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Optical properties of group-III nitride quantum wells and quantum boxes

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Abstract

We propose an overview of specific optical properties of quantum-size artificial structures made of group-III nitride semiconductors with natural wurtzite symmetry. We consider the cases of quantum wells and of quantum boxes obtained by the Stranski–Krastanov growth mode. We comment on results of continuous-wave and time-resolved optical spectroscopy, in comparison with our envelope-function calculations of excitonic energies and oscillator strengths. The influence on recombination dynamics of internal electric fields and carrier localization is discussed in detail.

1. Introduction

In the past few years, group-III nitride optoelectronic devices have received significant interest, especially after the demonstration of the first ultraviolet laser diode (LD) based on InGaN/GaN quantum well (QW) structures [1]. As a matter of fact, all efficient nitride-based light emitters obtained so far involve quantum-confinement systems, i.e. nanometric layers of InGaN [2] or of GaN [3]. Recent research revealed that these systems present several original and sometimes fascinating properties. These properties make nitride quantum systems not only good elements for light-emitting diodes (LEDs) and LDs, but also promising candidates for other types of optical application [4]. The first purpose of this paper is to summarize what these specific properties are, comparing them to more familiar systems, e.g. GaAs/AlGaAs QWs. Also, we will see that one serious problem encountered was to explain how nitride QWs can be such efficient emitters when the materials which they are made of are seldom of very high quality, mainly due to high densities of threading dislocations. The second purpose of this paper is to review what has been understood so far on GaN/AlGaN and InGaN/GaN QWs and quantum boxes (QBs), particularly in terms of recombination dynamics of excitons. In view of this, we will give several examples of results obtained by our group on specific samples grown by

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molecular beam epitaxy at the CRHEA-CNRS in Valbonne, France. Our third purpose is to draw the reader's attention towards some peculiar aspects of these novel objects, which may lead to original applications.

We will try to meet these three purposes through the following discussion of recent experimental and theoretical results. An introductory section will be devoted to specific properties of these materials, with emphasis placed on theoretical expectations concerning exciton binding energies and oscillator strengths. In the next section, we will present and discuss continuous-wave (cw) and time-resolved (TR) photoluminescence (PL) studies of GaN/AlGaN QWs. Indeed, we consider these objects as ideal model-systems which will allow us to face the much more complicated case of InGaN/GaN QWs and QBs. The latter will be the subject of the last section before short concluding remarks.

2. Specific properties of group III nitrides

As already mentioned, most nitride heterostructures available were grown with a strong residual strain [5], by heteroepitaxy on a variety of substrates: sapphire, in most cases, but also SiC [6, 7] or the (111) surface of Si [8]. Some cases of epitaxy of quantum structures on GaN substrates have been reported [9–11], but such substrates are really difficult to obtain and, still, their heavy n-doping induces some lattice mismatch with undoped GaN. Consequently, whatever the growth technique used to elaborate QWs or QBs, the samples embed high densities of threading dislocations [12]. In particular, for the samples studied by us, this density is close to 10^{10} cm^{-2}. We must mention that this density can be significantly reduced by growing layers on patterned substrates, in the so-called 'lateral-over-growth' mode [1, 13–15]. In fact, it is now clear that reducing this density is really a way of improving the room-temperature radiative efficiency of the samples. This seems particularly crucial in the case of blue–UV LDs [1]. This means that nonradiative recombination centres are related more or less directly to those dislocations, which is now commonly accepted.

The other original characteristic of nitrides is somehow a consequence of their wide band-gaps: electrons and holes have quite large effective masses, e.g. GaN $m_e = 0.22m_0$ for electrons and $m_h = 1.1m_0$ for heavy holes [16]. This is why the exciton binding energies are large, too: $\sim$26 meV for GaN [16, 17] and even more in the case of quantum confinement. This induces a good thermal stability of excitons at room temperature. Another consequence of large masses is the very small spatial extension of electronic wave-functions, e.g. in the case of excitons, Bohr radii as small as 3 nm in GaN. This also makes electrons and holes much more sensitive to short-range potential fluctuations than in materials like GaAs or InGaAs where these fluctuations are averaged over several tens of elementary cells. For GaN, note that the above-mentioned Bohr radius corresponds to only six cells and that the 'orbit' of the hole around the centre of mass is only 15% of this Bohr radius [18]. Recent *ab initio* calculations [19] emphasized the impact of such effects in the case of ternary alloys, where specific carrier localization and transport are predicted.

It is worth remarking, thirdly, that group-III nitrides are ionic, polar materials [20], although they belong to the III–V family. This, in particular, has important consequences for the coupling of excitons with LO phonons: phonon side-bands are easily observed in nitrides [21] and especially in low-dimensional systems [22]. The energy of the LO phonon in GaN is of 91 meV [23] i.e. nearly four times larger than in GaAs.

But the most spectacular property of nitride QWs and QBs certainly lies in the huge electric fields present along their growth axes. This is basically related to the wurtzite symmetry in which these materials naturally grow. Then, any artificial structure breaking the translation symmetry along the (0001) axis will permit the presence of internal polarization of the

materials, along the same direction. This is really similar to what has been produced by growing QWs made of zincblende III–V [24–26] or II–VI [27] compounds along the (111) axis. The main difference from these materials lies in the values of the relevant material constants for both spontaneous and piezoelectric polarizations in group-III nitrides [28, 29]: the electric fields induced in GaN/AlGaN or InGaN/GaN QWs reach values close to or larger than 1 MV cm^{-1}. This is at least one order of magnitude larger than what had been obtained for arsenides or tellurides. More specifically, InGaN and GaN mainly present a large difference of their piezoelectric polarizations [28], so that these effects are the principal source of electric fields. On the other hand, GaN and Al(Ga)N present sizeable differences in both their piezoelectric and spontaneous polarizations: both effects contribute to the electric field in the QWs *and in the surrounding barriers*. Recently, results on QWs and QBs fabricated in the *cubic* phase of GaN have been reported [30]. In these cases, no electric field effects were seen. In the following, we will restrict ourselves to the most common case of hexagonal materials.

