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Optical properties of nominally undoped n-type MOVPE GaN epilayers

ROBERT KUDRAWIEC, JAN MISIEWICZ

Institute of Physics, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50–370 Wrocław, Poland.

REGINA PASZKIEWICZ, BOGDAN PASZKIEWICZ, MAREK TŁACZAŁA

Institute of Microsystems Technology, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50–370 Wrocław, Poland.

Nominally undoped GaN epilayers have been grown by the metalorganic vapour phase epitaxy (MOVPE) technique on (0001) sapphire substrates. Various growth conditions result in different concentration of defects, which is strongly correlated with the electron concentration. For epilayers selected to these investigations the electron concentration changes from 5×10^{15} cm^{-3} to 5×10^{18} cm^{-3}. The optical methods like photoluminescence (PL), reflectance (R) and photoreflectance (PR) have been applied to define a correlation between quality and electron concentration of the GaN epilayer. It has been found that an improvement of optical properties, which is always associated with the improvement of the sample quality, appears to be connected with the decrease in electron concentration. The existence of free excitons has been observed for epilayer with the electron concentration lower than 10^{17} cm^{-3}.

1. Introduction

Gallium nitride has became one of the most promising wide band-gap semiconductor materials for use in the high temperature electronic and high brightness blue/green light emitting diodes and laser diodes [1], which are very important devices for applications in full-colour outdoor light emitting diode displays and optical storage devices. GaN layers are commonly grown on sapphire substrates, where the mismatch in the lattice constants and thermal expansion coefficients between substrates and GaN layers produce a large density of dislocations. It has been reported in the literature that the dislocation density as high as $10^8\sim10^{10}$ cm^{-2} [2] has been observed in the GaN films grown by conventional techniques. The electron concentration of nominally undoped GaN epilayers is induced by point defects. Nitrogen vacancies which produced shallow donors are most often proposed to explain the n-type conductivity of the GaN [3]. Also acceptor levels (induced p-type conductivity) can be produced by dislocations, but the density of acceptors is usually much lower than the density of donors. Generally it is known that nominally undoped GaN epilayers are usually n-type conductive.

The electron concentration is a very important parameter for electronic devices, but the transport properties depend also on the layer quality which decreases according to the increase in defect concentration. It is obvious that optical properties, which are the best indicator of the quality of semiconductor materials, have to depend on the electron concentration of GaN films. In consequence it is interesting to know how the epilayer quality depends on the electron concentration in the nominally undoped GaN epilayer. In this paper optical methods like PL, R and PR have been applied to define a correlation between the electron concentration in GaN epilayers and their quality. Our results show that free-excitons, which are characteristic of good quality materials, exist for epilayers where the electron concentration is lower than 10^{17} cm^{-3}. For GaN films with the electron concentration higher than 10^{17} cm^{-3} the density of point defects and dislocations is so big that free-excitons cannot exist. It means that the distance between defects has to be comparable with the exciton Bohr radius.

2. Experiment

GaN samples used in this study were grown on the c-plane sapphire substrate in atmospheric pressure, single wafer, vertical flow MOVPE system redesigned for nitrides deposition [4]. Trimeihylgallium (TMGa) and ammonia (NH_3) were used along with H_2 carrier gas. Before the growth process, the substrate was degreased in organic solvents and etched in a hot solution of H_2SO_4:H_3PO_4 (3:1). The growth procedure involved sapphire substrate annealing and nitridation, low temperature GaN layer growth and the high temperature GaN layers deposition. The epitaxial process parameters were optimised and were discussed earlier [4], [5]. The layers were grown at various parameters of the epitaxial process which resulted in different density of native defects and hence different concentrations of free-electrons originating from the shallow donor levels. All samples were nominally undoped, several micrometer thick, n-type epilayers. The electron concentration in epilayers was determined by the impedance spectroscopy method performed in the range 80 Hz – 10 MHz with HP4192A impedance meter using a mercury probe. The capacity and conductance versus frequency characteristics were measured over a range of DC biases and the results were fitted to the worked-out model [6].

PR measurements were performed at 295 K in the so-called bright configuration where the sample was illuminated by white light from a halogen lamp as a probe beam source at near normal incidence. The reflected light was dispersed through a 0.55 m focal length single grating monochromator and detected by an InGaAs -based photomultiplier. For the photomodulation a 300 nm line of an Ar^+ laser was used as a pump beam which was mechanically chopped at frequency of 36 Hz. The output power of the laser was kept on the level of 100 μW to minimize photovoltaic effects and to avoid the heating of the sample. The same equipment was used in photoluminescence and reflectance experiments. The samples were cooled down by a close-helium cryostat.

