QD environment with the annealing temperature. We related these information to the structural modification that the material undergoes during the annealing procedure by means of theoretical modeling of QD electronic structure and carrier thermal properties. We demonstrate that the post-annealing has as major effects the promotion of a sizeable interdiffusion of the group III species at the hetero-interfaces, the improvement of the overall material quality and the modification of the carrier dynamics with the temperature of the QD ensemble.

The work is organized as follows: in Section 2 we describe the samples and the experimental setup; in Section 3 we outline and discuss our cw and time resolved PL findings; Section 4 is devoted to the analysis of the PL temperature behavior. Conclusions are presented in Section 5.
2. Experimental details

The samples were grown by MDE. The process was performed in a Riber-32P MBE system with elemental sources and an EPI-valved As cracking source. The choice of the As cracking source, although only uncracked As is used in MDE, is motivated by the possibility offered by this type of sources of a rapid modulation of a high As flux. After the desorption of native oxides in the GaAs(001) wafer, 300 nm GaAs buffer layer and 500 nm Al$_{0.3}$Ga$_{0.7}$As barrier layer were grown at the temperature of 580°C. The substrate temperature is then lowered, the As valve closed and the As pressure in the growth chamber depleted. Droplet formation was carried out by supplying Ga on As-adsorbed $c(4 \times 4)$ surface at the substrate temperature of 180°C. The Ga flux was equivalent to that necessary for a GaAs growth rate of 0.5 MLs/s. Since there are 1.75 MLs excess As atoms on the $c(4 \times 4)$ surface [10], the initial group III atoms (in this case Ga) are incorporated into the surface, resulting in the appearance of a thin GaAs layer wetting the surface. The subsequent deposition of Ga, due to the low growth temperature, leads to the formation of metallic droplets on the top of the growth substrate. Sample A0 was obtained by covering the substrate with 4.75 MLs of Ga.

Following the deposition of the Ga droplets an As$_4$ molecular beam with the flux of $2 \times 10^{-4}$ Torr was irradiated on the surface. After the complete change of reflection high-energy electron diffraction (RHEED) pattern from halo to spots, an Al$_{0.3}$Ga$_{0.7}$As barrier layer of 10 nm was grown by migration enhanced epitaxy [11] at the same temperature (180°C) in order to prevent two-dimensional regrowth of the naked GaAs microcrystals [5]. Then, the growth temperature was raised back to 580°C and 90 nm of Al$_{0.3}$Ga$_{0.7}$As and 10 nm of GaAs as cap layer were grown by ordinary MBE. Surface (before the deposition of the capping layer) and cross section high resolution scanning electron microscope (HRSEM) demonstrate the formation of pyramidal shape nanocrystals with typical base sizes of 16 nm x 20 nm and a density of $\approx 1 \times 10^{10}$ cm$^{-2}$ [12]. Pieces cut from sample A0 were reloaded in the growth chamber and annealed for 60 min in $1.5 \times 10^{-5}$ Torr As$_4$ atmosphere at temperatures ($T_{\text{Ann}}$) in the 520–760°C range at 40°C steps (samples A1–A7).

CW PL spectra were measured in the 17–250 K temperature range. The PL was excited with an Ar$^+$ laser in multiline mode. The excitation power density $P_\text{exc}$ ranged from 5 to 5000 W/cm$^2$, with a spot diameter of 500 or 100 μm. PL spectra were measured by a grating monochromator operating with a GaAs photomultiplier. Time-resolved PL measurement was carried out with use of a second-harmonic output of a mode-locked Ti-sapphire laser with 76-MHz repetition. The excitation power was estimated to be between $\approx 1.3$ nJ/cm$^2$ and $\approx 130$ nJ/cm$^2$ per pulse. The PL signal was dispersed by a polychromator, and temporally resolved by a streak camera of 5 ps resolution. All experiments were performed at 5 K.

