Magnetic Resonance Studies of GaN:Fe

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We investigate one of the candidates for room temperature ferromagnetism, GaN:Fe grown by MOCVD, by means of electron spin resonance. In heavily Fe doped material we observe in addition to the signal due to isolated, substitutional Fe^{3+} ferromagnetic resonances with outstanding sensitivity. The anisotropy of the spectra allows to conclude on the crystal structure of the precipitates and we identify three different kinds. One of them most likely is Fe_4N.

Introduction

Following the prediction of carrier mediated, room-temperature ferromagnetism in wide-band-gap, diluted magnetic semiconductors substantial effort has been devoted to fabrication and investigation of transition-metal doped oxides and nitrides (GaMnN, GaFeN, AlCrN, ZnVO, ZnCoO). Numerous papers report ferromagnetic signatures of such materials, with Curie temperatures ranging from a few up to several hundred Kelvin. The highest apparent Curie temperatures are found, however, in samples in which the carrier mediated mechanism is not operative, so the origin of the ferromagnetism is not really understood. Here we report on magnetic resonance studies performed on a series of GaN:Fe samples grown by MOCVD at identical conditions but with the iron precursor flow rates differing in a wide range. These studies allowed us to determine the solid solubility limit of substitutional Fe in GaN as well as to demonstrate the presence of ferromagnetic precipitates of three different phases.

Experiments and Results

In all studied structures, independent of the iron concentration, a paramagnetic resonance signal of isolated, substitutional Fe^{3+} ions is observed. Figure 1(a) shows the concentration of Fe^{3+} estimated from the EPR signal intensity (circles) compared to the total Fe concentration measured by SIMS (triangles) as a function of the iron source flow rate for two series of samples (full and open symbols). With increasing iron precursor flow rate – up to about 200 sccm – the concentration of substitutional Fe^{3+} ions increases continuously, but at a lower rate than the total iron concentration in the sample. Above 200 sccm the Fe^{3+} content is reduced and considerable fluctuations are observed from sample to sample. We relate this effect to the change of the Fermi level position and, hence, greater occupancy of the Fe^{2+} charge state. In the high doping regime a drastic increase of the oxygen donor concentration, by about two orders of magnitude as compared to that of GaN:Fe grown at low Cp_2Fe flow rates, is detected by SIMS. The oxygen accumulation seems to be correlated with the enhanced sample roughness.

The algorithm used so far is based on peak maxima detection and the maximum intensity is interpreted as the peak center defining the relative correction shift. In this paper we present a novel algorithm which takes into account also the surrounding of the peak

maxima and results in more precise information on growth rate, composition and crystal quality.

The presence of Fe^{2+} ions cannot be determined directly by magnetic resonance since the ground state is a spin singlet state and there is no resonance transition observed in the X-band. We have detected a 20% increase of the EPR signal intensity of Fe^{3+} under illumination with light of energies above 1.2 eV, confirming the presence of Fe in the 2+ charge state, but no estimations of the actual concentration can be made from such experiments. Therefore, in order to estimate the total concentration of substitutional Fe ions in the sample, we have analyzed the width of the EPR absorption line of Fe^{3+}. At very low concentrations, the linewidth, σ, should be mainly governed by interactions with nuclear magnetic moments of the Ga and N isotopes, however, with increasing Fe concentration dipole-dipole interactions between iron ions should lead to line broadening. The broadening consists of two contributions: one due to the interaction with other 3+ ions and one related to the interaction with Fe ions in the 2+ charge state. Both contributions depend on the i^{th} to j^{th} ion distance, r_{ij}, as r_{ij}^{-3}. Assuming that the ions as well as their charges are uniformly distributed in the lattice, one can expect a linear correspondence between the dipolar broadening σ-σ_0 and the Fe concentration. Figure 1(b) gives the linewidth broadening as a function of iron precursor flow rate for the -1/2 → 1/2 transition of Fe^{3+} at B || [0001] for the same samples shown already in Fig. 1(a). As it can be seen, the linewidth increases continuously with the Cp_2Fe flow rate up to 250 sccm and saturates above this value. In the low doping regime we obtain exactly the same slope for the dipolar line broadening versus Cp_2Fe flow rate as that for the SIMS concentration. This allows us to set the solubility limit for substitutional iron in GaN at our growth conditions to 1.8×10^{20} cm^{-3}, *i.e.*, 0.4% [1].

