Photoluminescence and Raman study of compensation effects in Mg-doped GaN epilayers

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The compensation of Mg-doped GaN is systematically studied by low-temperature photoluminescence and Raman spectroscopy 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, each giving rise to deep unstructured donor-acceptor pair emission. © *1998 American Institute of Physics.* [S0021-8979(98)07420-9]

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] Little is known about the electronic structure of compensating defects and their 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 using intensity-dependent photoluminescence (PL) spectroscopy. We performed Raman-scattering experiments in order to determine the influence of the Mg doping on structural properties such as strain, doping, and disorder.

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 metalorganic vapor phase epitaxy (MOVPE) in an AIX 200 rf reactor. The layers were thermally annealed in N_2 atmosphere at 650 °C. 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 HeCd 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. The setup for the Raman-scattering experiments is described in Ref. 6.

The effects of Mg doping in GaN on strain and disorder can be studied conveniently and with high sensitivity by Raman spectroscopy.[4,5] Figure 1 shows two Raman spectra of GaN samples with different Mg content. As can be seen the A_1(TO) and the E_1(TO) modes, which are forbidden by selection rules in $z(..)\bar{z}$ configuration,[6] appear more pronounced for the sample with a higher Mg content. Obviously, the incorporation of Mg causes disorder and, therefore, a weakening of the selection rules. This allows the observation of the E_1(TO) mode. It is noticeable for all our samples that a higher Mg content yields a more intense E_1(TO) mode. The $E_1(\mathrm{TO})/E_2$ intensity ratio given in Table I is thus a measure for the disorder in the sample, caused by a high concentration of defects. Additionally the E_2 mode becomes broader with a higher Mg content, which can be attributed to the lower crystalline quality.

The inset of Fig. 1 shows the frequency of the E_2 mode as a function of the Mg content. A slight hardening can be observed, which is due to increasing compressive strain in the GaN epilayers. For the same reason the A_1(LO) mode exhibits a similar behavior.

It is important to note that we did not observe LO-phonon-plasmon (LPP) coupled modes. This indicates that the highly doped samples studied are at the same time highly compensated. The free hole concentration needs to be in the 10^{18} cm^{-3} range[7] to observe a shift of the LPP$^+$ mode from the value of the A_1(LO) frequency.

The information obtained from the Raman measurements is confirmed by PL experiments. Figure 2 shows low-temperature PL spectra of five epilayers grown using different precursor ratios as indicated. Below 0.3% the samples are *p* type and exhibit a pronounced donor-acceptor-pair (DAP) luminescence at 3.27 eV with characteristic LO replica.[8] From 0.3% upwards the samples are highly resistive indicating an effective compensation mechanism. This suggests that defects incorporated by the Mg doping itself play a key role for the compensation of the shallow Mg acceptor level. The PL spectra of the compensated samples exhibit a character-

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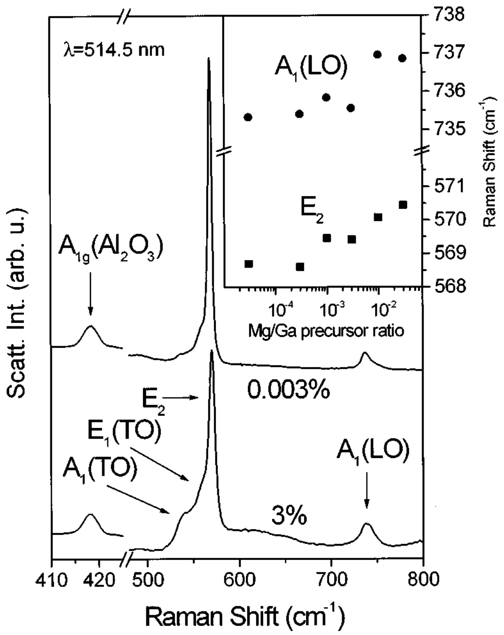

FIG. 1. Raman spectra of two Mg-doped GaN samples with Mg/Ga precursor ratios of 0.003% and 3%, Inset: line position of the A_1(LO) and E_2 mode.