3. Photoluminescence low temperature properties

The low temperature (17 K) PL spectrum of the non-annealed sample A0 is reported in Fig. 1a. It shows an asymmetric PL lineshapes, with FWHM around 90 meV and a tail on the high energy shoulder. Such PL spectral characteristics should be the outcome of a height self-limitation phenomenon which occurs during the high temperature capping layer growth stage due to the dissolution of the QD tops which exceed in height the capping layer thickness deposited at low temperature [12]. The PL intensity rise at high energy is attributed to defect emission in the AlGaAs barrier. By post-annealing, the PL spectra blue-shift, become more broad and Gaussian-like and the PL yield increases (Fig. 1a). The integrated PL intensity of sample A7 ($T_{\text{Ann}} = 760°C$) is around two orders of magnitude higher than that of the non-annealed sample A0. A summary of the PL spectral characteristics of the annealed samples, namely integrated intensity, peak energy and FWHM, as a function of the annealing temperature is presented in Figs. 1b–d.

A more accurate PL characterization has been performed on three samples (A0, A3 and A7) out of the set, which allow us to follow, with a
relatively coarse grain, the different aspects of the evolution of the emission characteristics with the annealing temperature. Increasing $P_{\text{exc}}$ at low temperature, in the 5–5000 W/cm$^2$ range, produces a clear band filling effect, as displayed in Fig. 1a for the samples A0, A3 and A7. While the ground state emission tends to saturate, a high-energy shoulder is superlinearly growing with $P_{\text{exc}}$. We attribute this emissions to excited state recombination. The ground to excited state energy separation is roughly stable with the post-annealing temperature, being 70, 65 and 85 meV in the samples A0, A3 and A7, respectively. The non-annealed sample shows a superlinear dependence of the QD PL integrated intensity with respect to $P_{\text{exc}}$. A trend towards the decrease of the superlinear dependence with the annealing temperature is observed. The PL integrated intensity dependence on $P_{\text{exc}}$ of the sample A7 is, in fact, slightly sublinear.

The time-resolved PL measurement was performed on the as-grown material (A0) and, to characterize the annealing effects, on a sample which is at the center of our annealing temperature range (A4). Typical time evolution of the emission at the peak energy of the PL bands for the annealed and non-annealed samples at

\[ \approx 1.3 \text{ nJ/cm}^2 \text{ per pulse and } 5 \text{ K} \] is reported in Fig. 2. The samples show a substantial equivalence of the decay profiles. On the other side, faster risetime is observed in non-annealed samples
respect to the annealed one. In order to get more quantitative results, the data have been fitted with a phenomenological model based on the difference between two exponential decays after a convolution with the experimental response function. The decay times of the samples are almost equal ($\tau_D \approx 350 \pm 30$ ps). The non-annealed sample show a fast risetime ($\approx 7 \pm 2$ ps), much lower than that measured for the annealed sample ($\approx 20 \pm 2$ ps). By changing energy per pulse over two orders of magnitude the two samples do not show any change in the decay profile. The risetime does not depend significantly, in this range, on the excitation power density.

Let us now discuss the phenomenology presented. Our experimental observations should stem from two intercorrelated phenomena promoted by the post-growth annealing process in highly disordered GaAs/AlGaAs hetero-structures [13,14]: the interdiffusion of group III species and the reduction of the defectivity of the material. In fact, Watanabe et al. [12] have observed, by means of HRSEM microscopic analysis, that during the thermal annealing of MDE–QD samples, a reduction of the mean size of the MDE–QDs and a possible washing out of the WL during the post-growth annealing step, most likely attributable to group III interdiffusion.

The interdiffusion process that possibly takes place during the annealing process in the MDE materials can be quantified by means of QD PL measurements. The QD wave functions are, in fact, very sensible nanoscale probes of the confining potential profile. The modifications of the potential due to thermal annealing are reflected in the optical transition energies as measured by PL. We can therefore estimate the interdiffusion length at the QD heterointerfaces by PL. This naturally implies a modeling of interdiffusion processes as well as the calculation of the induced changes in the QD transition energy caused by the modifications in the confining potential profile. We proceeded as follows. The QD electronic structure calculations have been performed within the effective mass approximation, following the method outlined in Ref. [15]. The dot shape, typically pyramidal, has been approximated, for computational purposes, by cone with the same height and base. On the other side, the took carefully into account the changes in the potential profile of the dot induced by the annealing procedure. A WL of 1.75 ML of GaAs, originating from the Ga stabilization of the $c(4 \times 4)$ reconstruction, has been added to the structure. The HRSEM microscopic analysis assigns to the MDE–QD a base size of $\approx 20$ nm and a height of $\approx 16$ nm. The calculated ground state transition for a QD with the same size is 1.61 eV, with ground-to-excited states energy separation of 70 meV, in nice agreement with the PL results of 1.63 eV for the ground state emission and 70 meV ground-to-excited state separation. The material parameters used in the calculation are reported in Table 1. By thermal annealing, group III species interdiffuse at the interfaces. The simplest model for interdiffusion involves and isotropic diffusion of Al and Ga with a diffusion coefficient independent of the Al concentration [13]. Under this crude approximation the Al concentration $X$ in the QD material varies as [16]

