

## Optical Properties of Mn-doped GaN

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### ABSTRACT

Molecular beam epitaxy-grown GaN with different Mn concentrations ( $5\text{-}23 \times 10^{19} \text{ cm}^{-3}$ ) and codoped with Si were investigated by cathodoluminescence (CL) spectroscopy and optical transmission measurements. In the GaN:Mn, an intense absorption peak at  $1.414 \pm 0.002 \text{ eV}$  was observed. This peak was attributed to an internal  ${}^5T_2 \rightarrow {}^5E$  transition of the deep neutral  $\text{Mn}^{3+}$  state since its intensity scaled with the  $\text{Mn}^{3+}$  concentration. The CL measurements showed that Mn-doping concentrations around  $10^{20} \text{ cm}^{-3}$  had three effects on the emission spectrum: (i) the donor bound exciton at  $3.460 \text{ eV}$  was reduced by more than one order of magnitude, (ii) the donor-acceptor-pair band at  $3.27 \text{ eV}$  was completely quenched and (iii) the yellow luminescence centered at  $2.2 \text{ eV}$  was strongly decreased. The latter two effects were attributed to a reduced concentration of  $V_{\text{Ga}}$ . In the infrared spectral range, three broad, Mn-doping related CL emission bands centered at  $1.01 \pm 0.02 \text{ eV}$ ,  $1.09 \pm 0.02 \text{ eV}$  and  $1.25 \pm 0.03 \text{ eV}$  were observed. These bands might be related to deep donor complexes, which are generated as a result of the heavy Mn-doping, rather than internal transitions at the Mn atom.

### INTRODUCTION

Transition metals in GaN have been studied in detail for more than 10 years [1], but regained attraction recently due to potential application for growth of high-resistivity GaN substrate material and for dilute magnetic semiconductors (DMS) showing ferromagnetic behaviour above room temperature [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 needs to support carrier-mediated ferromagnetism so that spin-polarised charge carriers may be injected into a nonmagnetic semiconductor [5]. Recent reports indicate that the  $\text{Mn}^{2+}$  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].

Optical studies represent one approach to identify the nature of deep levels, which are generated by the introduction of Mn in GaN. In this study, low temperature optical absorption measurements and cathodoluminescence (CL) spectroscopy were carried out to investigate the optical characteristics of GaN:Mn and GaN:Mn:Si layers. 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.

## EXPERIMENTAL DETAILS

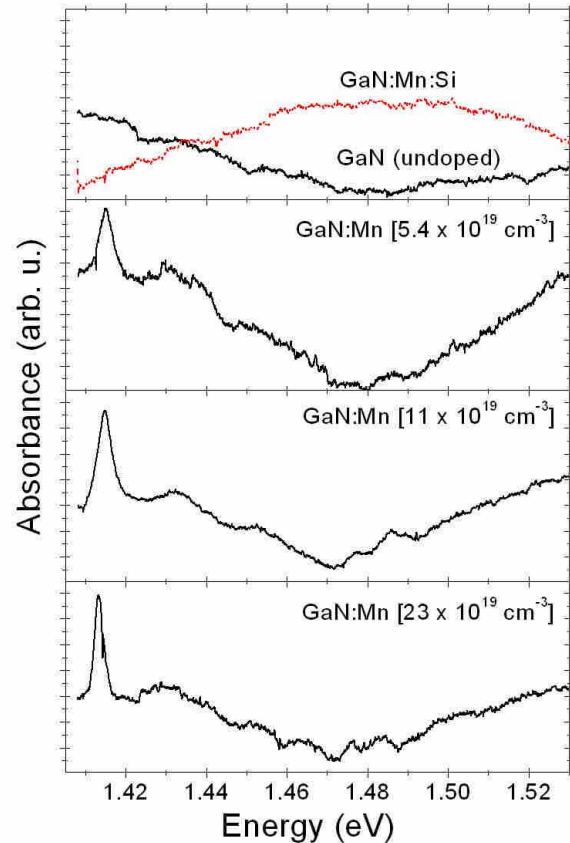
The 1  $\mu\text{m}$  thick samples under investigation were grown by plasma-induced molecular beam epitaxy on c-plane  $\text{Al}_2\text{O}_3$  substrate. The samples were either nominally undoped, Mn-doped with Mn concentrations of  $0.5 - 2.3 \times 10^{20} \text{ cm}^{-3}$ , as determined by elastic recoil detection, or intentionally codoped with Mn and Si ( $[\text{Mn}] \sim [\text{Si}] \sim 3 \times 10^{19} \text{ cm}^{-3}$ ). The absorption measurements were performed at 2 K with a 250 W tungsten-halogen lamp and spectrally dispersed by a 0.75 m double-grated monochromator with a resolution of 0.02 nm. A cooled Ge detector was used to detect the sample transmittance. The CL measurements were performed using an Oxford Instruments MonoCL2 system installed on a JEOL35C SEM. The UV-VIS CL spectra were collected using a 1200 lines/mm grating blazed at 500 nm and a Hamamatsu R943-02 Peltier cooled photomultiplier tube (PMT). The IR spectra were measured using a 600 lines/mm grating blazed at 1600 nm and a Hamamatsu R5509-72 PMT. All CL spectra were corrected for system response. The electron beam current,  $I_b$ , was measured using a Faraday cup.