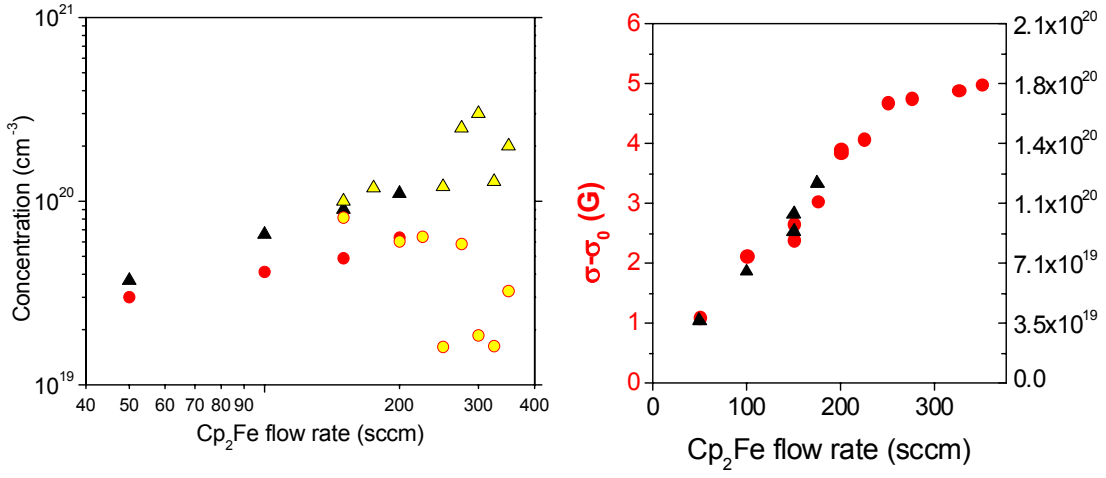

Fig. 1: (a) Fe^{3+} concentration estimated from the EPR signal intensity (circles) as compared to the total Fe concentration measured by SIMS (triangles) vs. the iron precursor flow rate. Full and open symbols identify two different sample series, grown at the same conditions. (b) EPR line broadening (left y-axis) as a function of the iron precursor flow rate (circles) for σ_0 = 12 G. The SIMS concentration (right y-axis, in units of cm^{-3}) at low flow rates, denoted by triangles, is shown for comparison.

In highly Fe doped samples additional resonance transitions are observed. In contrast to the Gaussian shaped paramagnetic resonance signals of Fe^{3+} the line shape of the new signals is Lorentzian. The signal amplitudes are almost temperature independent, as expected of a ferromagnet well below the Curie temperature. However, the angular dependence of the ferromagnetic resonance (FMR) peak positions, shown in Fig. 2,

reveals neither the sample shape anisotropy nor the hexagonal crystalline anisotropy of GaN. In contrast, the peak positions are very well described assuming cubic crystalline anisotropy only. This indicates that we deal with almost spherically shaped ferromagnetic precipitates of a cubic phase.

