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Time-resolved photoluminescence studies of InGaN/GaN multiple quantum wells

J. Allègre, P. Lefebvre, S. Juillaguet, W. Knap, J. Camassel
Groupe d'Etude des Semiconducteurs, GES-CNRS

Q. Chen, M. A. Khan
APA Optics Inc.

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Abstract

We report both cw and time resolved optical investigations performed on an InGaN/GaN multiple quantum well grown by MOVPE on <0001>-oriented sapphire substrate. At low temperature we find a strong "blue" luminescence band, of which energy position corresponds well with the wavelength of stimulated emission when excited with a nitrogen laser. We show that this PL band appears systematically red-shifted with respect to the QWs features, which supports a standard picture of fluctuations of the indium composition. Coming to the time-resolved data, we find at low temperature at least two "blue" band components which are both associated with long decay times (up to 4-5 ns at 8K). The decay time is temperature dependent and, when rising the temperature, the recombination rate increases. At room temperature, we reach typical values in the range ~100 to 500 ps.

1. Introduction

In the present state of the GaN technology, manufacturing InGaN/GaN single quantum well (SQW) structures on sapphire substrates appears to be one of thr most promising issues for producing efficient blue LEDs (light emitting diodes) at reasonable cost (see for instance Ref. [1] and references therein). Using the same basic design, but multiple quantum wells (MQWs) stacks in the active region, room temperature operations of laser diodes (LDs) working under pulsed operation conditions have also been demonstrated [2] [3].

Despite this series of technological breakthroughs, it is useful to remember that (opposite to the more mature material systems based on GaInAsP, for instance) most details of the capture process which rules the spatial localization of the electron-hole pairs in the thick InGaN epitaxial layers and, a fortiori, in the moderately narrow (single or multiple) QWs are still far from being understood.

Even the structural behavior of this peculiar alloy system sets problems. For instance, on thick 3-dimensional layers grown with a nominal 12% In composition, Harris et al. [4] reported energy-dependent recombination lifetimes. This suggested evidence of extrinsic localization effects, which were later confirmed by independent groups [1] [5]. These effects arise from uncontrolled fluctuations of the alloy composition. Direct correlation of these fluctuations with the change in PL emission energy under large excitation density (through the photorefractive effect) and with the change in PL linewidth with increasing alloy composition (through the piezoelectric effect) have been more recently suggested [6] [7].

In the case of single InGaN/GaN QWs, Jin Seo Im et al. [8] and C.-K. Sun et al [9] investigated the temperature dependence of the PL decay time. Similar to the simple epitaxial layers they found lifetimes ranging from about 250 to 600 ps at low temperature, which fastly decreased with increasing temperature. At 300K, typical values of about 75 to 130 ps were reported.

Finally, InGaN/InGaN MQWs structures have been examined [10] [11] [12] and, in this case, TEM

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investigations appear of special interest. Results have been first reported in Refs. [10], and next confirmed in Ref. [11], but up to now they concern only samples from the same origin. They show that the standard picture of a 2-dimensional square well-potential, like the one generally used for more conventional III-V alloys, is far from reality. When considered in the (x,y) planes, the quantum wells do not appear like uniform, but rather made of a mixture of conventional 2-dimensional wells and self-formed (In-rich) dotted-like regions. On such samples the dynamical studies have suggested that the n=1 excitons are first photogenerated in the large QW areas and next move, to be finally trapped in the low energy quantum dot-like structures [12]. At the present time it is not clear whether this is a general picture or can vary from grower to grower, depending of uncontrolled parameters.

Attempting to solve this problem, we have collected time-integrated (cw PL) and time-resolved photoluminescence (TRPL) measurements on a series of InGaN/GaN MQWs structure grown by MOVPE on sapphire substrates. They have rather close connection with the InGaAsP/InGaAsP family of strain-compensated structure and should display the same type of (complex) band alignment. In this work we focus only on a short period (8.5nm) structure which presents, when pumped by a N_2 laser, stimulated emission at 400 nm wavelength (purplish blue).

