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On a possible origin of the 2.87 eV optical transition in GaNP

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Abstract

Temperature dependent photoluminescence excitation spectroscopy is employed to evaluate basic physical properties of the 2.87 eV absorption peak, recently discovered for the GaN_xP_{1-x} alloys. Whereas the appearance of this transition is found to be facilitated by incorporation of N and also H atoms, its intensity does not scale with the N content in the alloys. This questions the possible association of this feature with an N-related localized state. On the basis of the results of temperature dependent measurements, it is concluded that the state involved has a non-Γ character. Excitation of the known N-related localized states via this state is found to be non-selective, unlike that between the N-related centres. The observed properties are shown to be barely consistent with those predicted for the higher lying localized state of the isolated N atom derived from the Γ conduction band minimum (CBM). Alternative explanations for the '2.87 eV' state as being due to either a t_2 component of the X_3^c (or L_1^c) CBM or a level arising from a complex of N and H (in some form) are also discussed.

1. Introduction

Physical properties of N in III–V compound semiconductors have remained a subject of extensive research effort for almost four decades and yet are still matters of controversy. The surprising discovery by Thomas and Hopfield [1] that this impurity, in spite of its isoelectronic origin, introduces a number of states in the forbidden band gap of GaP stimulated in-depth theoretical [2–4] and experimental [5–7] studies aiming at understanding the origin of perturbations induced by isoelectronic impurities in semiconductors. Further interest in N behaviour was ignited by successful attempts to fabricate dilute nitride alloys, by increasing the N content in GaP(As) beyond a doping limit. In this case, N incorporation has been found [8, 9] to induce unusual and dramatic modifications in the band structure of the forming alloys, such

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as the giant bowing in the bandgap energy accompanied by a splitting of the conduction band (CB) states into the so-called E_- and E_+ subbands [10]. The former represents the CB edge, whereas the latter, for GaNP alloys, stems from the higher lying Γ CB minimum (CBM). Energy positions of these states strongly depend on the N content and undergo anticrossing with increasing N content [10–12]. The exact physical mechanism responsible for these fascinating transformations of the band structure still remains highly controversial [10, 13, 14].

Recently, we have found [14] that in addition to the E_- and E_+ states, a new absorption peak at 2.87 eV, i.e. just below the energy of the Γ_{15}^{v}–Γ_{1}^{c} direct exciton, emerged in the photoluminescence (PL) excitation spectra of the N-related emissions in GaN_xP_{1-x} alloys within the range $x = 0.05$–0.9%. The energy position of this transition remained pinned at 2.87 eV independently of the N content, which pointed towards a distinctively different origin of the state involved as compared to the E_- and E_+ states. We tentatively attributed the 2.87 eV transition to a zero-phonon optical absorption between the valence band maximum (VBM) and a t_2 component of the L_1^c or X_3^c CB states [14]. The pinning of the energy position was explained by the expected insensitivity of this t_2 state to perturbation by the N state of a_1 symmetry. An alternative model for the origin of the 2.87 eV transition has most recently been suggested from supercell calculations [15], which has concluded that the perturbed host states are not involved as their energies are about 0.20–0.25 eV below the Γ CBM. Instead, it was ascribed to one of the previously unknown N-related localized states that lies *well above* the CB edge, just below the Γ CBM. The corresponding state has been concluded to have predominantly Γ character and was attributed to an isolated N atom. The PLE peak was also assigned to the direct exiton in a GaP buffer layer [16].

The purpose of the present work is to gain detailed knowledge on basic properties of the 2.87 eV transition that is important for identification of its physical origin and, therefore, for a better understanding of N behaviour in GaNP alloys. The role of N in promoting the 2.87 eV transition will be evaluated on the basis of its dependence on the N content. In order to experimentally determine the character of the state involved, the temperature dependence of the 2.87 eV transition will be analysed. We will also examine the efficiency of excitation transfer from the 2.87 eV state to the known N-related levels within the bandgap of GaNP and will compare it with the well-established energy transfer from the excitonic state related to the isolated substitutional N atom. All studies were performed by utilizing temperature dependent photoluminescence (PL) excitation (PLE) spectroscopy. Alternative optical absorption measurements were found to be difficult and not conclusive, due to a strong overlap with optical transitions from a GaP substrate that dominate in optical absorption spectra.

