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Doping-level-dependent optical properties of GaN:Mn

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The optical properties of molecular-beam-epitaxy-grown GaN with different Mn-doping levels ($5-23\times10^{19}$ cm^{-3}) were studied by cathodoluminescence (CL) and optical transmission spectroscopy. Transmission measurements at 2 K revealed an absorption peak at 1.414 ±0.002 eV, which was attributed to an internal $^5T_2\rightarrow{}^5E$ transition of the neutral Mn^{3+} state. The intensity of this Mn-related transmission peak was found to scale with the Mn^{3+} concentration. The CL measurements showed that Mn-doping concentrations around 10^{20} cm^{-3} reduced the near band edge emission intensity by around one order of magnitude. A complete quenching of the donor–acceptor-pair band at 3.27 eV and strong decrease of the yellow luminescence centered at 2.2 eV were attributed to a reduced concentration of V_{Ga}. In the infrared spectral range of 0.8–1.4 eV three broad, Mn-doping related CL emission bands centered at 1.01 ± 0.02, 1.09 ± 0.02, and 1.25 ± 0.03 eV were observed. Their origin is attributed to deep donor complexes, which are generated as a result of the heavy Mn-doping. © *2004 American Institute of Physics.*
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Transition metals in GaN have been studied in detail for more than 10 years,[1] but regained prominence recently due to potential application for growth of high-resistivity GaN substrate material and for dilute magnetic semiconductors.[2] GaN doped with Mn is a possible candidate for spintronics applications since a Curie temperature above room temperature has been reported.[3,4] However, a viable spintronics device has to fulfill a second requirement: it needs to support carrier-mediated ferromagnetism so that spin-polarized charge carriers may be injected into a nonmagnetic semiconductor.[5] Recent reports indicate that the Mn^{2+} acceptor level is located deep in the GaN band gap and not effective-mass-like as in GaAs:Mn,[6] suggesting that carrier-mediated ferromagnetism in GaN:Mn is rather unlikely.[7]

The aim of this work was to improve the understanding of how the manganese is incorporated into the GaN layers and how this process affects the defect structure of these films.

The 1-μm-thick samples under investigation were grown by plasma-induced molecular beam epitaxy on *c*-plane Al_2O_3 substrate. The samples were either nominally undoped or Mn-doped with Mn concentrations of $5-23\times10^{19}$ cm^{-3}, as determined by elastic recoil detection. For comparison purposes, a GaN sample intentionally codoped with Mn and Si ($[Mn]\sim[Si]\sim3\times10^{19}$ cm^{-3}) was grown under identical conditions. The absorption measurements were performed at 2 K with a 250 W tungsten–halogen lamp. The light was spectrally dispersed by a 0.75 m double-grated monochromator facilitating a resolution of 0.02 nm and detected by a Ge detector. The CL measurements were performed using an Oxford Instruments MonoCL2 system installed on a JEOL35C scanning electron microscope. The UV–visible CL spectra were collected using a Hamamatsu R943-02 Peltier cooled photomultiplier tube (PMT). The IR spectra were measured using a Hamamatsu R5509-72 PMT. All CL spectra were corrected for system response.

The optical absorption spectra recorded at 2 K of nominally undoped GaN, GaN:Mn, and GaN:Mn:Si are presented in Fig. 1. An absorption band with a zero phonon line (ZPL) at 1.414 ± 0.002 eV was observed in the GaN:Mn samples but neither in the nominally undoped nor the GaN:Si,Mn samples. The relative intensity of this ZPL was found to scale with the Mn concentration indicating a transition involving a Mn level. The ZPL was recently attributed either to the internal $^5T_2\rightarrow{}^5E$ transition of the deep neutral Mn^{3+} state[7] or to the optical transition from the valence band to the Mn^{2+} acceptor.[8,9] Our results rule out the latter interpretation since no ZPL was detected in the GaN:Mn:Si sample although much higher (more than one order of magnitude) concentrations of the Mn^{2+} acceptor (due to an electron transfer from the Si donor to the Mn acceptor) were found by ESR.[7] Therefore, the ZPL is most likely related to the neutral Mn^{3+} acceptor state. The five 3*d*-orbitals of the Mn^{3+} split into three t_2 and two *e* orbitals in the tetrahedral crystal field of the surrounding N ligands. Additionally, in GaN the t_2 orbitals of Mn^{3+} hybridize with the *p* orbitals of the valence band, shifting the occupied bonding states t^b into the valence band and the antibonding t^a states above the two nonbonding

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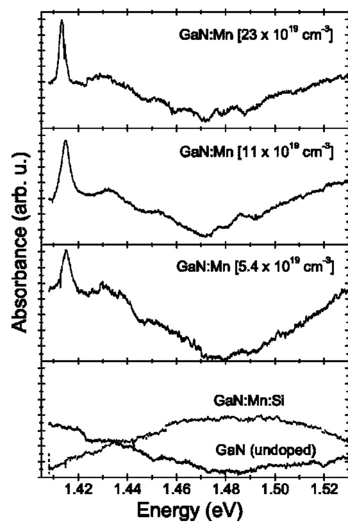

FIG. 1. Optical absorption spectra at 2 K for MBE-grown undoped, Mn-doped, and Mn:Si codoped GaN. The Mn concentration varied from 5.4 to 23×10^{19} cm^{-3}. The ZPL is at 1.414 ± 0.002 eV.