$$X(\vec{r}_1) = \frac{8}{(\pi \ell^2 T)^{3/2}} \int X_0(\vec{r}_1) \exp \left( -\frac{(\vec{r} - \vec{r}_1)^2}{4\ell^2(T)} \right) d\vec{r}_1. \quad (1)$$

Here $X_0(\vec{r}_1)$ is the initial Al distribution. In our QD the initial Al distribution is $X_0(\vec{r}_1) = 0.3$ everywhere except in the GaAs QD and WL volume. $\ell(T)$ is the temperature dependent interdiffusion length at the GaAs/Al$_x$Ga$_{1-x}$As interfaces. The Al profiles before and after the interdiffusion processes, for $\ell = 1$ and 2 nm, simulated through Eq. (1), are reported in Fig. 3. The Al interdiffusion smoothes the QD interface, reducing the QD effective size, and rapidly washes out the thin GaAs WL formed at the growth substrate during the droplet formation step. From the concentration profile the modified potential

<table>
<thead>
<tr>
<th>Material</th>
<th>$V_{\text{cont}}$ (eV)</th>
<th>$m_{\text{GaAs}}$ ($m_0$)</th>
<th>$m_{\text{AlGaAs}}$ ($m_0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrons</td>
<td>-0.293</td>
<td>0.067</td>
<td>0.093</td>
</tr>
<tr>
<td>Holes</td>
<td>0.157</td>
<td>0.51</td>
<td>0.57</td>
</tr>
</tbody>
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shape can be easily calculated. The calculated effects of the Al interdiffusion on the QD ground and excited state transitions are shown in Fig. 4a for increasing $\ell$. The ground and excited state transition energies are monotonically increasing functions of $\ell$, as observed experimentally. This gives us a way to correlate the experimentally observed PL blue-shift with $\ell$. The interface diffusion length characteristic of each annealing temperature was determined to best fit the calculated optical ground state transition to the measured value. This yields a procedure for relating interface diffusion length to each annealing temperature. The resulting diffusion length are reported in Fig. 4b. The theoretical predictions of the excited state transitions nicely agree with the measured ones (Fig. 4a). It is worth noting that interdiffusion lengths around 2 nm have been reported in annealed AlGaAs/GaAs multiple quantum wells disordered by implantation [13].

The interdiffusion length of our samples is already 1 nm in sample A1, annealed at 520°C, thus showing that a very strong interdiffusion of the group III species takes place in the MDE samples during the post-growth annealing procedure already at relatively low temperatures. This observation implies an unusually low activation energy for the interdiffusion processes (Ga and Al interdiffusion should become significant for temperatures above 800°C for GaAs/AlGaAs heterointerfaces grown by standard MBE [17]) which should be related to the high defectivity and to the under-stoichiometric composition respect to the group III species of the as-grown MDE material [12]. In fact, disordered materials show a huge increase of the interdiffusion of the Ga and Al species [13,18], promoted by group III vacancy assisted diffusion [13,14] and depending on the initial vacancy concentration only. On the other side, the $\ell$ shows only a weak dependence on the annealing temperature, compared with the usual steep dependencies reported in the literature [18].

Fig. 3. Calculated Al concentration profiles at different interdiffusion length: 0 nm (a), 1 nm (b) and 2 nm (c).