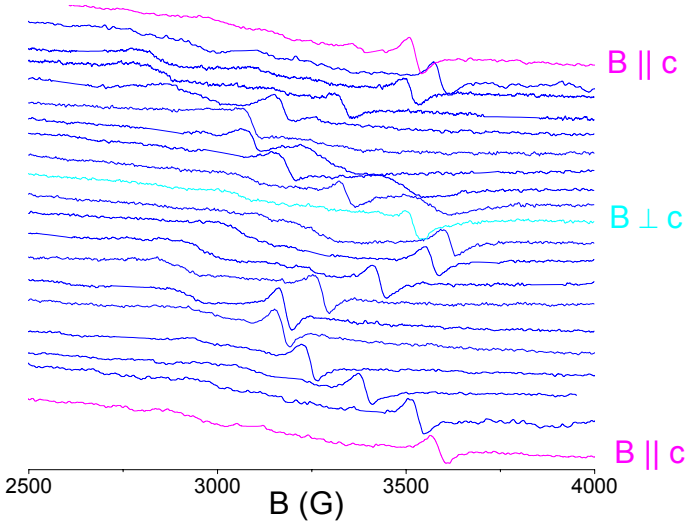

Fig. 2: As measured ferromagnetic resonance spectra at room temperature. The magnetic field is rotated in the $(1\bar{1}00)$ plane of GaN.

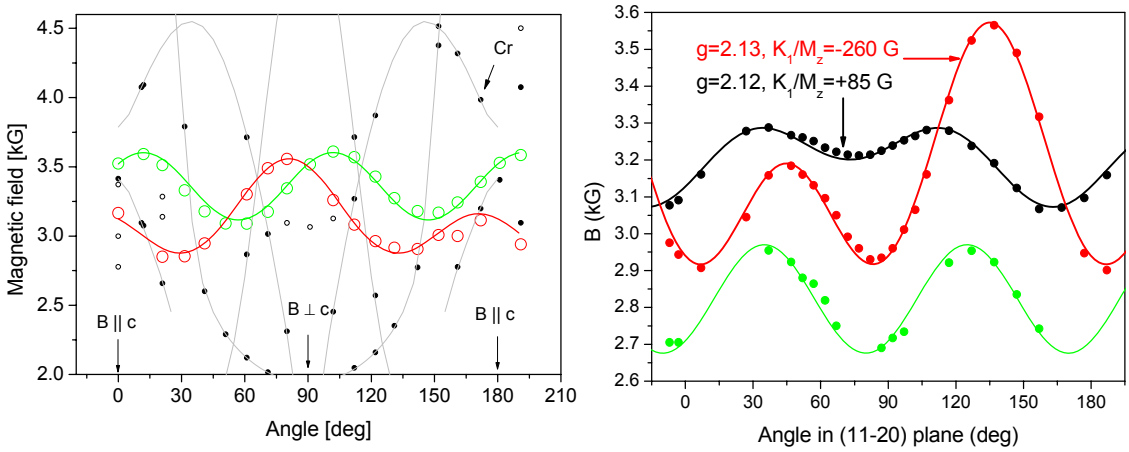

Fig. 3: Angular dependencies of FMR signals in two samples grown at the same conditions.

Conclusions

Altogether, we have identified three different kinds of ferromagnetic precipitates in GaN:Fe. The first kind has a negative first order cubic anisotropy constant, K_1, with the easy magnetization, M, direction along [111]. This is expected for ferromagnetically ordered ions occupying *fcc* lattice sites. In addition, the value of K_1/M=-260 G, determined from the fit of the angular dependence of the FMR peak positions (red lines in

Fig. 3) is consistent with that of *fcc* Fe_4N. The Fe_4N precipitates grow preferentially with a [100] axis along one of the in-plane crystallographic axes of GaN. The second kind of precipitate has a positive cubic anisotropy constant and an easy magnetization axis along [100], like bcc Fe. However, the determined value of K_1/M=85 G (black line in Fig. 3) is considerably smaller than 270 G observed in bulk Fe. This may be due to possible size effects. We also detected ferromagnetic precipitates growing with one of the [100] directions along the in-plane crystallographic axes of GaN. Here (green line in Fig. 3) we can only estimate the absolute value of $|K_1/M|$=200 G and, hence, cannot determine the exact crystallographic structure. This value, however, is very close to that expected for magnetite, Fe_3O, which has a stable cubic phase at room temperature. Moreover, the FMR peak positions were found to depend strongly on temperature in the region close to 200 K and disappear at lower temperatures, consistent with the transition of magnetite to a tetragonal symmetry phase.

The magnetic moment of each kind of precipitate estimated from the FMR signal amplitude is of the order of 10^{12} Bohr magnetons, which is well below the SQUID detection limit.

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References

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