Paramagnetic GaN:Fe and Ferromagnetic (Ga,Fe)N: Relation between Structural, Electronic and Magnetic Properties

A. Bonanni[1], C. Simbrunner[1], M. Kiecana[2], Tian Li[1], M. Wegscheider[1], A. Navarro-Quezada[1], M. Quast[1], H. Przybylinska[2], T. Dietl[2]

[1]Institut für Halbleiter- und Festkörperphysik, Johannes Kepler Universität Linz, A-4040 Linz,

[2]Institute of Physics, Polish Academy of Sciences, Warsaw, Poland

GaN:Fe and (Ga,Fe)N layers have been grown by means of metalorganic chemical vapor deposition on c-sapphire substrates and thoroughly characterized via high-resolution x-ray diffraction, transmission electron microscopy (TEM), spatially-resolved energy dispersive X-ray spectroscopy (EDS), secondary-ion mass spectroscopy, photoluminescence, Hall-effect and SQUID magnetometry. A combination of TEM and EDS reveals the presence of coherent nanocrystals, presumably Fe_xN with the composition and lattice parameter imposed by the host. In layers with iron content $x > 0.4\%$ the presence of ferromagnetic signatures, such as magnetization hysteresis and spontaneous magnetization, have been detected. The ferromagnetic-like response is shown to arise from the (Ga,Fe)N epilayers, it increases with the iron concentration, it persists up to room temperature, and it is anisotropic.

In recent years, it has become more and more clear that wide band-gap semiconductors and oxides doped with transition metals (TM) constitute a new class of materials system exhibiting magnetic properties whose origin and methods of control are still not understood [1]. While extensive studies have been conducted on (Ga,Mn)N as promising workbench for future applications in spintronics, only little is known about (Ga,Fe)N. In the attempt to compensate this gap, we have carried out a comprehensive study [2] of the GaN:Fe (below the solubility limit of Fe into GaN at our growth conditions) and (Ga,Fe)N materials systems, beginning with a careful on-line control of the metalorganic chemical vapor deposition (MOCVD) process and proceeding with a possibly thorough investigation of the structural, electrical, optical and magnetic properties in order to shed new light into the mechanisms responsible for the paramagnetic and high-temperature ferromagnetic response of these novel material.

The studied epilayers have been fabricated in an AIXTRON 200RF horizontal-tube MOCVD reactor. All structures have been deposited on c-plane sapphire substrates according to a well established growth procedure [3]. The employed reactor offers the unique possibility of controlling in real time the deposition process via simultaneous on-line spectroscopic ellipsometry and X-ray diffraction [4]. A combination of transmission electron microscopy (TEM) and spatially resolved energy dispersive X-ray spectroscopy (EDS) analysis reveals the presence of coherent nanocrystals, presumably Fe_xN with the composition imposed by the host, like the one reported in Fig. 1. From both TEM and secondary ion mass spectroscopy (SIMS) studies, it is stated that the density of nanocrystals, and thus the Fe concentration increases towards the sample surface.

According to Hall effect measurements, electrons from residual donors are trapped by mid-gap Fe acceptor states in the limit of iron content $x < 0.4\%$, indicating that the concentration of Fe^{2+} ions increases at the expense of Fe ions in the 3+ charge state. This effect is witnessed by photoluminescence measurements as changes in the intensity of

the Fe^{3+}-related intra-ionic transition, which can be controlled by co-doping with Si donors and Mg acceptors. In this regime, EPR of Fe^{3+} ions and Curie-like magnetic susceptibility are observed. As a result of the spin-orbit interaction, Fe^{2+} does not produce any EPR response. However, the presence of Fe ions in the 2+ charge state may account for a temperature-independent Van Vleck-type paramagnetic signal that we observe by SQUID magnetometry.

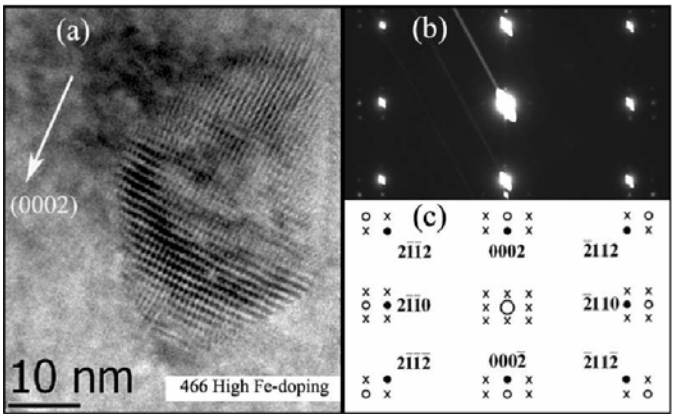

Fig. 1: (a) Elongated nanocrystal observed in an HRTEM image of Moiré fringes contrast. (b) SADP pattern acquired in the region around the precipitate along the (1010) zone axis; (c) the corresponding schematic graph for indexing of the diffraction spots.

