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PHOTOLUMINESCENCE BETWEEN 3.36 eV and 3.4 eV FROM GaN EPITAXIAL LAYERS

22

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1. INTRODUCTION

GaN, its alloys, QW's and MQW's have gained an important place among short-wavelength optical emitters and high temperature electronic devices [1,2]. The performance of such devices is limited by the presence of native and impurity defects. The understanding of the optical properties of the basic material allows us to improve its quality and thus increase the performance of these materials.

In non intentionally doped (nid) hexagonal good quality GaN layers grown on sapphire, 6H-SiC and Si, free exciton (FXC, FXB, FXA), donor bound exciton (DX), acceptor bound exciton (AX) and donor-acceptor pair (DAP) recombinations have been reported by several authors [3, and references therein]. Besides these typical emissions, emission lines in the range 3.3 – 3.44 eV have been observed in nid and intentionally doped hexagonal GaN layers. However the nature of these recombinations is not completely clarified. Some authors assigned them to a superposition of LO phonon assisted transitions of DX and FX [3-8], excitons bound to neutral donors with deeper donor levels [5], band to impurity transitions and/or free to bound emission involving oxygen [9-11], DAP transitions [12-14], shallow bound excitons of cubic phases [15], excitons bound to structural defects [16-20] and Zn related recombinations [21].

In this work we analyse the luminescence between 3.36 eV and 3.41 eV of nid hexagonal GaN samples grown on sapphire. We found sample dependent emission lines with no DAP behaviour. From the data we are able to identify different kinds of recombination processes in the same spectral region.

2. EXPERIMENT

Hexagonal GaN layers of ca. 2 μm where grown by MOCVD on (0001) sapphire substrates. Steady state (SS) photoluminescence (PL) is excited by the 325 nm line of a He-Cd laser. The luminescence signal was dispersed by a SPEX 1704 1m monochromator and detected by a Hamamatsu photomultiplier. Excitation intensity was varied by neutral density (ND) filters. Time resolved (TR) measurements were carried out with a pulsed Xe lamp as an excitation source and a boxcar system for detection. The samples were mounted on a cold finger of a closed-cycle He cryostat and the temperature of the samples was varied between 12-300K.

Samples are oxygen free and present a background concentration of about $5 \times 10^{17} \text{ cm}^{-3}$.

3. RESULTS

Fig. 1 shows SSPL and TRPL of a oxygen free sample (sample A) where besides the excitonic emissions at 3.47 eV, DAP recombination at 3.27 eV and yellow band (YB) recombination a set of lines can be observed in the range between 3.3 and 3.43 eV, namely at 3.4 eV, 3.342 and 3.328 eV (Fig. 2).

Fig. 1: SS and TRPL of sample A at 10K

Fig. 2: Temperature dependent PL spectra of sample A

From time dependent analysis of luminescence we are able to assume that all high energy side emissions are fast, shorter than microseconds as they do not appear in time resolved spectra. The TRPL spectra show that only the 3.27 eV DAP and the YB transitions have contributions with lifetimes above 10 μs . With increasing temperature the excitonic emissions shift to lower energies while the 3.400 eV emission shifts to higher energies (Fig. 2) indicating that they have different origin although they show a similar quenching. The 60 meV energy separation indicates that the 3.4 eV emission cannot be a LO assisted phonon replica of the excitonic recombinations. Also the relative intensity of the 3.4 eV band and excitonic emissions is spatial dependent.

There is no significant shift of the peak position of the 3.4 eV band with varying excitation density while under low levels of photoexcitation density a high energy shift of the excitonic emission is observed (Fig. 3).

Fig. 3: Excitation Intensity Dependence of PL of sample A

Fig. 4: Emission intensity for various excitation intensities (sample A)

On the other hand a superlinear behaviour of the 3.4 eV band with increasing excitation intensity can be observed (Fig. 4)

Some of the mid samples present only excitonic lines and their vibronic replicas. However in some samples an overlapping of several high energy emission lines (peaked between 3.3 to 3.43 eV) with LO phonon assisted replicas of excitonic transitions are observed as shown in Fig. 5 and 6 (sample B). Some of these lines show a smaller quenching than the excitonic emissions. It is interesting to note that a line that appears at 3.402 eV (very close in energy to the 3.400 eV emission of sample A) shifts to lower energies with increasing temperature (broken line in Fig. 5)

The line at 3.383 eV (sample B) shows a quite different evolution with temperature. In Fig. 7 and 8 a plot of luminescence intensity versus temperature is shown for the 3.400 eV line and DX emission of sample A and the 3.373 eV, 3.383 eV, 3.402 eV and DX line of sample B. The overall shape of the quenching curve of emissions of sample A and B are generally described by equations (1) and (2)

$$I(T) = I(0) [1 + C_i \exp(-E_{oi}/k_B T) + C_j \exp(-E_{oj}/k_B T)]^{-1} \quad (1)$$

$$I(T) = I(0) [1 + C_k \exp(-E_{ok}/k_B T)]^{-1} \quad (2)$$

Where the weighting factors C_z express the weights of nonradiative dissociation channels and E_z stands for the thermal activation energy of the quenching processes. For the different lines these values are given in table 1.

