Electronic and Magnetic Properties of GaN:Fe

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Here we report on metal-organic chemical vapor deposition growth of GaN:Fe and its characterization by means of high-resolution X-ray diffraction, secondary ion mass spectroscopy, photoluminescence, electron spin resonance, and magnetization measurements. Both electron spin resonance and photoluminescence demonstrate the existence of Fe in the isolated $3d^5$ (Fe^{3+}) state. The magnetization measurements show, apart from Curie paramagnetism due to Fe^{3+}, a temperature independent contribution which we attribute tentatively to van Vleck paramagnetism of Fe in the 2+ state. We conclude that the Fe ions coexist in two charge states in the investigated samples. The fraction of Fe^{3+} ions was found to increase upon additional co-doping with Mg acceptors, both in ESR as well as in magnetization. In the latter one a significant reduction of the temperature independent magnetic moment was simultaneously observed. High field magnetization data yield Fe concentration in the $x \approx 10^{-3}$ range, which compares well with secondary ion mass spectroscopy results.

Introduction

Transition metal doped GaN is one of the predicted candidates for obtaining Zener-type ferromagnetism with T_c > 300K. As a necessary condition, the transition metal ion should be incorporated on isolated (*i.e.* not clustered) substitutional sites and exhibit a high-spin ground state. So far, the Mn dopant in GaN has been investigated thoroughly, as it was expected to act as an acceptor providing besides the S = 5/2 spin also the high hole concentration necessary to mediate the exchange coupling among the Mn ions. More recently it has been shown, however, that unlike Mn in GaAs the 3+/2+ acceptor level of Mn in GaN is deep (>1.7 eV above the valence band edge) and the hole is localized on Mn, leaving it in the $3d^4$ state. Hence, Zener magnetism is not expected for the GaN:Mn system. In this respect the GaN:Fe seems to be more promising, especially with p-type co-doping.

Experimental

Sample Preparation

All samples have been fabricated in an AIXTRON 200RF horizontal tube metal-organic chemical vapor deposition (MOCVD) reactor. The growth of the device quality layers was carried out on c-plane sapphire substrates by using TMGa, NH, Cp Fe, Cp Mg and SiH as precursors and H as carrier gas. The deposition process has been performed according to a well established procedure consisting of substrate nitridation, low temperature (540 °C) GaN nucleation layer growth, annealing of the nucleation layer under

NH leading to re-crystallization and GaN buffer growth (1 µm). On top, iron doped GaN layers (1 µm) were grown at different temperatures (800 – 1050°C) and Cp_2Fe fluxes (50 – 200 scams).

Measurements

Crystal Quality

High-resolution x-ray diffraction measurements were performed routinely on the grown samples. Rocking curves showed a full width at half maximum (FWHM) of the order of 260 up to 320 deg, which is comparable to the state-of-the-art device material. Increasing the iron flux resulted in a broadening of the GaN (0002) reflex.

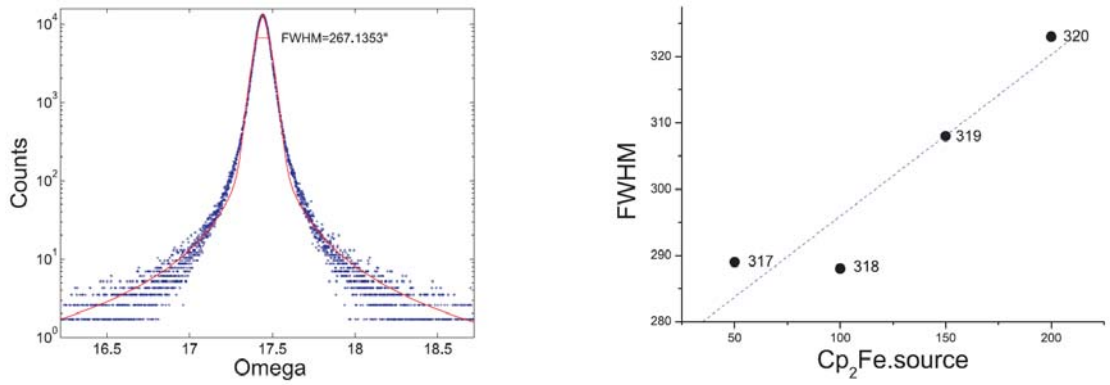

Fig. 1: Rocking curve of the GaN (0002) reflex measured for GaN:Fe epilayers (left panel) and the FWHM as a function of Fe flux (Cp_2Fe) (right panel).

