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Yellow Band and Deep levels in Undoped MOVPE GaN.

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Abstract

Undoped layers of GaN grown by MOVPE on sapphire substrates have been characterized by photoluminescence, photocapacitance and photoinduced current transient spectroscopy (PICTS). Photocapacitance reveals in all samples two specific signatures at photon energies of 1 eV and 2.5 eV. The photocapacitance decrease observed at 1 eV seems to be due to an electron capture process from the valence band, whereas the capacitance increase at 2.5 eV is related to an electron emission process. The fact that the capacitance step at 1 eV is only seen after photoionization at energies above 2.5 eV, and the observed correlation between its amplitude and the photoluminescence intensity of the “yellow band», lead us to conclude that both transitions are linked to the same trap, which is also suggested to be responsible for the yellow band. The position of this trap, at 2.5 eV below the conduction band, is confirmed by PICTS measurements, that show a hole thermal emission activation energy of 0.9 eV at 350 K.

1. Introduction

The origin and role of native defects and impurities in GaN is essential to understand their potential effects in device performance. Despite the fact that efficient devices based on GaN layers and its alloys (GaAlN, GaInN), showing a high density of dislocations (>10^{10} cm^{-2}), have been achieved, the presence of extended and point defects can be detrimental on the device performance in the long term. It has been suggested that point defects like V_N , Ga_I , and V_{Ga} , among others, may be responsible for the high residual n-type character of undoped GaN, and for a reduced doping efficiency [1]. Ga_I are also suspected to generate a deep donor state in GaN that might be related to the ubiquitous “yellow band» in this material [2] [3] [4]. Other deep states related to impurities have been reported, like Fe, which is believed to generate an acceptor trap at E_V + 2.5 eV [5].

Although Deep Level Transient Spectroscopy (DLTS) has been used by several authors to study the presence of deep defects in GaN, like Götz et al. in Si- doped GaN [6] and Hacke et al. in undoped and Mg-doped GaN [7] [8], there is no evidence about the origin of most of these traps. However, since the ability of this technique to detect deep traps in wide gap materials is limited by temperature, other techniques based on photoemission, have been used. Götz et al. [9] and Balagurov et al. [10] have recently observed several optical threshold energies by photoemission capacitance and optical transmission respectively, that could be related to the 2.2 eV luminescence band (yellow band). However, none of the spectra were giving sharp transitions, and the results from the two groups cannot be directly compared since they belong to Si-doped and undoped samples.

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Several models have been proposed in the literature to explain the origin of the “Yellow Band». The model by Glaser et al. [2] [3] relates the yellow luminescence to a transition from a deep (A_1) donor state (E_c - 0.8 eV) to an effective mass (EM) like acceptor. On the contrary, another model proposed by Ogino et al. [11] and Hofmann et al. [12], presents an opposite levels scheme, where a recombination process from a shallow donor to a deep level located at 0.9 eV above the VB should originate the yellow luminescence.

In this work we present photoemission capacitance spectra, taken over a photon energy range of 0.6 eV to 3.5 eV, where optical transitions at 2.5 eV and 1 eV have been observed in a variety of undoped GaN samples. A correlation between capacitance amplitudes and photoluminescence intensities of the 2.2 eV band has been established. Photoinduced Current Transient Spectroscopy (PICTS) spectra show a hole emission thermally activated process at 350 K with an energy around 0.9 eV, that we relate to the former optical threshold at 1 eV.