Coming to the consequences of these particular properties on nitride QWs and QBs, let us start with excitonic binding energies, E_{1s}, in-plane pseudo Bohr radii, a_{1s}, transition energies and oscillator strengths, for the ground-state transition, usually denoted e1h1. These quantities are easily computed within the envelope-function approximation, using the so-called effective-potential method [31] and a two-dimensional trial function, which has proven to be relevant for QWs with electric fields [27]. Figures 1 and 2 display plots of these quantities for ideal free excitons versus the well width, L_w, for GaN/$Al_{0.3}Ga_{0.7}N$ QWs. For narrow wells, the quasi-bidimensional confinement enhances E_{1s} up to 50 meV and the in-plane Bohr radius is as low as 2 nm. The squared overlap integral of electron and hole envelope functions is maximum. In fact, the electric field, which we can estimate as $\sim$1.65 MV cm^{-1} from previous works [32], does not affect the wave functions, for ultra-narrow QWs. On the other hand, for increased L_w, the overlap integral decreases nearly exponentially, due to the spatial separation of electron and hole by the field, as noticed for nitride QWs by several groups [33–40]. This separation also dramatically reduces E_{1s}, thus increasing the in-plane extension of the exciton wave function. Nevertheless, it is worth noting that, for reasonably wide QWs, E_{1s} remains comparable to or larger than values obtained for GaAs QWs, for instance. We remark, too, that, in nitrides, a 20 monolayer (ML) wide QW should be regarded as a wide QW, although $L_w \sim 5$ nm, because this is equivalent to 1.7 times the three-dimensional Bohr radius. Figure 1 also shows that, although it increases with L_w, a_{1s} remains relatively small, especially when compared with the typical in-plane size of QBs obtained by the so-called Stranski–Krastanov [41] growth mode (*see below*). This has an important impact on the physics of excitons in such QBs: the effects of in-plane confinement will always remain quite weak. In other words, the energies and oscillator strengths of excitons are mainly sensitive to the QB height (L) via electric field effects, just as if these excitons were in QWs with the same L. In fact, the lateral confinement has a sizeable impact on the escape of carriers towards nonradiative centres, as shown below and its role is thus limited to carrier localization. In the rest of this section, all comments related to exciton transition energies and oscillator strengths in nitride QWs are directly applicable to QBs.

Figure 2 illustrates the so-called quantum confined Stark effect on the e1h1 transition energy and oscillator strength. Clearly, we see that one can almost directly measure the electric field in the well, F_w, if one elaborates a sequence of QWs of increasing widths. Indeed, for sufficiently wide QWs, the transition energy is nearly a linear function of L_w. The slope, measured in meV nm^{-1}, gives directly F_w. This method has been used in previous works to determine F_w in GaN/AlGaN QWs, with various well and barrier widths [32, 42]. It turns out that there is some scattering in the values of F_w determined by several groups on comparable GaN/AlGaN or InGaN/GaN QWs [35–38, 43] and that these fields are always weaker than those predicted theoretically by Bernardini *et al* [28]. The reasons for this are not totally clear

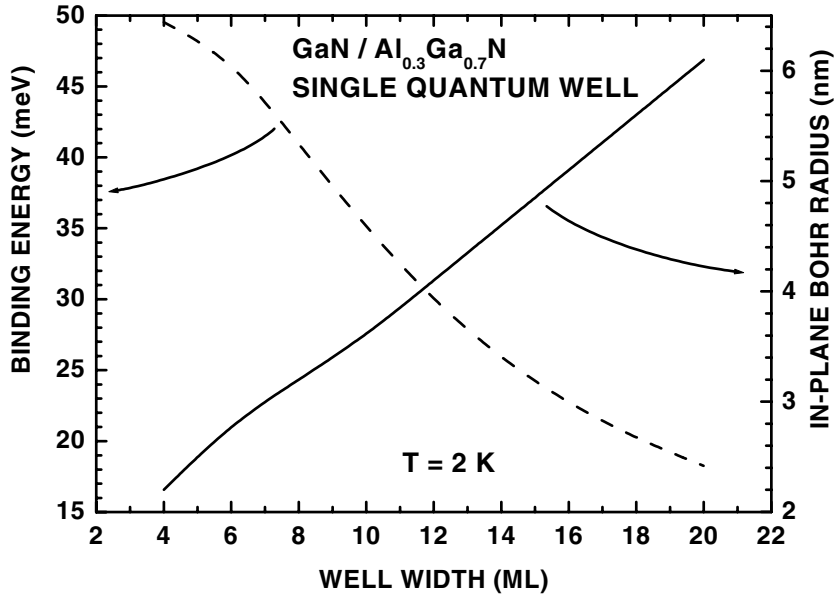

Figure 1. Calculated well-width dependence of the exciton binding energy (E_{1s}) and of the in-plane pseudo-Bohr radius (a_{1s}) for GaN/$Al_{0.3}Ga_{0.7}$N QWs. We have considered the situation of a single QW with infinite barriers, with an electric field in the QW of $F_W = 1.65$ MV cm^{-1}.

yet, although some effects have been invoked such as the partial neutralization of charges at the sample surface by some adsorbates [44, 45], the screening of fields by free electrons in these materials which are residually n doped [46, 47], or segregation of species at the QW boundaries during growth, yielding nonplanar interfaces and an underestimation of the field via optical spectroscopy [47].

Anyway, these electric fields are strong enough to make the e1h1 transition almost 'forbidden' in wide enough QWs, to the point that the PL decay time can reach several tens of microseconds [44, 48]. We can even predict, by our calculations, decay times of milliseconds, e.g. for GaN/AlN QWs or QBs, where F_w can reach 7 MV cm^{-1} [49, 50]. This possibility is certainly not interesting for efficient optoelectronic light-emitters, mainly due to the presence of AlN, with a band-gap of 6.2 eV [51]. On the other hand, this offers novel perspectives in terms of 'tailor-made' photorefractive materials, for instance. Such long decay times are preserved at room temperature, due to the exceptional gap difference between GaN and AlN (2.7 eV). Then, reasonably weak photo-injection of carriers can yield a significant screening of the internal field, inducing strong optical nonlinearity in the system. The PL from such samples has been excited by photons with energies *below the AlN band-gap* [49, 50], which proves that these photons are resonant with transitions involving the numerous electron and hole excited states. No interband transition is totally forbidden or totally allowed in nitride QWs. Figure 3 presents the interband absorption spectrum that we have calculated for GaN/$Al_{0.3}Ga_{0.7}$N QWs of various widths. The quasi-continuous absorption onset for the wider QWs simply results from the accumulation of excited states. By the way, we also want to remark that allowed inter-subband (intraband) transitions [4] in nitride QWs benefit from the natural asymmetry induced by the electric field, in contrast to the case of arsenide QWs, for which this asymmetry had to be induced artificially via sophisticated sample profiles [52].

