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Journal of Crystal Growth 189/190 (1998) 523–527

JOURNAL OF CRYSTAL GROWTH

Compensation effects in Mg-doped GaN epilayers

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Abstract

The compensation of Mg-doped GaN is systematically studied by low-temperature photoluminescence (PL) using a series of samples with different Mg concentrations. Strongly doped samples are found to be highly compensated in electrical measurements. The compensation mechanism is directly related to the incorporation of Mg. Three different deep donor levels are found at 240 ± 30, 350 ± 30 and 850 ± 30 meV from the conduction band. With increasing excitation density in photoluminescence measurements these levels are subsequently neutralized giving rise to a deep unstructured donor–acceptor pair (DAP) emission. These emissions exhibit a blue shift that saturates at higher densities, thus excluding band fluctuations as the prime mechanism for the low energy of the observed DAP bands. © 1998 Elsevier Science B.V. All rights reserved.

PACS: 71.55.Eq; 78.55.Cr

Keywords: GaN; P-doping; Compensation; Photoluminescence; Deep levels

1. Introduction

One of the major advances in semiconductor technology during the recent years was the realization of p-conductivity in GaN, leading to optoelectronic devices in the blue spectral range like high-power light-emitting diodes. The major problem to be solved first was the compensation of the incorporated Mg acceptors which resulted in highly resistive material even at high dopant concentrations. After the breakthrough by Amano et al. [1] using a low-energy electron beam treatment of their p-doped samples, Nakamura et al. showed that hydrogen plays an active role in the compensation process [2]. The latter authors also developed the technique of thermal annealing in nitrogen atmosphere to prevent the formation of Mg–H complexes. Today it is clear that despite this success the compensation of acceptors is still a major problem with the nitrides. It limits the number of active

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PII S0022-0248(98)00344-3

acceptors to about 10^{18} cm^{-3} even if the concentration of Mg is much higher. Little is known on the electronic structure of compensating defects and the effects on the optical properties of GaN. We therefore investigated a series of p- and n-type GaN samples with a systematically varied concentration of Mg to gain further insight into the electronic and optical implications of compensation in GaN.

2. Experimental procedure

The samples investigated are GaN : Mg epilayers of 500 nm thickness grown at 1100°C on a GaN buffer layer and *c*-plane sapphire substrates by MOVPE in an AIX 200 RF reactor. (The precursors used were TEGa/TMGa, NH_3, and Cp_2Mg with N_2 and H_2 as carrier gases.) The ratio between Cp_2Mg and TEGa was varied between 0.003 and 3% for different samples to obtain a series of Mg concentrations. The layers were thermally annealed in N_2 atmosphere at 650°C. X-ray rocking curves revealed an increase in the FWHM for increasing Mg-content. Room-temperature Hall measurements and potential profiling were performed to establish the nature of conductivity in these samples [3].

Low-temperature photoluminescence (PL) measurements were performed with either a He–Cd laser or, for higher excitation densities, using the third harmonic at 355 nm of an actively mode-locked Nd : YAG laser giving pulses of 80 ps duration with 76 MHz repetition rate. The samples were kept at 1.8 K in an immersion cryostat.

3. Results

The photoluminescence of Mg-doped GaN depends in a very sensitive manner on the concentration of Mg in the sample and the degree of compensation. Fig. 1 shows low-temperature PL spectra of five epilayers grown using different Cp_2Mg/TEGa ratios as indicated. Below 0.3% the samples are p-type and exhibit a pronounced donor–acceptor-pair luminescence at 3.27 eV with characteristic LO-replicas [4]. Excitonic emissions are hardly visible. From 0.3% upwards the samples are highly resistive indicating an effective compensation mechanism dependent on the concentration of Mg present in the sample. This suggests that defects incorporated by the Mg-doping itself play a key role for the compensation of the shallow Mg acceptor level in these samples. The PL spectra of the compensated samples exhibit a characteristic change of the line shape of the DAP band. Instead of a series of LO replica of the zero-phonon line around 3.27 eV, only one broad band with no phonon replica is observed. Its peak is shifted strongly to lower energies. This behavior is typical for the DAP emission in strongly doped and at the same time highly compensated semiconductors and has been observed, e.g., in ZnSe [5] or GaAs [6] before. An explanation for this behavior was discussed in detail by Shklovskii and Efros [7]. It involves strong fluctuations in the band gap at different positions in the sample caused by an electric field of a high number of compensated and, thus, ionized donors and acceptors, which are

