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Element specific investigations of the structural and magnetic properties of Gd:GaN

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The authors present element specific measurements of the x-ray linear dichroism and the x-ray magnetic circular dichroism (XMCD) on Gd:GaN samples. They can show that the majority of the Gd dopant atoms goes to substitutional Ga sites and that a small XMCD is detectable for Gd. There are significant deviations of the magnetic hysteresis recorded for Gd compared to superconducting quantum interference device measurements. Our measurements show that the magnetic signal from the Gd dopant atom itself is rather small highlighting the role of magnetic contributions of the GaN host crystal. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2750542]

Dilute magnetic semiconductors (DMS) are considered to be useful materials for spintronic applications. However, the origin of the long range magnetic order in DMS materials has not yet been adequately understood. Recently long range magnetic order above room temperature has been demonstrated for the dilute magnetic nitride (DMN) Gd:GaN even in the very dilute limit of the order of 10^{16} at./cm^3.[1,2] This phenomenon is accompanied by a huge effective magnetic moment per Gd atom an effect which is even more pronounced in Gd-ion-implanted GaN.[3] However, at higher Gd concentrations the effective magnetic moment drops to the well-known atomic value.[1,3] The occurrence of magnetic order was phenomenologically explained by large spheres of influence surrounding the Gd dopant atoms where the GaN matrix is magnetically polarized the order of $10^{-3}\mu_B$/atom.[1]

Here we present element specific investigations of Gd:GaN at the Gd L_3 edge and the Ga K edge, respectively, measuring the x-ray linear dichroism (XLD) as well as the x-ray magnetic circular dichroism (XMCD). We are able to show that the Gd:GaN remains in the GaN wurtzite structure and that about 85% of the Gd goes to Ga substitutional sites. Further we are able to detect a XMCD signal for Gd consistent with its atomic magnetic moment. The element specific hysteresis at the Gd-edge deviates significantly from the hysteresis measured by superconducting quantum interference device (SQUID).

The Gd:GaN(0001) samples investigated here are highly resistive and were grown on SiC(0001) substrates using ammonia-assisted molecular beam epitaxy (MBE), which were previously investigated in great detail.[1,2] The results shown here were measured predominantly on one sample having a dopant concentration of about 2×10^{19}/cm^3 (about 0.05%). For smaller dopant concentrations it was not possible to detect a Gd absorption edge. The x-ray absorption near edge spectra (XANES) were taken at the ESRF ID 12 beamline in total fluorescence yield,[4] and all absorption spectra were normalized with respect to the edge jump. For the XLD measurements a quarter wave plate was used to flip the linear polarization of the synchrotron light from vertical to horizontal as described in greater detail elsewhere;[5] the angle of incidence was 10° with respect to the sample surface. The XMCD measurements were done using a 6 T superconducting magnet and taking the direct difference of two XANES spectra recorded with right and left circular polarized light under grazing incidence ($\sim$10°). The direction of the magnetic field was reversed as well to minimize artifacts. The spectra were simulated using the FDMNES code[6] using the multiple scattering formalism within the muffin tin approximation. Additional in-plane magnetic measurements have been performed using a commercial SQUID magnetometer.

Figure 1 shows the measured (full symbols) and calculated (open symbols) XANES spectra recorded at the Ga K edge at room temperature with the electrical field vector parallel (squares) and perpendicular (circles) to the c axis of the Gd:GaN sample (a) and the respective XLD signal, which is a pure structural effect (b). Identical spectra could be recorded for other, less doped GaN samples (10^{16}, 5×10^{18}, and 1×10^{19}/cm^3) without any significant difference, especially regarding the size of the XLD signal. For the simulations the bulk values of the lattice constants (a=3.189 Å and c=5.185 Å) for wurtzite GaN were taken together with a core hole lifetime of 1.82 eV for Ga. The u parameter of 0.377 for wurtzite GaN was taken from Ref. 7. The experimental and theoretical spectra were normalized at the same energies and they agree well with previously measured spectra from (Ga,Mn)N samples,[5] thus our Gd:GaN samples are in the bulk GaN wurtzite structure.

