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# The $\text{Mn}^{3+/2+}$ acceptor level in group III nitrides

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Molecular-beam-epitaxy grown GaN:Mn and AlN:Mn layers with Mn concentrations around  $10^{20} \text{ cm}^{-3}$  were investigated by optical absorption and photoconductivity measurements. From electron spin resonance Mn is known to be mostly present in the neutral acceptor state in GaN without codoping. This leads to a reassignment of the optical absorption features to a charge transfer from the neutral  $\text{Mn}^{3+}$  oxidation state, either by direct photoionization at 1.8 eV or through a photothermal ionization process via an excited state at 1.42 eV above the  $\text{Mn}^{3+}$  ground state by spin-allowed  $\text{Mn}^{3+} {}^5\text{E} \rightarrow {}^5\text{T}$  internal absorption. The position of the  $\text{Mn}^{3+/2+}$  acceptor level at 1.8 eV above the valence-band edge of GaN makes the realization of carrier-mediated ferromagnetism rather unlikely in GaN:Mn. © 2002 American Institute of Physics.

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A large potential for novel device applications is anticipated for dilute magnetic semiconductor (DMS) materials exhibiting ferromagnetism above room temperature. Extrapolating the carrier-mediated magnetic interaction from GaMnAs to GaN:Mn, room-temperature ferromagnetism would be expected at doping concentrations of 5%.<sup>1</sup> This prediction triggered significant experimental efforts<sup>2–6</sup> and ferromagnetism with Curie temperatures as high as 940 K was reported for some GaN:Mn layers. However, because of possible inclusions of various  $\text{Mn}_x\text{N}_y$  phases,<sup>7,8</sup> the magnetization data alone is insufficient to verify the existence of carrier-mediated ferromagnetism. Remarkably, no *p*-type conductivity was observed in GaMnN unlike the metallic conductivity observed in GaMnAs at similar doping concentrations. According to the model of Ref. 1, itinerant holes are essential for the mediation of the long-range ferromagnetic interactions. Such a coexistence of extended holes and localized spins is enabled by an effective-mass-like  $\text{Mn}^{2+}-\text{h}^+$  acceptor complex in GaAs:Mn.<sup>9,10</sup>

In GaN:Mn, optical absorption measurements with indications for an unidentified deep gap state of Mn in GaN have been reported.<sup>6</sup> We correlate this optical absorption with electron spin resonance (ESR) and with photoconductivity experiments, which suggest that the Mn-bound holes in group III nitrides are not effective-mass-like, but are localized within the  $\text{Mn}^{3+}$  *d*-shell, in accordance with the empirical Langer–Heinrich rule for the vacuum-level-related valence-band offsets and with theoretical calculations for the gap states of GaN:Mn.

The Mn-doped GaN and AlN films investigated were grown epitaxially with a thickness of about 1  $\mu\text{m}$  on  $\text{Al}_2\text{O}_3$  substrates by plasma-induced molecular beam epitaxy with Mn concentrations around  $10^{20} \text{ cm}^{-3}$ , as determined from elastic recoil detection (ERD). Electrical measurements were performed with interdigit Ti/Al contacts with a spacing of 50

$\mu\text{m}$ . Unambiguous Hall measurements are prohibited by a resistivity above  $10^{10} \Omega \text{ cm}$  at room temperature. Microscopic information on the Mn lattice site and oxidation state was obtained by ESR, as reported elsewhere.<sup>11,12</sup> For  $\text{Mn}^{2+}$ , a large axial crystal field  $D_{\text{GaN}} = -234 \text{ G}$  is observed due to the GaN wurtzite structure, and the strong polarization of the Mn–N bonds results in an increased (negative) Fermi–contact interaction  $A_{\text{GaN}} = -69 \text{ G}$ , compared to  $A_{\text{GaAs}} = -56 \text{ G}$  for the less polar Mn–As bonds.<sup>12</sup> Whereas these ESR experiments provide important microscopic information about the localized  $\text{Mn}^{2+}$  spins, no information can be deduced about Mn-bound holes, which are absent in the case of a negatively charged acceptor.