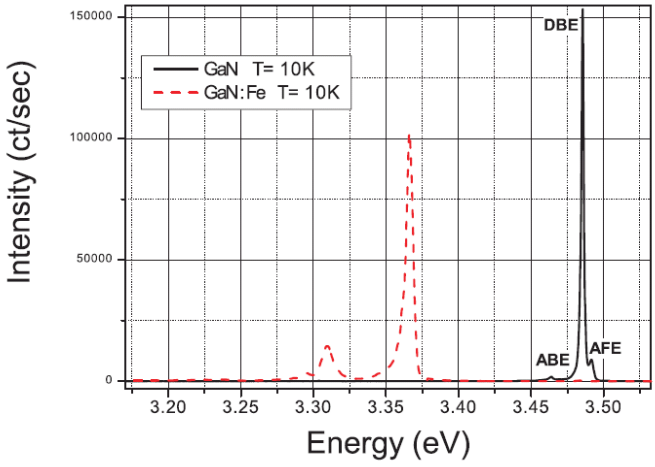

Fig. 2: Photoluminescence spectra of GaN and GaN:Fe samples showing excitonic transitions: AFE, DBE, ABE, as well as unidentified lines due to the Fe dopant.

Photoluminescence Measurements

Figure 2 shows a comparative photoluminescence (PL) study of pure GaN and GaN:Fe. The peaks were identified as an acceptor-free exciton (AFE), a donor bound exciton (DBE) as well as an acceptor bound exciton (ABE). The DBE may be bound to Si or O, which lead to the unintentional n-type behavior of pure GaN, the ABE may be bound to Mg [1]. The peaks assigned to iron have not been identified so far.

Figure 3 shows an infrared PL band at 1.289 eV, that is assigned to a $^4T_1(G)$ - $^6A_1(S)$ crystal field transition of Fe^{3+} (d^5 configuration) [2]. The strong crystal field is typical for GaN due to its small lattice constant and the high electronegativity of nitrogen.

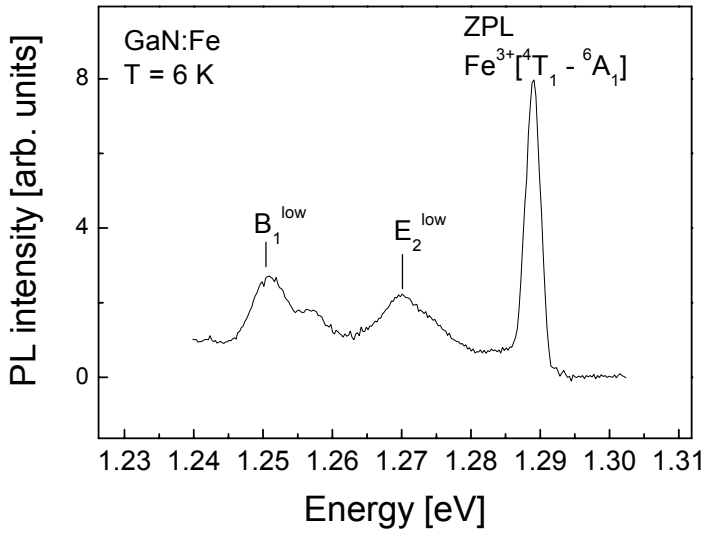

Fig. 3: Photoluminescence spectrum of an intracenter transition $^4T_1(G)$ - $^6A_1(S)$ within $Fe^{3+}(d^5)$ configuration of iron in GaN. The zero-phonon line at 1.289 is accompanied by GaN phonon replicas. E_2^{low} and B_1^{low} GaN phonons are marked.

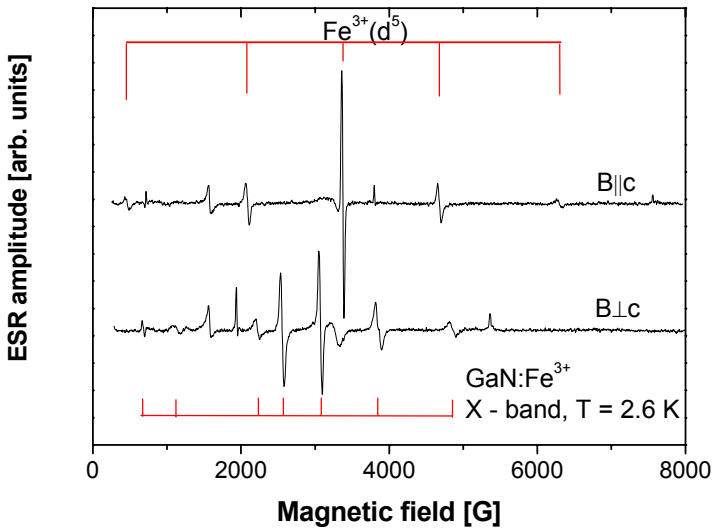

Fig. 4: ESR spectra of $Fe^{3+}(d^5)$ in wurtzite GaN epilayers collected in B || c and B $\perp$ c configuration.