2. Experimental

The samples were undoped, hexagonal GaN layers grown by Metallorganic Vapor Phase Epitaxy (MOVPE) on sapphire substrates along the c axis. Some samples had an AlN buffer layer (100 Å) grown at high temperature (1050°C), and all samples had a low temperature (600°C) GaN buffer layer. In all cases, the active GaN layer was grown at 1050°C in a vertical reactor using TMGa and ammonia. Layer thicknesses were between 1 and 3 µm, and Hall measurements revealed residual donor concentrations between 10^{17} and 10^{18} cm^{-3}. Schottky barriers were formed with Au or Pt, and ohmic contacts were obtained with Ti/Al. A Boonton 7200 capacitance meter and a monocromator Yobin-Ivon H25 with a 600 W Globar (quartz-tungsten) lamp was used for photoemission capacitance measurements. Selected band and long pass interferential filters were used to avoid replicas. Samples were cooled down in a closed cycle He cryostat. Photoluminescence was excited with the 334 nm (3.7 eV) line of an Ar laser, analyzed by a Yobin-Ivon THC1000 monochromator, and detected with a GaAs photomultiplier. Finally, PICTS was performed in a specially designed cryostat working from 77K to 500K, and pulsed blue and yellow LEDs were used as excitation sources.

Figure 1 shows typical photoemission capacitance spectra taken from 0.6 eV to 3.5 eV. There is an optical threshold at around 2.5 eV and the signature of the near band gap absorption at 3.5 eV. Besides, a non resolved capacitance step is observed in some samples near 1.4 eV. It has to be remarked that the step observed for the optical transition at 2.5 eV was always observed, although its sharpness was sample-dependent. These spectra were taken after cooling down the sample to 20K in the dark. Then, after 1 hour delay to ensure thermal equilibrium (i.e. steady capacitance values), a very slow photon energy scan (4 hours) was performed. The sample remained always at zero bias. Correction of these spectra by the system response changed only the relative amplitudes but not the threshold positions. Quite similar spectra are obtained by photocurrent spectroscopy in the same samples. It has to be pointed out that, at any photon energy, the photocapacitance remains persistent after a partial thermal recovery, which is quite nonexponential and very slow. Although none of these thresholds have a clear origin so far, the one at 1.4 eV is sample-dependent and might be related to contamination by impurities. Oxygen, that seems to be a rather frequent source of contamination generating both shallow [13] and deep donor states [14], might be a candidate.

Figure 2 shows various spectra taken at low temperature after sample illumination at different photon energies. The measuring process, at zero bias, was the following: a) cooling down to 20 K; b) sample illumination at a given photon energy for 30 min.; c) the sample remains in the dark until a complete stabilization of the capacitance value is reached (70 min.); and d) a scan in photon energy is performed like the ones in figure 1. Step c) in this process was necessary since after the photocapacitance increase under light excitation there was always a strong non-exponential thermal capture of carriers, so that, the final persistent value of the capacitance was smaller. This behavior is identical to the one reported previously by Johnson et al. [15]. On the other hand, when illuminating the samples at the energies shown in Figure 2, there is always a non exponential increase of the capacitance that needs at least 30 min to saturate. This might indicate that more than one trap is contributing to the photoionization process.

For sample illumination at photon energies below a threshold at around 2.5 eV, Figure 2 shows just a persistent increase of the photocapacitance, similar to the one observed at 2.5 eV in Figure 1. However, after sample illumination with photons of 2.8 eV and above, an abrupt decrease of the photocapacitance is observed at 1 eV. This is a much sharper feature than the one at 2.5 eV (positive step) in Figure 1, and its amplitude increases when illuminating with higher photon energies. This behavior has been observed in all kind of samples, with and without AlN buffer layer.

In an n-type sample, an increase of the capacitance is associated with an increase of the total positive charge. The positive step (increase) observed at 2.5 eV (Figure 1) can be interpreted as generated by electron emission to the conduction band (CB). Its (partial) persistent character can be explained, without involving capture barriers of metastable character, by the unability of electrons to climb up the Schottky depletion region. However, the

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photocapacitance decrease observed at 1 eV cannot be explained by electron emission to the CB, but rather by electron emission from the VB to a trap placed 1 eV above. This picture is backed by the fact that the step at 1 eV is not detected unless light illumination is above 2.5 eV, that is, until a trap located at 2.5 eV below the CB is emptied. Now, it seems straighforward to conclude that a single trap is the origin of both transitions, at 1 eV and 2.5 eV, respectively, and that this trap is located at 2.5 eV below the CB edge (inset in Figure 2).