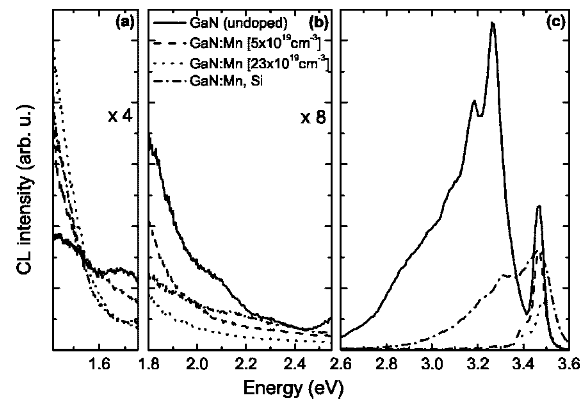

FIG. 2. CL spectra [$E_b=8$ keV, 45 μm$\times$36 μm] at 80 K for undoped GaN (solid line), GaN:Mn [5.4×10^{19} cm^{-3}] (dashed line), GaN:Mn [23×10^{19} cm^{-3}] (dotted line), and GaN:Mn codoped with Si (dash-dotted line). The spectra were collected at 20 nA (a), and 5 nA (b), (c). While spectrum (a) was multiplied by a factor of 4, spectrum (b) was multiplied by a factor of 8.

e states.[10] As a result, one (spin-allowed) transition $T_2\rightarrow E$ is expected in optical absorption spectra of Mn-doped GaN. Calculation based on the tight-binding linear-muffin-tin-orbital method yield an energy difference, ΔE, between the t_2 and e states of $\Delta E=E_{t2g}-E_{eg}\sim1.35$ eV for zinc-blende GaN:Mn,[11] while calculations within the local spin density approximation gave a respective energy difference of approximately 1.2–1.3 eV for the wurtzite structure of GaN:Mn,[10] both of which roughly agree with the experimentally observed absorption peak at 1.414 eV. Thus, we attribute this absorption line to an internal $^5T_2\rightarrow{}^5E$ transition of the deep neutral Mn^{3+} state, in agreement with previous reports.[7,12] The series of satellite peaks on the higher energy side of the ZPL with an energetic distance of 20 ± 1 meV and 73 ± 3 meV, respectively, is attributed to pseudolocal vibrational modes of the Mn level.[8]

The luminescence properties of nominally undoped GaN, GaN:Mn, and GaN:Mn:Si were investigated by CL spectroscopy. It should be noted that the purely Mn-doped samples were charging when irradiated with the electron beam during CL,[13] indicating a semi-insulating behavior due to doping with deep Mn acceptors. A comparison of absolute intensities of doped and undoped samples is presented in Fig. 2. We observe that Mn-doping concentrations around 10^{20} cm^{-3} reduce the near band edge emission intensity by around one order of magnitude. Moreover, no donor–acceptor-pair (DAP) emission centered at 3.27 eV with its characteristic LO phonon replica[14] and a strongly reduced yellow luminescence (YL) around 2.1–2.2 eV[15] are observed in the Mn-doped samples. Manganese doping promotes nonradiative recombination and effectively quenches the CL in the visible part of the spectrum. Since V_{Ga} are suggested to be responsible for the YL[16,17] and to form acceptor complexes involved in the 3.27 eV DAP in undoped GaN,[18] the introduction of Mn_{Ga} acceptors might affect the concentration of V_{Ga}: first, by occupying the Ga lattice site and second, by downshifting the position of Fermi level to the midgap region and consequently increasing the formation energy of residual V_{Ga} acceptors.[16]

Figure 2 reveals two additional features: (i) the GaN:Mn,Si sample exhibits a broad multipeak emission band between 3.2 and 3.5 eV and (ii) we observe the onset of an infrared emission band in both the doped and the codoped GaN. The former feature is illustrated in more detail in Fig. 3 where the undoped, codoped, and the samples doped with the highest and the lowest Mn concentration are compared. The spectrum of the GaN:Mn,Si sample consists of at least three peaks at 3.46, 3.39, and 3.30 eV. The 3.46 eV near band edge emission (NBE) is attributed to a superposition of bound and free excitons at 80 K. The latter two of these peaks can also be found in both GaN:Mn and undoped samples and are therefore attributed to structural defects. Microcavity effects can be ruled out due to the energetic distance of these peaks. Although the nature of the 3.39 eV emission remains to be determined, the emission at 3.30 eV is suggested to be its first LO phonon replica. The Mn-doped GaN exhibits a blueshift of the NBE with increasing Mn concentration, which is attributed to biaxial compressive strain.[19] The NBE, centered at 3.460 eV in the undoped GaN, shifts 12 meV to 3.472 eV