At this stage, it is important to mention that PL experiments in QWs at low temperatures

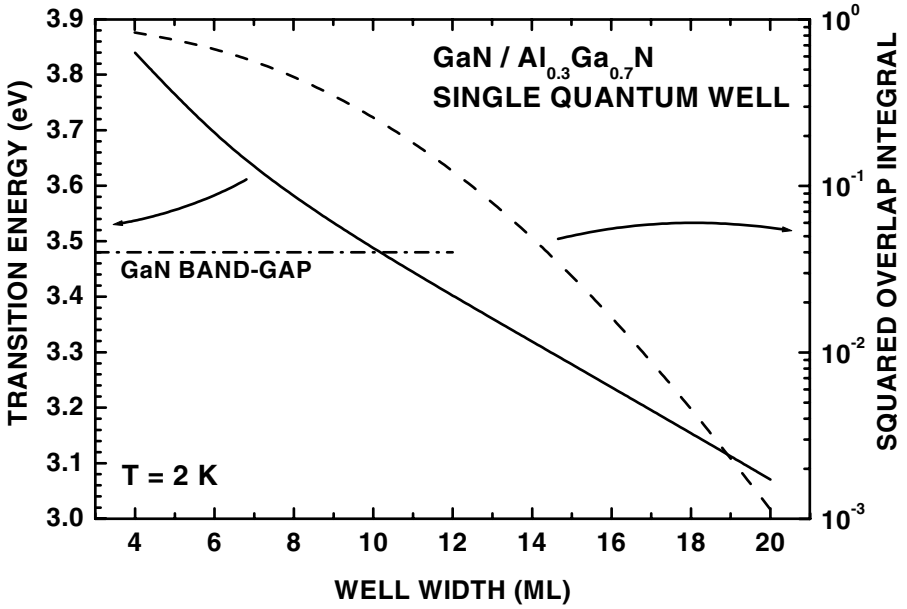

Figure 2. Calculated well-width dependence of the ground-state excitonic transition energy (e1h1) and of the electron–hole envelope-function overlap integral (I^2_{eh}) for GaN/$Al_{0.3}Ga_{0.7}N$ QWs.

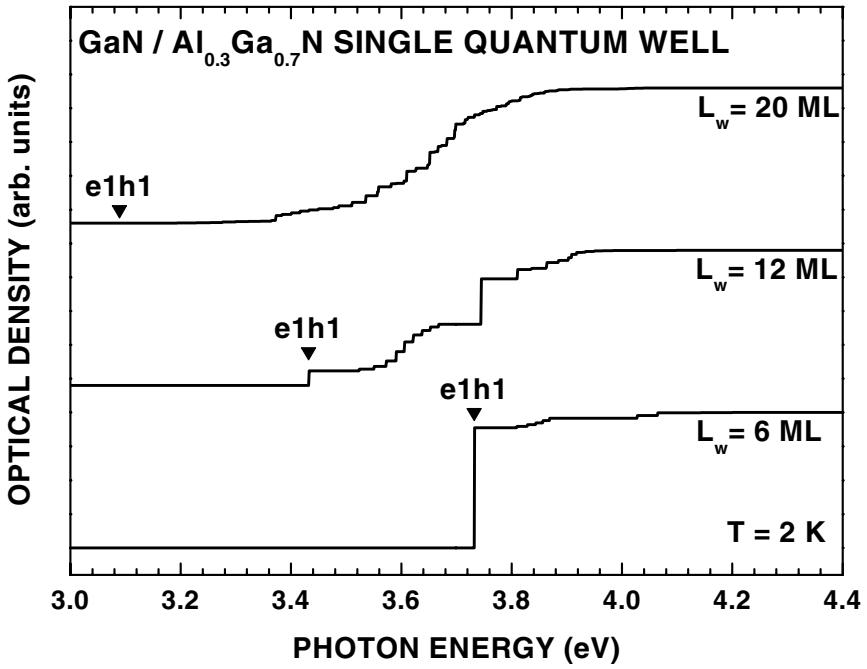

Figure 3. Calculated interband absorption spectra for three GaN/$Al_{0.3}Ga_{0.7}N$ QWs, of respective widths 6, 12 and 20 atomic monolayers. Arrows show the energies of the corresponding e1h1 transition, which is allowed for narrow wells and very weak for wider ones.

principally involve *localized excitons*. We will see, in the next sections, that this is particularly the case for nitride QWs and not only at low temperatures. Basically, the properties discussed above are the same for localized excitons, as far as electric field effects are concerned. But carrier localization is in fact the key to the success of nitride-based QWs as room-temperature light-emitters. The control, at the growth stage, of this localization yields the control of the nonradiative lifetime of carriers. The challenge is to keep this nonradiative lifetime larger than the radiative lifetime, while the latter itself can be made large by electric field effects. In the next section, we report some results of TR-PL obtained for a series of GaN/AlGaN QWs, showing the respective roles played by electric fields and by carrier localization in terms of radiative and nonradiative lifetimes.

3. Time-resolved PL of GaN/AlGaN QWs

Our experimental set-up has been described elsewhere [53]: 2 ps laser pulses are used to excite the samples, at a repetition frequency which we can adjust from 82 MHz down to 4 kHz. This avoids quasi-continuous excitation of the PL in case of very slow decays. The photon energy of the laser is either close to 3.1 eV, which we use for exciting InGaN systems, or close to 4.7 eV, which we use for GaN QWs and QBs.

