RADIATIVE AND NONRADIATIVE RELAXATION OF EXCITONS IN GaN

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ABSTRACT

We report on investigations of the excitonic quantum efficiency in GaN epilayers as function of buffer layer thickness, buffer layer material, sample thickness and residual oxygen content. These values are compared to that of GaN bulk material. The quantum efficiency of the free excitons rises with increasing buffer layer thickness, increasing sample thickness and decreasing residual oxygen content. The influence of oxygen on the quantum efficiency is stronger than that of the buffer layer thickness. Additionally, the homoepitaxial growth of GaN shows higher quantum efficiencies than the growth with an AlN buffer layer. In general, the observed quantum efficiencies in GaN epilayers are below 20% indicating the strong impact of nonradiative relaxation and recombination processes in the excitonic range. Only, GaN bulk material shows quantum efficiencies of 25 % for the free A-exciton X_A and of 50 % for the donor-bound exciton complex D^0,X).

INTRODUCTION

Nonradiative recombination processes are detrimental to the laser action in III-V-nitride devices [1]. Since there is still scarce information on these nonradiative processes we performed low-temperature time-resolved photoluminescence and calorimetric experiments near the band gap on a series of GaN epilayers grown on (0001) sapphire by MOCVD. The excitonic luminescences dominating in this spectral range exhibit decay times between 10 and 300 ps. Using the simultaneous and highly sensitive detection of the calorimetric absorption, transmission, and reflection at 50mK we determine the quantum efficiency of the excitonic decay processes involved [2]. From these data a detail picture of radiative and nonradiative relaxation and recombination processes in the spectral range near the band gap energy is obtained.

EXPERIMENTAL SETUP

We investigated GaN epilayers grown by metal organic chemical vapor deposition (MOCVD) on sapphire with an AlN or a GaN buffer layer. The V/III molar ratio used during growth differs from 8000 to 10000. The thickness of the buffer layers varied from 250 to 500 Å and the thickness of the epilayers from 1 to 2 µm. In addition, samples with different amounts of residual oxygen content (10^{16} - 10^{18} cm^{-3}) were investigated [3].

The measurement of the radiative relaxation of the epilayers was done using time-integrated and time-resolved photoluminescence (PL). The time-resolved measurements were performed with a Nd:YAG pumped dye laser with a time resolution of 15 ps. To obtain information about the nonradiative relaxation we used the calorimetric absorption spectroscopy (CAS) at mK temperatures. The excitation light source is a xenon lamp XBO. With this technique it is possible

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temperatures. The excitation light source is a Xenon lamp XBO. With this technique it is possible to measure simultaneously the nonradiative relaxation (CAS spectrum), the transmission (CTS spectrum) and the reflection (CRS spectrum) of a crystal. Due to the additional recording of the power of the exciting light the calculation of the total absorbed light (ABS spectrum) can be done. This value contains besides the nonradiative part which leads to a heating of the crystal (CAS spectrum) also the part which relaxes radiatively. With these data given in units of power the quantum efficiency (qe) of the crystal can be calculated according to

$$qe = 1 - \frac{P_{CAS}}{P_{ABS}} \tag{1}$$

With the CAS we are able to measure on the one hand the heating (absorption) of a thick sample also without a detectable transmission signal and on the other hand also an absorption of very thin layers where the transmission signal does not show any resonances [4]. This is due to the very high sensitivity of the CAS of a few hundred fW. For more details concerning the CAS-method see [2].

RESULTS

The characterization of the samples concerning their light emitting properties was made by PL spectroscopy. All samples showed similar PL data. A typical PL spectrum of a thin GaN epilayer grown by MOCVD is presented in Fig. 1. The photoluminescence spectrum is dominated by the (D^0,X) resonance at 3.480 eV. Additionally, the resonances of the free excitons X_A and X_B can be observed in the PL spectrum at 3.486 eV and 3.493 eV, respectively. Due to the blue energy shift of the X_A peak of the epilayer in comparison to the excitonic spectrum of a GaN bulk crystal a compressive strain of the epilayers has to be assumed. The FWHM of the (D^0,X) line in Fig. 1 is 4 meV which indicates a relatively low defect density. Beside the excitonic resonances to the donor-acceptor-pair (DAP) luminescence at 3.267 eV can be detected. Finally, the yellow luminescence at 2.34 eV is very weak.

