

Mn charge states in GaMnN as a function of Mn concentration and co-doping

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ABSTRACT

In the context of the pursuit of a dilute magnetic semiconductor for spintronic applications, a set of GaMnN samples with varying Mn concentration and Si or Mg co-doping was investigated by optical and electron spin resonance spectroscopy. The results clearly demonstrate how the charge state of Mn is changed between 2+, 3+ and 4+ by Mg and Si co-doping. For p-type GaMnN we show that the introduction of the Mn^{3+/4+} donor can be compensated by Mg co-doping lowering the Fermi energy below the Mn^{3+/4+} level. While our results are in agreement with the hypothesis that the infrared photoluminescence appearing in GaMnN upon Mg doping originates from Mn⁴⁺, an unambiguous proof is still to be presented. Under this assumption, our measurements show that the Mn⁴⁺ center must be excited via an extra-center process at 2.54 eV.

INTRODUCTION

The development of semiconductor based spintronic devices requires a ferromagnetic spin-coupling at room temperature in a dilute magnetic semiconductor (DMS). Theoretical models predict a great potential to achieve this goal for p-type doped GaMnN [1]. In order to purposefully design such a DMS, the following issues need to be clarified: (1) the charge state of Mn found in n- and p-type GaN, i.e., the position of the acceptor and donor levels formed by Mn within the band gap, (2) the electronic structure of the respective charge states, (3) details on the incorporation of Mn into the host lattice (site, strain, complex formation). In this work we address these issues by means of optical and magnetic studies on GaMnN samples with varying Mn concentrations and co-doping.

A general problem of achieving p-type GaMnN is the fact that the Mn^{3+/4+} donor level is believed to be found within the band gap compensating p-type doping [2]. This is supported by the observation of a structured luminescence band that occurs around 1 eV in Mg co-doped GaMnN and that is attributed to the internal ⁴T₂(F) — ⁴T₁(F) transition of Mn⁴⁺[3]. However to our knowledge, there is no unambiguous proof of this assignment. According to Ref. [3] the numerous zero phonon lines (ZPL's) of the emission feature are the result of different defect complexes involving Mn⁴⁺ and probably Mg. While some of our results are in good agreement with this interpretation others are rather difficult to explain. While discussing our results on this luminescence we need to take into account that it might originate from a different defect than Mn⁴⁺.

On the contrary, Mn^{3+} in GaN is well established [4-6]. The ^5D ground state of the d^4 ion is split by the tetrahedral crystal field into a $^5\text{T}_2$ ground state and a ^5E excited state. The $^5\text{T}_2 \rightarrow ^5\text{E}$ transition is observed in absorption and luminescence spectra at 1.41 eV [4-6].

EXPERIMENTAL

GaMnN films co-doped with Si or Mg were grown by metal-organic vapor deposition (MOCVD) on sapphire (0001) substrates with GaN templates [7]. The respective thickness varies between 300 and 800 μm . The Mn concentration and co-doping as determined by secondary ion mass spectroscopy can be seen in Fig. 1. For photoluminescence (PL) and transmission experiments, the samples were immersed in liquid helium. PL was excited using the 488 nm line of an Ar-ion laser. A 250 W halogen-tungsten lamp was used for polychromatic transmission spectroscopy. The emitted and transmitted light was dispersed by a 1-m Spex monochromator and detected by a nitrogen-cooled photomultiplier (PMT) with a Ge cathode and by a peltier-cooled PMT with a GaAs cathode, respectively. Electron spin resonance (ESR) measurements were carried out using a Bruker ESP 300E spectrometer operating in the X band (≈ 9.5 GHz). Temperatures were varied with an Oxford Instruments continuous-flow cryostat.