The samples were all grown by molecular beam epitaxy on micrometric GaN buffer layers, themselves deposited on sapphire substrates. Details of the growth have been given in previous papers [42]. We will comment here on the results obtained for a series of samples, each embedding four GaN/$Al_{0.17}Ga_{0.83}N$ QWs of respective widths 4, 8, 12 and 16 MLs, from the surface towards the substrate. The only difference between these samples was the width of the barriers, L_B, between them: 5, 10, 15 and 50 nm, respectively for the four samples. In a first step, it has been verified by cw PL studies [42] that F_W in a multiple QW is roughly proportional to $L_B/(L_B+L_W)$, as expected from simple electrostatics [54]. In these samples, F_W was found to vary between 0.8 MV cm^{-1} for $L_B = 50$ nm down to 0.5 MV cm^{-1} for $L_B = 5$ nm. In the second step, we have tried to check the variation of the radiative lifetime, τ_R, versus L_B, by measuring the PL decay times, τ_{PL}, for each well width, at $T = 8$ K. The results are shown in figure 4, along with the variations of the radiative lifetime expected from envelope-function calculations. Clearly, the observed reduction of τ_{PL}, when L_B is reduced, is much faster than the calculated variation of τ_R. This indicates that efficient nonradiative processes are enhanced when L_B is small. In other words, τ_{PL} is nearly equal to the nonradiative lifetime, τ_{NR}, which decreases exponentially when L_B decreases. A detailed explanation for this observation is still difficult to provide. Nevertheless, we remark that reducing L_B increases the tunnel effect between the QWs and may even induce resonant tunnel effects, e.g. between hole levels which are numerous, due to heavy masses. This would induce an inter-well transfer of carriers, thus reducing τ_{NR} and the subsequent radiative efficiency. Another process, derived from the previous one, can be invoked. The electrons and holes are localized on local fluctuations of the well width. This is a well known phenomenon in QWs made of a binary compound and this is even amplified in nitrides, as we comment below. We believe that the increased possibility of crossing the barrier, for small L_B, may result in an increased probability for carriers of moving along the plane of the sample, eventually into nonradiative centres. On the other hand, for wide barriers, if the presence probability in the barriers is weak, then the carriers can remain localized and the radiative efficiency is preserved.

The specific localization behaviour in nitride QWs is exemplified by the results shown in figure 5: for a nominally 16 ML wide QW, high-resolution PL [55] reveals a doublet which we assign to two localization states. These states correspond, respectively, to areas where the QW width is of 18 MLs (lower energy: E_{18}) and of 17 MLs (higher energy: E_{17}). Following the

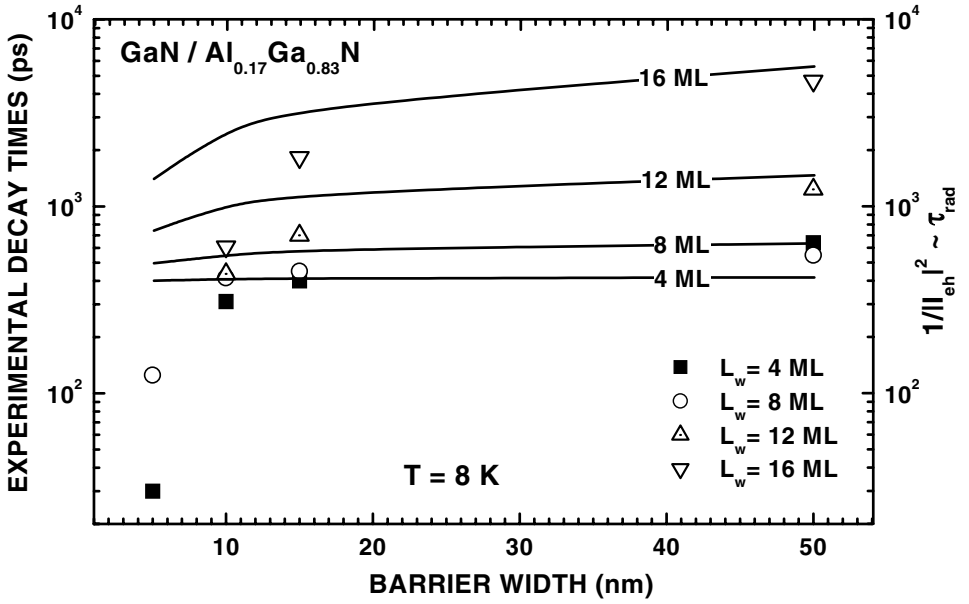

Figure 4. Symbols represent experimental PL decay times measured for GaN/$Al_{0.17}Ga_{0.83}N$ QWs of nominal widths 4, 8, 12 and 16 MLs, plotted against the width of the barriers between these wells, for the samples described in the text. Solid curves show the result of theoretical calculations of the inverse oscillator strength against the same barrier width, via the subsequent change of the internal field.

peak of the low-resolution PL of the same sample against temperature, T, we observe the well known transition between localized excitons, at low T and free excitons at higher T. Only above ∼130 K, the energy of the line tends to follow the nearly parabolic variation parallel to that of the GaN band-gap. By extrapolation of this curve, fitted by the empirical model of Varshni [55, 56], at $T = 0$ K, we obtain the energy of excitons for the 16 ML wide QW. We could not measure the spectra above 120 K, simply because in-plane free excitons become extremely sensitive to captures by nonradiative centres and the PL signal decreases exponentially versus T. In the low-T range, we remark that the average PL peak, centred between the two localization states, first tends to decrease with T, before increasing due to thermal excitation towards the free exciton regime. We assign the low-T results to the thermally enhanced transfer from the high-energy state towards the low-energy one. The time-resolved data in figure 6 show the dynamics of this transfer: the low-energy state decays only by radiative recombination of excitons, whereas the high-energy state decays also via the relatively slow transfer towards its low-energy companion. We believe that the slowness of this transfer partly results from the presence of the electric field, for two reasons: (1) a one-ML fluctuation induces a localization energy of ∼20 meV, which is much larger than what is observed for other semiconductors, without electric fields, (2) the field pushes the electron and hole wave functions towards the interfaces, making the in-plane motion more difficult than for other systems like GaAs/AlGaAs QWs. We see that the transfer between the two states is accelerated when slightly increasing T, which explains the small red-shift observed in time-integrated spectra.