## DISCUSSION

In order to elucidate the nature of the Mn dopant in GaN, optical absorption measurements of nominally undoped GaN, GaN:Mn and GaN:Mn:Si were carried out at 2 K (Fig. 1). In the spectra of the purely Mn-doped GaN, an intense absorption peak at  $1.414 \pm 0.002$  eV was observed. This line was not selected in either the nominally undoped or the GaN:Si:Mn samples. The relative intensity of this absorption peak was found to scale with the Mn concentration indicating a transition related to a Mn center. The absorption peak was recently attributed either to the internal  ${}^5T_2 \rightarrow {}^5E$  transition of the deep neutral  $\text{Mn}^{3+}$  state [7] or to the optical transition from the valence band to the  $\text{Mn}^{2+}$  acceptor [8,9]. If the latter interpretation was correct, a strongly pronounced absorption peak would be expected in GaN:Mn:Si, where a much higher (more than one order of magnitude) concentration of the  $\text{Mn}^{2+}$  acceptors was measured by ESR [7]. The absence of this line in GaN:Mn:Si contradicts the latter interpretation and makes the former assignment more likely.

Based on a comparison with the position of the  $\text{Mn}^{2+}$  acceptor level (with respect to the vacuum energy) in GaAs, GaP and InP, the  $\text{Mn}^{2+}$  level in GaN is expected at  $2.0 \pm 0.1$  eV above the valence band [10]. Therefore, the absorption peak is more likely related to the neutral  $\text{Mn}^{3+}$  acceptor state. Due to the splitting of the five d orbitals of the  $\text{Mn}^{3+}$  into three  $t_2$  and two e orbitals in the tetrahedral crystal field of the surrounding N ligands, one (spin-allowed) transition  $T_2 \rightarrow E$  is expected in optical absorption spectra. However, in GaN the  $t_2$  orbitals of  $\text{Mn}^{3+}$  hybridise 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 e states [11]. Calculation based on the tight-binding linear-muffin-tin-orbital method indicated an energy difference,  $\Delta E$ , between the gap states of  $\Delta E = E_{t_2g} - E_{eg} \sim 1.35$  eV for zincblende GaN:Mn [12], 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 [11], 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  $\text{Mn}^{3+}$  state, in agreement with previous reports [7,13]. The series of satellite peaks on the higher energy side of the ZPL with an energetic distance of  $20 \pm 1$  meV is attributed to pseudolocal vibrational modes of the Mn level [8].

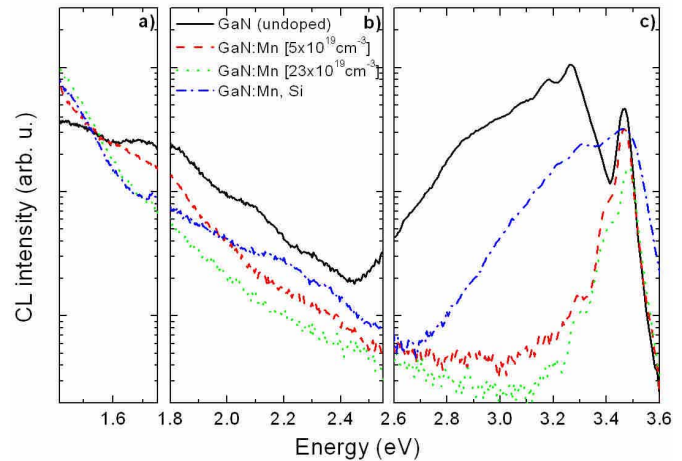
**Figure 1.** Optical absorption spectra at 2 K for MBE-grown undoped, Mn-doped and Mn:Si codoped GaN. The Mn-concentration varied from  $5.4$  to  $23 \times 10^{19} \text{ cm}^{-3}$ . The ZPL is at  $1.414 \pm 0.002 \text{ eV}$ . The spectra were corrected from  $\lambda_{\text{air}}$  to  $\lambda_{\text{vacuum}}$  and calibrated using the  $8853.87 \text{ \AA}$  and  $9148.68 \text{ \AA}$  lines of a Ne spectral lamp.