The  $\text{Mn}^{2+}$  concentration measured by ESR is below  $2 \times 10^{18} \text{ cm}^{-3}$  in the GaN:Mn samples, indicating that less than 2% of the Mn impurities were negatively charged by the capture of residual electrons from the GaN host crystal. The number of negatively charged  $\text{Mn}^{2+}$  acceptors is increased to  $3 \times 10^{19} \text{ cm}^{-3}$  in intentionally codoped GaN:Mn:Si samples with  $[\text{Mn}] \sim [\text{Si}] \sim 3 \times 10^{19} \text{ cm}^{-3}$ . In the pure GaN:Mn samples, the remaining 98% of the Mn centers are therefore supposed to be in the neutral  $\text{Mn}^{3+}$  (or  $\text{Mn}^{2+}-\text{h}^+$ ) acceptor state. X-band ESR identification of these states has been impossible in GaN so far because both the shallow  $\text{Mn}^{2+}-\text{h}^+$  complex and the deep high-spin state of  $\text{Mn}^{3+}$  are subject to distortions by the static Jahn–Teller effect, or by residual strain.<sup>9,13,14</sup> However, superconducting quantum interference device (SQUID) measurements of the saturation of the total magnetization at 2 K and up to 7 T indicate that the majority of the Mn atoms are in a high-spin state, which is probably  $\text{Mn}^{3+}$ .

Figure 1 shows room-temperature absorption spectra of GaN:Mn and AlN:Mn samples with  $[\text{Mn}] \sim 10^{20} \text{ cm}^{-3}$ , measured with photothermal deflection spectroscopy in the region of low absorbance, and with transmission and reflection measurements at higher absorbances close to the band gap. The pure GaN:Mn samples show strong Mn-related absorption features (a broad band A with an onset  $h\nu_A \sim 1.8 \text{ eV}$ ,

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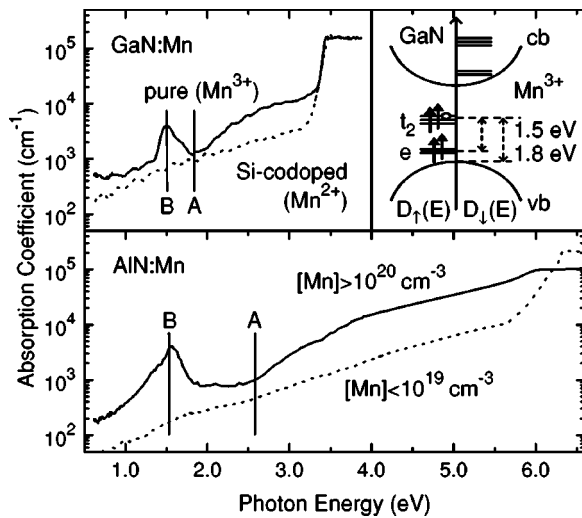


FIG. 1. Optical absorption of GaN:Mn, GaN:Mn:Si, and AlN:Mn with  $[Mn] \sim 10^{20} \text{ cm}^{-3}$ . Transition A with the onset around 1.8 eV in GaN is assigned to the direct emission of holes from  $Mn^{3+}$  acceptors to the valence band, and transition B around 1.5 eV to the internal spin-allowed  ${}^5E \rightarrow {}^5T$  transition of the deep neutral  $Mn^{3+}$  state, as shown in the inset with the spin-polarized one-electron densities of states  $D_{\uparrow}(E)$  and  $D_{\downarrow}(E)$ .

and a peak B around  $h\nu_B \sim 1.5 \text{ eV}$ ) that were tentatively assigned to  $Mn^{2+}$  in previous studies.<sup>6,15</sup> This assignment has to be revised, since much larger concentrations of  $Mn^{2+}$  are found by ESR in GaN:Mn:Si samples, that do not show the Mn-related absorption (dashed curve in Fig. 1). Rather, the initial state of both transitions seems to be the neutral acceptor  $Mn^{3+}$  or  $Mn^{2+} - h^+$ . In Refs. 6 and 15, a zero-phonon line at 1.42 eV was resolved for transition B at lower temperatures, which merges with its photon replica to a broad peak at 1.5 eV at higher temperatures. A similar absorption peak at about 1.5 eV is also observed for AlN:Mn in Fig. 1 as well as a photoionization shoulder at 2.6 eV. The relative intensities of both features are similar in both materials.

Only those absorption processes that affect the number of carriers in the bands contribute to photoconductivity measurements as shown in Fig. 2 for pure GaN:Mn samples. At all temperatures, the broad absorption band A above 1.8 eV is observed, confirming that carriers are excited directly to the valence or conduction band. This associates the energy position  $h\nu_A$  either with a  $Mn^{3+/2+}$  acceptor or a  $Mn^{3+/4+}$  donor level. Of both interpretations, the large absorption coefficient  $\alpha_{\text{max}} \sim 5 \times 10^3 \text{ cm}^{-1}$  at  $[Mn] \sim 10^{20} \text{ cm}^{-3}$  suggests hole emission from  $Mn^{3+}$  acceptors involving the  $p-d$  coupling to the valence band. Further evidence for their assignment is presented below based on the band alignment of different III-V materials. Because the energy dependence of the transition matrix elements is not known *a priori*, the energy  $h\nu_A = 1.8 \text{ eV}$  was estimated from the onset of A, assuming low-energy tails similar to those below the band gap and below the zero-phonon line of transition B. Photoconductivity experiments on AlN:Mn, similar to those shown for GaN:Mn in Fig. 2 would require very high temperatures.