Our studies of GaN/AlGaN QWs have shown us that electric fields have a crucial influence on the value of the radiative lifetime, but also that in-plane localization is really what prevents the carriers from nonradiative recombinations. We have observed, too, that transfers between

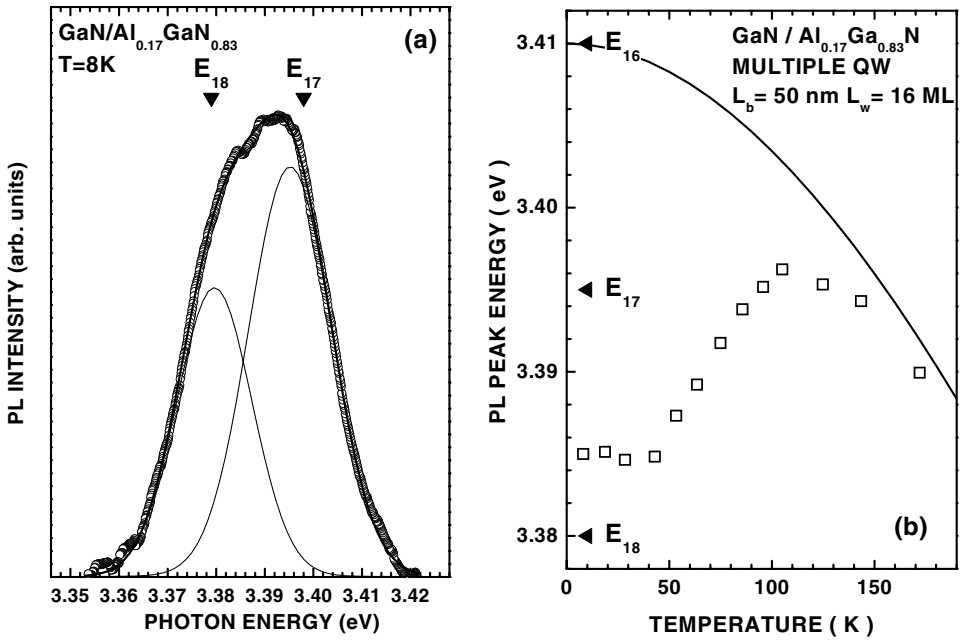

Figure 5. (a) Time-integrated PL spectrum, obtained with a high-resolution set-up, for a nominally 16 ML wide GaN/$Al_{0.17}Ga_{0.83}N$ QW. (b) Plot of the low-resolution PL peak energy versus temperature for the same sample. Low resolution was used in order to obtain a better signal-to-noise ratio, especially in the higher temperature range. Exciton energies for the nominal 16 ML wide QW and for 17 and 18 ML wide QWs are indicated.

different localization states are possible but relatively slow, certainly due to the conjunction of electric fields, large localization energies and large effective masses. To confirm the role of localization, we wish to mention here the remarkable results obtained by two groups on wurtzite GaN/AlN QBs [49, 50]. Emission at wavelengths ranging from the UV to the dark orange has been obtained, monitored by the size of the boxes along the (0001) axis. In these systems, the in-plane localization of excitons is so strong that intense PL is obtained even at room temperature, although the radiative lifetime can reach several hundred microseconds, for low-energy emission.

In fact, all the above results will help us understand the more complicated case of InGaN QWs and QBs, because GaN/AlGaN QWs have revealed to us all the essential ingredients.

4. InGaN/GaN quantum wells and quantum boxes

As mentioned, InGaN is a disordered alloy for which the local variations of chemical potential are very large. Formation of In-rich nano-clusters has been invoked [57, 58] to support the idea of self-formed quantum dots in InGaN/GaN QWs. In fact, the random distribution of In atoms, in itself, leads to complex local configurations [59]. Electronic wave functions would somehow average such fluctuations if effective masses were smaller, as for InGaAs. For nitrides, the masses are large. In other words, the Wannier functions of the carriers are limited to one or few elementary cells. Consequently, electronic excitations, namely excitons, can 'feel' such deep and localized fluctuations. The result is a large variety of localized states, each having its own energy and oscillator strength. Carrier transfers are allowed between these states, leading

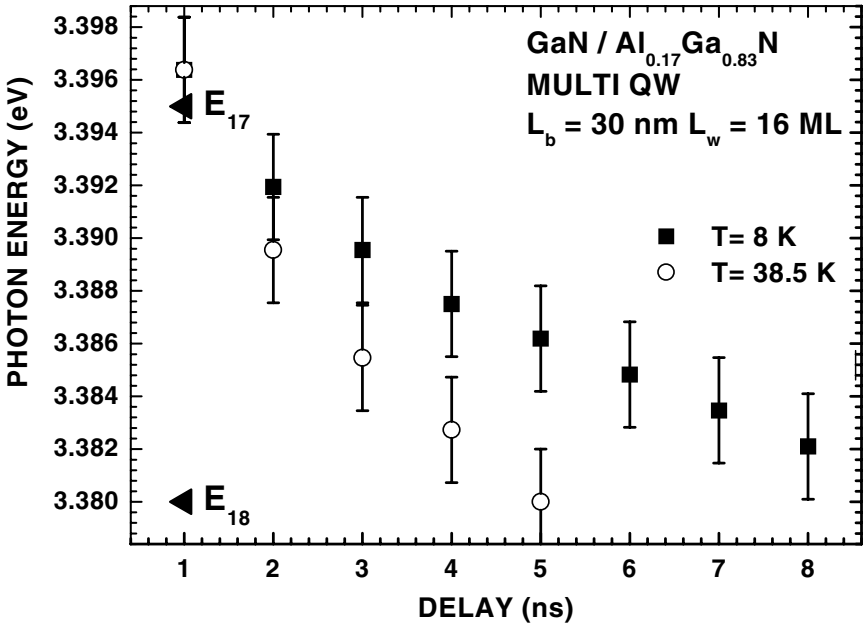

Figure 6. Plot of the PL peak energy recorded at various delays after optical excitation for a nominally 16 ML wide GaN/$Al_{0.17}Ga_{0.83}N$ QW. This energy shifts from a value close to that for a 17 ML wide QW towards a value close to that for a 18 ML wide QW. This process becomes faster when the temperature is slightly raised.

to complex, non-exponential PL time-decays.