RESULTS

Figure 1 presents photoluminescence and absorbance spectra of GaMnN for samples with different Mn concentrations and Si and Mg co-doping. The luminescence feature around 1 eV is attributed to the internal transition $^4\text{T}_2(\text{F}) \rightarrow ^4\text{T}_1(\text{F})$ of the Mn^{4+} center involved in different defect complexes [3]. Where no spectrum is displayed, the sample does not show any luminescence features at all. The prominent peak found in the absorption spectra originates from the internal $^5\text{T}_2 \rightarrow ^5\text{E}$ transition of Mn^{3+} [5, 6].

In general, the presumable Mn^{4+} luminescence only shows up in Mg co-doped samples which is in agreement with the literature [8]. The appearance of the luminescence band in the non co-doped GaMnN sample ($[\text{Mn}] = 0.2\%$) is treated as an exception and is discussed below. In the cases in which this luminescence feature is present, it hardly shows any dependence on the Mn or co-doping concentration. On the contrary, the Mn^{3+} absorption is quite sensitive against the Mn concentration and co-doping. With rising Mn content the intensity and FWHM of the absorption line increase. Moreover, for high Mn concentrations and Mg or Si co-doping, the line shifts to higher energies. This effect can be explained by strain induced by the high concentration of impurities. As a result, the splitting caused by the crystal field increases slightly. Co-doping also affects the intensity of the Mn^{3+} absorption line. On the one hand, the impurity induced strain and degradation of the crystal quality lead to a broadening. On the other hand, co-doping also causes a charge transfer from Mn^{3+} into other charge states reducing the number of absorbing Mn^{3+} centers.

In order to clarify whether the samples that exhibit the luminescence band around 1 eV actually contain Mn in the 4+ charge state, we carried out ESR measurements. Unfortunately, at magnetic field strengths at which we would expect to see the Mn^{4+} resonances, the spectrum is dominated by strong signals originating from Fe, Cr and Mo impurities in the sapphire substrate outshining potentially present Mn^{4+} .