The distinct behavior of the photoconductivity at different temperatures shows that transition B is not related to a direct photoionization, but to internal optical excitation followed by thermal ionization with an activation energy  $E_A \sim 0.3 \text{ eV}$  (see inset of Fig. 2). This is confirmed by the total

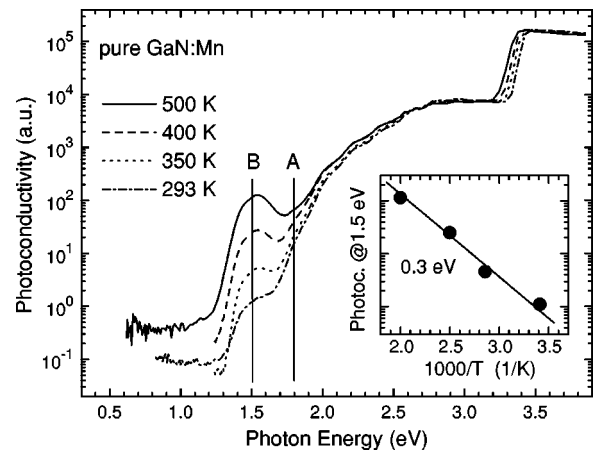


FIG. 2. Temperature dependence of the spectrally resolved photoconductivity spectra of GaN:Mn. Photoionization across the band gap is observed around 3.4 eV. At high temperatures, this threshold decreases by 0.4 meV/K, in good agreement with the numbers reported for the excitonic luminescence in Ref. 30. Absorption around 1.8 eV enables the emission of holes from deep neutral  $Mn^{3+}$  acceptors, which occurs photothermally in a two-step process B via an internal transition to an excited  $(Mn^{3+})^*$  state assigned to the zero-phonon absorption line of Ref. 7, followed by thermal emission with an activation energy  $E_A \sim 0.3 \text{ eV}$ , as seen in the inset.

energy difference  $h\nu_A = h\nu_B + E_A = 1.8 \text{ eV}$  between the final and initial state of A. To summarize, the photoionization processes in GaN:Mn have been identified as

$$(A) \quad Mn^{3+} + h\nu_A \rightarrow Mn^{2+} + h^+,$$

$$(B) \quad Mn^{3+} + h\nu_B \rightarrow (Mn^{3+})^*, \quad \text{followed by}$$

$$(Mn^{3+})^* + E_A \rightarrow Mn^{2+} + h^+.$$

A one-electron scheme for these processes is shown in the inset of Fig. 1. The tetrahedral crystal field of the surrounding N ligands splits the five  $d$  orbitals of the Mn ion into two  $e$  orbitals and three  $t_2$  orbitals. The latter are split once more by the trigonal distortion present in group III nitrides. In a covalent picture, the  $t_2$  orbitals are hybridized with those of the surrounding nitrogen atoms, shifting the occupied bonding  $t_2$  orbitals (not shown) into the valence band, and the antibonding  $t_2$  orbitals above the two nonbonding  $e$  orbitals.<sup>16,17</sup> The spin-up and spin-down levels are offset by the exchange energy  $\Delta E_{\text{ex}}$ . In the  $Mn^{3+}$  ground state with  ${}^5T_2$  symmetry, one  $t_2$  orbital is occupied by a strongly acceptor-bound hole. If additional electrons are provided via codoping, the Mn acceptor is converted into  $Mn^{2+}$  ( ${}^6A_1$ ).

