	Experiment title: Where do the holes reside in (Ga,Fe)N doped with Mg?	Experiment number: HS-3919
Beamline: BM08	Date of experiment: from: 2009-09-17 to: 2009-09-24	Date of report: 2010-02-15
Shifts: 18	Local contact(s): Francesco d'Acapito	<i>Received at ESRF:</i>
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Report

The x-ray absorption fine structure experiment n. HS-3919 is conducted at the Italian CRG beamline “GILDA” (BM08) on a series of (Ga,Fe)N:Mg magnetic semiconductors produced at the Institute for Semiconductors and Solid State Physics, Johannes Kepler University (Linz, Austria) via metal-organic vapour phase epitaxy (MOVPE) as described elsewhere [1]. The experiment is conducted in fluorescence mode at Fe K-edge (7112 eV) with a double Si[311]-equipped sagittally focusing monochromator and a pair of Pd mirrors for harmonics rejection. The data are collected at room temperature with 1° incidence angle and the polarization vector perpendicular to the GaN *c*-axis. During the allocated 18 shifts, both near-edge (XANES) and extended (EXAFS) spectra are collected on a series of six samples as described in Tab. 1 and, despite 8 shifts lost due to technical failures of the beam-line equipment (monochromator refrigerating system), the resulting acquired data present a good signal-to-noise ratio as shown in Fig. 1. This has been possible collecting several spectra (≈ 4) for each sample and manually removing the glitches due to Bragg diffraction or excluding the fluorescence channels affected by distortions due to secondary effects as standing-waves.

Sample #	Cp ₂ Fe (sccm)	TMGa (sccm)	T _g (°C)
995	200	12	850
993	300	12	850
618	100	12	950
873	100	12	950
615	200	12	950
875	300	12	950

Table 1: Main growth parameters for the GaFeN:Mg characterized samples: ferrocene (Cp₂ Fe) and trimethylgallium (TMGa) flow rates in standard cubic centimeters per minute (sccm) and the growth temperature (T_g). The cyclopentadienyl-Mg source is kept at 300 sccm.

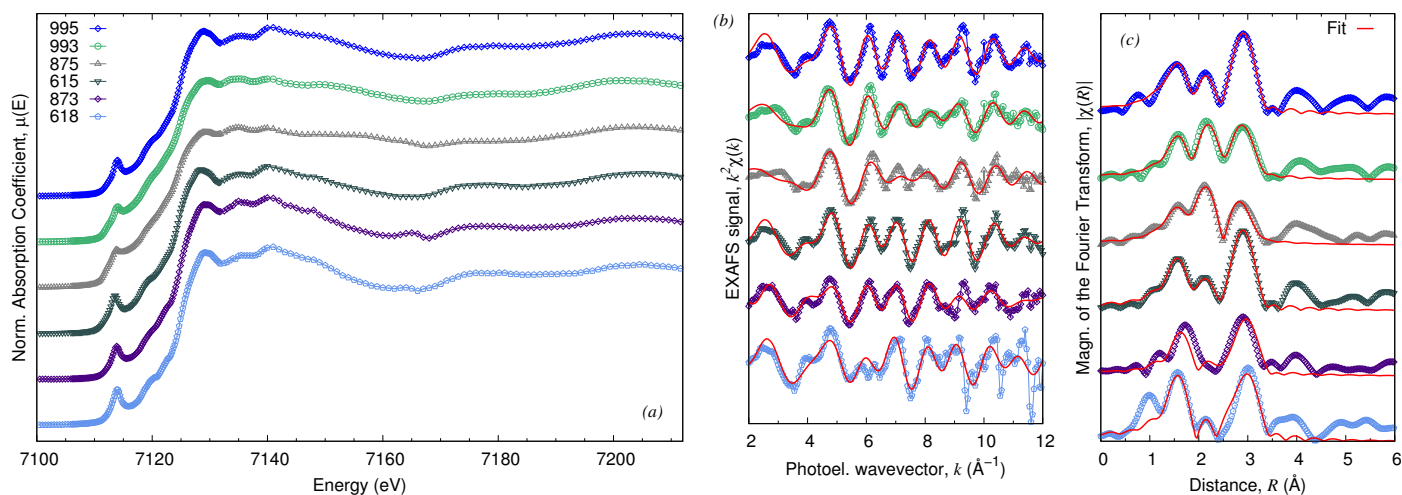


Figure 1: (a) XANES part of the collected average spectra; (b) extracted EXAFS signal and (c) Fourier-transformed data with relative best fits (red lines).