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 [14], indicating a semi-insulating character due to doping with deep Mn acceptors. A comparison of the absolute intensities of the doped and undoped samples is presented in Fig 2. Mn-doping concentrations around  $10^{20} \text{ cm}^{-3}$  reduce the donor bound exciton ( $D^0X$ ) emission intensity by almost one order of magnitude. Moreover, the shallow donor-acceptor-pair (DAP) emission centred at  $3.27 \text{ eV}$  with its characteristic LO phonon replica [15] is completely quenched and yellow luminescence (YL) around  $2.1\text{-}2.2 \text{ eV}$  [16] is strongly reduced in the Mn-doped samples. The Mn doping promotes nonradiative recombination and effectively quenches the CL in visible part of the spectrum. In addition, the introduction of  $\text{Mn}_{\text{Ga}}$  acceptors reduces the concentration of  $V_{\text{Ga}}$  in two ways. First, Mn occupies the Ga lattice site and second, the downshifting of the position of Fermi-level to the midgap region results in a higher formation energy of residual  $V_{\text{Ga}}$  acceptors [17]. The  $V_{\text{Ga}}$  are suggested to be responsible the YL [17,18] and to form acceptor complexes involved in the  $3.27 \text{ eV}$  DAP in nominally undoped GaN [19].

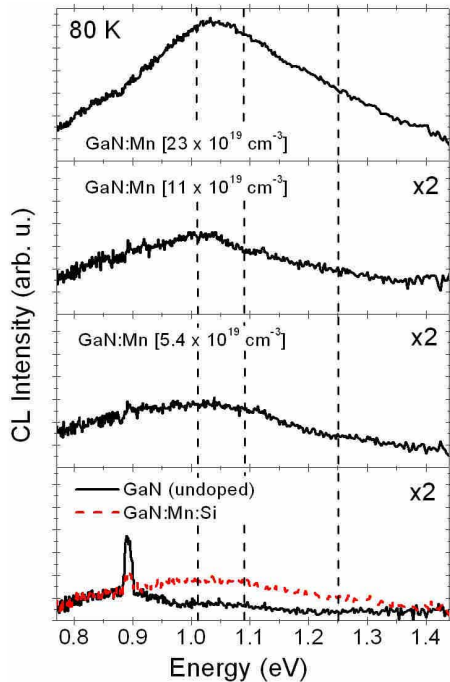
However, Fig. 2 reveals two additional features: (i) the GaN:Mn:Si sample exhibits a broad multippeak emission band between  $3.2$  and  $3.5 \text{ eV}$  and (ii) the onset of an infrared emission band in both the doped and the codoped GaN. The former feature is attributed to an accumulation of defect centers in the GaN:Mn:Si and currently under investigation.

**Figure 2.** CL spectra [ $E_b=8$  keV,  $45 \mu\text{m} \times 36 \mu\text{m}$ ] at 80 K for undoped GaN (solid line), GaN:Mn [ $5.4 \times 10^{19} \text{cm}^{-3}$ ] (dashed line), GaN:Mn [ $23 \times 10^{19} \text{cm}^{-3}$ ] (dotted line) and GaN:Mn codoped with Si (dash-dotted line). The spectra were collected at 20 nA (a), and 5 nA (b,c). Spectrum (a) was divided by a factor of 4. While spectrum c) was collected without any filter, a 400 nm and a 650 nm filter were used for acquisition of spectra b) and a), respectively.