The amplitude of the step at 1 eV increases very much when “emptying» band gap light is used. Following the above picture, this might show that the emptying of the electron trap at 2.5 eV is quite enhanced by the generation of holes.

There is still a pending question about the observed thermal electron capture processes after turning off the light, that seem to be always present, even at room temperature, although with different rate. The presence of residual shallow donors cannot account for this slow capture process at room temperature. Shallow donors generated by nitrogen vacancies or oxygen contamination have ionization energies from 20 to 70 meV. There have to be, in addition to these shallow and deep electron traps, other electron states, possibly located over a rather wide range of energies. This picture lead us to think on states generated at grain boundaries in “polycrystalline» columnar-like material, and/or extended defects like dislocations.

Figure 3 shows the experimental correlation found between the “yellow band» PL intensity and the corresponding capacitance step at 1 eV in various samples with and without AlN buffer layer. From this fact, we suggest that the electron trap located at 2.5 eV below the CB is the one responsible for the luminescence signal at 2.2 eV. The insert in this figure shows the proposed model for the electron trap structure in GaN.

The essence of PICTS measurements is to perform a standard DLTS measurement on the current signal in a GaN sample between two ohmic contacts. A pulsed light source (LED) illuminates the sample, which is kept under 5 volts bias. Then, the current decay during the LED off-period, converted to voltage in a test resistor, is analyzed by the DLTS system. The transients are thermally activated and a peak with a thermal acivation energy of 0.9 eV is produced at 350 K (Figure 4. (a) and inset). This process corresponds to electrons from the VB being captured (hole emission) by a trap located 0.9 eV above it. This generation of holes reduces by recombination the number of electrons in the CB, and a thermally dependent current decrease is observed. This picture is consistent with the presence of an electron trap at 2.5 eV below the CB. Note that this peak does not show up for light pulses below 2.5 eV (Figure 4. b). This leads us again to the scheme of a deep electron trap that, once it has been emptied with photon energies above 2.5 eV, can be filled again with electrons coming from the VB. The fact that the GaN band energy at 350K is reduced some 150 meV in respect to that at 20 K, makes it suitable to consider the transitions at 1 eV and that at 0.9 eV being the same. This would imply that the electron trap at 2.5 eV below the CB is tracking it.

Standard DLTS has also been tried on these samples from 20 K to 600 K in either Mo, Au or Pt Schottky diodes, where electron traps at 0.35, 0.40 and 0.66 eV have been observed. For the trap at E_C - 0.40 eV, a capture barrier of 200 meV has been measured. These electron traps have already been reported in the literature, and their origin is, so far, unknown. However, since their appearance is very much dependent on the sample, we rule out any relationship with the phenomena described in this work, observed in all samples. This result is in open contradiction with the presence of a deep donor state at E_C - 0.8 eV [2] [3].

In summary, an electron trap located at around 2.5 eV below the CB has been characterized through several spectroscopic techniques. From photocapacitance and photoluminescence measurements, a relationship between the relative concentration of this trap and the intensity of the yellow band has been established. This relatioship makes this trap a good candidate as the origin of the yellow band. The results presented in this work support the model proposed by Ogino et al. [11], that finds an energy of 0.86 eV for the thermal quenching of the yellow luminescence, very close to our value obtained by PICTS. These results are in clear contradiction with the model proposed by Glaser and Kennedy [2] [3].

