REGULAR PAPER

Temperature-Dependence of Exciton Radiative Recombination in (Al,Ga)N/GaN Quantum Wells Grown on *a*-Plane GaN Substrates

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This article presents the dynamics of excitons in *a*-plane (Al,Ga)N/GaN single quantum wells of various thicknesses grown on bulk GaN substrates. For all quantum well samples, recombination is observed to be predominantly radiative in the low-temperature range. At higher temperatures, the escape of charge carriers from the quantum well to the (Al,Ga)N barriers is accompanied by a reduction in internal quantum efficiency. Based on the temperature-dependence of time-resolved photoluminescence experiments, we also show how the local disorder affects the exciton radiative lifetime at low temperature and the exciton non-radiative lifetime at high temperature.

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1. Introduction

One of the most important remaining bottlenecks regarding the use of III–nitride based light emitting diodes for high power applications is the reduction in efficiency at high injection current, the so-called "efficiency droop".[1] Although the origin of the efficiency droop is still the subject of controversy,[1–4] many studies suggest that it could originate from efficient Auger recombination of charge carriers confined in the quantum well (QW) plane.[2] One natural way to decrease the efficiency of Auger recombination is to decrease the charge carrier density in the QW, which can be achieved by increasing the thickness of the QW. However, in GaN-based heterostructures grown along the [0001] axis, the discontinuity of the polarization field at the interfaces of the QW leads to a built-in electric field that spatially separates the electron and hole wave functions[5] and causes therefore a dramatic increase in radiative decay time for QW thicknesses larger than about 3 nm. Non-polar planes allow for the growth of thick QWs with an optimal overlap between electron and hole wave functions,[6] but the use of lattice-mismatched substrates induces high densities of stacking faults and dislocations. Then, even at low temperature, the decay of excitons in non-polar QWs is dominated by their capture on extended defects.[7,8] We have recently shown that depositing non-polar (Al,Ga)N/GaN QWs directly on the *a*-facet of GaN crystals allows for a significant increase of the radiative efficiency at 300 K.[9,10] Based on room-temperature cathodoluminescence experiments, we deduced a dislocation density of $2 \times 10^5 \, \text{cm}^{-2}$ in the QW and an exciton diffusion length of 100 nm, demonstrating that dislocations do not affect QW excitons at room temperature.[9] Then, from time-resolved photoluminescence (PL) measurements, we showed that the radiative efficiency at high temperature of these non-polar QW samples was related to the non-radiative recombination in

the (Al,Ga)N barriers of charge carriers thermally emitted from the QW plane.[10]

In the present paper, we describe the dynamics of excitons in non-polar (Al,Ga)N/GaN single QW samples deposited on *a*-plane GaN crystals. For all the investigated QW samples, the mechanism limiting the radiative efficiency at 300 K is related to the thermal escape of carriers from the QW to the (Al,Ga)N barriers. We detail in particular how disorder affects the dynamics of excitons confined in the QW plane. At low temperature, we observe spatial variations in the exciton radiative decay time, which we ascribe to fluctuations in localization centre density along the QW plane. At room temperature, we observe that the larger the density of localization centres in the QW, the shorter the QW PL decay time. This leads us to the conclusion that there is a spatial correlation between the density of localization centres in the QW and the density of non-radiative point defects in the (Al,Ga)N barriers.

2. Experiments

We study by non-resonant time-resolved PL experiments $Al_{0.06}Ga_{0.94}N/GaN$ single QWs deposited by NH_3 molecular beam epitaxy on the *a*-facet of GaN substrates produced by the high-pressure solution method. The investigated samples have QW widths of 2, 4, and 7 nm. As reported in Ref. 9, the resulting QW structures exhibits a threading dislocation density of the order of $2 \times 10^5 \, \text{cm}^{-2}$. For time-resolved PL experiments, the QW samples were excited with the third harmonic ($\lambda = 280 \, \text{nm}$) of a $Ti:Al_2O_3$ laser with 2 ps pulse width and 80.7 MHz repetition rate. We estimate the photogenerated carrier density to $5 \times 10^{10} \, \text{cm}^{-2}$. The emission from the QW samples was analysed with a monochromator (focal length of 36 cm and grating of 1200 g/mm) followed by a streak camera using a photon counting mode. Continuous-wave (cw) PL experiments have been carried out using a HeCd laser ($\lambda = 325 \, \text{nm}$). The QW emission was analysed with a monochromator (focal length of 64 cm and 1200 grooves per mm grating) followed by detection on a Peltier-cooled CCD.