2. Experimental details

2.1. Samples

The sample used in this work has been grown using a low pressure metal-organic chemical vapor deposition (MOCVD) system. First, a thin GaN buffer layer was deposited, then a thick (~1μm) GaN layer was grown. On top of this layer, a stack of five different InGaN/GaN quantum wells was deposited. All wells had nominal composition ~22.5 % indium and thickness 3.5 nm. They were separated by 5 nm barriers of pure GaN. For clarity, a schematic drawing is shown in Figure 1. An important point to outline is that, taking into account the nominal values of lattice parameters [13] for GaN (a = 3.189 Å, c = 5.185 Å) and InN (a = 3.548 Å, c = 5.760 Å) respectively, one can calculate a rather large value (~2.5 %) of compressive strain in the wells. To lower this quantity, an additional buffer layer has been grown. It is ~30nm-thick and made of InGaN with typical composition 10-15 %. Depending on the final value of indium composition and stress, this should result in a more balanced strain structure, (similar to that already encountered in the case of InGaAsP MQWs lasers [14]). Assuming complete relaxation, the strain components should be alternatively negative (contractile) in the wells and positive (tensile) in the barriers, with reasonable values in the range of 1-1.5 %.

2.2. PL set up

Our cw PL set-up is a conventional one. The excitation is provided by the UV lines (at 333 nm) of a 5 W Ar+-ion laser, focused by a concave mirror to a spot diameter of about $1mm^2$. The sample is glued on the cold finger of a cryostat and the temperature can be adjusted from 5K to 300K. The emitted spectrum is analyzed using a HR 460 Jobin-Yvon spectrometer, equipped with a cooled GaAs photomultiplier (R943-02 from Hamamatsu) and standard photon counting electronics.

The TRPL setup is less conventional. The excitation consists of UV laser pulses, centered at ~272 nm, with a repetition frequency of 82 MHz and a temporal width of ~1.6 picosecond. Starting from the ~816 nm wavelength of a Ti-sapphire cavity pumped by a high power Ar+ ion laser, the pulses have been obtained by, first doubling and then admixing the second harmonic with the fundamental frequency by using a non-linear BBO crystal. The 272 nm outpout was then focused on the samples kept at regulated temperature on the cold finger of a second (closed-cycle helium) cryostat. The temperature range investigated was 8 K to 300 K. The emitted PL light was analyzed through a 0.5 m focal length spectrometer and detected by a C4334 Hamamatsu synchroscan streak camera. Starting from the 2 ps short pulse laser excitation, the overall temporal response of the setup is then broadened to a typical full width at half maximum (FWHM) of ~15 ps. After deconvolution of the PL decay from this response, the temporal resolution comes back to about 5 ps. The current repetition rate of one pulse every 12 ns prevents any accurate measurements of decay times larger than ~25 ns. Finally, when necessary, transmission spectra were collected at low temperature (8K) using a halogen lamp as source and detecting with the camera.

3. Experimental results and discussion

3.1. Band lineup

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Up to now, there are very few available (and reliable) results concerning the band alignment in InGaN/GaN QWs. As a consequence, we have found useful to start by reviewing the different contributions which result in the final energy position of the confined levels in this III-V peculiar system. First, using data from Ref. [13], we compute from the nominal In composition a raw band offset :

$$\Delta E_c + \Delta E_v = 0.45 \text{ eV} \quad (1)$$

of which we assume a standard repartition $\Delta Ec = 2 \Delta Ev$. Next we take into account the strain contribution. Neglecting all parameters which describe the (weak) spin-orbit interaction [15], this results in a very simple picture of triplet (X-,Y-,Z-like) states split by the in-plane (alternatively tensile or compressive) strain. From the work of Ref. [16], we get simply :

$$E(\Gamma_7^c\text{-}\Gamma_9^v) = E_{X,Y,Z} + (C_1\text{-}T_1\text{-}T_3)\, e_{zz} + (C_2\text{-}T_2\text{-}T_4)\,(e_{xx} + e_{yy}) \quad (2a)$$

$$E(\Gamma_7^c\text{-}\Gamma_7^{v+}) = E_{X,Y,Z} + (C_1\text{-}T_1\text{-}T_3)\, e_{zz} + (C_2\text{-}T_2\text{-}T_4)\,(e_{xx} + e_{yy}) \quad (2b)$$

$$E(\Gamma_7^c\text{-}\Gamma_7^{v-}) = E_{X,Y,Z} + (C_1\text{-}T_1)\, e_{zz} + (C_2\text{-}T_2)\,(e_{xx} + e_{yy}) \quad (2c)$$

where all C_i and T_i deformation potential refer to the conduction and (triplet) valence band, respectively. Since there are rather large discrepancies concerning experimental values in GaN [17] [18], we shall only use these results to make numerical estimates. Neglecting the crystal compressibility, i.e. assuming a constant ratio $e_{zz} = -(e_{xx} + e_{yy})$, we take all deformation potentials from the work of Ref. [18] and, neglecting the composition dependence, we find :