Localization is known to increase the exciton lifetime, simply because it introduces non-vanishing components away from the photon wave vector in the exciton–polariton wave function [60–62]. As a matter of fact, typical PL decay times of several nanoseconds have been measured for InGaN QWs emitting blue–UV light. But it would be a *serious mistake* to state that the localization alone is responsible for such slow decays: electric fields are present, too. We will show below how we have unravelled the respective roles played by localization and electric fields in InGaN/GaN QWs and QBs. The latter samples were all grown by molecular beam epitaxy [63]. For QBs, the Stranski–Krastanov 2D–3D growth mode transition was used to produce planes of boxes, with densities of a few 10^{11} cm^{-2}. The wetting layer (typically 1 nm thick) was covered by hexagonal truncated pyramids of InGaN with typical base sizes varying around 10 nm and height varying between 1 and 5 nm. The aim of growing these boxes was to localize carriers to protect them against nonradiative capture at threading dislocations. This idea had already been successfully applied for InGaAs/GaAs QBs [64].

First, we will illustrate the electric field effects on PL decay times for InGaN/GaN QWs, multiple QWs and QBs. Figure 7 presents a collection of results gathered from the literature [40, 58, 65–80] and from our experiments, aimed at demonstrating any correlation between the PL decay time and the PL energy. This correlation exists, but there is some scattering in the data, with variations of τ_{PL} as large as two orders of magnitude for a given transition energy. We can explain this scattering, first, by the average In compositions of the samples, which vary between 6 and 30%. The second explanation lies in the variable nano-texture of the ternary alloy, depending on the growth method and on the growth conditions. Indeed, these parameters control the influence of localization on the decay time and the overall shape of the

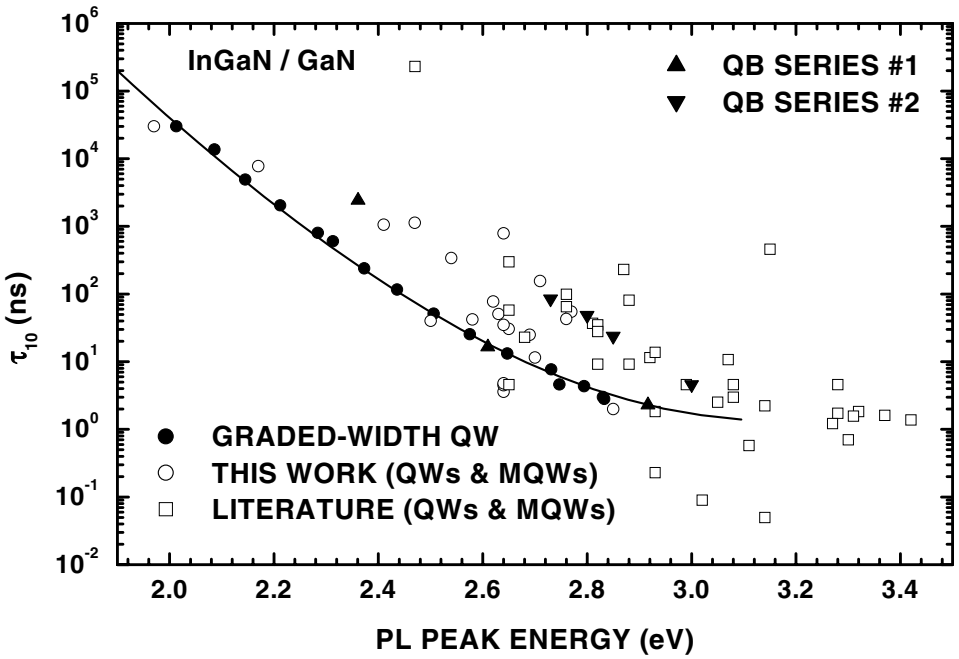

Figure 7. Open squares show a plot of PL decay times extracted from literature versus the corresponding average PL energy. These results were obtained on a variety of InGaN/GaN quantum-well systems. Circles show the results obtained by our group on different QW and multiple-QW samples (open circles) and on a special graded-width InGaN/GaN QW sample (solid circles). Our results on two different sets of InGaN/GaN QB samples are shown by triangles. The fit to the data for the graded-width QW is shown by the solid curve (*see text*).

PL decay (see figure 8). Finally, we have also understood, in several instances [81, 82] that the excitation conditions (e.g. laser wavelength and intensity) may have a sizeable effect on the apparent decay dynamics of excitons in the QWs or QBs. Moreover, these dynamics also strongly depend on the overall structure involved, i.e. a non-intentionally doped structure or a p–i–n structure built for an LED or an LD.

Nevertheless, there is a general trend, which is basically an exponential increase of decay times from nanoseconds, for systems emitting UV light, to tens of microseconds, for systems emitting red light. We have proved that this trend is a manifestation of the electric field F_W by measuring the PL spectra and their decays along a graded-width InGaN/GaN QW [48]. This sample was specially designed so that its emission covers the entire visible range from one end of the sample to the other, whereas the In composition remains constant everywhere. This composition lies in the range of 0.15–0.20, which is the case for all samples studied by us. The measured PL decays are never exponential in this sample and they are not, either, for any of our QWs, multiple-QWs or QB planes (figure 8). This is why we chose to plot, in figure 7, the characteristic time, denoted τ_{10}, for which the intensity is reduced by a factor of 10 (solid circles). For data extracted from the literature, in figure 7, the decay times resulted from a fit with exponential shape and we simply have plotted the reported decay times multiplied by ln(10), for consistency. The result of our experiments is a smooth, monotonic variation of τ_{10} over more than four orders of magnitude. This variation is not precisely an exponential. In fact, our envelope-function calculation of the inverse oscillator strength gave an excellent fit to this variation, the only parameter being the electric field which we found equal to