Fig. 4. Panel (a): calculated ground (continuous line) and excited (dotted line) state transition shifts of ground and excited states, calculated respect to the A0 ground state emission, as a function of the interdiffusion length. Squares (ground state) and circles (excited states) indicates the measured values, for the samples A0, A3 and A7, respectively. Panel (b): interdiffusion length dependence as a function of the annealing temperature as deduced from the comparison between calculated and observed values (see text).
The sample A7, annealed at 760°C, shows a diffusion length of only twice that of sample A1. As a matter of fact, the ultralow growth temperature of the MDE samples (180°C) introduces a variety of lattice defects, including type III and V vacancies, interstitials and defect complexes. Interdiffusion can be, in principle, promoted by any of these defects. The more probable involves vacancies on the group III sublattice [14], which are expected to be dominant defect in MDE materials [12]. At each time $t$ during the annealing procedure the interdiffusion coefficient is then proportional to the concentration of vacancies, and to their diffusion coefficient at the annealing temperature: $D(t, T) = D_v(T)N_v(t, T)$. The diffusion length describing the interdiffusion after the annealing for a time $t$ is

$$
\ell^2(t, T) = \int_0^t D(t', T) \, dt' = D_v(T) \int_0^t N_v(t', T) \, dt' = D_v(T)N_v^{\text{eff}}(t, T). \tag{2}
$$

This implies a dependence of the interdiffusion process on the vacancy lifetime $\tau_v$ [13]. In the long time limit, $N_v^{\text{eff}}(\infty, T) \propto \tau_v$. Thus, a shorter vacancy lifetime implies a reduction of $N_v^{\text{eff}}$. For systems starting from out-of-equilibrium concentrations of vacancies, like the MDE materials, thermal annealing produces a depletion of the vacancy concentration with time, due to surface evaporation or trap driven decay of the excess, non-equilibrium, vacancies [13,18]. This process becomes more effective as the temperature increases. This phenomenon induces a reduction of $N_v^{\text{eff}}(t, T)$ for increasing annealing temperatures. Our observation of a weak dependence of the interdiffusion process on the temperature at fixed annealing times (60 min) should then stem from the compensation of the temperature dependence of diffusion coefficient by a steeper reduction of $N_v(t, T)$ with time for increasing annealing temperatures.

The reduction of the vacancy content with the increasing annealing temperature should leave its fingerprints in a lower defectivity of the annealed materials. The better crystalline quality of the higher temperature annealed samples is demonstrated by the enhancement of the PL yield with the annealing temperature. In this regard, we observe that both annealed and non-annealed samples show long and equivalent decay times, whose values do not depend on the photogenerated carrier density. Thus, in both non-annealed and annealed samples the decay dynamics of the carrier trapped in the QDs can be considered intrinsic and the emitting dots are defect free. As a matter of fact, the annealing procedures are then not changing the quality of the emitting QDs. The observed enhancement of the emission efficiency with the annealing must be therefore searched for in a more effective capture of the photogenerated carriers by the QDs in annealed samples. The improvement of barrier quality due to the removal of trap states works in that direction. It is possible to evidence that this is the case by two observations: first, a noticeable lengthening of the QD PL risetime with the annealing process; second, the non-annealed sample show a marked superlinear dependence on $P_{\text{exc}}$ and such superlinearity tends to disappear in the annealed samples. Let us discuss these points more clearly. The 20 ps risetime shown by the annealed samples compares well with the intrinsic QD risetime, as previously reported in SK InAs/GaAs QDs [19]. Then, the reduction of the risetime in non-annealed samples is attributable to extrinsic effects. A short lifetime of the photogenerated carrier density in the barrier, shorter than the intrinsic capture time in the QDs, gives rise to a reduction of the QD PL risetime, which is now dominated by the depletion of the carriers in the barrier. The increase of photogenerated carriers tends to saturate the non-radiative recombination channels in the barrier, thus extending the carrier lifetime in the barrier and therefore the QD risetime. This is confirmed also by the superlinear behavior of the PL integrated intensity on $P_{\text{exc}}$, which witnesses the presence of an efficient non-radiative channel in the barrier which tends to be saturated by the increase of photogenerated carriers. The annealing procedure reduces the importance of this non-radiative channel. In fact, together with the enhancement of the PL yield as the post-annealing temperature increases, also the superlinear dependence of the emission efficiency with $P_{\text{exc}}$ is strongly reduced.
4. Photoluminescence temperature dependence