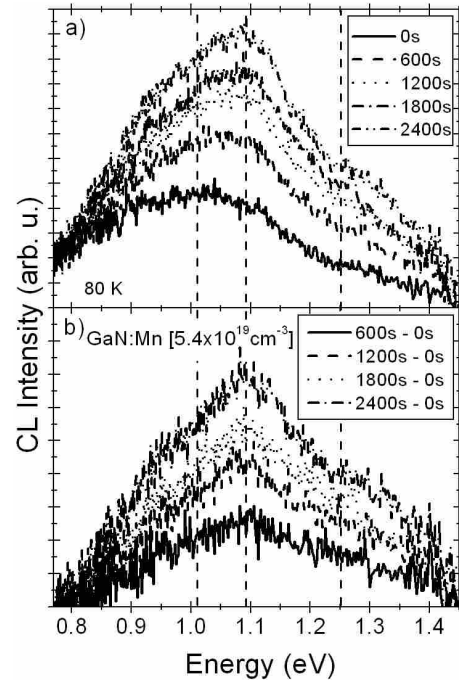


In the infrared spectral range of  $0.8 - 1.4$  eV three broad, Mn-doping related CL emission bands centered at  $1.01 \pm 0.02$  eV,  $1.09 \pm 0.02$  eV and  $1.25 \pm 0.03$  eV were observed (Figs. 3 and 4), which were found to be highly beam sensitive. Continuous electron exposure resulted in an increased intensity, facilitating the determination of the energetic peak position by subtracting the spectra from each other (Fig. 4). The luminescence band at  $1.25 \pm 0.03$  eV was recently attributed to the spin-forbidden  ${}^4T_1(G) - {}^6A_1(S)$  transition at the  $\text{Mn}^{2+} d^5$  ion [20]. However, the GaN:Mn with the highest doping level displayed a much stronger IR emission intensity than GaN:Mn,Si, which has a one order of magnitude higher concentration of  $\text{Mn}^{2+}$ . 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 the light of these results, we propose the following model to account for the IR emission bands. Heavy Mn-doping ( $>3-5 \times 10^{19} \text{cm}^{-3}$ ) leads to a downshift of the Fermi-level and promotes the formation of compensating donor-like 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 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 the strong electron beam sensitivity of the IR emission bands, which could be understood in terms of defect complex dissociation [24,25]. 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 and tentatively attributed to  $\text{Mn}^{3+}$ -donor and  $\text{Mn}^{2+}$ -donor complexes [20]. Finally, it should be noted that the IR peaks in Fig. 4 cannot stem from the sapphire underneath, since (i) the 2<sup>nd</sup> order of the  $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$  peak at 0.893 eV is always the strongest sapphire emission in our samples and cannot be observed in the doped samples and (ii) nearly all CL signal is generated within the GaN layer for an electron beam energy of 12 kV [26].



**Figure 3.** 80 K CL spectra [ $E_b=12$  keV,  $I_b=150$  nA,  $67 \mu\text{m} \times 53 \mu\text{m}$ ] in the near-infrared region of undoped, Mn-doped and Mn:Si codoped GaN. Compared with the intensity of the top spectrum all other spectra are multiplied by a factor of 2. The Mn-doping related CL emission bands centered at  $1.01 \pm 0.02$  eV,  $1.09 \pm 0.02$  eV and  $1.25 \pm 0.03$  eV are marked by dashed lines.



**Figure 4.** a) 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  $5.4 \times 10^{19} \text{cm}^{-3}$ . b) Successive changes of the CL spectra, expressed as the difference between the first spectrum and each of the following spectra.

## CONCLUSIONS

In purely Mn-doped GaN, an absorption peak at  $1.414 \pm 0.002$  eV was observed at 2 K, which was attributed to an internal  ${}^5T_2 \rightarrow {}^5E$  transition of the deep neutral  $\text{Mn}^{3+}$  state and was found to scale in intensity with the  $\text{Mn}^{3+}$  concentration. The CL measurements revealed that Mn-doping concentrations around  $10^{20} \text{cm}^{-3}$  reduced the donor bound exciton emission intensity by almost one order of magnitude. Moreover, the shallow donor-acceptor-pair band at 3.27 eV was completely quenched, whereas the yellow luminescence was strongly decreased. These effects were attributed to the reduced concentration in  $V_{\text{Ga}}$ . In the infrared spectral range, three broad, Mn-doping related CL emission bands centered at  $1.01 \pm 0.02$  eV,  $1.09 \pm 0.02$  eV and  $1.25 \pm 0.03$  eV were observed. Their origin is tentatively attributed to deep donor complexes, which are generated as a result of the heavy Mn-doping.

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