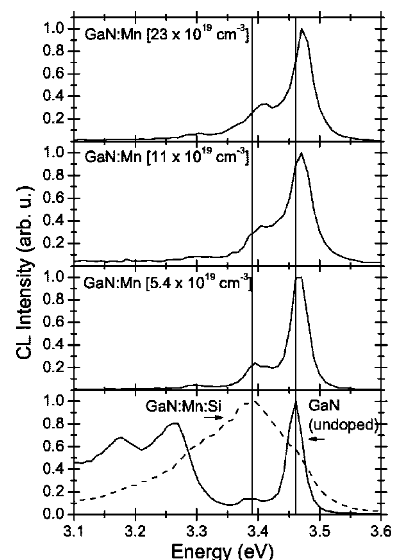

FIG. 3. 80 K CL emission spectra [$E_b=12$ keV, $I_b=25$ nA, 67 μm $\times$53 μm] of undoped, Mn-doped, and Mn:Si codoped GaN. The solid lines at 3.46 and 3.39 eV are a guide to the eye to assess the blueshift of the near band edge emission lines with higher Mn concentration.

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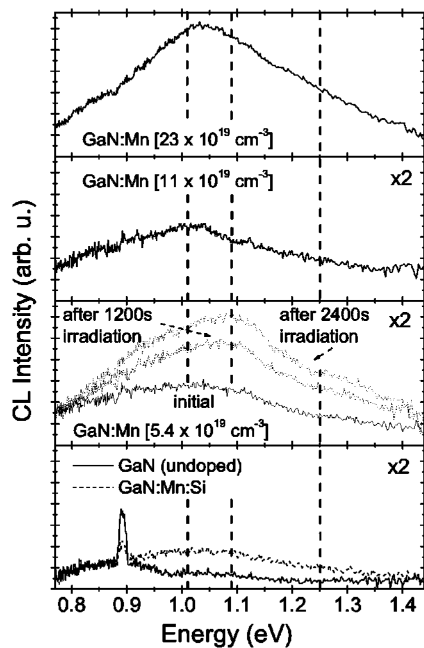

FIG. 4. 80 K CL spectra [$E_b = 12$ keV, $I_b = 150$ nA, 67 μm$\times$53 μm] in the near-infrared region of undoped, Mn-doped, and Mn:Si codoped GaN. Compared with the intensity of the upper spectrum all other spectra are multiplied by a factor of 2. The change of the CL spectra during electron beam irradiation with a relatively high dose is illustrated exemplarily for the GaN doped with Mn concentration of 5.4×10^{19} cm^{-3}. The Mn doping related CL emission bands centered at 1.01 ± 0.02, 1.09 ± 0.02, and 1.25 ± 0.03 eV are marked by dashed lines.

in the GaN:Mn [23×10^{19} cm^{-3}], indicating a significant amount of compressive strain.

In the infrared spectral range between 0.8 and 1.4 eV three broad, Mn-doping related CL emission bands were observed, centered at 1.01 ± 0.02, 1.09 ± 0.02, and 1.25 ±0.03 eV (Fig. 4), which were found to be highly beam sensitive. Continuous electron exposure resulted in an increased intensity. The exact position of these three bands was determined by applying sensible fitting techniques both to the original and to the difference spectra. The luminescence band at 1.25 ± 0.03 eV was recently attributed to the spin-forbidden $^4T_1(G)$-$^6A_1(S)$ transition at the Mn^{2+} d^5 ion due to long decay times in the ms range.[20] However, we found a much stronger IR emission intensity in GaN:Mn with the highest doping level compared to GaN:Mn,Si, which has a one order of magnitude higher concentration of Mn^{2+}. Moreover, neither a ZPL nor the fine structure, which is typical for internal transitions, was observed and the broad shape of this band is rather an indication for deep defects with strong phonon coupling. In light of these results, we propose the following model to account for the IR emission bands. It is known that heavy Mn doping ($>3-5\times10^{19}$ cm^{-3}) leads to a downshift of the Fermi level and promotes the formation of compensating defect complexes[21] (e.g. Mn–H[22] and Mn–V_N), i.e., doping-driven self-compensation mechanisms similar to conventional Mg doping in GaN.[23] Although theoretical calculations of energies for Mn-related complexes are not available yet, our results indicate that these complexes form deep donor levels, probably with a strong phonon coupling. This is supported by strong electron beam sensitivity of the IR emission bands, which could be understood in terms of defect complex dissociation.[24–26] Thus, in GaN:Mn codoped with Mg an even more pronounced IR emission intensity is expected since Mg codoping will further downshift the Fermi level and promote the generation of compensating donors. Recently, this was indeed observed in PL experiments on GaN:Mn,Mg.[20] Finally, it should be noted that the IR peaks in Fig. 4 cannot originate from the sapphire substrate underneath. First, the ruby ($Al_2O_2:Cr^{3+}$) lines appearing in second order at 0.893 eV in Fig. 4 are always the strongest sapphire emission in our undoped samples. In the doped samples they are buried under the doping related emission bands. Second, nearly all CL signal is generated within the GaN layer for an electron beam energy of 12 kV.[27]

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