The temperature dependence of the PL integrated intensities, FWHMs and peak energies of three samples out of the series (A0, A3 and A7) is reported in Fig. 5. The spectra were recorded at the same excitation level of 10 W/cm². The chosen value of $P_{\text{exc}}$ is below that necessary for the onset of the emission from the QD excited states. Therefore, due to the random nature of the carrier capture processes in QDs, we can consider the PL lineshape as a reliable image of the size distribution [20,21] of QDs in the sample. In the sample series, the emission shows a decrease of the high temperature efficiency, relative to 20 K, with the post-annealing temperature. If, on one side, in virtue of its good barrier quality, the sample A7 remains the most efficient even at high temperature, the ratio with the PL yield of the sample A0 is reduced by more than one order of magnitude by increasing the temperature. Puzzling, such reduction is not accompanied by a decrease, but rather by an increase, of the quenching activation energy, as can be seen from the PL integrated intensity Arrhenius plot slopes at high temperatures.

The FWHM and the peak energy behavior of the sample A0 differ strongly from the other two samples in the series. Samples A3 and A7 show a strong decrease, with the increasing temperature, of the FWHM, from $\approx 130$ to $\approx 70$ meV. The decrease of the FWHM in sample A0 is much more less marked. Also the red-shift of the peak position with the temperature is faster in the annealed samples than in sample A0. The change in the spectral characteristics shows no correlation with the energy position of the QD PL band and only slightly on the initial PL bandwidth.

In the droplet epitaxy growth procedure, a wetting layer of 1.75 ML is formed at the base of the QDs. The post-annealing procedure should wash out this thin layer, due to interdiffusion of Ga and Al as demonstrated by the PL spectral analysis shown in the previous section. This fact should have a direct consequence on the PL temperature characteristics of non-annealed and annealed samples.

The electronic structure of the non-annealed MDE–QDs is, in principle, similar to that of the SK–QDs. In SK–QDs the WL has been shown to play a major role in determining the PL quenching mechanism and the thermalization of the QD ensemble [22]. Coupling through the WL state has been considered responsible for the anomalous temperature behavior of the PL FWHM and peak position [22–24]. On the other side, the lack of a WL connecting the dots should change the thermal behavior of carriers in the QD ensemble. However, if the energy distance between the QD and the barrier states is not too large the role of the WL, as principal quenching channel and coupling state for the dot ensemble, can be played by the barrier states.

In order to assess the nature of the coupling and quenching channel in the non-annealed and annealed samples we fitted the PL integrated intensity with the rate equation model of Ref. [22] which mimics the exact electronic structure of the SK–QD materials. The results of the fit procedure for the sample A0 are reported in Fig. 5 and the simulated spectra in Fig. 6. The reproduction of the PL spectra and integrated intensity is pretty good. The best fit gives the energy position of the coupling state at $1.90 \pm 0.20$ eV. This value is very close to the theoretical one for a 1.75 ML GaAs quantum well in $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ ($\approx 1.93$ eV). The analysis of the quenched carrier flows permits to us to conclude that the quenching channel in the case of sample A0 is provided by the WL. As expected, attempts
to fit the PL integrated intensity data of the annealed samples A7 and A3 with the model of Ref. [22] gave the coupling channel energy almost coincident with that of the AlGaAs barrier. The quenching channel of the annealed samples is then compatible with a mechanism involving excitation of the carrier from the QDs directly into the AlGaAs barrier.

In order to make a more quantitative comparison we tried to simulate PL spectra of the annealed samples A3 and A7 at various temperature on the basis of a rate equation model which mimics the electronic structure of QD sample without WL. The model parameters will be derived by a fit procedure on the PL integrated intensity temperature dependence only.