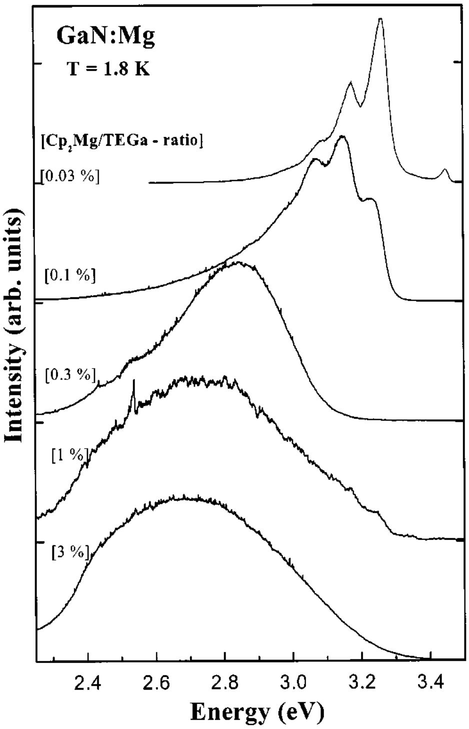

Fig. 1. Low-temperature photoluminescence GaN epilayers doped with Mg at different concentrations.

randomly distributed in the sample. At low excitation densities radiative DAP recombination takes place between the energetically lowest neutral donors and acceptors since photoexcited carriers relax quickly to these levels. A test of this model is the intensity dependence of the emission since at high excitation densities the concentration of photoexcited carriers is high enough to neutralize most donors and acceptors and the band fluctuations should vanish. Thus, at the highest densities the well-known structured DAP emission line shape as seen for samples with low compensation should be observed. This was indeed the case for compensated ZnSe : N [5].

To test this model for GaN : Mg, we studied the intensity dependence of the PL of the highly resistive sample grown with a Cp_2Mg/TEGa ratio of 0.3%. It is shown in Fig. 2a and Fig. 2b for two different excitation conditions. In Fig. 2a we used a focused continuous-wave (cw) He–Cd laser with a maximum density of 2 kW/cm^2, in Fig. 2b the focus of the pulsed Nd : YAG laser system described above to obtain even higher excitation densities. Starting from the lowest excitation intensities in Fig. 2a, we observe two broad emission bands around 2.45 and 2.8 eV. Assuming a Gaussian line shape for both luminescences, we fitted the spectra of Fig. 2a and obtained very good agreement with the measurements. Raising the excitation density the high-energy band exhibits a growth in integrated intensity with a slope of 1, exactly the same as that observed for compensated ZnSe : N [5]. Also the observed logarithmic shift of the peak energy to higher energies with increasing excitation density is in agreement with the behavior of other strongly doped and compensated semiconductors. This shift is equal for both emission bands.

The total blue shift of the high-energy band between 20 mW/cm^2 and 2 kW/cm^2 is as high as 153 meV. Using the pulsed laser source the

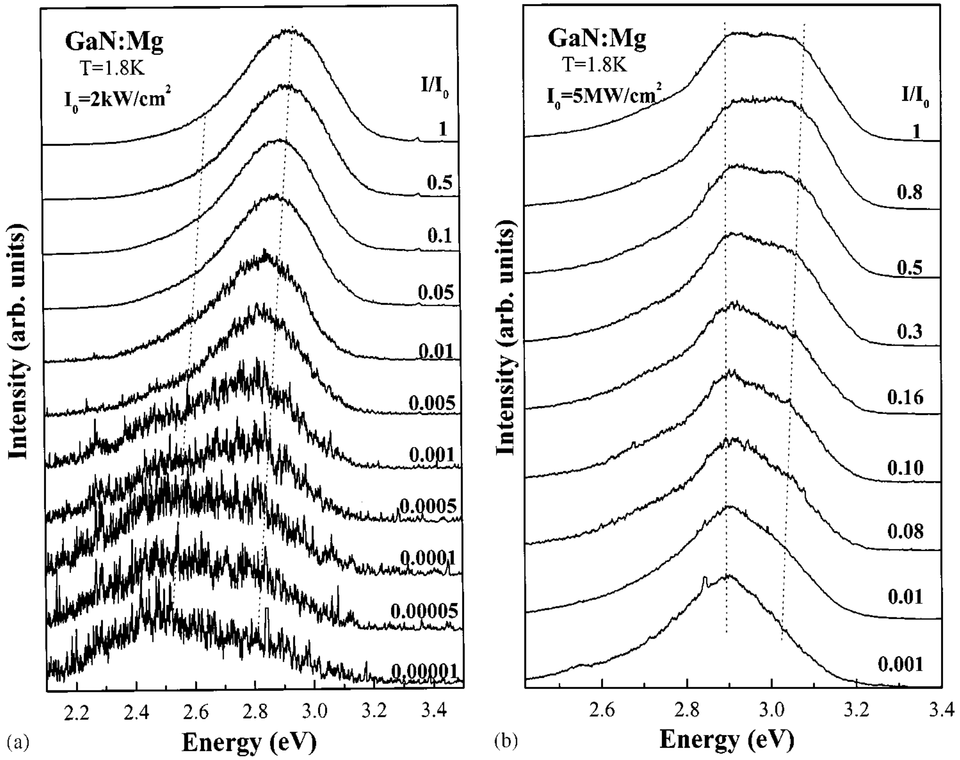

Fig. 2. Intensity dependence of the normalized PL of a p-type GaN epilayer doped with 0.3 Mg: (a) measured with a cw-He–Cd laser up to 2 kW/cm^2; (b) measured with the third harmonic of a pulsed Nd : YAG laser with pulse intensities up to 5 MW/cm^2.