Fig. 5: Temperature dependent PL spectra of sample B

Fig. 6: PL spectra of sample B for 3 different temperatures

Fig. 7: Temperature quenching of sample A

Fig. 8: Temperature quenching of sample B

Sample A					Sample B				
Line (eV)	C ₁	C ₂	E _{a1} (meV)	E _{a2} (meV)	Line (eV)	C ₃	E _{a3} (meV)	C ₄	E _{a4} (meV)
3.46 (exc.)	5.8	30	5.2	18.8	3.461 (DX)	140	13.6		
3.400	5.0	233	3.5	17.4	3.402	5.0	5.6	340	44
					3.383	68	29		
					3.373	592	10		

Table 1: Quenching parameters of the emission lines

4. Discussion

In the spectral region between 3.33 and 3.43 eV several sample dependent emission lines can be observed. The origin of the emission lines is discussed in detail for two samples.

4.1 Sample A

In this sample besides the characteristic 3.27 eV DAP emission no other lines reveal donor acceptor pair behaviour. In fact the 3.400 eV line shows a shift to higher energies with increasing temperature as recently reported in literature [11,12]. However no shift of the peak position to higher energies with increasing excitation density and no long lived luminescence (provided from distant pairs) was observed indicating that in our samples the 3.400 eV line is not a DAP recombination. It has been reported that this luminescence was attributed to oxygen related transitions [9] but as our samples are oxygen free as assessed by SIMS, this luminescence cannot be related to oxygen.

In our spectra no shoulder is observed at the 3.400 eV luminescence and no enhancement of the luminescence was observed when the sample was excited from the backside as has been mentioned in recent reports [19] indicating that no structural defects at the interface are involved in this recombination line.

While the exciton energy accompanies the band gap dependence on temperature the 3.400 eV line shifts to higher energies. This clearly shows that although both DX and the 3.400 eV line show similar temperature quenching they have different origins. A shift to higher energies usually indicates a free to bound or a bound to free transition. A free to bound transition occurs usually when at low temperature DAP emission is quenched due to ionisation of the donor. In our case no evidence of DAP is found. So we may assume that the 3.400 eV emission may be due to a bound to free transition. This would fit the following peak energy law [11]: $h\nu = E_g - E_d + nkT$ with $n=1$. This value accounts for the degeneracy of the top of the valence band. The donor level would be located about 100 meV below the conduction band. The similar quenching may suggest that this donor is populated from DX.

4.2 Sample B

As in previous reports [3-8] some samples show only excitonic lines and their LO phonon replicas 92 meV apart. However, in some samples an overlap of several emission lines can be observed as in our sample B. In this sample the increase of the FX emission with temperature is clearly observed. Furthermore the quenching of the DX emission gives an activation energy equal to the spectroscopic separation between the FX and DX emissions (13.6 meV).

In this sample the 3.383 eV line is close to 92 meV below the free exciton. Previous results [7,8] clearly indicate a very small phonon coupling of the free exciton but in sample B the emission at 3.383 eV reaches the intensity of the free exciton emission at 100K. Therefore we can exclude a LO phonon replica. DAP transitions have been ascribed to the recombination mechanisms of a 3.383 eV line in Be doped samples [15,16]. Also a line at 3.382 eV has been ascribed to a strong phonon replica of a 1_X bound exciton peaked at 3.4735 eV [22]. However in our undoped sample B the 3.383 eV line does not change in peak position with temperature, photoexcitation density and

delay times indicating that this emission is not a DAP recombination. On the other hand no I_X line was observed as in ref. [22].

10 meV lower in energy (3.373 eV) another line is observed. This line shows a different quenching process than the other lines and cannot be ascribed to a LO phonon replica of the DX emission. Although the 3.402 eV line appears very close in energy to the 3.400 eV emission of sample A and presents a similar quenching process the line in sample B shows a low energy shift with temperature while the line of sample A shifts to higher energies. So the two lines cannot be attributed to the same defect.

5. CONCLUSIONS

Emissions in GaN between the excitonic region and the 3.27 eV DAP transitions are very complex and sample dependent. We show that lines that appear in the same spectral region, or very close in energies in different samples present some common behaviour but also differ in fundamental characteristics so that they can be ascribed to different transitions. Even lines that might be LO phonon replicas due to their peak position are shown to be of different origin due to their different temperature behaviour.

These results show that different recombination channels are present due to donor and/or acceptor levels which are introduced in these samples.

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