2. Experiment

The GaN_xP_{1-x} epilayers studied in this work were grown by gas-source molecular beam epitaxy (GS MBE) on (100) GaP substrates. The thickness of the epilayers with N compositions ranging between 0.05% and 0.8% was 0.25 μm, whereas the GaN_xP_{1-x} epilayers with $x \geqslant 0.9\%$ were 0.75 μm thick. Secondary-ion mass spectrometry (SIMS) measurements were done using a Cameca system and a Cs^+ ion beam. PL was excited by either a xenon lamp assembled with a grating monochromator for a wide spectral range or by a tunable dye laser for high resolution studies over a narrow spectral range near the Γ_{15}^{v}–Γ_{1}^{c} transition. The resulting PL was detected by a GaAs photomultiplier through a double-grating monochromator. All PLE spectra were measured by monitoring emissions from N-related localized states except for a reference GaP sample, where the PLE spectrum was detected for the dominant 2.309 eV PL line from a residual dopant of unknown origin.

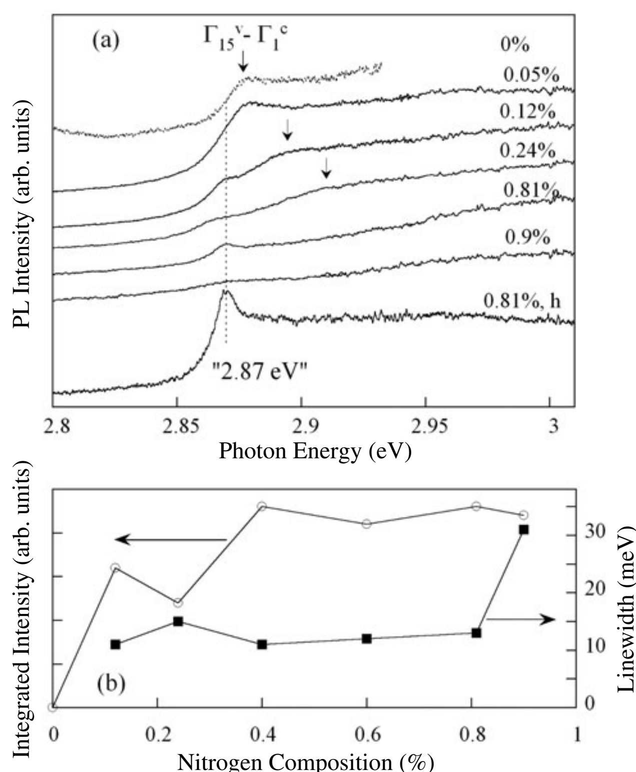

Figure 1. (a) Effects of N incorporation on PLE spectra of N-related emissions measured in the vicinity of the direct bandgap of GaP. The detection energy during all measurements was set at 2.101 eV except that the PLE spectrum of the reference GaP sample (shown by the dotted line) was detected at 2.309 eV. For comparison, also shown is the PLE spectrum of the $GaN_{0.081}P_{0.979}$ epilayer subjected to post-growth hydrogenation to the dose of 2×10^{18} cm^{-2} (the lowest curve), from [17]. Arrows indicate spectral positions of the E_+ transition which stems from the Γ_{15}^{v}–Γ_{1}^{c} transition. The spectra are normalized to their intensity at the highest energy and are shifted vertically for clarity. (b) Compositional dependence of the integrated intensity and the FWHM of the 2.87 eV peak.

3. Experimental results

Understanding the origin of the electronic state involved in the 2.87 eV transition requires detailed knowledge of its basic physical properties. These properties will be discussed below on the basis of the compositional and temperature dependences of the 2.87 eV transition, as well as efficiency of excitation transfer from this state to the known localized N-related centres.

3.1. Compositional dependence

Figure 1 demonstrates the compositional dependence of the 2.87 eV transition in the GaN_xP_{1-x} alloys. For the N-free reference sample, optical absorption in the energy range of 2.8–2.9 eV is dominated by the Γ_{15}^{v}–Γ_{1}^{c} direct exciton—see the dotted curve in figure 1. This transition rapidly shifts towards higher energy with increasing x (indicated by arrows in figure 1(a)) and represents the E_+ transition in GaN_xP_{1-x} alloys [10–12]. Simultaneously, a new peak pinned at 2.87 eV emerges. The intensity and linewidth of the 2.87 eV PLE peak were found