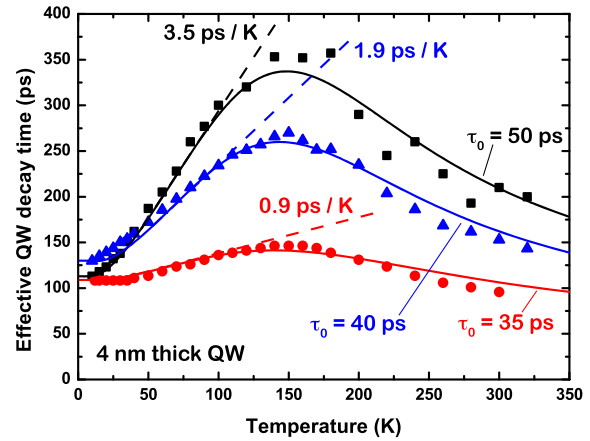†Present address: CEA-LETI, Minatec Campus, 17 rue des Martyrs, 39054 Grenoble, France.

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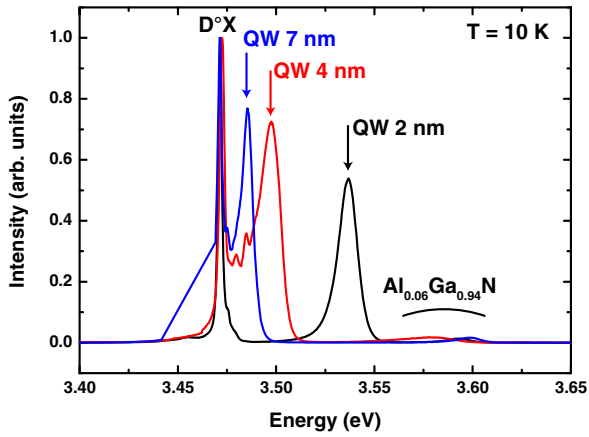
Fig. 1. (Color online) Time-integrated PL spectra taken at 10 K on 2-, 4-, and 7-nm-thick $Al_{0.06}Ga_{0.94}N$/GaN single QWs (black, red, and blue lines, respectively).

Fig. 2. (Color online) Effective QW PL decay time as a function of temperature for a 4-nm-thick $Al_{0.06}Ga_{0.94}N$/GaN single QW, for three different excitation spots (symbols). The result of the fitting procedure using Eq. (1) is shown by solid lines. Dashed lines show the linear increase of exciton radiative lifetime with respect to temperature.

3. Results and Discussion

3.1 Impact of disorder on the low-temperature exciton dynamics

We display in Fig. 1 the cw-PL spectra at 10 K for the three QW samples. When increasing the QW thickness from 2 to 7 nm, the QW emission energy decreases from 3.540 to 3.483 eV. From the dependence of the QW emission energy on the QW thickness, we confirm the absence of built-in electric fields in our samples.[7] In parallel, the emission linewidth goes from 13 to 8 meV, due to the reduced effect of interface roughness and barrier alloy disorder on the quantized energies for the thickest QWs.[7,11] We attribute the weak emission band observed in the 3.57–3.60 eV range to the recombination of excitons in the $Al_{0.06}Ga_{0.94}N$ barriers. Concerning the narrow emission line centred at 3.471 eV, it corresponds to the recombination of donor bound excitons (D^0X) in the GaN substrate.[9,12] We also note the absence of any emission in the 3.42 eV range, indicating the absence of basal plane stacking faults in our samples.[13,14] When moving the excitation spot across the samples, there is no noticeable change in QW emission energy and emission linewidth. This means that both the barrier Al-content and the QW thickness remain nearly constant across the sample. We present in Fig. 2 the PL decays τ_{PL} measured on the 4-nm-thick QW sample with respect to temperature, for three different excitation spots. At 10 K, excitons are mostly localized along the QW plane and τ_{PL} is given by the radiative decay time of localized excitons τ_{loc}. Scanning the excitation spot across the sample, the QW PL decay time at 10 K fluctuates between 105 and 130 ps. The decay time of localized excitons is inversely proportional to the coherence volume of the exciton,[15] which in the present case is given by the volume of the localization centre.[16] Consequently, as the QW thickness is constant across the sample, we attribute the variation in τ_{loc} to local change in the spatial extension of exciton localization centres.