$$E(\Gamma_7^c\text{-}\Gamma_9^v) \sim E_{X,Y,Z} - 2.16\,(e_{xx} + e_{yy}) \quad (3a)$$

$$E(\Gamma_7^c\text{-}\Gamma_7^{v+}) \sim E_{X,Y,Z} - 2.16\,(e_{xx} + e_{yy}) \quad (3b)$$

$$E(\Gamma_7^c\text{-}\Gamma_7^{v-}) \sim E_{X,Y,Z} \quad (3c)$$

This shows clearly that, for any contractile strain, the transition energy associated with the lowest direct band gap must experience a blue shift of, typically, 40 meV per percent. The last point is to estimate the confinement energies. Taking a constant effective mass 0.2 m_0 (after Ref. [19]), we estimate for a 3.5 nm thickness E (n=1) = 0.15 eV. The final (correct) value is not important but, altogether, these results deserve the following comment.

Because of the natural tendency to equilibrate the strain within a multilayer structure, both type I and type II transitions should be observed. Type I transitions correspond with carriers localized in the wells and, while the final transition energy should vary depending on the more or less efficient cancellation of the strain within a given set of layers, in our case the corresponding value should be expected ~3.24 eV. The selection rule should correspond with direct recombination of confined electrons and Z-like holes (E//Z). The type II transitions correspond with carriers confined in different places in real space : while the electrons are still in the wells, the holes are now confined in the (strained) barriers. The corresponding transition energy is, of course, very dependent on the final value of the band parameters but a reasonable estimate is again close to 3.25 eV. The selection rules correspond now with E ^ C (X- and Y-like states).

3.2. Continuous PL

Typical spectra collected at 5K, on two different points of the surface, are shown in Figure 2. They evidence, both, common features and inhomogeneous behavior. The most important common feature is the strong purple (hereafter called "blue") band which manifests at ~3.05 eV. This blue band corresponds well with the wavelength of stimulated emission (400 nm) of the same sample, when pumped by a N_2 laser, and cannot come from intrinsic transitions. Indeed, with 22.5 % indium composition in the well, we have already established (see previous section) that no intrinsic transition should appear below 3.24 eV. The blue band corresponds well to the energy position of the 3-dimensional band gap of the alloy which constitutes the wells

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but, considering the structure, it has to be corrected for strain and confinement effects. Both contributions add to increase the transition energy up to 3.24 eV. As a consequence, from this first series of experiments, we conclude that the PL cannot originate from intrinsic origin. This is similar to the results already reported in Refs. [10] [11] [12] and suggests carrier localization effects in In-rich zones.

The second series of common features are the (weak) transitions observed from 3.2 to 3.5 eV. While corresponding better with the intrinsic transition energies expected from the consideration of band alignment in section III-A, they do not shift much when changing the well width and probably come from extrinsic origin. Unresolved admixture of QW states and deep GaN donor-acceptor pair transitions is also possible (see the sharp GaN excitonic transition resolved around 3.5 eV).

Most of the nonuniform behavior comes from a strong band (centered around 3.15 eV) which manifests itself more or less strongly depending upon the spectrum under consideration. Because this is in the energy range where the stimulated emission appears, we have focused out TRPL investigation on this feature.

3.3. TRPL spectra

Figure 3 shows a time-integrated PL spectrum collected at low temperature (8K). The time-integration is 5 ns and, similar to the pure cw spectrum, we see clearly that the strong extrinsic blue band dominates the spectrum. We attribute the small differences in absolute energy positions to the difference in excitation frequency and power. Since we believe that In-rich zones are involved, to confirm this hypothesis, we have inspected the transmission spectra. We have found the following :

A clear absorption structure appears around 3.25 eV, at 8K. It has been indicated in Figure 3 by the high energy arrow labeled "Absorption". Coming back to the above results, we find that it agrees well with either the direct creation of free n=1 excitons in the unstrained InGaN buffer layer (balanced strain structure) and/or the creation of indirect (in real space) type II excitons in the MQWs stack. As a consequence, from this first absorption feature, we conclude that the major contribution to the joint density of states (DOS) in the InGaN range comes from either the strain-free buffer layer with 12.5 % indium composition and/or the MQWs stack with type II structure.