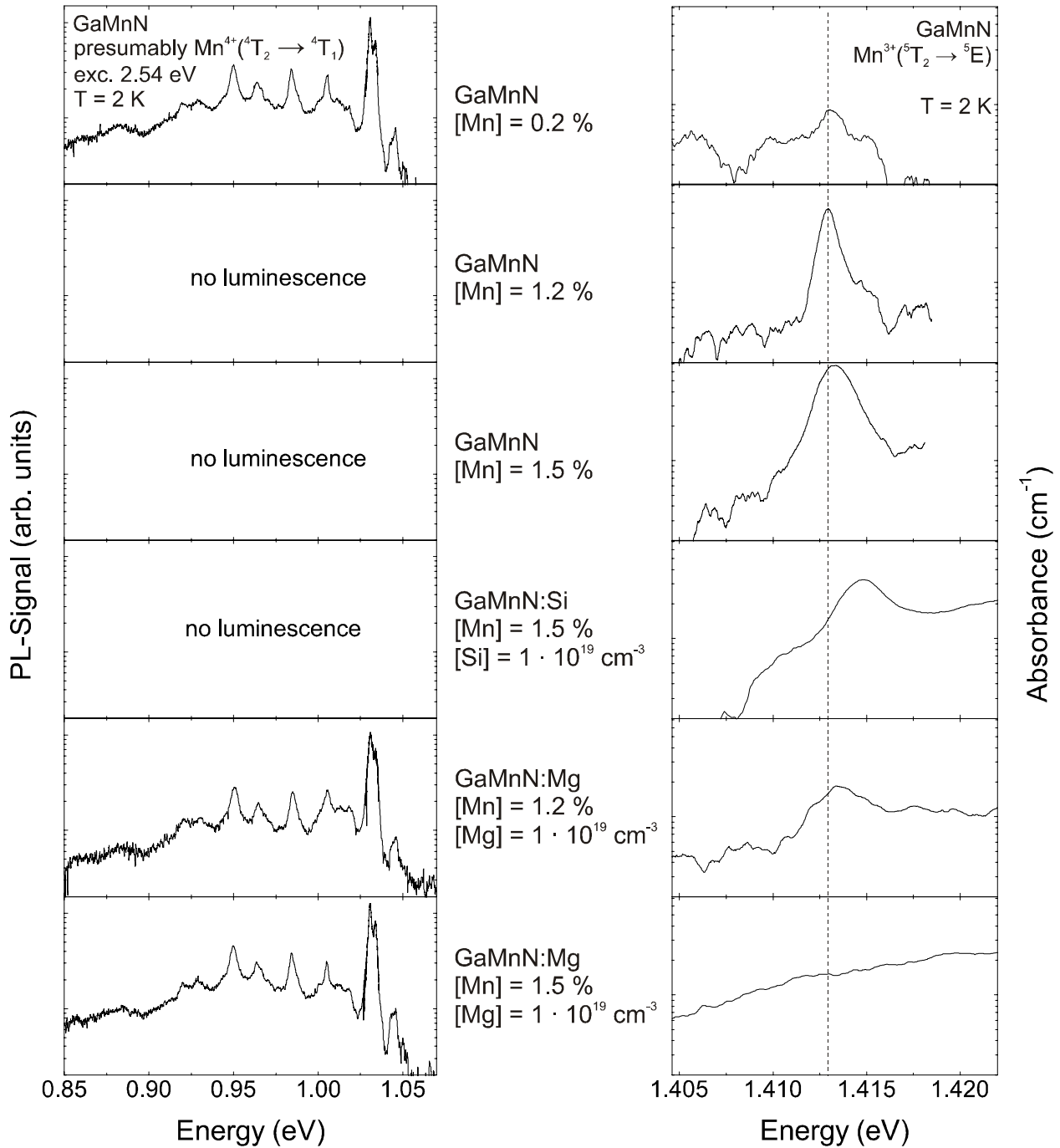


Figure 1. Photoluminescence and absorbance spectra of Si and Mg co-doped GaMnN recorded at $T = 2$ K on logarithmic scale. The PL spectra on the left display the near infrared luminescence occurring in Mg co-doped GaMnN under irradiation by the 488 nm line of an Ar laser (2.54 eV). This emission feature has been attributed to the internal $d-d$ transition in Mn^{4+} involved in different defect complexes [3]. No spectra were recorded for samples that do not exhibit any emission features in the given spectral region. The absorbance spectra on the right show the ZPL that is assigned unambiguously to the $Mn^{3+} {}^5T_2 \rightarrow {}^5E$ transition [5, 6].

DISCUSSION

For a first interpretation of the dependence of the optical properties on the Mn concentration and co-doping, we neglect the appearance of the 1-eV luminescence band in the sample containing 0.2 % Mn. Besides strain effects, the change of intensities observed in Fig. 1 can be explained consistently by a shift of the Fermi level as a result of Si and Mg co-doping. Si acting as a donor in GaN causes the Fermi energy to rise changing the charge state of Mn from isoelectric 3+ to 2+. As a result, the Mn^{3+} absorption decreases. We also observe an increase of the Mn^{2+} ESR signal upon Si doping confirming the charge transfer from Mn^{3+} to Mn^{2+} . The GaMnN sample with a Mn concentration of 1.5 % and a Si concentration of $1 \cdot 10^{19} \text{ cm}^{-3}$ shown in Fig. 1 still exhibits the Mn^{3+} absorption. Hence, both charge states 3+ and 2+ are present at the same time meaning that the Fermi level is pinned to the $\text{Mn}^{3+/2+}$ level.