A comparison of the PL spectra of the epilayer and the GaN bulk crystal shows a FWHM of the D^0,X complex of approximately 4 meV for the epilayer and below 1 meV for the bulk material [4]. This leads to the assumption that the damping constant and also the defect density in the bulk crystals is lower than that in the epilayers. A higher density of defects would yield to more nonradiative recombinations so that the excitonic life time of the of the bulk crystal should decrease for the epilayers. To achieve information about this we performed time resolved spectroscopy. In Fig. 2 results of the time resolved measurements of a GaN

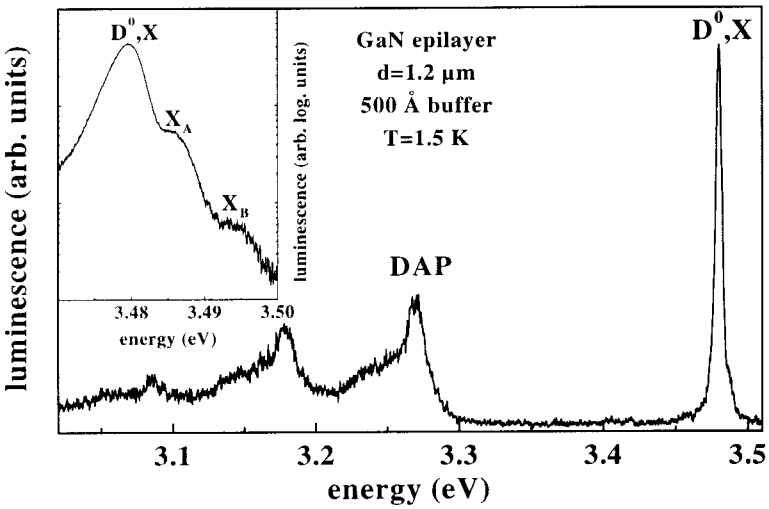

Figure 1: Photoluminescence spectrum of a 1.2 µm thick GaN epilayer. In the inset is the (D^0,X) resonance and the X_A and X_B resonances are enlarged shown.

epilayer are exemplary depicted. The decay time of the (D^0,X) complex is 40 ps while the decay times of the resonances of the free excitons are below the detection limit of 15 ps. The other investigated epilayers show even shorter lifetimes of the (D^0,X) complex and a similar behavior concerning the decay time of the X_A and the X_B resonances. Therefore, the values of the densities of defects cannot be estimated. The statement we receive from these measurements is a faster decay of the resonances in the epilayers in comparison to these in bulk material where the decay time of the (D^0,X) complex is up to 300 ps. This exhibits an increase of the radiative relaxation and a lower defect density in the bulk material.

Another access to characterize optical properties is the reflection spectroscopy. With this technique it is possible to obtain data from the surface of the sample. The free excitons X_A and X_B can be treated as Lorentz oscillators and they show because of their oscillator strength typical reflection structures by resonant excitation. From these reflection data we obtain material parameters like the damping constant Γ and the longitudinal transversal splitting ω_{LT} by fitting these spectra in a two oscillator model including the interaction of the free A- and the free B-exciton, spatial dispersion and dead layers.

