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Effect of annealing on metastable shallow acceptors in Mg-doped GaN layers grown on GaN substrates

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Mg-doped GaN layers grown by metal-organic vapor phase epitaxy on GaN substrates produced by the halide vapor phase technique demonstrate metastability of the near-band-gap photoluminescence (PL). The acceptor bound exciton (ABE) line possibly related to the C acceptor vanishes in as-grown samples within a few minutes under UV laser illumination. Annealing activates the more stable Mg acceptors and passivates C acceptors. Consequently, only the ABE line related to Mg is dominant in PL spectra for the annealed samples. The temporal changes in PL are permanent at low temperatures; however, they can be recovered after heating to 100 K or higher. © 2008 American Institute of Physics. [DOI: 10.1063/1.2909541]

GaN is one of the most important III-V compound semiconductors for the modern electronics and optoelectronics. Scientific efforts are concentrated on further understanding of the fundamental properties of GaN and on further improvement of the crystalline quality. Developing GaN substrates and homoepitaxial growth result in a significant reduction of the threading dislocation density in the material, making it suitable for such demanding devices as long lifetime laser diodes. However, there are still unsolved problems; one of them is related to the properties of *p*-type GaN, a bottleneck for the performance of GaN-based devices. More research is needed to optimize highly *p*-doped GaN. To achieve the necessary hole concentration (usually in the range of 10^{17} – 10^{18} cm⁻³), the magnesium concentration in the GaN has to exceed $\sim 1 \times 10^{19}$ cm⁻³, which leads in turn to formation of microstructural defects.^{1,2} An additional post-growth annealing step is needed to activate the Mg acceptor. We have previously reported a strong metastable behavior of the UV cathodoluminescence (CL) observed in high quality Mg-doped GaN layers grown on quasibulk GaN templates.³ Mg concentrations were varied in the range of $(1-5) \times 10^{19}$ cm⁻³. We have noticed that UV photoluminescence (PL) in such GaN layers is also metastable, however, the temporal transformation of PL was very different from the metastable changes in CL. For adequate optical measurements, i.e., detection and interpretation of PL spectra, it is very important to be aware of optical metastability of the near-band-gap PL in Mg-doped GaN. For example, excitation power dependent measurements can be misrepresented due to temporal changes introduced by the UV laser. Spectra detected after an exposure to UV laser light will have a transformed shape, etc. Thus, the aim of this paper is to elucidate the time-dependent behavior of the low-temperature UV PL under cw excitation conditions, with emphasis on metastability of shallow acceptors and the effect of annealing.

GaN layers doped with Mg at rather high concentrations between 1×10^{19} and 1×10^{20} cm⁻³ were grown by metal-organic vapor phase epitaxy (MOVPE) on freestanding

200 μ m thick GaN substrates produced by the halide vapor phase epitaxy (HVPE) technique (type I samples). For each Mg concentration, the epitaxial growth has been done simultaneously using two similar pieces of GaN substrates with size of $\sim 7 \times 7$ mm². After that, one piece remained as-grown while the other has been annealed under 10 min at 800 °C in nitrogen atmosphere. From CV-measurements we could conclude that the (N_A-N_D) concentration is by a factor of ~ 10 higher in the annealed samples (2×10^{17} cm⁻³ before annealing and $\sim 5 \times 10^{18}$ cm⁻³ after annealing in the layer with Mg concentration of 1.5×10^{19} cm⁻³). For comparison, we have also done experiments on similar Mg-doped GaN layers fabricated on 200 μ m thick GaN templates grown by HVPE on sapphire (samples type II). Both types of GaN:Mg layers are grown in the same reactor with the same growth conditions. The type I samples are expected to have somewhat reduced threading dislocation density and a smaller residual strain as compared with the type II samples. PL was measured using the fourth harmonic ($\lambda_e=266$ nm) of a cw Nd:Vanadate laser as an excitation source. The samples were placed in a liquid-He cryostat providing temperatures in the range of 2–300 K. The PL signal was detected using a charge-coupled device camera.

With metastability of PL in the studied GaN layers we mean temporal changes of the spectral shape and relative intensities of the emission peaks in the region of 2.4–3.5 eV. Following the previously introduced procedure,^{3,4} we compare the whole transformation process for each sample and each excitation power within a certain time interval. The laser power density of 50 W cm⁻² was kept constant in the experiments described below to avoid any additional effects of the excitation density on the PL spectral shape. We note here that the effect of the excitation density in the range between 2 and 80 W cm⁻² on the temporal behavior of the PL spectra was negligible. We also introduce a delay time Δt , which is a time between the start of the excitation of PL and the start of the signal detection.