A weaker (and broader) absorption feature (shoulder) appears also around 3.1 eV. It corresponds to the high energy range of the low temperature PL spectrum, close to the lasing wavelength. To check how much of the PL intensity is directly collected from these In-rich areas, we have performed a Gaussian fit to the experimental spectrum. The results are shown as solid line. We find mainly two components. The first one dominates the spectrum, the second one agrees more with the absorption onset.

From these results we conclude that both nominal QWs and In-rich domains exist. The range of In-rich compositions is rather narrow, but not strictly limited to the value which corresponds to the maximum of the blue PL band. Indeed, most of the DOS appears at slightly higher energy (lower In composition). This explains the simultaneous observation, in the blue band of two different series of lines. The high energy one correspond with the average In-rich zones, with a rather well-defined In composition. The low energy one (i.e. the maximum energy of the blue PL band) corresponds with the fluctuations. Since it is typically Stokes-shifted by 60 meV from the maximum of the DOS (absorption edge shoulder), we estimate ~3 % fluctuation. The time-dependent results confirm this analysis. In Figure 4 we show three different PL spectra, all collected at low temperature and integrated on time intervals of 100 and 200 ps. The difference is only the time delay, at the beginning of each interval, with respect to the excitation : solid circles (t=0), open circles (t=500 ps) and solid squares (t=1 ns), respectively.

This figure demonstrates clearly that there is, during the first 100 ps, a broad continuum of transitions which extends, roughly speaking, from the n=1 absorption edge (~3.25 eV) to the In-rich zone (~3.1 eV). In the TRPL experiments, it displays no specific features but results in a high energy luminescence tail. Extending the delay between excitation and detection, the relative contribution of this tail decreases rapidly and, after 1 ns, most of the emission left is from the long-lived (red-shifted) blue PL band. This gives PL spectra very similar to the one plotted in Figure 3. To evaluate how fast is the cooling from the In-rich zone to the Stokes-shifted tail, we have performed a second series of oscillator fits. We considered only two components and find that, versus time, the ratio of integrated areas changes from 15 % at t=0 to about 7% after 300 ps and, then, do not change very much.

This probably indicates that there is, for some carriers, no direct connection between the main density of states and the red-shifted main PL band. As a consequence we conclude, from this third series of experiments, that most of the optically excited carriers after being created in the QWs diffuse into the In-rich areas where they

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can find either a relative or an absolute (further red-shifted) minimum of energy. The time delay which corresponds to the transfer mechanism is on the 300 ps time-scale. Since, depending on whether they correspond with relative or absolute energy minima, the decay of the long-lived components will be associated with more or less complex mechanisms, we have considered the temperature dependence of the decay times associated with the two different zones identified in the blue band. Results have been shown in Figure 5 and Figure 6. They correspond to the maximum DOS of the In-rich zone and to the center of the dominant PL contribution at 3.05 eV, respectively. We find clearly that the decay time decreases with, both, increasing energy and increasing temperature. The change with energy comes from the band tailing effect [4] [5] [12], the change with temperature is more interesting. We find indeed that the recombination rate increases almost linearly with temperature. This is shown in Figure 7. We believe that such a result rules out the hypothesis of electron and holes separated by well defined potential fluctuations (and thermally de-trapped from these fluctuations). Rather, our results suggest an initial spatial separation of electrons and holes. This separation may arise from strain-induced internal piezoelectric fields,which are likely to be present due to the non-centrosymmetric nature of the crystals. Then, electrons and holes would need kinetic energy to encounter. The larger the In composition, the larger the field and the longer the lifetime.

4. Conclusion

Investigating the optical properties of a short period (8.5 nm) InGaN/GaN MQW sample, we have found that non homogeneous indium incorporation problems play a major role in the definition of the main blue PL band observed at low temperature. While the fundamental energy transition is about 3.25 eV, the main (purple-blue) PL band resolves around 3.05 eV.

Finally, coming to the TRPL, we have found that the decay time of the blue band at low temperature was always long, with time constants in the range 1 to 5 ns. Rising the temperature, the recombination rate increases and, at room temperature, the decay time was in the range of 100 ps.