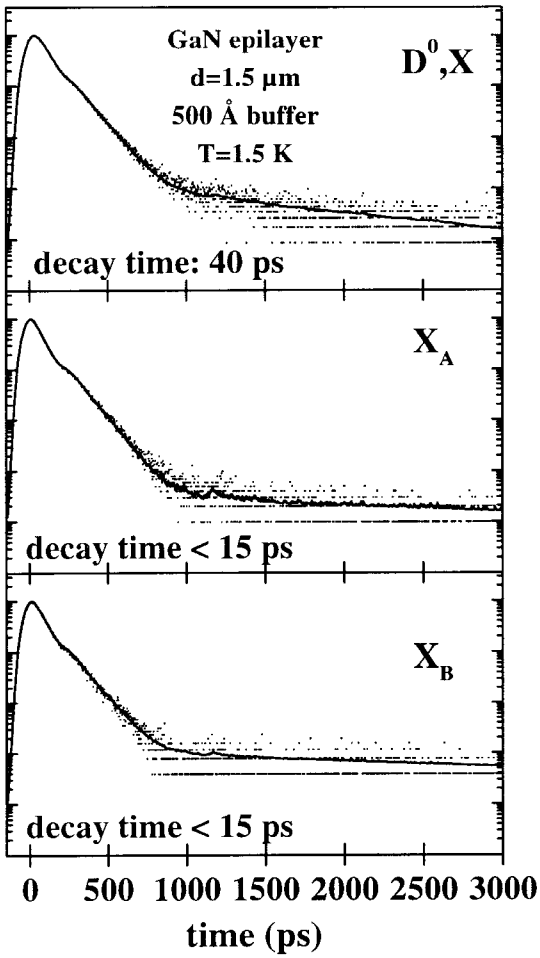

Figure 2: Time-resolved photoluminescence spectra of a GaN epilayer for the (D^0,X), the X_A and the X_B resonance.

The analysis of the reflection spectra yield similar values for the ω_{LT} splitting for the epilayer and for bulk material with 0.9 meV. But as it was expected the damping constant of both samples differs significantly. The epilayer has a damping constant of 3 meV and the bulk crystal of 0.65 meV. This shows that there is a strong impact of defects on the optical properties of the epilayer.

With all the presented methods it is only possible to detect the nonradiative relaxation processes qualitatively and indirectly. On the contrary, the CAS measurements yield information about the nonradiative relaxation of the GaN epilayer. The results of these investigations are shown in Fig. 3 and Fig. 4. The lower parts show the measured CAS, CTS and CRS spectra and the calculated ABS data, whereas in the upper part the quantum efficiency of the GaN epilayers derived from Eq. 1 is presented. The resonances of the A- and the B-exciton can be observed as well in the CAS as in the CRS spectrum. The CRS data show also Fabry-Perot interferences in the lower-energy range which are due to the crystal shape of the epilayers. By looking at the low-energy side of the CAS spectra one can see that there is still a heating of the sample below the band gap energy. This indicates a relatively high density of defects in GaN epilayers in comparison to that in other materials, e.g. CdS, ZnSe [5]. The quantum efficiencies of the epilayers shown in the upper parts of the figures are below 20 % for the whole excitonic region.

To receive a more detailed picture of the quantum efficiency as a function of other parameters like the epilayer thickness, the buffer layer thickness and the residual oxygen content, crystals with various properties in these ranges were investigated. The results of these CAS

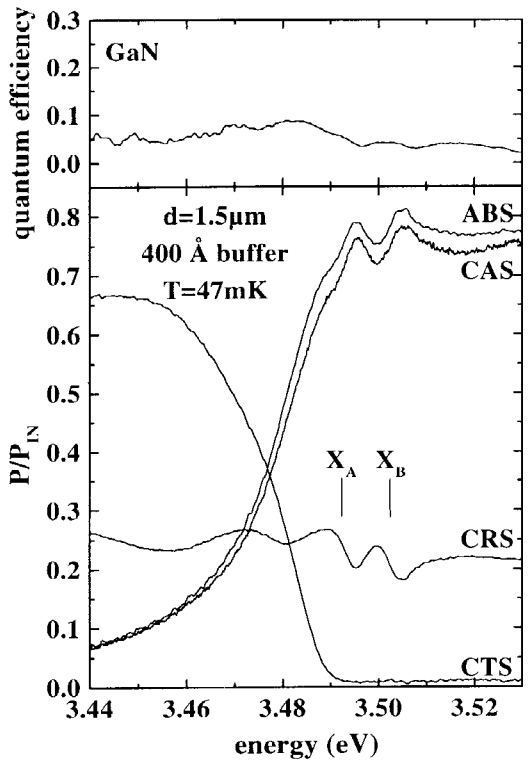

Figure 3:CAS,CTS,CRS and ABS spectrum of a GaN epilayer, in the upper part the quantum efficiency is shown.