P-type doping by Mg lowers the Fermi level eventually leading to a charge transfer from Mn^{3+} to Mn^{4+} . The appearance of the 1-eV emission upon Mg doping does not necessarily prove it to be related to Mn^{4+} . It might as well originate from another defect center that is activated by the low Fermi level. Alternatively, the low Fermi level may activate an involved excitation mechanism. Here again, the absorbance spectra indicate that, in the Mg co-doped sample containing 1.2 % Mn, the Fermi level is pinned to the $\text{Mn}^{3+/4+}$ donor level meaning that both charge states coexist. On the contrary, in the Mg co-doped sample with a Mn concentration of 1.5 %, the Fermi level seems to be below the $\text{Mn}^{3+/4+}$ level. As a consequence, the Mn incorporation does not completely compensate the p-type doping and all Mn centers are in the 4+ charge state. The latter sample exhibits slightly better luminescence properties suggesting that it is of better crystal quality. A resulting smaller concentration of native defects acting as donors may be responsible for the lower degree of compensation despite the higher Mn concentration.

The excitation and temperature dependent behavior of the luminescence lines clearly demonstrate the involvement of the luminescent center in different complexes. However, no such signs were found neither in the optical spectra of Mn^{3+} nor in the ESR spectra of Mn^{2+} in GaN samples grown under similar conditions. As a consequence, we conclude that Mn^{4+} has a strong tendency to form such complexes.

Since we were not able to unambiguously verify the presence of Mn^{4+} by ESR experiments, the assignment of the luminescence feature shown in Fig. 1 to an internal Mn^{4+} transition is still hypothetical. Under this assumption, the observation of the luminescence in the sample with a Mn concentration of 0.2 % and no co-doping is difficult to explain. In this sample, the Fermi level is expected to be governed by the intrinsic defects in GaN acting as donors. However, the presumable Mn^{4+} emission has not been reported for similar samples with even smaller concentrations of Mn [9]. Thus, we rule out excitation mechanisms that are only present at small Mn concentrations. As a consequence, we assume that, in our sample, unintentional p-type doping lowers the Fermi level down to the $\text{Mn}^{3+/4+}$ level where it stays pinned.

The relative independency of the luminescence intensity from the Mn and co-doping concentrations suggests that, at least for excitation at 2.54 eV, the excitation channel representing the bottleneck of the excitation process is unrelated to Mn or Mg. Hence, the origin of the broad band in the excitation spectrum of the presumable Mn^{4+} emission [10] needs to be reconsidered. A comparable situation was found for the excitation of Fe^{3+} in GaN. Here, the bottleneck is the generation of free holes via intrinsic defects appearing as a broad band in the excitation spectrum of Fe^{3+} [11, 12].

In the literature, Mn^{4+} related defects involving Mg were put forward as the origin of the luminescence [3]. However, the independency of the Mg concentration rather suggests the involvement of other defects than Mg.

For our thin GaMnN films we cannot rule out that impurities like Fe, Cr or Mo that were found in the sapphire substrate diffused into the GaMnN layer during the growth process. Also Mn or Mg may have migrated into the substrate. However, the luminescence was also observed at excitation energies above the absorption edge of GaN in thick GaMnN layers with a GaN buffer layer between them and the substrate [8].

CONCLUSIONS

A set of GaMnN samples with varying Mn concentration and Si or Mg co-doping was investigated by optical and ESR spectroscopy. For non co-doped material, the $\text{Mn}^{3+}({}^3\text{T}_2 \rightarrow {}^5\text{E})$ absorption scales with the Mn concentration and slightly shifts to higher energies due to strain at high overall doping. The dependency of the proportion of the Mn charge states 2+, 3+ and 4+ on the Si and Mg co-doping can be explained almost completely by a shift of the Fermi level. An exception is the observation of the presumable Mn^{4+} luminescence in a sample with relatively low Mn concentration and without nominal p-type co-doping. For p-type GaMnN, we demonstrated that the introduction of the $\text{Mn}^{3+/4+}$ donor can be compensated by Mg co-doping lowering the Fermi energy below the $\text{Mn}^{3+/4+}$ level. While our results are in agreement with the hypothesis that the 1-eV luminescence in Mg co-doped samples originates from Mn^{4+} involved in different complexes, this hypothesis could not be verified. The independence of the PL on the Mn concentration suggests a dominant extra-center excitation process at an excitation energy of 2.54 eV.

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