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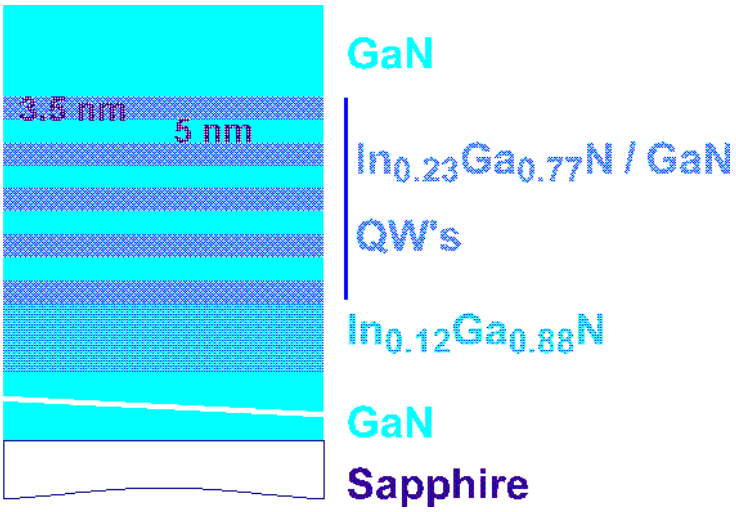

Figure 1. Schematic view of the multi-quantum well used for the present optical investigations.

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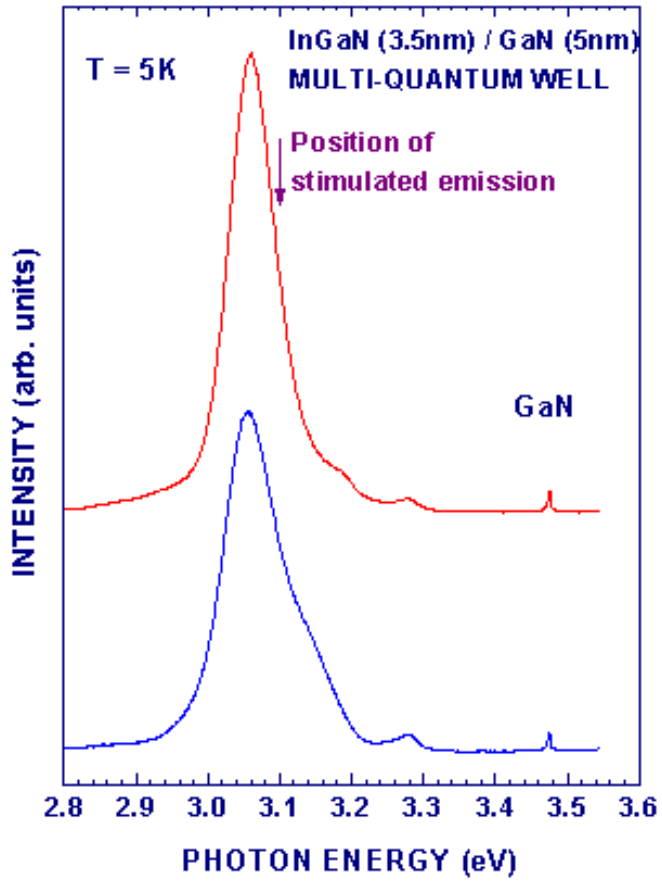

Figure 2. Continuous PL spectra taken at two different points of the sample.

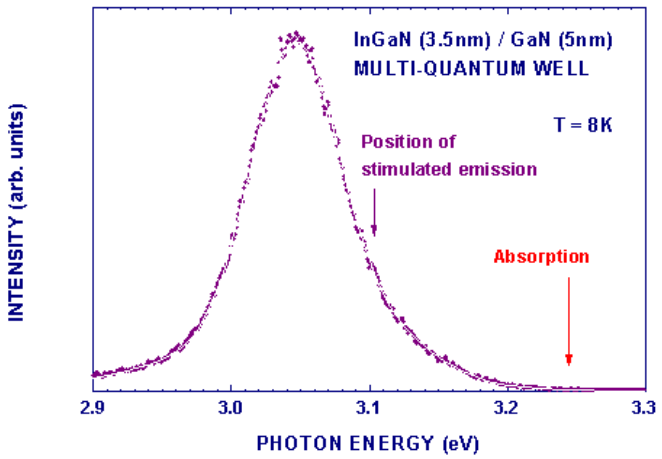

Figure 3. Plot of the time-integrated PL spectrum of a 3.5nm / 5nm InGaN / GaN quantum well excited by 272 nm laser pulses.