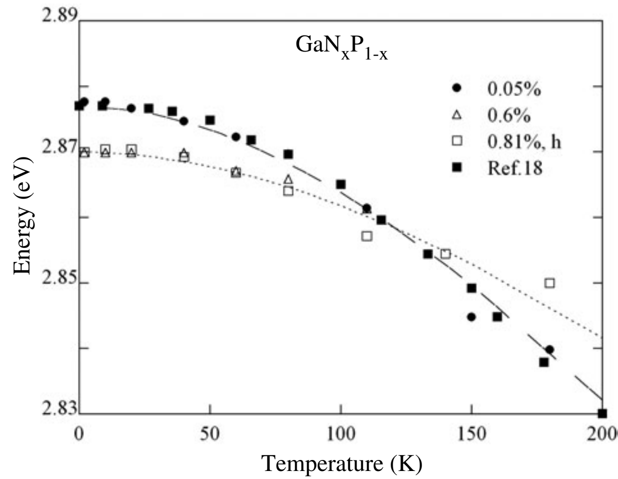

Figure 2. Experimentally determined energy positions of the Γ_{15}^{v}–Γ_{1}^{c} (solid dots) and the 2.87 eV transition (open symbols) as a function of measurement temperature. The data were obtained from the GaNP alloys with the specified N compositions and H treatment. Also shown (filled squares) is the expected thermal shift of the Γ_{15}^{v}–Γ_{1}^{c} transition in bulk GaP, taken from [18] (vertically shifted by about 5 meV for easier comparison). The dashed and dotted lines are the fitting curves for equation (1) with the corresponding fitting parameters $\alpha = 7.2 \times 10^{-4}$ and 5.4×10^{-4} eV K^{-1} for the Γ_{15}^{v}–Γ_{1}^{c} and the 2.87 eV transition, respectively.

to strongly depend on the concentrations of N, H and the structural quality. To illustrate these facts, compositional dependences of the integrated intensity (open dots) and the full width at half-maximum (FWHM) (filled squares) of the 2.87 eV transition are summarized in figure 1(b). (The data were obtained after subtracting background absorption due to the Γ_{15}^{v}–X_{1}^{c} and Γ_{15}^{v}–Γ_{1}^{c} transitions.) The abrupt broadening of the 2.87 peak is probably related to an increasing non-uniformity in strain distribution within the GaNP epilayers as it is observed for the partially relaxed GaNP epilayers with the thickness of 0.75 μm. It is worth mentioning that the intensity of the 2.87 eV transition is dramatically enhanced (i.e. by 5–6 times) by post-growth hydrogenation—see the lowest curve in figure 1(a) where the PLE spectrum from the hydrogenated $GaN_{0.081}P_{0.979}$ epilayer to the dose of 2×10^{18} cm^{-2} is shown (from [17]). The observed sensitivity of the 2.87 eV transition to N and H contents indicates that it does not originate from the GaP buffer layer [16], as N and H are known to be confined within the GaNP epilayers.

3.2. Temperature dependence

Increasing measurement temperature causes red shifts of all absorption transitions in GaP to a degree that is determined by the character of the state involved, e.g. the Γ_{15}^{v}–Γ_{1}^{c} direct bandgap is known to be appreciably more sensitive to a variation in temperature than the Γ_{15}^{v}–X_{1}^{c} indirect bandgap. In order to elucidate the character of the state involved in the 2.87 eV transition, we have studied the temperature dependence of the PLE spectra of the GaNP alloys. In figure 2 we show the energy of the 2.87 eV peak in the GaNP epilayers (with the specified N compositions) as a function of measurement temperature, determined by PLE. The thermal shift of the Γ_{15}^{v}–Γ_{1}^{c} direct exciton energy over the same temperature range [18] is also shown in figure 2, for comparison. From figure 2 it is clear that the thermal variation for the Γ_{15}^{v}–Γ_{1}^{c} direct exciton obtained from the $GaN_{0.0005}P_{0.9995}$ epilayer is identical to that reported in earlier

studies of bulk GaP [18] (shown by filled squares), which confirms the identical origins of the two transitions. On the other hand, the 2.87 eV PLE peak exhibits a markedly smaller red shift with increasing temperature as compared to that of the Γ_{15}^{v}–Γ_{1}^{c} absorption. This implies that the state involved is unlikely to be of Γ character and has a distinctly different origin as compared with the Γ_{1}^{c} states, contrary to the findings of [16]. To obtain quantitative information on the energy shifts, the temperature dependences of both transitions have been analysed using the Varshni equation [19]:

$$E = E(0) - \frac{\alpha T^2}{(T + \beta)}. \tag{1}$$

Here $E(0)$ is the corresponding energy position at 0 K, $\beta = 460$ K [19] is approximately the Debye temperature at 0 K and α is an empirical constant. The results of the fitting for the direct excitonic bandgap of GaP and the 2.87 eV transition are shown in figure 2 by the dashed and dotted lines, respectively, with the corresponding fitting constants $\alpha = 7.2 \times 10^{-4}$ and 5.4×10^{-4} eV K^{-1}. The latter value is somewhat below the known temperature coefficient for the Γ_{15}^{v}–X_{1}^{c} absorption of 6.2×10^{-4} eV K^{-1} [20]. (Experimental data describing thermal variations of other CB extrema are currently lacking, unfortunately.)

3.3. Excitation transfer to N-related localized states

Intensities of different PLE transitions are determined not only by their corresponding oscillator strengths but also by how efficiently the photoexcited carriers, which are created as a result of a particular absorption process, will be transferred to monitored luminescence centres. In the case of a band-to-band absorption, this transfer is usually not selective for a luminescent centre. Differences in the PLE intensities of different luminescent centres reflect differences in their concentrations and capture cross-sections for photoexcited electron–hole (e–h) pairs. In contrast, excitation transfer between different localized states often depends on their origins. Therefore optical excitation to a certain localized state is often selectively enhanced for ‘matching’ emissions, i.e. it exhibits a strong dependence on the detection energy.

Figure 3 shows PLE spectra of the N-related emissions detected at the specified emission energies, taking as an example the GaNP alloys with N compositions of $x = 0.05\%$ (a) and $x = 0.4\%$ (b). The corresponding PL spectra are also shown in the insets, for easy reference. In addition to the Γ_{15}^{v}–Γ_{1}^{c} and 2.87 eV transitions discussed above, and also structureless Γ_{15}^{v}–X_{1}^{c} band-to-band absorption that is dominant within the 2.35–2.8 eV spectral range, the PLE spectra contain excitonic lines related to the localized states of an isolated N atom (N_A) and also the NN_3 and NN_1 pairs. The intensity of these bound exciton transitions is considerably higher when the PLE spectra are recorded for PL emissions from shallow N states. For example, for the $GaN_{0.0005}P_{0.9995}$ alloy the PLE intensity at the N_A transition energy is about 1.8 times higher on monitoring the NN_3 line (curve 1 in figure 3(a)) as compared to that on monitoring the deeper NN_1 exciton (curve 2) or the cluster-related emissions (curve 3)—see figure 3(a). A similar trend is also observed for alloys with higher N compositions—see figure 3(b). The observed behaviour is common for N-related localized states in the parent GaP and reflects a higher efficiency of energy transfer via exciton tunnelling to the shallower states that are more abundant [6, 7]. On the other hand, such selectivity is not observed either for the band-to-band excitations or for the 2.87 eV transition. Close-ups of the PLE spectra for the same detection energies as those in figure 3 are shown in figure 4, within the narrow spectral range of 2.8–2.92 eV with a better spectral resolution. No significant differences were found between the PLE spectra, confirming that the excitations of various localized N states via the Γ_{15}^{v}–Γ_{1}^{c} and 2.87 eV transitions are not selective.

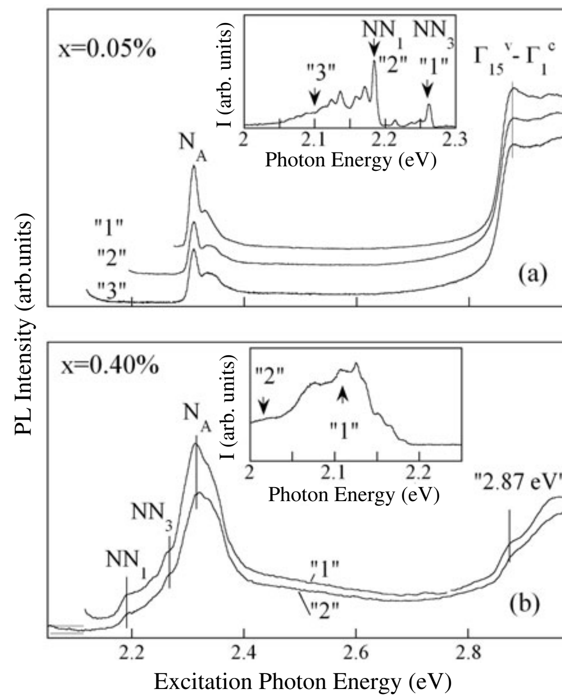

Figure 3. PLE spectra recorded for various N-related emissions, taking as an example the GaNP alloys with N compositions of 0.05% (a) and 0.4% (b). The PL spectra are also shown in the inset of each figure, for easy reference. Arrows denote detection energies used for the PLE measurements. The dominant features in the PL and PLE spectra are identified in terms of the states involved. The spectra are normalized to their intensity at the highest energy and are shifted vertically for clarity.