3. Results and discussion

Figure 1 shows room temperature PL (**a**) and PR (**b**) spectra recorded for n-type GaN epilayers whose electron concentration varies from 5×10^{15} cm^{-3} to 5×10^{18} cm^{-3}. For the epilayer with the lowest electron concentration (5×10^{15} cm^{-3}) three peaks are observed in PL. The peak at 3.422 eV is due to the free-exciton recombination. The peaks at energies 3.378 eV and 3.350 eV are attributed to excitons bound to deep centres localized at dislocations near the substrate-epilayer interface [7]. So far, two separate peaks bellow the emission at 3.422 eV have never been observed. The spectral shape of the near band edge emission most often reported in literature is similar to the PL line shape of the sample 2. The emergence of two separate lines could be associated with the lower electron concentration that influences the full width half maximum (FWHM) of emission peaks.

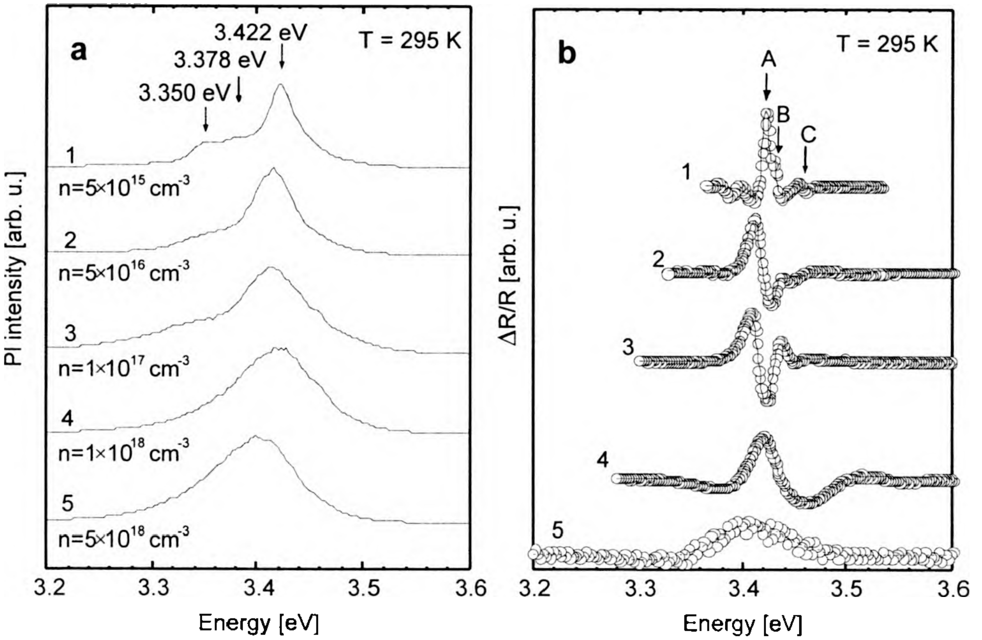

Fig. 1. Room temperature photoluminescence (**a**) and photoreflectance (**b**) spectra of nominally undoped GaN epilayers with various electron concentrations. 1, 2, 3, 4, 5 – number of sample.

A character of the recombination process at 3.422 eV changes according to the increase in the electron concentration. It has been found that at room temperature the FWHM of the band edge (BE) emission increases with the increase in the electron concentration (see Fig. 1). The point defects decreas the exciton population through the binding of the excitons on a local fluctuations of a potential and/or destroying the excitons by a local electric field. Also the screening effect, which is stronger for higher free-carrier concentration, decreases the binding energy of the exciton and in consequence it also changes the exciton population. For these reasons the character of the BE emission at room temperature changes from free-exciton to free-carriers recombination according to the increase in the electron concentration. In the low quality samples, where the electron concentration is bigger than $10^{17}\,cm^{-3}$, in the emission a free-carrier recombination through defect states take place. The further increase in the quantity of defects generates a bigger band tailing that induces a red shift and broadening of the BE emission peak (see PL for sample 5 in Fig. 1**a**). Such scenario is consistent with previous results observed in PR experiment [8] (see Fig. 1**b**).