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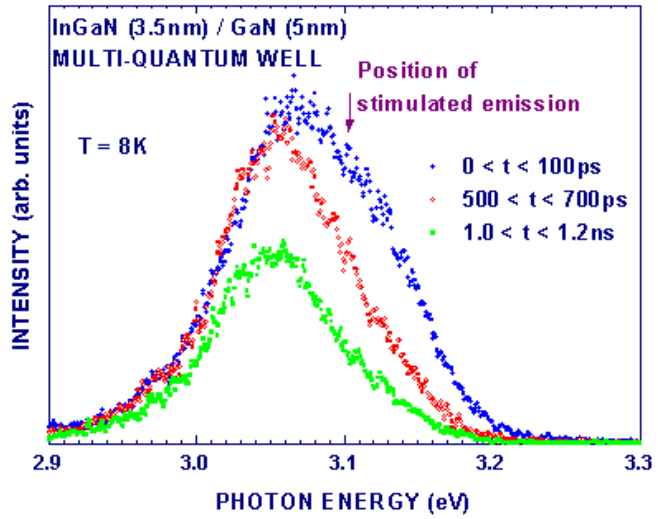

Figure 4. Evolution versus time, of the PL spectrum of a InGaN / GaN multi quantum well.

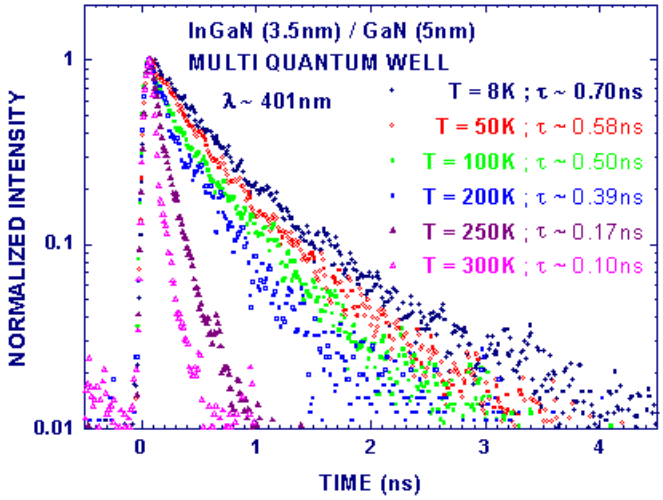

Figure 5. Decay of PL intensity at the wavelength of stimulated emission, at various temperatures.

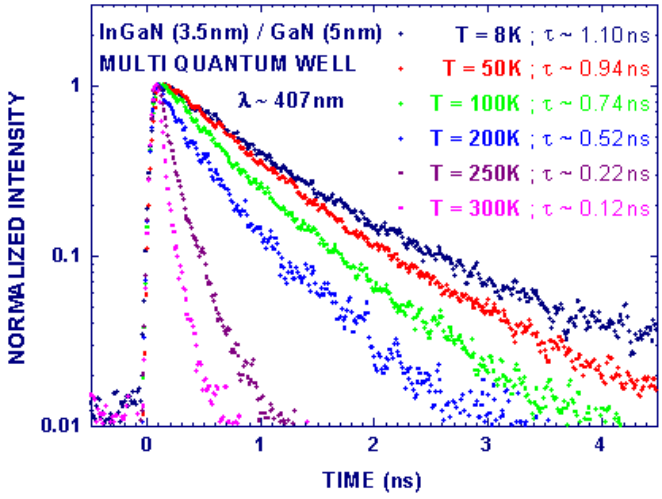

Figure 6. The same as Figure 5, but for the PL signal recorded at the maximum of PL spectrum.

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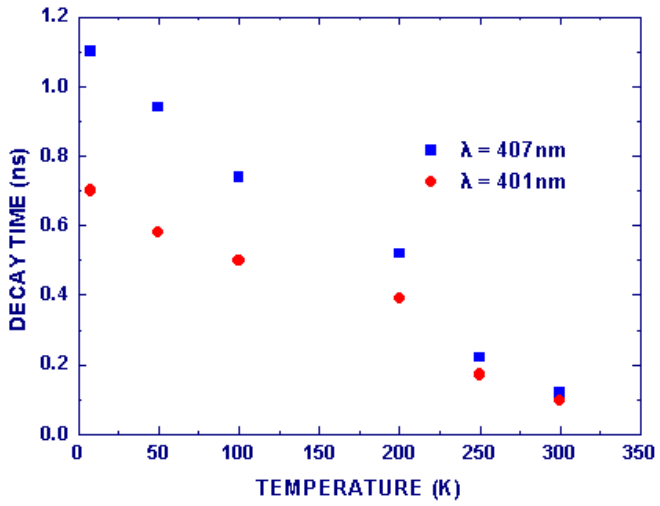

Figure 7. Temperature dependence of the decay times measured at two different spectral positions.

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