4. Discussion

We can now compare the basic properties of the 2.87 eV transition revealed in this work with those expected from different physical models proposed for the transition. Let us start with the idea of [15] that the corresponding state is related to the isolated N atom and is mainly built up from the higher lying Γ CB states. This model can account for the appearance of the 2.87 eV transition with N doping as well as its high oscillator strength, determined by the Γ character of the localized state involved. However, a number of experimental observations seem to be inconsistent with the model. First of all, the state involved is in fact not of Γ character, as revealed by the results of the temperature dependent measurements (figure 2). Secondly, assuming that the 2.87 eV state originates from the isolated N atom, its concentration should continuously increase with increasing x as long as the majority of N atoms remain isolated and do not interact with each other. This is true for the whole range of N compositions studied in this work, i.e. $x \leqslant 0.9\%$. Indeed, the average distance between the N atoms even for the alloy with the highest N content of 0.9% is about 16 Å, i.e. it exceeds the spatial separation between the N atoms in the most distant NN_{10} pair (12 Å) known to date [1]. In contrast, the intensity of the 2.87 eV transition saturates when $x > 0.24\%$ (figure 1(b)). Moreover, this model cannot explain the observed strong enhancement of the 2.87 eV transition after hydrogen passivation. For example, the intensity of the 2.87 eV transition in the hydrogenated sample (figure 1(a)) is ~6 times stronger than that observed in the untreated samples with the

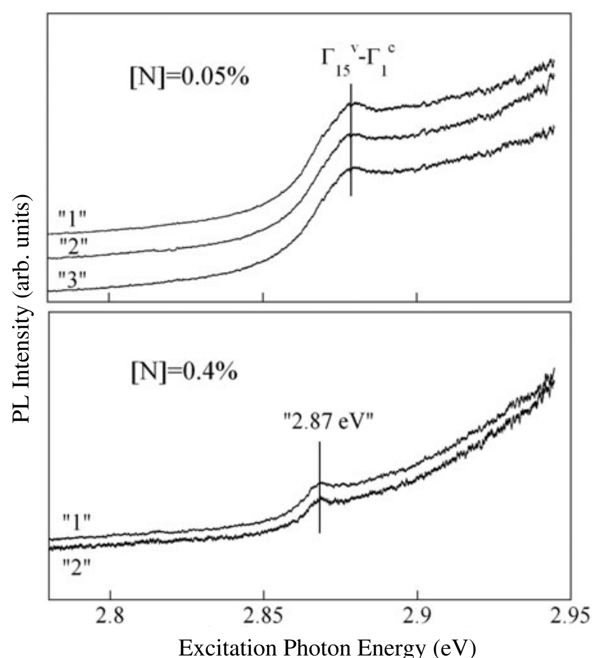

Figure 4. Close-ups of the PLE spectra as presented in figure 3, measured with a higher resolution by employing a tunable dye laser. In each case, the excitation power was chosen to be low enough to avoid any saturation effects.

same apparent N content of about 0.12–0.24% [17]. And finally, also rather surprising is a lack of selectivity of the excitation transfer from this state to other N-related states. Indeed, it is natural to expect that fast intracentre energy relaxation from the 'excited' state (i.e. the 2.87 eV state) to the ground bandgap state of the same N atom will precede relatively slow intercentre energy transfer to other N-related levels that is typically in the range of hundreds of ns [7]. This should lead to a correlation between intensities of the 2.87 eV and A-line transitions in the PLE spectra, which is not observed experimentally—see figures 3 and 4.