Acknowledgments

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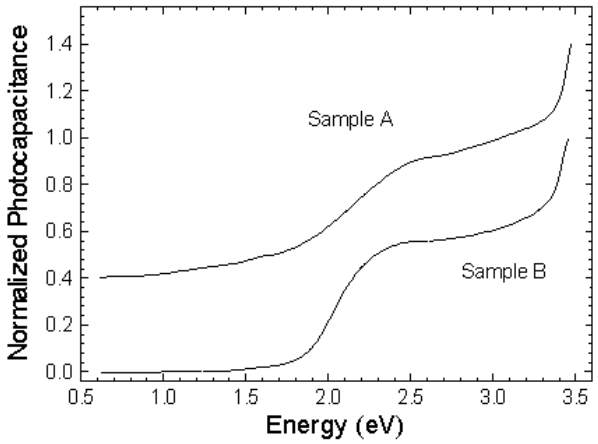

Figure 1. Photoemission capacitance spectra of two different samples, presenting a clear optical threshold at 2.5 eV and the near band gap absorption at 3.5 eV.

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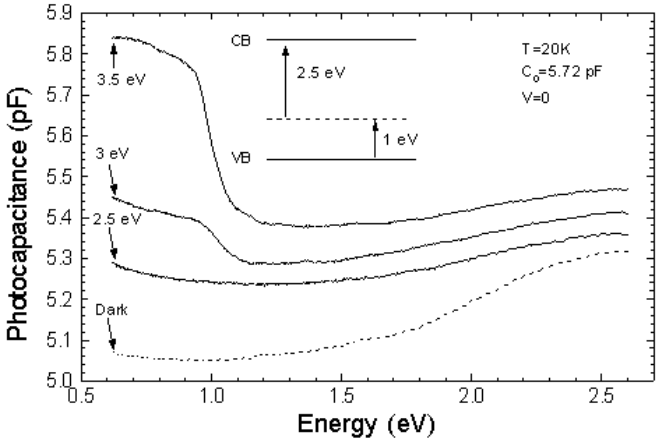

Figure 2. Photocapacitance spectra taken after sample illumination at different photon energies.

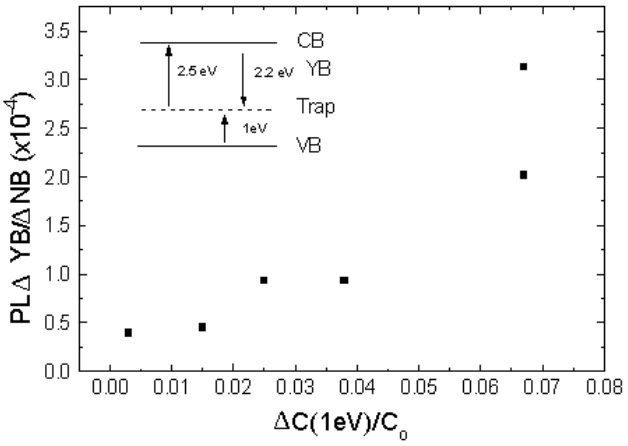

Figure 3. Experimental correlation between the yellow band (YB) PL intensity, normalized to the near band gap (NB) PL one, and the corresponding capacitance step at 1.0 eV, normalized to the value at RT (Co).

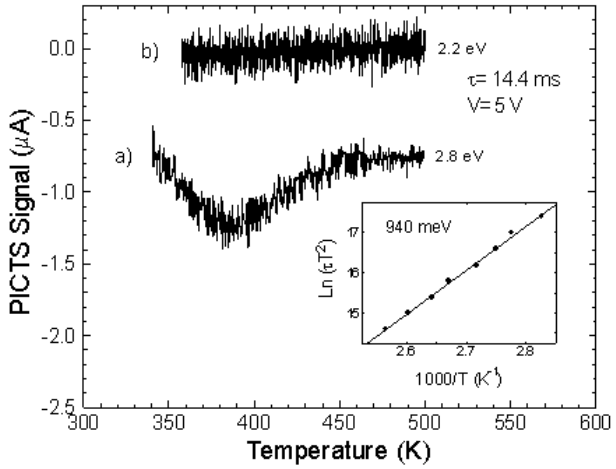

Figure 4. PICTS spectra with excitation light at 2.5 and 2.8 eV showing the transition energy of the electron capture from the valence band.

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