excitation density per pulse can be increased up to 5 MW/cm^2. The result of this experiment for the compensated 0.3% sample is shown in Fig. 2b. We find that the blue shift of the high-energy band saturates around 2.91 eV. On the high-energy shoulder of this band a new emission line grows, again shifting to higher energies with increasing excitation intensity. At the highest density of 5 MW/cm^2 it is found at 3.06 eV, 210 meV below the well-known DAP ZPL in weakly compensated GaN. Summarizing the results, in GaN a transition from a structured DAP band to a broad emission band shifted to lower energies is observed with increasing concentration of Mg acceptors. This is in agreement with observations on the other compensated semiconductors. The compensation mechanism seems to be correlated directly to the increased incorporation of Mg into GaN. For a highly compensated sample studied in the intensity-dependent measurements the expected observation of a structured DAP band at the highest excitation densities, following the model of Shklovskii and Efros cannot be accomplished up to 5 MW/cm^2. Instead of a continuous shift of the emission peak to higher energies a saturation of the blue shift accompanied by the growth of a new emission is observed.

4. Discussion

In our intensity-dependent experiments we identified three broad emissions: the band peaking at 2.45 eV is most prominent at the lowest excitation densities but experiences a blue shift just like the second band found around 2.8 eV under weak excitation. This second emission band, however, becomes dominant at intermediate intensities up to 2 kW/cm^2. It does not shift any further than 2.953 eV in our experiments. The third band is only observed at high excitation densities and its maximum reaches 3.06 eV at the highest density of 5 MW/cm^2 employed. No sign of a saturation of the blue shift is observed for this band at the intensities employed. Our findings, especially at high excitation densities, show that band fluctuations according to the model of Shklovskii and Efros cannot give a satisfying explanation of the observed PL properties of highly doped GaN : Mg.

In a recent paper, Hacke et al. used deep-level transient spectroscopy on weakly Mg-doped MOCVD GaN employing also Cp$_2$Mg as a Mg precursor for doping [8]. They found three Mg-related deep donor levels below the conduction band edge, one at 265 ± 15 meV, a second broad level around 400 meV, and a third level at 615 ± 20 meV. A deep DAP emission between these levels and the shallow Mg-acceptor should appear at an energy given by their distance to the conduction band, plus that of the shallow Mg acceptor level to the valence band (about 220 meV), subtracted from the low-temperature band edge of 3.5 eV. Therefore, on the basis of the paper by Hacke et al. one expects deep DAP emissions around 2.68, 2.9 and 3.04 eV. This is in a very good agreement to our observation of at least the two emission bands around 2.95 and 3.06 eV. The low-energy emission band we observed at 2.45 eV corresponds to a donor level at 850 ± 30 meV below the conduction band. We used the energy position of the respective bands at the lowest possible density for the calculation.

In a highly compensated GaN : Mg sample these deep donor levels and the shallow Mg acceptor level will be ionized. Creating free carriers at low density by low-power laser irradiation, we neutralize a small number of acceptors and donors so that radiative DAP recombination can take place. The created electrons relax fast to the lowest donor levels. Increasing the excitation density, the existing deep donor levels will be subsequently neutralized according to their energetic position. This is one of the reasons for the observed blue shift of all DAP emissions in Fig. 2a and Fig. 2b. The other reason is the well known Coulomb interaction between the ionized donor and acceptor involved in the recombination process [9]. The observed saturation in the blue shift is explained by a complete neutralization of the respective donors. Thus, in our optical experiments we can prove the presence of deep levels observed by Hacke et al. They are strongly related to the Mg dopant and act as deep donors efficiently compensating the shallow acceptor. In our PL measurements photoexcited electrons are bound to these deep levels before recombining with holes captured by the shallow Mg acceptor level.

5. Conclusions

In our intensity-dependent PL measurements on highly compensated p-doped GaN : Mg, we showed that different deep donor levels related to the Mg-doping are responsible for the compensation of the shallow acceptor. We found three deep donors at 240 ± 30, 350 ± 30 and 850 ± 30 meV from the conduction band. They are subsequently neutralized with increasing excitation density giving rise to deep unstructured donor–acceptor pair emissions. Thus, deep defects and not band fluctuations are the dominant mechanism for the observation of the deep DAP emissions in GaN : Mg.

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