Figure 2(a) shows simulations of the XLD at the Gd L_3 edge from a $Ga_{23}GdN_{24}$ supercell, the core hole lifetime for Gd is 4.01 eV. The two spectra shown correspond to Gd on a substitutional Ga site (squares) and on a substitutional N

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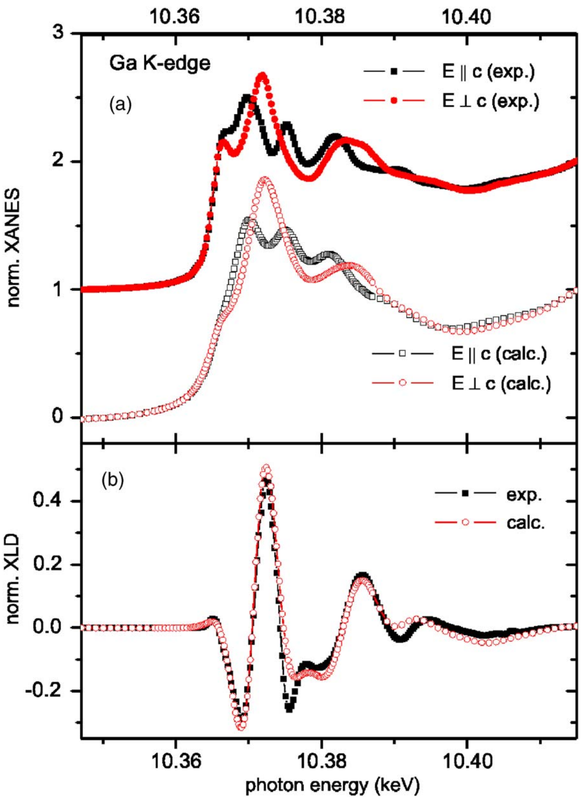

FIG. 1. (Color online) (a) Measured and calculated normalized XANES spectra of the Ga K edge of GaN for two perpendicular orientations of the linearly polarized light. The measurements were taken at 300 K under 10° grazing incidence. (b) Resulting calculated and measured XLD signature of the wurtzite structure of GaN.

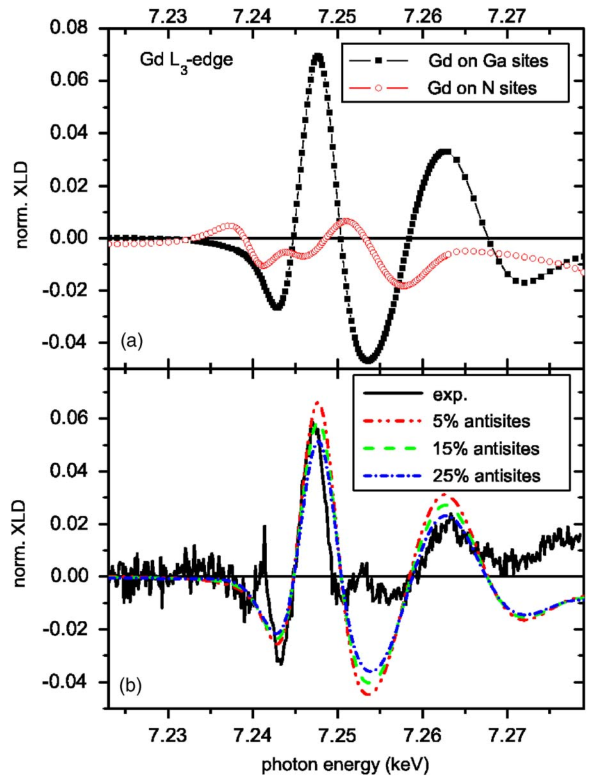

FIG. 2. (Color online) (a) XLD spectra at the Gd L_3 edge for Gd on Ga sites (squares) and at N sites (antisites, cirles) calculated for a wurtzite $Ga_{23}GdN_{24}$ supercell. (b) Comparison between the measured (300 K) and simulated XLD spectra for 5%, 15%, and 25% of Gd on N sites.