We shall now discuss the model of [14] in which the state responsible for the 2.87 eV transition represents the t_2 component of the X_3^c (or L_1^c) CBM. This t_2 state should not be perturbed by the N state of a_1 symmetry, i.e. it is expected to remain pinned in energy with increasing N content, as is indeed observed experimentally. The intensity of the corresponding transition should not be directly determined by the number of N atoms inserted in the crystal lattice, consistent with the experimental findings of figure 1. Instead, it should reflect relaxation of momentum conservation requirements for this formally forbidden transition due to alloy disorder. The higher intensity of the 2.87 eV transition in the hydrogenated samples can then be attributed to an increasing degree of disorder caused by the simultaneous presence of N and H atoms. Moreover, the corresponding state should be of either X or L character and therefore should be considerably less sensitive to the measurement temperature than the Γ CBM, as is indeed seen in the temperature dependent studies—figure 2. In line with this model, no selectivity of energy transfer to various N-related states is expected from this CB state, as fast energy relaxation to the bottom of the conduction band (of the order of tens of picoseconds for intervalley energy relaxation [21]) will probably precede trapping of the photoexcited carriers to the localized states, in agreement with the results given in figures 3 and 4. We can thus

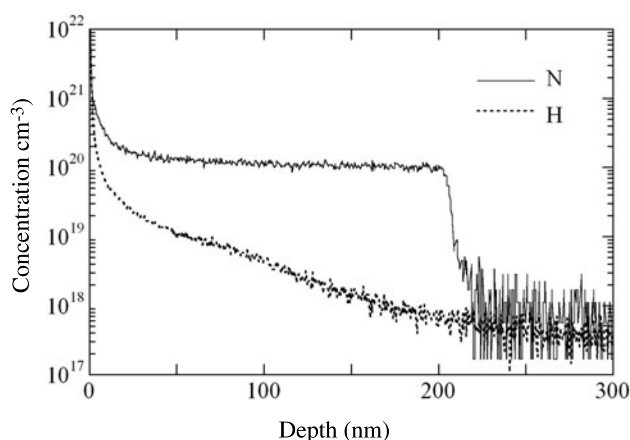

Figure 5. SIMS profiles of N and H concentrations in the as-grown $GaN_{0.006}P_{0.994}$ epilayer.

conclude that the involvement of the t_2 state from the X_3^c (or L_1^c) CBM in the 2.87 eV transition is more consistent with the experimental facts. However, several considerations question the validity of this model. First of all, the theoretically predicted energy for the Γ_{15}^v–X_3^c (L_1^c) transition deviates significantly from 2.87 eV and is around 2.64 (2.56) eV [15]. Secondly, it is not clear whether the disorder-induced breaking of selection rules can enhance the intensity of the formally forbidden transition to a degree comparable with the direct Γ_{15}^v–Γ_1^c transitions.

The third model for the 2.87 eV transition can be related to a complex of N and H atoms (in some form) bearing in mind the observed dependence of the transition on both N and H incorporation. Such a complex is expected to have an energy level deep in the conduction band, to explain the experimentally observed neutralization of N in GaNP by post-growth hydrogenation [17, 22]. The concentration of the corresponding centres should then depend not only on N composition but also on H concentration in the alloys, to account for the experimentally observed consistent increase in intensity of this transition with increasing hydrogen dose. Within this model, the presence of the 2.87 eV transition in the as-grown samples implies a high background doping level of H. This was indeed confirmed by our SIMS measurements performed for the as-grown $GaN_{0.006}P_{0.994}$ epilayer (figure 5), which shows a very high H concentration especially in the near-surface region. The incorporation of H in the as-grown samples is not surprising as H is known to be rather abundant during the GS-MBE growth.

5. Summary

In summary, we have employed temperature dependent PLE measurements to determine basic physical properties of the 2.87 eV absorption peak recently discovered for the GaN_xP_{1-x} alloys [14]. We have shown that whereas the appearance of this transition is facilitated by N and also H incorporation, its intensity does not scale with the N content and remains constant for x ranging between 0.24 and 0.9%. On the basis of the results from the temperature dependent measurements, a non-Γ character of the state involved is concluded. The energy transfer from this state to the localized N-related states within the bandgap is found to be largely non-selective. The observed properties are found to be barely consistent with those predicted for the higher lying localized state of the isolated N impurity derived from the Γ CBM [15]. Alternative explanations for the '2.87 eV' state as being due to either the t_2 component of the

X_3^c (or L_1^c) CBM or a level arising from a complex of N and H (in some form unknown so far) are also discussed. This work calls for future studies, to establish the exact origin of the 2.87 eV transition, important for a complete understanding of N behaviour in dilute nitrides.

Acknowledgments

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