The preliminary analysis has been focused in determining the position of the pre-edge peak(s) in the XANES spectra in order to get information on the Fe valence state and the Fe-Fe contribution in the EXAFS signal in order to have an idea of the precipitation level or chemical aggregation as a function of the investigated growth parameters. Regarding the XANES, only one pre-edge peak is found from a Gaussian fit of the background-subtracted spectra (using an *arctan*-like function) with a stable position at ≈ 7114 eV (second column in Tab. 2), suggesting a Fe^{3+} valence state. For the EXAFS part, the fine structure, $\chi(k)$, is extracted using the VIPER software (Fig. 1(a)) and the data analysis is conducted using the IFEFFIT package in the Fourier transformed (FT) R -space obtained filtering the k^2 -weighted $\chi(k)$ signal using Hanning window in the k -range [3.0–11.0] \AA^{-1} with slope parameter $dk=1$. A simple “3-distances” theoretical model is used to fit the first three main peaks visible in the in the FT spectra (Fig. 1(c)) using the Fe-N, Fe-Fe and Fe-Ga single scattering paths calculated with the FEFF8 software from Fe substitutional in GaN (Fe_{Ga}) and the $\epsilon\text{-Fe}_3\text{N}$. The global amplitude factor, S_0^2 , is kept fixed at 0.9 during the fit, while the free parameters consists in: a common correction to the chosen edge energy $E_0=7118$ eV (ΔE_0) and, for each theoretical paths, the coordination number (N_i), the distance (R_i) and the Debye-Waller factor (σ_i). The results of this model are plotted in Fig. 1(b),(c) and reported quantitatively in Tab. 2. Apart the 100 sccm Cp_2Fe samples where only the Fe_{Ga} phase is present, in all other probed samples a Fe-Fe coordination is found and increases with the Fe concentration and growth temperature. In addition, from the R_{Fe} distance it is possible to state that the Fe_xN precipitation is predominant (crystallographic: ≈ 2.75 \AA) while in one case (615) the shorter distance suggests a metallic inclusion (crystallographic: ≈ 2.55 \AA).

Sample #	XANES (eV)	ΔE_0 (eV)	N_{N}	N_{Fe}	N_{Ga}	R_{N} (\AA)	R_{Fe} (\AA)	R_{Ga} (\AA)	σ_{N} (10^{-3}\AA^2)	σ_{Fe} (10^{-3}\AA^2)	σ_{Ga} (10^{-3}\AA^2)
995	7113.6(4)	0(2)	2.6(6)	2(1)	8(3)	1.95(4)	2.70(8)	3.14(4)	5(3)	10(8)	8(3)
993	7113.8(4)	-0(3)	1.5(6)	4(2)	4(3)	1.94(5)	2.75(8)	3.13(7)	2(1)	12(8)	6(4)
875	7113.6(4)	-5(3)	1.4(8)	5(2)	2(2)	1.90(7)	2.75(7)	3.01(7)	3(2)	11(8)	3(2)
615	7113.5(4)	0(1)	2.1(4)	1.4(6)	9(2)	1.96(2)	2.53(4)	3.14(3)	2(1)	6(5)	8(4)
873	7113.8(4)	4(3)	1.6(9)	-	10(4)	2.07(7)	-	3.25(9)	4(2)	-	-
618	7113.9(4)	3(3)	2.4(8)	-	12(3)	1.97(5)	-	3.29(7)	4(3)	-	-

Table 2: Results of the preliminary quantitative analysis of the XANES (position of the pre-edge peak) and EXAFS (3-distances model described in the text).

In conclusion, the main results found from this preliminary analysis are that, to respect the previously studied (Ga,Fe)N [2], the Mg co-doping does not introduce a change in the Fe valence state, being stable in a Fe^{3+} configuration, while enhances the precipitation in additional phases or chemical inhomogeneities coexisting with the main Fe_{Ga} phase. These results are in line with recent synchrotron x-ray diffraction measurements [3] that, identifying the precipitated phases, will permit to extend the present analysis to multiple scattering contributions and have a better description of the local environment to better understand the role played by the Mg co-doping on the Fe solubility limit in GaN.

References

- [1] A. Bonanni *et al.*, *Phys. Rev. B* **75**, 125210 (2007).
- [2] M. Rovezzi *et al.*, *Phys. Rev. B* **79**, 195209 (2009).
- [3] R. T. Lechner *et al.*, ESRF report n. SI-1797 (2009).