site (circles); note, that the absolute size of the XLD at the L edge is much smaller (about a factor of 10) compared to K edge, nevertheless a clear difference between Gd on Ga sites and N sites (antisites) is visible. Other possible Gd positions or neighboring Gd atoms are significantly different. Comparing the simulations with the experimental data recorded at 300 K in Fig. 2(b) one sees that the Gd is predominantly on substitutional Ga sites in a comparable wurtzite environment (the negative peak at 7.243 keV and the positive peak at 7.247 eV correspond well with the respective peaks of Ga at 10.369 and 10.373 keV, respectively, see Fig. 1); the deviations around 13 eV above the edge (at 7.253 keV) are also visible in the K edge XLD of pure GaN (at 10.377 keV) which originate from the muffin-tin approximation.[6] Because of the smaller overall XLD signal at the L_3 edge they are more pronounced here. Note that Gd on random interstitial sites would only reduce the overall size of the normalized XLD signal since it has no XLD signature at all. We show exemplarily the linear superposition of 5%, 15%, and 25% of Gd on antisites to illustrate that the experimental data are conclusive with (85±5)% of Gd on substitutional Ga sites, since 5% show a too large and 25% a too low XLD intesitiy at 7.247 keV, which is the dominant XLD feature for the wurtzite cystal. In particular, we can exclude phase separation (Gd–N–Gd bonds), or metallic Gd clusters (Gd–Gd bonds) within a few percentage of the overall doping level, which would show a significantly different XLD signature; only a small fraction of antisites cannot be excluded. Within the accuracy of our measurement we can thus conclude that the Gd:GaN samples are good DMN with low antisite disorder and without any detectable clustering in agreement with earlier x-ray diffraction studies.[1,2]

Figure 3 shows the normalized XANES and XMCD spectra recorded at the Gd L_3 edge at 40 K. The XMCD signal is the direct difference between two normalized XANES spectra recorded with right and left circular polarized lights, respectively. In addition, to minimize artifacts, the difference spectra were recorded in an external magnetic field of ±6 T. A clear dichroic signal of the order of 3% with respect to the edge jump is visible. The XMCD signal increases to about 7.5% at 7 K (not shown). The spectral shape of the XANES and the XMCD signal compare well with

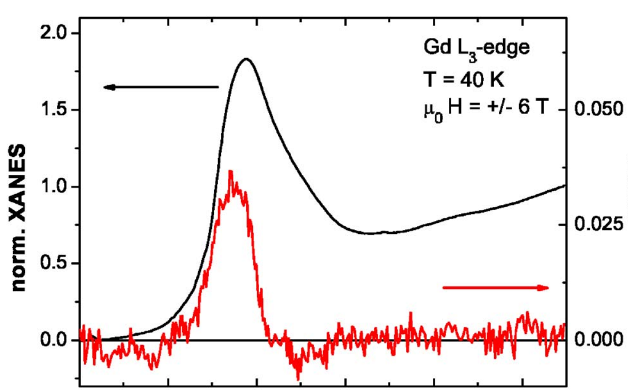

FIG. 3. (Color online) Normalized XANES and XMCD spectra recorded at the Gd L_3 edge at 40 K. For the XMCD signal the direct difference between the normalized XANES spectra with right and left circular polarized light was taken and in addition these difference spectra were taken in a magnetic field of ±6 T. The maximum size of the XMCD signal is about 3%.

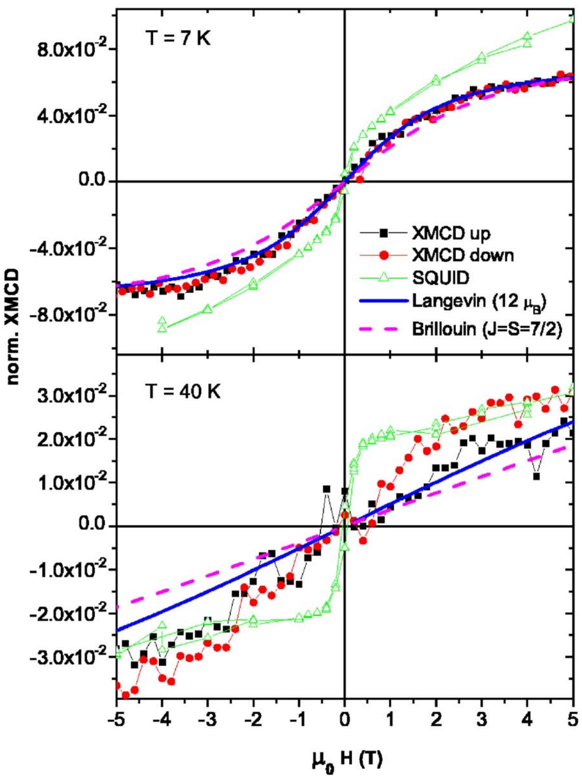

FIG. 4. (Color online) SQUID (open triangles) and XMCD hysteresis (solid squares and circles) for Gd:GaN at 7 and 40 K taken at the Gd L_3 edge. The SQUID data were normalized to the norm. The XMCD signal is at 40 K between 4 and 5 T. The fits using the Lagevin (solid line) and the Brillouin (dashed line) functions were calculated with a saturation magnetization of 0.076.