At higher temperatures, excitons are delocalized along the QW plane and τ_{PL} now corresponds to the decay of a thermalized distribution of localized and free QW excitons.[17] With N_{loc} and N_{fr} the density of localized and free QW excitons, respectively, one gets, in the simplest possible picture:

$$\tau_{PL} = \frac{N_{loc} + N_{fr}}{N_{loc}/\tau_{loc} + N_{fr}/\tau_{fr}} . \tag{1}$$

The free exciton decay time τ_{fr} is given by $\tau_{fr}^{-1} = \tau_r^{-1} + \tau_{nr}^{-1}$, where τ_r and τ_{nr} are QW free exciton radiative and non-radiative lifetimes, respectively. The density of localized excitons N_{loc} is a function of temperature (T), of the localization centre density N_D and of the exciton localization energy E_{loc}. As shown in Refs. 9 and 17, it is possible to express the ratio between localized and free exciton densities as

$$\frac{N_{loc}}{N_{fr}} = \frac{N_D \pi \hbar^2}{2MkT} \exp\left(\frac{E_{loc}}{kT}\right), \tag{2}$$

where M is the exciton mass. To compute E_{loc}, we use envelope function calculations that include a variational modeling of excitonic effects.[18] We assume that exciton localization occurs on monolayer fluctuation of the QW thickness[19] and we get $E_{loc} = 8$, 3, and 1 meV for the 2-, 4-, and 7-nm-thick QWs. The computed QW width dependence of E_{loc} agrees qualitatively with the localization energies deduced from the temperature-dependent PL experiments reported in Ref. 10. In addition, since we do not observe any change in QW emission linewidth when scanning across a sample of given QW thickness, we assume that E_{loc} is constant along the QW plane. Regarding τ_{loc}, it only depends on the coherence volume of the localized exciton[15,16] and we take it to be constant with temperature. In contrast, τ_r depends on M and on the oscillator strength f_{osc}, and increases linearly with temperature, due to the population of states lying out of the light cone (i.e., exciton states that do not couple to light).[20,21] Consequently, in the absence of non-radiative recombination, exciton delocalization leads to an increase in τ_{PL}. Experimentally, between 10 and 150 K, we observe that τ_{PL} for the 4-nm-thick QW sample increases with temperature (Fig. 2), proving the dominance of radiative recombination over non-radiative processes in this temperature range. Consistent with this, we find that for temperature below 150 K, the QW emission intensity remains nearly constant (Fig. 3).
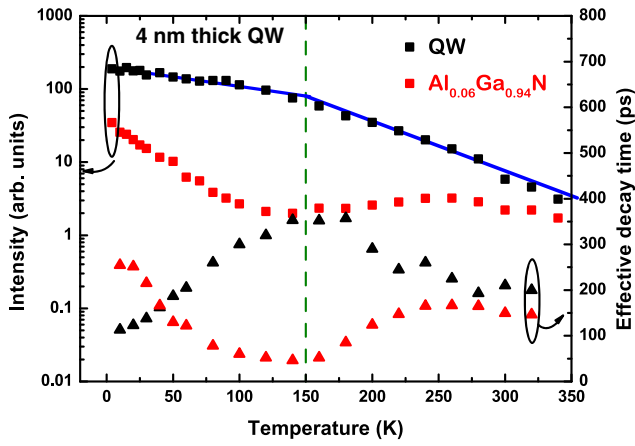
Fig. 3. (Color online) QW (black) and $Al_{0.06}Ga_{0.94}N$ barrier (red) emission intensity (squares) and effective decay time (triangles) as a function of temperature for a 4-nm-thick $Al_{0.06}Ga_{0.94}N$/GaN single QW. Solid and dashed lines are guides to the eye.

Fig. 4. (Color online) Effective QW PL decay time taken as a function of temperature for a 2 (black), 4 (red), and 7 nm (blue) thick $Al_{0.06}Ga_{0.94}N$/ GaN single QW samples. Solid lines show the result of the fitting procedure using Eq. (1).

It is to be noted that the gradient of τ_{PL} is not the same over the whole sample. We observe that this gradient lies between 0.9 and 3.5 ps/K (Fig. 2). Using the formalism presented in Ref. 9, and assuming that M and f_{osc} do not depend on the local disorder amplitude, the increase of τ_{PL} with temperature in the low-temperature range can be fitted with only a single free parameter: the density of localization centres N_D. We deduce from the data displayed in Fig. 2 that N_D varies between 2×10^{12} and 2×10^{13} cm^{-2}. We emphasize that we do not evidence any correlation between the coherence volume of localized exciton and the density of exciton localization centre. Note also that the localization centre densities computed here should be taken as indications of the relative local disorder amplitude rather than as absolute values characterizing the QW interface roughness at the local scale.