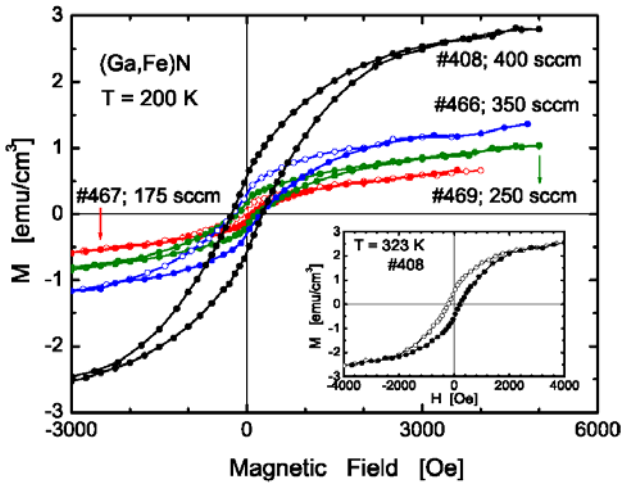

Fig. 2: Magnetization at 200 K for a series of (Ga,Fe)N samples with various Fe content (solid symbols). Inset: above room temperature M(H) for a sample with 3% Fe content.

Surprisingly, at higher Fe concentrations, the electron density is found to increase substantially with the Fe content. The co-existence of electrons in the conduction band and Fe in the 3+ charge state is linked to the gradient in the Fe concentration. In layers with iron content x > 0.4% the presence of ferromagnetic signatures, such as magnetization hysteresis and spontaneous magnetization, have been detected. A set of precautions has been undertaken in order to rule out possible sources of spurious ferromagnetic contributions. Under these conditions, a ferromagnetic-like response is shown to arise from the (Ga,Fe)N epilayers, it increases with the iron concentration, it persists up to

room temperature, and it is anisotropic – i.e., the saturation value of the magnetization is higher for in-plane magnetic field.

According to the findings summarized in Fig. 2, the ferromagnetic signal does not diminish remarkably when the temperature is increased to 200 K, and it persists up to above room temperature, as shown in the inset. The set of magnetization curves obtained in the full available temperature and field range allows to establish the temperature variation of spontaneous magnetization MS, determined from the Arrot plot, as depicted in Fig. 3. If the ideal Brillouin MS(T) dependence is assumed, the data displayed in the inset point to an apparent Curie temperature T_C of ~ 500 K.

We link the presence of ferromagnetic signatures to the formation of Fe-rich nanocrystals, as evidenced by TEM and EDS studies. This interpretation is supported by magnetization measurements after cooling in- and without an external magnetic field, pointing to superparamagnetic properties of the system.

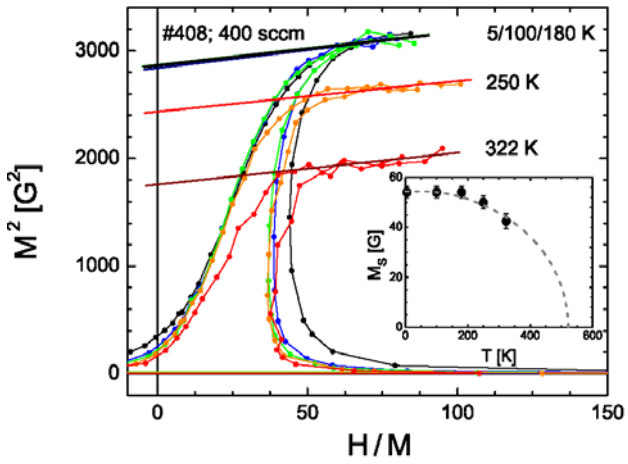

Fig. 3: Determination of the spontaneous magnetization at various temperatures obtained by plotting the square of the magnetization vs. the ratio of the magnetic field to the magnetization (Arrot plot). The inset shows the established spontaneous magnetization as a function of temperature. The extrapolation leads to an apparent Curie temperature of 500 K.

From our findings, we can argue that the high temperature ferromagnetic response due to spinodal decomposition into regions with small and large concentration of the magnetic component is a generic property of diluted magnetic semiconductors and diluted magnetic oxides showing high apparent Curie temperature.

References

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