Figure 1**b** shows PR spectra for the same GaN epilayers. The experimental data are shown by open circles and the theoretical fits, according to the low-field electromodulation Lorentzian line shape functional form [9], [10], are shown by solid lines. For the sample 1 three well resolved sharp PR features, which have been attributed to excitonic transitions [8], [11], [12], are seen in the spectrum. These transitions are labelled by A, B and C and are related to the $\Gamma_9^v-\Gamma_7^c$, Γ_7^v (upper band), Γ_7^c and Γ_7^v (lower band), Γ_7^c interband transitions of wurtzite GaN [13], respectively. The energy positions of the A, B and C excitons are 3.422, 3.430 and 3.453 eV, respectively. The energy position of the A exciton, within experimental error, is the same as the energy position of the main peak observed in emission. It proves that for the sample 1 the free-exciton recombination process is observed in PL. Excitonic transitions dominate PR spectrum for samples 1, 2, and 3. Above 10^{17} cm^{-3} electron concentration in PR spectrum band-to-band transitions take place [8].

On the basis of room temperature PL and PR experiments it has been shown that the quality of nominally undoped GaN epilayer is strongly correlated with the electron concentration. The validity of this conclusion has been also examined at low temperatures. With the decrease in kT energy the excitonic transitions clearly start to dominate in high quality materials. In this case excitons are a sensitive indicator of material quality. Mechanism which broaden or shift the excitonic resonance such as defects, impurities and strain, in turn broaden and shift the energy position of excitonic transitions.

Figure 2 shows PL (solid lines) and reflectance (dashed lines) spectra of samples 1, 3, and 5 recorded at 15 K. The photoluminescence of the sample 1 is dominated by one strong peak associated with a donor bound-exciton recombination [14] (in Fig. 2 this transition is labelled as DX). Above the dominating peak also a weaker peak attributed to the free-exciton recombination (A exciton) is observed. Free -excitons are very clearly and sharply visible in reflectance spectrum. These transitions in Fig. 2 are marked by arrows and are labelled according to the previous description (see PR spectrum of the sample 1). The oscillations on the lower energy side of the R spectrum are caused by the interference effect. For the epilayer with higher electron concentration (sample 3) both PL and R spectra have changed. Generally, all transitions have become less distinguishable. It is associated with an increase in the broadening parameter (FWHM for photoluminescence peaks

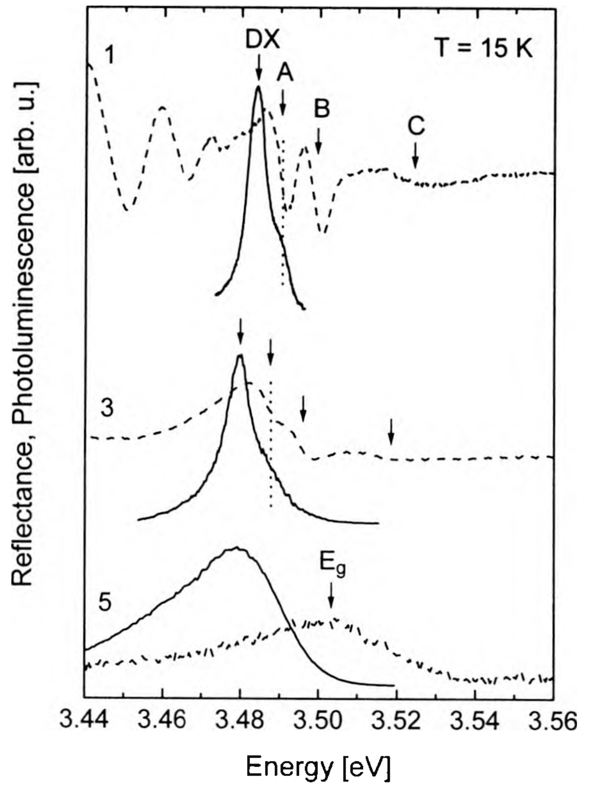

Fig. 2. Low temperature photoluminescence (solid lines) and reflectance (dashed lines) spectra of nominally undoped GaN epilayers with various electron concentrations. 1, 2, 3 — number of sample.