Electron Spin Resonance Measurements

Electron spin resonance (ESR) experiments show the presence of $Fe^{3+}(d^5)$ substituting Ga in all studied GaN samples. The examples of ESR spectra collected at the magnetic field parallel or perpendicular to the GaN c-axis are shown in Fig. 4. The amplitude of the ESR signal (proportional to the number of Fe^{3+} centers), increases after co-doping with Mg acceptors. This is the indication of a mixed valence state of the Fe impurity in GaN samples – *i.e.*, the co-existence of the $Fe^{3+}(d^5)$ and most probably the $Fe^{2+}(d^6)$ charge states.

Magnetic Properties

Magnetization measurements of GaN:Fe epilayers were performed by a superconducting quantum interference device magnetometer (SQUID). Figure 5 shows the temperature dependence of the magnetization as obtained from measurements at constant magnetic field on GaN:Fe with different Fe content. In addition to a Curie type of magnetism due to $Fe^{3+}(d^5)$ there is clearly a temperature independent contribution which we attribute to Van-Vleck magnetism, most possibly originating from $Fe^{2+}(d^6)$ configuration of iron. In some of the measured samples an additional ferromagnetic contribution to the magnetization was observed. However, there is no experimental evidence so far that this fraction originates from the homogeneously doped GaFeN layer.

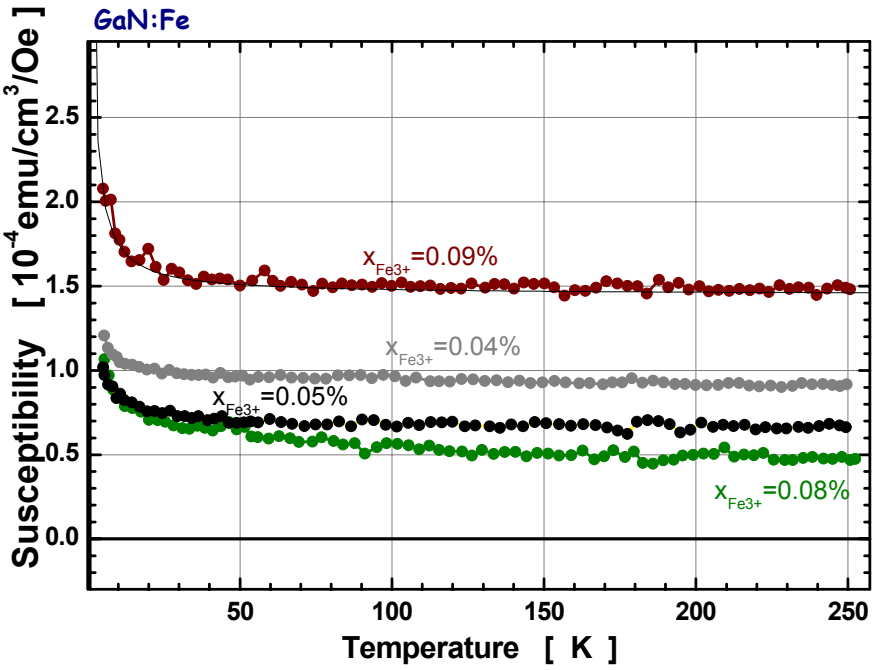

Fig. 5: Susceptibility (M/H) of GaN:Fe as a function of temperature measured at 10000 Oe. The paramagnetic contribution due to Fe^{3+} and the Van Vleck paramagnetism due to Fe^{2+} may be distinguished.

Conclusion

Both ESR and PL demonstrate the existence of Fe in the isolated $3d^5$ (Fe^{3+}) state. The magnetization measurements show, apart from Curie paramagnetism due to Fe^{3+}, a temperature independent contribution which we attribute tentatively to van Vleck para-

magnetism of Fe in the 2+ state. The fraction of Fe^{3+} ions was found to increase upon additional co-doping with Mg acceptors, both in ESR as well as in magnetization. In the latter one a significant reduction of the temperature independent magnetic moment was simultaneously observed. High field SQUID data yield Fe concentration in the $x \cong 10^{-3}$ range, in agreement with SIMS results. A small ferromagnetic contribution to magnetization was also observed, but as far there is no evidence that this fraction originates from homogeneous GaFeN.

References

[1] B. Monemar: “Bound excitons in GaN”, J. Phys: Condens. Matter, Vol. 13, 2001, pp. 7011-7026.

[2] R. Heitz, P. Maxim, L. Eckey, P. Thurian, A. Hoffmann, I. Broser, K. Pressel, and B. K. Meyer: “Excited states of Fe^{3+} in GaN”, Phys. Rev. B, Vol. 55, 1997, pp. 4382–4387.