Figure 1 shows normalized low-temperature PL spectra measured with delay time $\Delta t=0$ min for as-grown (solid lines) and annealed (dashed lines) samples of type I. PL spectra for samples with Mg concentration below 2

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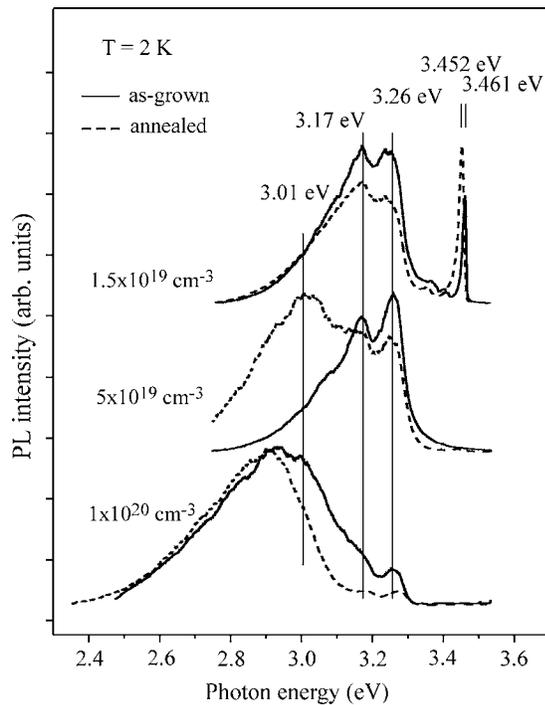


FIG. 1. PL spectra measured at 2 K for as-grown (solid lines) and annealed (dashed lines) GaN layers of type I with three Mg concentrations. An excitation density of 50 W cm^{-2} was used.

$\times 10^{19} \text{ cm}^{-3}$ are dominated by a shallow acceptor bound exciton (ABE) transition at $\sim 3.461 \text{ eV}$ (labeled here ABE1) and by two peaks at ~ 3.26 and $\sim 3.17 \text{ eV}$, which are likely a donor-acceptor pair (DAP) recombination and its LO phonon replica. The actual position of the ABE peak depends on the residual stress in the layer, while the actual position of the DAP emission is mainly dependent on the doping concentration and on the excitation power. With increasing Mg concentration, the shallow ABE1 line became weaker while the lower energy emissions at $2.9\text{--}3.27 \text{ eV}$ became stronger and finally, the PL spectrum is dominated by the broad band centered at $\sim 2.9 \text{ eV}$ in samples with the highest Mg concentration of $\sim 1 \times 10^{20} \text{ cm}^{-3}$. Annealing affects the PL spectrum as follows: (i) All samples with a pronounced PL related to the ABE1 line at 3.461 eV after annealing demonstrate instead another ABE at the lower energy 3.452 eV (labeled here ABE2). (ii) In the medium doped samples, a broad background band at $\sim 3.0 \text{ eV}$ became dominant. (iii) In the highly doped GaN layers the entire PL spectrum now centered at $\sim 2.9 \text{ eV}$ is narrowed due to reduced intensity of the emissions in the range of $3.0\text{--}3.3 \text{ eV}$. (iv) The effect of metastability is reduced, but does not disappear.

The temporal behavior of PL measured with 30–60 min intervals under continuous laser illumination is shown in Fig. 2 for as-grown (solid lines) and annealed (dashed lines) GaN layers of type I with two Mg concentrations of 1.5×10^{19} and $5 \times 10^{19} \text{ cm}^{-3}$, respectively. We have noticed that for samples with a high doping level of $\sim 1 \times 10^{20} \text{ cm}^{-3}$ the effect of metastability in PL is negligible, i.e., no pronounced changes in PL spectral shape have been observed within $\sim 1 \text{ h}$. For the UV PL in Mg-doped GaN layers with concentrations between $1 \times 10^{19}\text{--}5 \times 10^{19} \text{ cm}^{-3}$ a reduction of the ABE intensity, changes of the relative intensities of peaks in the region $3.26\text{--}3.0 \text{ eV}$ and a redshift of the 3.26 eV line are typical effects of prolonged laser irradiation. A similar be-