The photoionization process A can be understood as hole emission from the neutral Mn acceptor into the valence band, and the internal transition B as the  ${}^5T_2 \rightarrow {}^5E$  transition between the  $e$  and  $t_2$  gap levels with the same spin orientation, consistent with the observed large optical absorption cross-section  $\sigma \sim 10^{-16} \text{ cm}^2$ . In contrast, the spin-forbidden internal transition  ${}^6A_1 \rightarrow {}^4T_1$  of  $Mn^{2+}$  or  $Fe^{3+}$  is typically observed in photoluminescence (PL) only.<sup>18</sup> In AlN, this transition has been ascribed to a green Mn-related luminescence band around 2.0 eV.<sup>19</sup> If  $\Delta E_{\text{ex}}$  were similar in GaN: $Mn^{2+}$ , the unoccupied spin-down  $e$  orbitals of  $Mn^{2+}$  would be within the conduction band similar to GaAs: $Mn^{2+}$ . However, the PL energy of a zero-phonon line ascribed to

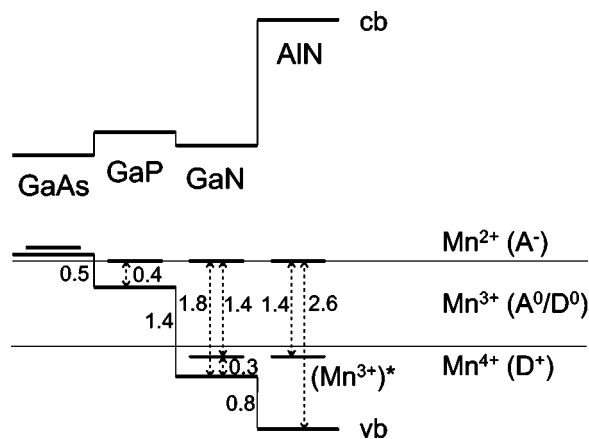


FIG. 3. Band alignment of the  $\text{Mn}^{3+/2+}$  acceptor level in different III-V materials with energy differences given in eV. The valence-band offsets have been taken from the literature (Ref. 23). A  $\text{Mn}^{3+/4+}$  donor level below the  $\text{Mn}^{3+/2+}$  acceptor level and close to the observed  $(\text{Mn}^{3+})^*$  acceptor level was predicted by *ab initio* calculations in Ref. 26.

this internal transition was reported to be as low as 1.53 eV in GaP,<sup>20</sup> so that further experimental studies are required to identify this transition in GaN:Mn.

The energy required for a charge transfer at the  $\text{Mn}^{3+/2+}$  level can be estimated from the vacuum-level-related band offsets.<sup>21,22</sup> Since the valence-band offset between GaN and GaP is known to be about  $\Delta_{\text{VB}} \sim 1.4$  eV,<sup>23</sup> the energy position of the  $\text{Mn}^{3+/2+}$  acceptor level can be extrapolated to GaN with the help of the known acceptor ionization energy  $E_{\text{GaP}} = 0.4$  eV of  $\text{GaP:Mn}^{3+}$ ,<sup>13,20,24</sup> as shown in Fig. 3. The resulting energy,  $E_{\text{GaN}} \sim E_{\text{GaP}} + \Delta_{\text{VB}} = 0.4 \text{ eV} + 1.4 \text{ eV}$ , is consistent with both photoionization processes. The same level alignment also works reasonably well for GaAs with  $E_{\text{AlN}} \sim 0.4 \text{ eV} + 2.2 \text{ eV}$ .<sup>23</sup> Although strong hybridization makes this extrapolation probably invalid for GaAs, it is interesting to note that the valence-band edge would be located above the Mn  $t_2$  orbitals in GaAs, which would make it energetically favorable for holes to occupy extended effective-mass acceptor states  $\text{Mn}^{2+} - h^+$  instead of the localized  $d$  orbitals, enabling the long-range mediation of magnetic interactions in ferromagnetic DMS.

*Ab initio* calculations based on the local-spin-density approximation<sup>16,17,25–28</sup> obtain a similarly deep  $\text{Mn}^{3+/2+}$  acceptor and  $\text{Mn}^{3+/4+}$  donor level in GaN, which would hinder the presence of free electrons or holes in GaN:Mn. This is consistent with the high resistivity also reported in Ref. 6. The optical peak absorption around 1.3 eV calculated in Ref. 25 agrees well with the zero-phonon line at 1.42 eV of Ref. 6. In the codoped GaN:Mn:Mg samples of Ref. 29, a large number of PL transitions was observed around 1.1 eV, which could be interpreted as the spin-allowed  $^4T_2 \rightarrow ^4T_1$  internal transitions of the  $3d^3$  system of ionized  $\text{Mn}^{4+}$  donors.<sup>24</sup>

In conclusion, the optical absorption features of GaN:Mn were assigned to direct (A) and photothermal (B) ionization

to the valence band. The  $\text{Mn}^{3+/2+}$  acceptor level is located close to the middle of the GaN band gap, suggesting that the acceptor wave function is very different from an effective-mass state like the  $\text{Mn}^{2+} - h^+$  complex in GaAs:Mn. This makes the assumption of carrier-mediated ferromagnetism in GaN:Mn rather unlikely.

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