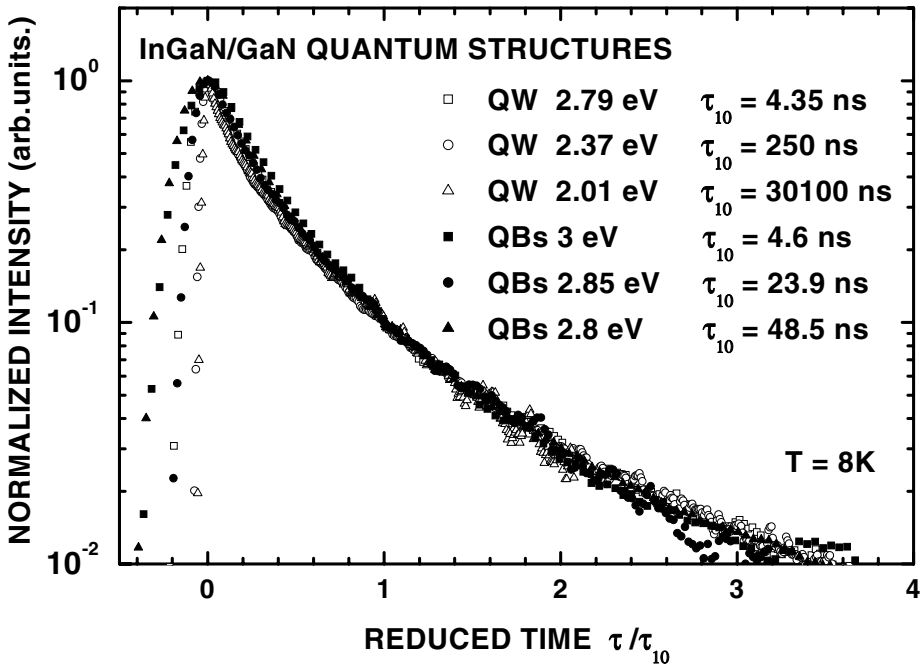

Figure 8. PL intensity decays plotted against a reduced time-scale, obtained from various InGaN/GaN QW and QB samples grown by molecular beam epitaxy under the conditions described in [48] and [63], in the same set-up. The corresponding characteristic times are listed in the figure.

$2.45\pm0.25\,\mathrm{MV\,cm^{-1}}$. The fit is shown by the solid curve in figure 7. In fact, we have understood that *there is* a localization effect, which contributes, e.g. to the Stokes shift of the PL line by a constant amount comparable to the PL linewidth ($\sim$120 meV throughout the entire sample). This localization certainly contributes, too, to the value of the decay time, but in a way which is the same in all regions of the sample. In other words, this effect is somehow modulated (or *enveloped*) by the electron–hole separation along the (0001) axis, induced by the electric field.

Interestingly, the shape of the decays, plotted against a reduced time-scale in figure 8, is constant throughout the sample [48]. This is also the case for the PL line-shape. In fact, figure 8 shows that for InGaN/GaN QBs grown in comparable conditions, this decay shape is the same, too. By a careful examination, we found that all PL lines measured tend to red-shift with time, which is related to the non-exponential shape of the decays. We believe that these findings are the consequence of the conjunction of radiative decays and carrier transfers between a variety of localized states, related to potential fluctuations in the ternary alloy. We believe that we have here a complex version of the transfer between two localized states commented on above for GaN/AlGaN QWs. We understand that the shapes of the lines and of their decays may be characteristic of given growth conditions and that they may be different for samples grown by other techniques or at different temperatures. On the other hand, for the present growth technique and the present growth conditions, the decay shapes are the same for QWs and QBs. This is a first indication that there is basically no difference between the two types of quantum structure, in terms of recombination dynamics. Figure 9 shows further evidence of this, by showing the temperature dependence of the PL peak energy for an InGaN/GaN QW and for a plane of InGaN/GaN QBs. The so-called 's-shape' of this variation is easily explained [83] by the existence of different localization centres, separated by some potential barriers, all distributed

in a stochastic way. The average PL energy results from the quasi-equilibrium established by the optical excitation and by the above-mentioned conjunction of radiative decays and carrier transfers. Slightly increasing the temperature displaces this equilibrium towards lower energies because the shallower potential fluctuations are thermally emptied to the benefit of deeper ones. By further increasing the temperature, at some point (∼130 K), thermal excitation becomes sufficient to excite some carriers out of the potential fluctuations. Then the average PL energy increases again. The full width at half maximum of the PL lines also increases steeply. For $T \sim 200$ K and above, the PL is dominated by free, quasi-two-dimensional carriers: then the temperature dependence is parallel to that of the band-gap of InGaN.

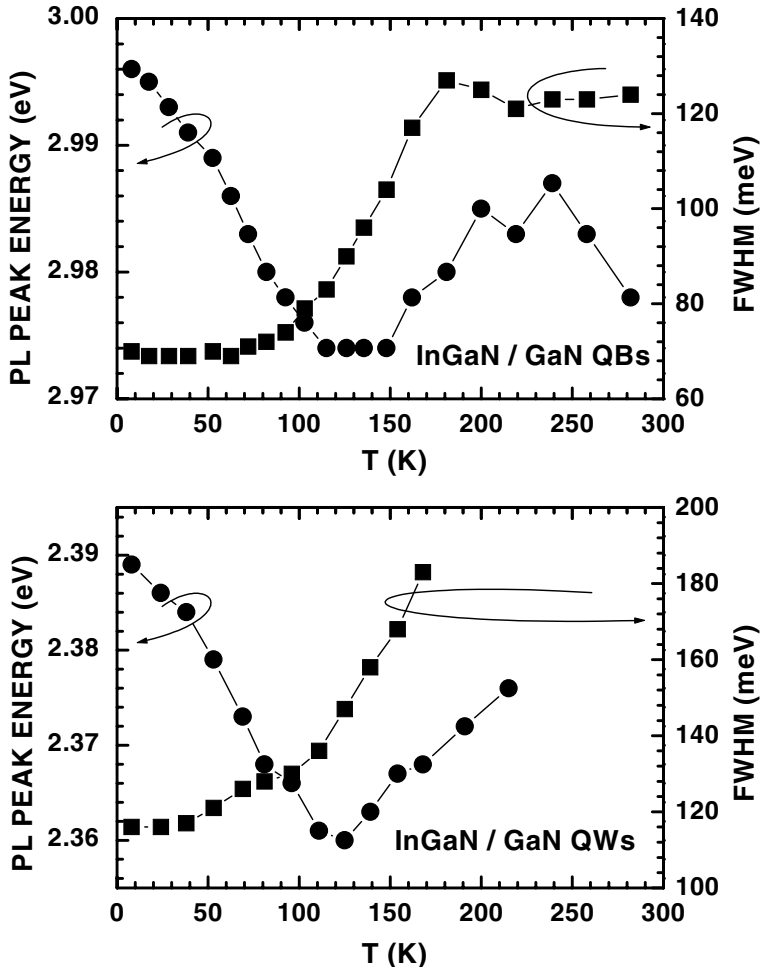

Figure 9. 'S-shaped' temperature dependence of the PL peak energy for an InGaN/GaN QW and for an InGaN/GaN single plane of QBs. The In composition is in the 0.15–0.20 range. The corresponding variations of full widths at half maximum (FWHM) of the PL lines are also plotted.