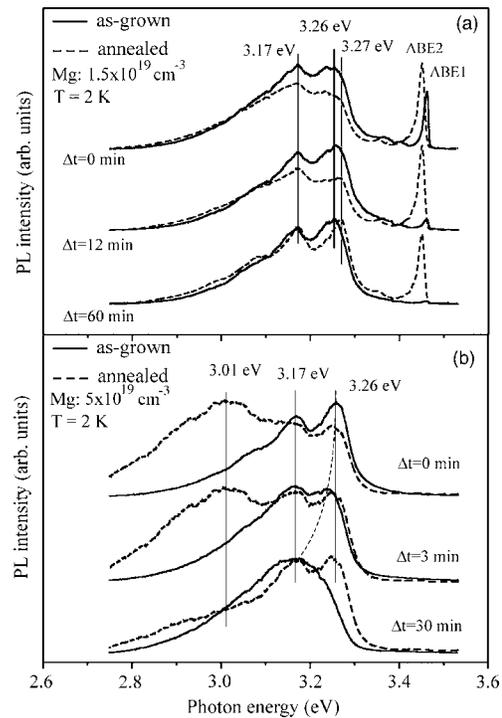


FIG. 2. (a) PL spectra measured at 2 K for the as-grown (solid lines) and annealed (dashed lines) sample of type I with Mg concentration of $1.5 \times 10^{19} \text{ cm}^{-3}$. PL spectra are shown for three different delay times after the beginning of the illumination by the laser light. (b) Similar PL data are shown at 2 K for the as-grown (solid lines) and annealed (dashed lines) sample of type I with Mg concentration of $5 \times 10^{19} \text{ cm}^{-3}$.

havior has been observed for samples of type II as well as for the GaN layers directly grown directly on sapphire. A comparison of different samples both homo- and heteroepitaxially grown has indicated that such structural properties as threading dislocation density or residual strain are unlikely responsible for the metastable behavior of shallow acceptors in *p*-type GaN. However, details of the metastable behavior seem to depend on the actual acceptor concentration and can vary from sample to sample even if they have been grown with the same Mg precursor flow. Annealing at $800 \text{ }^\circ\text{C}$ likely activates a more stable lower energy acceptor; thus, the intensity of the ABE2 line at 3.452 eV that is visible after annealing only slowly reduces in comparison to the ABE1 line at 3.461 eV before annealing. The redshift of the 3.26 eV emission in as-grown samples varies between $0\text{--}100 \text{ meV}$ after 30 min, increasing with Mg concentration. After annealing, no redshift has been observed for this emission within 30 min under laser excitation.

We have checked whether these changes in PL are permanent and in what temperature range these changes persist. The results of these experiments are shown in Fig. 3, where the type II sample with both pronounced ABE emission at $\Delta t = 0 \text{ min}$ and with a clear redshift of the 3.26 eV line is chosen for convenience. The PL spectra have practically the same shape at low temperatures $< 30 \text{ K}$ as well as the same temporal behavior and the same thermal recovery. Below 30 K , the temporal changes in PL are permanent, as can be seen from Fig. 3(a), where the sample at 10 K was first illuminated by the laser during 30 min (spectra are shown for delay time $\Delta t = 0$ and 30 min, respectively), then the laser beam was blocked and the sample was kept in the dark during 30 min. After that, the laser light was opened and the PL

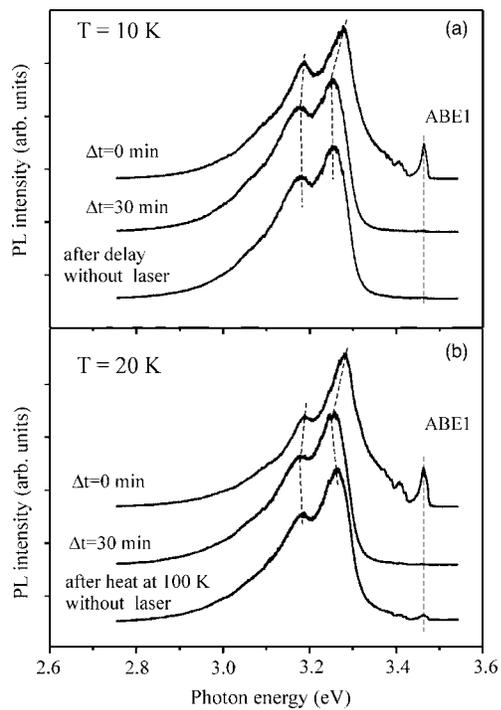


FIG. 3. (a) PL spectra measured at 10 K for the as-grown sample of type II with Mg concentration of $1.5 \times 10^{19} \text{ cm}^{-3}$ at the delay times $\Delta t=0$ and 30 min, respectively, under the continuous laser illumination and after a delay of 30 min in darkness. (b) PL spectra measured at 20 K for the same sample with $\Delta t=0$ and 30 min and after the sample has been heated (in darkness) to 100 K. Excitation power density for (a) and (b) was 50 W cm^{-2} .