recently investigated GdN films measured at the same beamline under comparable conditions.[8] Note, that the amount of Gd in our sample corresponds only to about one atomic layer of Gd measured on a large background signal of a bulklike GaN/SiC(0001). On the other hand, the size of the XMCD measured here is about a factor of 2 smaller compared to the GdN film. Since GdN possesses a magnetic moment of $7\mu_B$/Gd atom, we can infer an average magnetic moment of about $(4\pm1)\mu_B$/Gd atom in our Gd:GaN film by direct comparison to the bulk reference sample, i.e., our findings are compatible with an atomiclike magnetic moment for the Gd. The effective magnetic moment per Gd atom inferred from SQUID measurements in this doping range is about $10\mu_B$–$20\mu_B$,[1] which indicates that the GaN host crystal plays a crucial role for the magnetic signal as measured by the SQUID.

This assumption is further supported by comparing the element specific hysteresis recorded at the Gd L_3 edge to SQUID measurements at the same temperatures, as shown in Fig. 4. The hysteresis was taken at 7.25 keV for ±6 T and both helicities of the light. We show the maximum XMCD signal taken at 7.248 keV versus external magnetic field at 7 and 40 K, i.e., the XMCD signal at 40 K and 6 T corresponds to the maximum size of the normalized XMCD spectrum in Fig. 3. To compare the field dependence with the SQUID data, we have normalized the magnetization values of the SQUID between 4 and 5 T at 40 K to the XMCD signal. It can be noted that the overall magnetization measured by SQUID at 7 K is systematically higher than for the Gd contribution measured by XMCD which can be explained by either paramagnetic impurities or a paramagnetic response of the GaN host itself. At 40 K the low-field behavior as measured by the SQUID shows magnetic saturation between 0.5 and 1 T, whereas the Gd signal shows a different field dependence. Especially at low magnetic fields, where the XMCD signal at the Gd L_3 edge is negligibly small, the magnetizaiton measured by the SQUID does not originate from the Gd. Nevertheless, the Gd plays a crucial role in activating the magnetic signal. From our previous work on undoped GaN/SiC(0001) samples we know that they do not show any magnetic signal beyond pure diamagnetism,[3] only if Gd atoms are inserted—in this case implanted—a magnetic hysteresis is detectable by the SQUID. Contaminations were also ruled out for the MBE grown Gd-doped samples.[2] Thus, the Gd atoms are needed to activate the magnetic signal, presumably due to their large ionic radius straining the GaN crystal locally.[2] However, they do not significantly contribute to the overall magnetic signal at low magnetic fields. We also fitted the XMCD signal of the Gd using either the Langevin (solid line) or the Brillouin (dahed line) function, see Fig. 4. For the Brillouin function we assumed $J=S=7/2$ for the Gd^{3+} ion. The agreement with the 7 K XMCD hysteresis is quite good assuming a saturation magnetization of 0.076, corresponding to the normalized XMCD signal however, using the same parameters the agreement with the 40 K data is not good, especially the weak curvature of the XMCD data is not reproduced well. Also the fit using the Langevin function with an effective moment of $12\mu_B$ leads to a clear disagreement with the 40 K data, whereas it reproduces the 7 K data well, also here the saturation magnetizaiton was 0.076. Therefore, we can exclude that the Gd behaves paramagnetic or superparamagnetic, since both models fail to reproduce the temperature dependence of the shape of the XMCD hysteresis.

In conclusion we demonstrate that Gd:GaN is a DMN material with little if any phase segregation and only low Gd antisite disorder. A clear XMCD signal could be measured as well as element specific hysteresis loops at the Gd L_3 edge. The moment per Gd atom is of the same order of magnitude as for bulk GdN. The comparison of the element specific hysteresis at the Gd L_3 edge with SQUID measurements demonstrate that a large portion of the overall magnetization does not originate from the Gd itself but is only activated by the dopant, thus highlighting the important role of the GaN host matrix for the overall magnetic properties of Gd:GaN DMN.

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