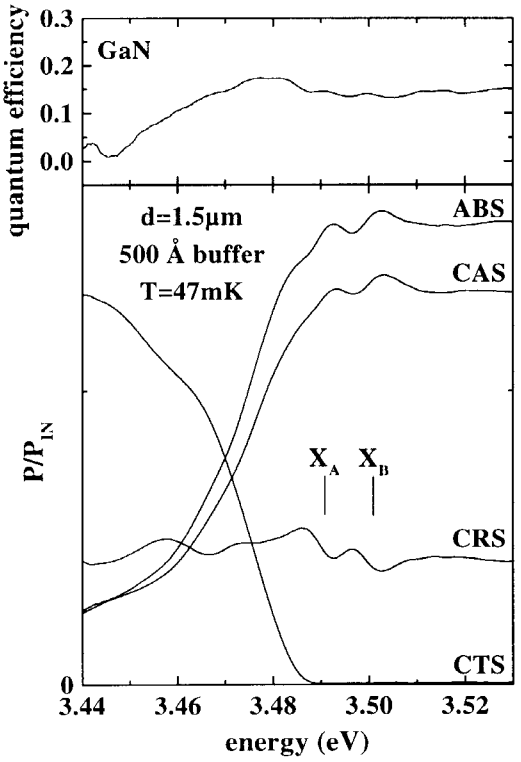

Figure 4: CAS,CTS,CRS and ABS spectrum of a GaN epilayer with less residual oxygen, in the upper part the quantum efficiency is shown.

measurements are depicted in Fig. 5. The quantum efficiencies of the X_A resonances (■) and the X_B resonances (●) are presented.

DISCUSSION

The quantum efficiency depends directly on parameters like the residual oxygen content, the buffer layer thickness and the thickness of the sample.

■ RESIDUAL OXYGEN CONTENT

One of the most important properties of the sample with regard to the quantum efficiency is the residual oxygen content. As one can see in Fig. 5 the quantum efficiencies of the crystals with lower residual oxygen content ($\approx 10^{16}$ cm^{-3}) show higher values than of the samples with a higher oxygen content ($\approx 10^{18}$ cm^{-3}). With these amounts incorporated the quantum efficiency of samples with lower oxygen content increases approximately by the factor of two.

■ BUFFER LAYER THICKNESS

The dependence of the quantum efficiency on the buffer layer thickness was also investigated. The quantum efficiency values rise with increasing buffer layer thickness (see Fig. 5). The increase of the quantum efficiency is due to the reduction of structural defects with a thicker buffer layer [6]. In the upper image in Fig. 5 it can be seen that the quantum efficiency of GaN epilayers with same residual oxygen content but different buffer layer thickness (250 and 500 µm) are identical. It has to emphasized that the epilayer (250 µm) has a GaN buffer layer. The homoepitaxial growth of this sample leads to a reduction of strain, structural defects and

therefore to fewer nonradiative relaxation channels. Only the increase of the AlN buffer layer thickness by a factor of two shows a comparable quantum efficiency. This leads to the assumption that the homoepitaxial growth of GaN exhibits lower defect densities.

■ THICKNESS OF THE SAMPLE

Finally, the influence of the sample thickness on the quantum efficiency was analyzed. Therefore, epilayers with same residual oxygen content (10^{16} cm^{-3}) and same buffer layer thickness (500 Å) but different thicknesses of the epilayer were compared. The bigger the buffer layer thickness the higher is the quantum efficiency of the free excitons. This behavior is caused by a reduction of defects near the surface due to the bigger sample thickness. By looking at the results for quantum efficiencies of a GaN bulk crystal grown by HVPE with a thickness of 400 µm one can see that the X_A resonance has a quantum efficiency of 25 % (see Fig. 6), which is higher than all the values of the epilayers. The results concerning the quantum efficiency in dependence of the sample thickness are consistent with this additional point.

The (D^0,X) complex of the bulk crystal exhibits with 50 % the highest quantum efficiency of all excitonic resonances. This can be already seen from the CAS spectrum in Fig. 6, where the dip indicates already an increase of radiative processes. This result concerning the quantum efficiency of the (D^0,X) complex is expected due to the giant oscillator strength and the breakdown of the k-selection rule [7].