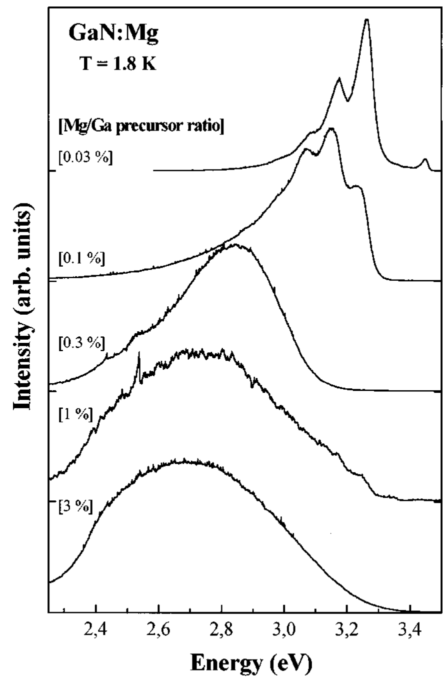

FIG. 2. Low-temperature PL of GaN epilayers doped with Mg at different concentrations.

istic 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 maximum of intensity is strongly shifted 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[9] or GaAs[10] before. An explanation for this behavior was discussed in detail by Shlovskii and Efros.[11] It involves strong fluctuations in the band gap at different positions in the sample caused by the electric field of a high number of compensated and, thus, ionized donors and acceptors, which are 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 therefore 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.[9]

To test this model for GaN:Mg we studied the intensity dependence of the PL of the most resistive sample grown with a Mg/Ga precursor ratio of 0.3%. It is shown in Figs. 3(a) and 3(b) for two different excitation conditions. Starting from lowest excitation intensities in Fig. 3(a) 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. 3(a) 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.[9] 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.

TABLE I. Dependence of the $E_1(TO)/E_2$ intensity ratio and FWHM of the E_2 mode on the Mg content.

Mg/Ga precursor ratio	0.003%	0.03%	0.1%	0.3%	1%	3%
$E_1(TO)/E_2$	0.235	0.271	0.317	0.303	0.436	0.676
FWHM E_2/cm^{-1}	4.2	3.7	3.8	5.3	6.5	7.0

The total blueshift of the high-energy band between 20 mW/cm^2 and 2 kW/cm^2 is as high as 153 meV. We find that the blueshift 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.

Both our Raman and PL investigations show that with increasing Mg doping additional defects are created in the GaN epilayers. They cause disorder and compensate the effects of the shallow acceptor level of Mg. In our intensity-dependent experiments we identified three broad emissions. 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 grown GaN.[12] They found three Mg-related deep donor levels below the conduction band edge, one at 265±15 meV, a second broad level around 400

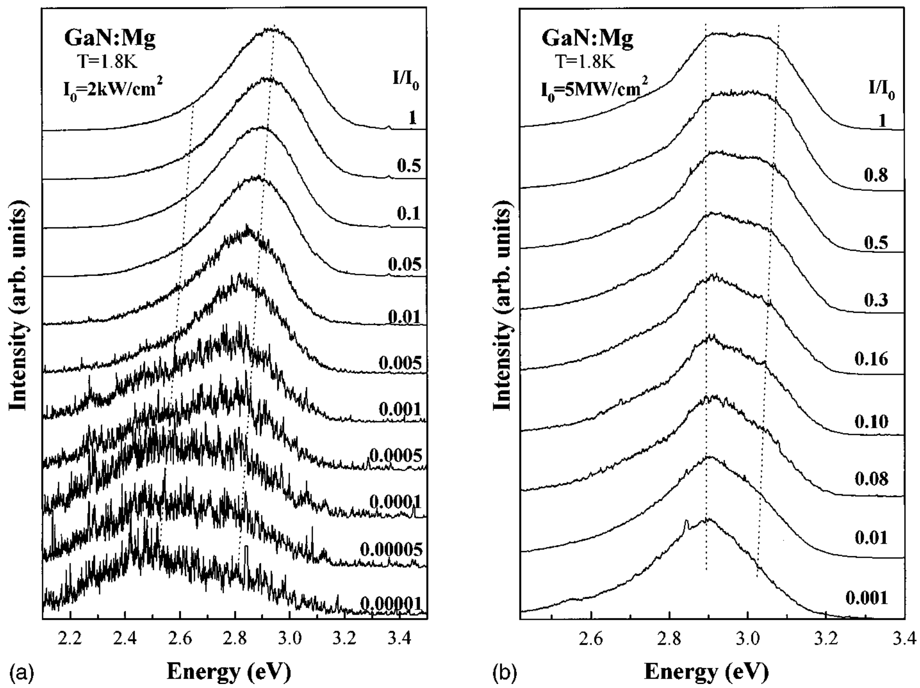

FIG. 3. Intensity dependence of the normalized PL of a *p*-type GaN epilayer doped with 0.3% Mg (a) measured with a cw-HeCd laser at up to 2 kW/cm^2, (b) measured with the third harmonic of a pulsed Nd:YAG laser with puls intensities up to 5 MW/cm^2.

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 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 reason for the observed blue shift of all DAP emissions in Figs. 3(a) and 3(b). The other reason is the well-known Coulomb interaction between the ionized donor and acceptor involved in the recombination process.[13] The observed saturation in the blueshift 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.*

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