spectrum has been immediately registered. This spectrum (with delay without laser) is identical to the previous spectrum detected with $\Delta t=30$ min. To reverse metastable changes in PL, the samples have to be heated up to 100 K or higher. This is demonstrated in Fig. 3(b), where the sample after 30 min illumination by the laser at 20 K showed a vanishing of the ABE line and a redshift of the 3.26 eV line. However, after heating at ~ 100 K in darkness and consequent cooling down to 20 K one can see that the PL is partly recovered. The redshift is decreased while the ABE1 line intensity is increased. Heating to room temperature completely recovers the initial PL spectrum shape. We have also observed that partial recovery of PL can be achieved even at 2 K under below band gap illumination using a green light emitting diode.

The following properties have to be explained: (i) in the as-grown samples we see only the metastable ABE1, while after annealing there is only ABE2; (ii) a vanishing of the ABE1 line under the UV laser illumination; (iii) the redshift of 3.26 eV transition is present only in as-grown samples; and (iv) the thermal recovery of the PL shape at low temperatures.

Two shallow acceptors have been previously reported in Mg-doped GaN.^{5,6} The typical signatures of the shallow acceptor A1 are ABE1 at ~ 3.462 eV and DAP at ~ 3.27 eV with its two LO phonon replicas. The second acceptor A2 is associated with ABE2 at ~ 3.453 eV and with a broad band at ~ 3.1 eV. It was suggested that A2 is related to Mg,⁷ while A1 has been recently assigned to the shallow C_N acceptor.⁸ In Mg-doped as-grown samples with Mg concentrations $< 2 \times 10^{19} \text{ cm}^{-3}$ we should have both acceptors, but we have observed only ABE1 related to A1. It means that the second

acceptor A2 is not active, due to H passivation and possibly formation of the neutral $V_N\text{-Mg-H}$ complexes during MOVPE growth. Still, there is evidence for a weak contribution from the A2 acceptor via the 3.1 eV band in PL spectra in such samples since the relative intensities of the DAP peak and phonon replicas are different as compared to more lightly Mg-doped GaN layers with Mg concentrations $< 1 \times 10^{19} \text{ cm}^{-3}$, where the DAP emission dominates over phonon replicas at the used excitation power density of 0.5 W cm^{-2} .⁶ Postgrowth annealing at 800 °C activates more stable A2 acceptors (associated to Mg) and passivates A1 acceptors since we have observed only ABE2 after annealing. The activation of Mg acceptors is then also correlated with the more dominant 3.1 eV PL in the annealed GaN layers with Mg concentrations $(1\text{--}5) \times 10^{19} \text{ cm}^{-3}$. Vanishing of the ABE1 line in as-grown samples under UV excitation or under electron irradiation can be explained by passivation of A1 by H. Mobile H is provided by the dissociation of the Mg-H complexes caused by the excess energy supplied by $e\text{-}h$ pair recombination. This explains also the redshift of the 3.26 eV band since, with reduction of the number of A1 acceptors, the corresponding DAP peak shifts to the lower energy. The observed recovery of PL at 2 K by the sample heating to 100–200 K rules out a simple assignment of the passivated A1 acceptor to stable $C_N\text{-H}$ complexes, since the binding energy of H with C is 1.66 eV,⁸ which makes dissociation process at 100–200 K improbable. Instead we suggest that the passivated A1 acceptor is residing in an optically nonactive metastable state (possibly an excited $C_N\text{-H}$ state) with relatively low activation energy. This state can be transformed to the initial configuration (i.e., optically active A1) by heating to 100–200 K or under below band-gap illumination.

In conclusion, we have observed for Mg-doped GaN layers temporal changes in the PL spectral shape caused by 266 nm cw laser illumination. Two acceptors are involved in the recombination process. In as-grown samples the possible candidate for the metastable acceptor is C_N , while after annealing the second more stable acceptor related to Mg became active. Thermal heating to 100–200 K is enough for partial recovery of the initial PL shape at 2 K. A similar recovery effect can be achieved by illumination below band gap at 2 K.

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