3.2 Impact of disorder on the high-temperature exciton dynamics

For temperatures higher than 150 K, we observe for the 4-nm-thick QW sample a decrease in τ_{PL} and in QW emission intensity, indicating the activation of a non-radiative recombination process. It is worth noting that whatever the local density of localization centres, τ_{PL} starts decreasing above the same temperature $T = 150$ K (Fig. 2). In parallel, we observe between 150 and 250 K the increase of both the (Al,Ga)N barriers PL intensity and lifetime (Fig. 3). This demonstrates that the non-radiative recombination of QW excitons is activated at the same temperature as the thermal escape of carriers from the QW to the (Al,Ga)N barriers (Fig. 3). As the decay of carriers in $Al_{0.06}Ga_{0.94}N$ is mainly non-radiative for temperatures higher than 100 K,[10] we attribute the decrease in τ_{PL} to the non-radiative recombination in the (Al,Ga)N barriers of charge carriers that have thermally escaped the QW. To account for this non-radiative recombination channel, we consider that the non-radiative recombination decay time is given by

$$\tau_{nr}(T) = \tau_0 \exp\left(\frac{E_a}{kT}\right), \quad (3)$$
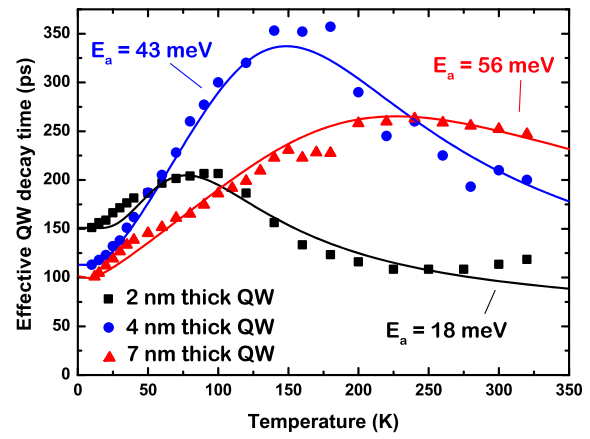
where E_a is an activation energy that characterizes the depth of the QW and τ_0 depends on details of the mechanisms of interaction between charge carriers and non-radiative recombination centres in the (Al,Ga)N. Note, however, that in agreement with what reported in Ref. 22, the E_a obtained from temperature-dependent PL experiments cannot be directly compared to the electron and hole confinement energies. When aiming at describing the thermal escape of carriers from a QW, one needs to account for (i) the ionization of excitonic complexes into electron–hole pairs,[10,23] (ii) the difference in density of states between the (Al,Ga)N barriers and the GaN QW (three and two dimensional, respectively),[10] (iii) B and C excitons, as well as the excited states of the three exciton branches[22] and (iv) the disorder in both the QW plane and the (Al,Ga)N barriers.[10,23] As expected, we manage to fit the temperature dependence of τ_{PL} for the different excitation spots keeping a constant E_a, which we find equal to 43 meV (Fig. 2). Regarding τ_0, it ranges between 30 and 50 ps. As a matter of fact, we notice that τ_0 and the local density in localization centres are correlated: the larger the local density of localization centres, the smaller τ_0 and therefore the more efficient the non-radiative recombination in the (Al,Ga)N barriers.

Performing time-resolved PL experiments on the 2- and 7-nm-thick QW samples fully corroborates the results obtained on the 4-nm-thick QW sample (Fig. 4). First, we observe for all samples an increasing τ_{PL} in the low-temperature range, indicating purely radiative exciton recombination. We find that the local density of localization centres in the QW is the main parameter setting the temperature dependence of exciton radiative lifetime and consequently the slope of τ_{PL} versus temperature. Second, and similarly to what is seen for the 4-nm-thick QW sample, we observe for the 2- and 7-nm-thick QW a decrease in τ_{PL} in the high-temperature range. For a given barrier Al-content, the thicker the QW, the larger the temperature range of increasing τ_{PL} (Fig. 4), as expected for non-radiative recombination processes related to the thermal escape of carriers from the QW to the barriers.[10] Using Eq. (1) to fit

the temperature-dependence of τ_{PL}, we find $E_a = 18$ and 56 meV for the 2- and 7-nm-thick QW samples, respectively, which verifies our earlier deductions. Coming to the values of τ_0, we find them to be equal to 50 ± 13 and 66 ± 15 ps, respectively, indicating that there is no relation between τ_0 and the QW width, as one might have anticipated for non-radiative recombination occurring in the barriers.

4. Conclusions

In conclusion, we have performed time-resolved photoluminescence experiments on *a*-plane (Al,Ga)N/GaN quantum wells grown on bulk GaN substrates for temperatures between 10 and 320 K. From the increase with temperature of the exciton effective decay time in the quantum well together with the nearly constant integrated emission intensity, we show that exciton recombination is mainly radiative for temperatures below 150 K. At higher temperatures, the decreases in effective decay time and emission intensity give evidences for the activation of non-radiative recombination, which we relate to the escape of carriers from the quantum well. We show that in the low-temperature range, variations in quantum well interface roughness lead to large fluctuations of exciton radiative decay time. We then show that the larger the density of localization centres in the quantum well, the more efficient the non-radiative recombination in the (Al,Ga)N barriers. This demonstrates a clear spatial correlation between disorder in the quantum well and in the (Al,Ga)N barriers.

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