and Γ for reflectance resonances), which depends on the epilayer quality. A difference (less than 2 meV) between the energy position of excitonic transitions of sample 1 and sample 3 can be explained by a different residual biaxial compressive strain in GaN/sapphire epitaxial layers of various thicknesses [15], [16], and/or also by various electron concentrations, which leads to the different band gap shift due to the band gap renormalization effect ($\Delta E_g = -3.2 \times 10^{-8}\ n^{1/3}$, where n is electron concentration [17]). Generally, observed energies of excitonic transitions agree with energies reported in literature and are not in detail analysed in this article. Significant differences in the line shape of PL and R spectra have been observed for sample 5. In this case the change is associated with a change of the character of optical transitions. In reflectance spectrum the peak, labelled as E_g, is not associated with the excitonic transition. The peak is attributed to the band-to-band transition. In PL spectrum of the sample 5 a broad band of the emission associated with excitons localised on defect states is observed. Between emission (PL experiment) and absorption (R experiment) transitions a big shift (equal to 20 meV) appears, which is the evidence of the low quality of the epilayer. Results obtained for the sample 5 show that nominally undoped GaN epilayers whose electron concentration is higher than 10^{17} cm^{-3} have such high defect concentration that free-excitons cannot exist in the epilayer. In such a case, the average distance between point defects has to be comparable with the exciton Bohr radius.

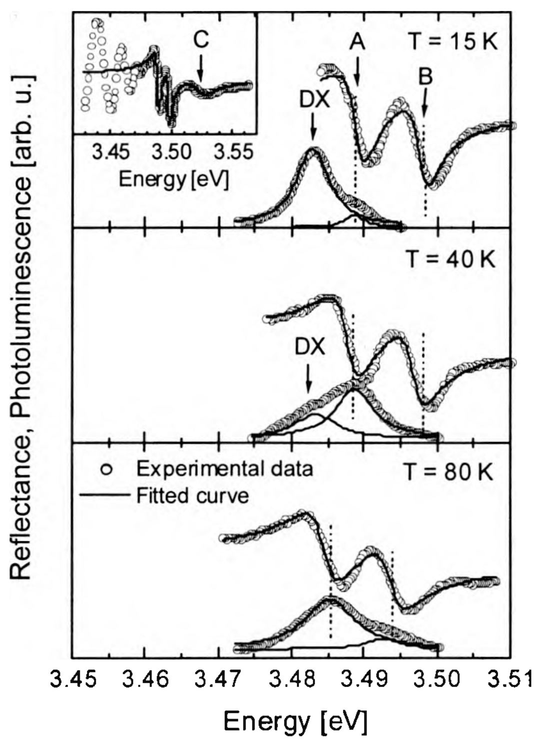

Fig. 3. Photoluminescence and reflectance spectra of the sample 1 recorded at various temperatures.

The bound-exciton DX observed for samples 1 and 3 is characteristic of GaN epilayers at low temperatures and it has been repeatedly studied [14], [18], [19]. The behaviour of the bound-exciton at various temperatures has been also examined in this article. Figure 3 shows PL and R spectra at selected temperatures. Experimental points are shown by open circles and theoretical fits are shown by solid lines. Photoluminescence spectra have been fitted by Lorentzian line shape. Reflectance spectra have been fitted by the following equation:

$$R(E) = R_0 + R_X \mathrm{Re}\left(\frac{E_X - E + i\Gamma_X}{\Gamma_X^2 + (E - E_X)^2} \exp(i\Theta)\right) \tag{1}$$

where R_X is an amplitude, E_X – an energy, and Γ_X – a broadening parameter of exciton X, R_0 – a background and Θ – a phase. To reduce the number of fitting parameters, it has been assumed that $R_A = R_B$, $\Gamma_A = \Gamma_B$, and $\Theta_A = \Theta_B$. In this way the energy of transitions observed in PL and R can be exactly compared and a nature of emission lines can be explained. Generally, it has been observed that the donor bound-exciton line dominates in the emission to 20 K. At 30 K bound-exciton and free-exciton lines are comparable. Above 40 K the donor line rapidly decreases and at 80 K is not observed. Above 80 K only free-exciton recombination (A exciton and B exciton) takes place. The E_A and E_B values obtained from reflectance are the same (within experimental error) as obtained from PL measurements. Very similar behaviour of the emission band has been observed for samples 2 and 3.

4. Conclusions

A correlation between electron concentration of nominally undoped GaN epilayers and quality of the epilayer has been investigated by photoluminescence, reflectance and photoreflectance. It has been shown that the electron concentration is strongly correlated with the epilayer quality. The improvement of the sample quality, which has been detected by optical methods, appears according to the decrease in electron concentration. Free-excitons have been observed below the electron concentration equal to 10^{17} cm^{-3}. Above this concentration the average distance between point defects is comparable to the exciton Bohr radius and in consequence free-excitons cannot exist in such epilayers.

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