Because the samples lack of the WL, the electronic structure of the QD system is greatly simplified. Once the carriers are captured in the QDs, which are defect free, the only escape process permitted is the thermal promotion to the barrier. However, this is not the only process active for the reduction of the PL yield with the increasing temperature. As pointed out by Mukai et al. [25], other non-radiative processes, outside the QDs, influence the PL intensity efficiency for the increasing temperature. They proposed thermally activated nonradiative recombination in the barrier, during the capture process, to explain the decreasing, with the temperature, emission efficiency of their dots. The activation energy of this process is therefore characteristic of the non-radiative recombination centers. In our samples we expect a fairly high number of defects. Then, the PL intensity of a single QD, within this model, is given by

$$I_{PL}(T) = \frac{g}{1 + (\tau_{nrb}/\tau_{c}) \exp(-Q/kT)} \times \left(1 + (\tau_{r}/\tau_{e}) \exp((E_{QD} - E_{bar})/kT)\right)$$

where $g$ is the photogenerated carrier injection density, $\tau_{nrb}$, $\tau_{c}$, $\tau_{r}$ and $\tau_{e}$ are the non-radiative lifetime, the QD capture time, the QD radiative lifetime and the lifetime for the QD to barrier thermal lifetime, respectively. $Q$ is the activation energy for the non-radiative processes in the barrier, $E_{QD}$ and $E_{bar}$ are the QD and the barrier energies, respectively. Since the process of QD population is intrinsically random [20] the QD density of states (DOS) is assumed to be proportional to the low temperature PL emission band. The model assumes that the retrapping is negligible in these QD structures, due to highly defective nature of the barrier. The PL spectra at various temperatures are then obtained by multiplying the $I_{PL}(T)$ for the QD–DOS. The PL integrated intensity is then obtained by simple integration over the inhomogeneous QD band. The free parameters of the model are two, namely the ratios $\tau_{nrb}/\tau_{c}$ and $\tau_{r}/\tau_{e}$. The activation energy $Q$, on the basis of the results of Ref. [25], is fixed $Q$ to 40 meV. The barrier energy $E_{bar}$ is 1.97 eV. $g$ is a normalization factor.

The fit results, obtained using the parameters of Table 2, are shown in Fig. 5. The simulated spectra of the sample A7 are reported in Fig. 6. The model correctly reproduces both the PL integrated intensity and the PL spectrum dependence on the temperature, thus showing that the barrier states determine QD temperature activated coupling and PL quenching in annealed samples.

The conflicting observation of an enhancement of the PL quenching going along with an increase of the same process is hence due to the change of the PL quenching channel. Carrier thermal escape
towards the barrier should be more probable, at constant activation energy, than towards the WL, because of the larger density of final states. However, when the WL quenching channel is present, as in the A0 sample, its lower activation energy makes it the dominant QD PL quenching channel.

5. Conclusions

We presented a detailed analysis of the post-annealing effects on the optical properties of self-assembled GaAs/AlGaAs quantum dots grown by MDE. The post-annealing procedure strongly affects the optical properties of the MDE QDs. Modifications involve emission spectra (QD PL blue-shift and broadening) and yield, as well as PL excitation power density and temperature dependencies.

As a matter of fact, the post-annealing creates structural modifications of the MDE–QD heterostructure by promoting the intermixing of the group III elements. We quantitatively estimated the interdiffusion process in the MDE–QD structures using the QD wave functions themselves as nanoprobes of the changes in the group III species concentration profiles. The assessment of the modifications of the QD eigenstates and of the QD environment have been performed via optical measurements. We determined a sizeable interdiffusion of Ga and Al (\(\ell = 1 \text{ nm}\)) already at relatively low annealing temperatures (520°C), with a relatively slow increase with the annealing temperature. The strong interdiffusion process and its annealing temperature dependence are attributed to the presence of a high concentration of out-of-equilibrium group III vacancies, introduced in the material during the low temperature growth stages of QD formation and capping. The out-of-equilibrium density of defects is strongly reduced during the intermixing process, due to vacancy evaporation at surface of trap decay, giving a better material quality which reflects itself in an increase of the QD emission yield with the annealing temperature.

As result of intermixing, the thin GaAs layer wetting the surface should be washed out. The temperature dependence of the spectral characteristics of the samples shows, in fact, a change in the active quenching processes, which are dominated by the WL in the non-annealed sample and by direct promotion of carrier from the dot into the barrier in the annealed ones.

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