Indeed, the above scenario is similar to that commented on above for the model system GaN/AlGaN, where the two 'in-plane' localization states are now replaced by a quasi-continuum of 'in-volume' potential fluctuations. Figure 10 confirms our analysis, for a variety of QW and QB samples (for the latter, the nominal thickness deposited is indicated). In the low-

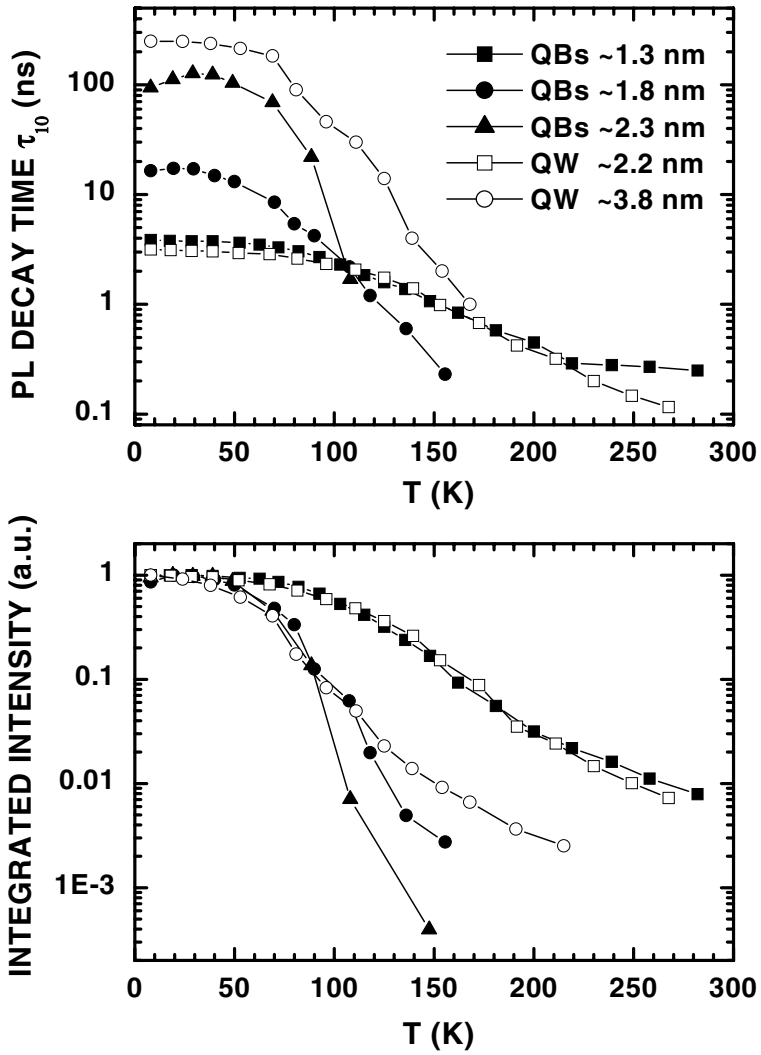

Figure 10. Plots of PL decay times and of PL integrated intensities versus temperature, for a variety of InGaN/GaN QW and QB samples. The widths indicated are the nominal, average widths, which means that the vertical sizes for QBs are somewhat larger than the values shown.

T range the PL decay times remain fairly constant, which is expected for the radiative lifetime of localized excitons [60–62, 84]. The spectrally integrated PL intensity is also constant. Both results confirm that nonradiative processes are still not fast enough to reduce the PL decay time or the PL efficiency. On the other hand, for T larger than $\sim$100 K, the thermally enhanced escape of carriers from localization centres strongly increases the probability of nonradiative recombination. This is why both the PL decay time and the PL intensity collapse nearly exponentially. Roughly speaking, the larger the initial low-T decay time (radiative lifetime) the faster the collapse. We remark, however, that growing QBs instead of QWs does not particularly protect the carriers against nonradiative effects.

For example, two of our samples (one QW and one QB plane) emit light around 2.9 eV and have thus comparable decay times, at low T, near 3–4 ns. There is not a large difference between

the temperature behaviours of these two samples, except, maybe, in the high-temperature range. The step taken by the variation of PL decay time versus T may result from the presence of boxes, but the effect on the loss of PL intensity is small. In fact, our systematic studies [48, 81, 82] have shown us that any attempt at improving the room-temperature radiative efficiency had basically the same effect on QW and on QB samples. These results have convinced us that, indeed, strong carrier localization reduces nonradiative recombinations in InGaN systems but also that the spatial extension of the localization centres is much smaller than the average size of our QBs, i.e. a few nanometres. In other words, the stochastic distribution of In atoms and the small extension of carrier wave-functions (the heavy masses) contribute naturally to avoid nonradiative recombination of electron–hole pairs.

In the case of InGaN/GaN systems, growing QBs is not really necessary if one only aims at improving radiative efficiency. This makes the important difference with GaN/Al(Ga)N systems, where localization *has to be* induced artificially by growing QBs.

In summary, we have seen that internal electric fields truly control the well-width dependence of radiative lifetimes for InGaN/GaN QWs and QBs. These radiative lifetimes can be measured directly because they are equivalent to PL decay times, at low temperatures only, due to carrier localization. This localization or rather the thermally enhanced de-localization of carriers is what controls the nonradiative lifetime and thus the room-temperature radiative efficiency. Improving this efficiency implies, of course, a reduction of densities of threading dislocations, if possible. But it also implies that one increases somehow the strength of localization, e.g. by inducing higher potential barriers between localization centres. We have seen that growing QBs instead of QWs had only a small effect in that sense.

5. Conclusion

Quantum-confinement systems based on wurtzite group-III nitrides have numerous original optical properties. We have shown their ability to emit light over the entire visible range, which makes them good candidates for white-light emission. We have analysed in detail the energies and dynamics of optical recombinations in quantum wells and quantum boxes. Electric field effects drastically affect oscillator strengths, thus radiative lifetimes. Localization effects, either natural (ternary alloys) or artificially induced (quantum boxes of binaries) are crucial to explain the limitation of nonradiative recombinations in these materials with large densities of defects.

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