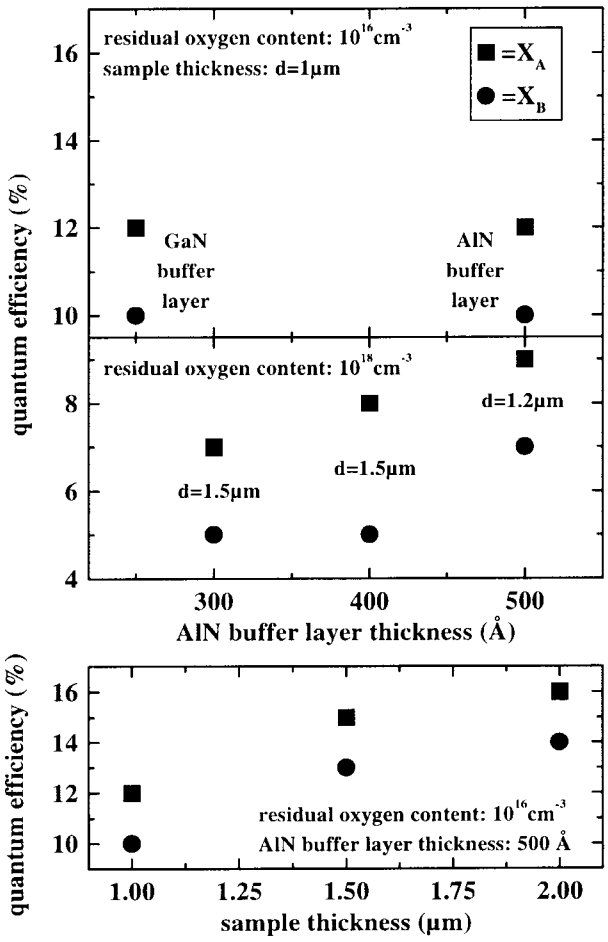

Figure 5: Quantum efficiencies of the X_A (■) and the X_B (●) resonance of GaN epilayers in dependence on the buffer layer thickness for different amounts of residual oxygen content and different sample thickness.

CONCLUSION

The presented investigations show strong dependence of the quantum efficiencies of excitonic resonances in GaN epilayers on buffer layer thickness, buffer layer material, sample thickness and residual oxygen content. An increasing buffer layer thickness enhances the quantum efficiency of the free excitons. The same behavior occurs by increasing the sample thickness. Both effects are due to a reduction of structural defects. Additionally, the material of the buffer layer plays an important role for the quantum efficiency. Homoepitaxial growth of GaN epilayers shows higher quantum efficiencies than the growth with an AlN buffer layer. It has to be emphasized that the quantum efficiency increases significantly with decreasing oxygen content. This effect is even stronger than the increase of the other parameters.

Nevertheless, the highest quantum efficiencies are observed for GaN, e.g. 25 % for the X_A resonance and 50 % for the (D^0,X) complex.

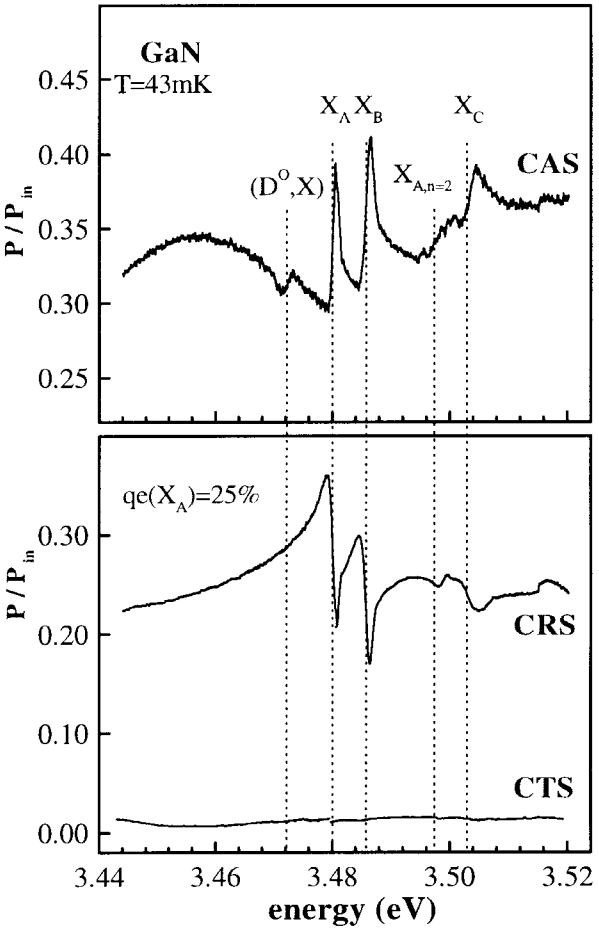

Figure 6: CAS, CTS and CRS spectrum of a GaN bulk crystal (400 µm). The quantum efficiencies of the X_A is 25 % and of the (D^0,X) complex 50 %.

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