ESRF	**Experiment title:** Dopant location and element specific magnetic properties probed by XLD and XMCD in rare earth ion implanted ZnO samples	**Experiment number**: HE-2860
Beamline: ID 12	**Date of experiment**: from: 19.11.2009 to: 26.11.2009	**Date of report**: 05.03.2009
Shifts: 18	**Local contact(s)**: A. Rogalev, F. Wilhelm	*Received at ESRF:*

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Report:

The aim of this experiment was to clarify the dopant location of rare-earth (RE) ion impanted ZnO substrates and the respective thin films grown on sapphire. The latter types of samples were restricted to Gd-doped ZnO epitaxial films grown by reactive magnetron sputtering. Ion implantation was done using Eu, Sm, Ho and Gd ions. The maximum dose of 3 x 10^{15}/cm^2 was only achieved for Gd, for the other RE elements it was 1 x 10^{15}/cm^2. Figure 1 shows the XANES of the Eu L_3-edge measured with a total integration time of 10 sec per energy point and without the quarterwave plate. The edge shape and position demonstrates that the Eu is in its 3+ oxidation state, which was also the chosen charge state for the ion implantation. No obvious changes are visible after high vacuum annealing, although the integral magnetic properties as measured by SQUID are slightly alteres at low temperatures (not shown). Unfortunately, the required integration time for these kind of spectra is too long to study such samples using x-ray linear dichroism (XLD). This is illustrated by Figure 2. Here, a Gd-ion implanted sample with a dose of 3 x 10^{15}/cm^2 was studied using XLD. The overall intensity of the synchrotron radiation is reduced because of the quarter wave plate and the integration time had to be reduced to minimize artefacts from drifts. Obviously the absorption signal is strongly reduced so that it is dominated by the background and no quantitative information can be extracted from the XLD. Therefore, further investigations using XLD had to be restricted to magnetron sputtered Gd-doped ZnO samples, where the Gd concentration could be as high as 16%. Figure 3 shows a series of Gd-doped ZnO epitaxial films

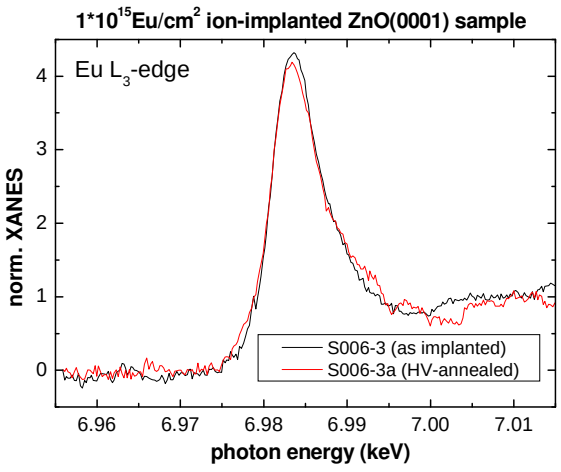

Figure 1: XANES spectra of Eu-ion implanted ZnO(0001) substrates as-imganted and after high vacuum annealing at 350°C. No obvious differences are visible and the typical XANES for Eu in its 3+ oxidation state is seen.

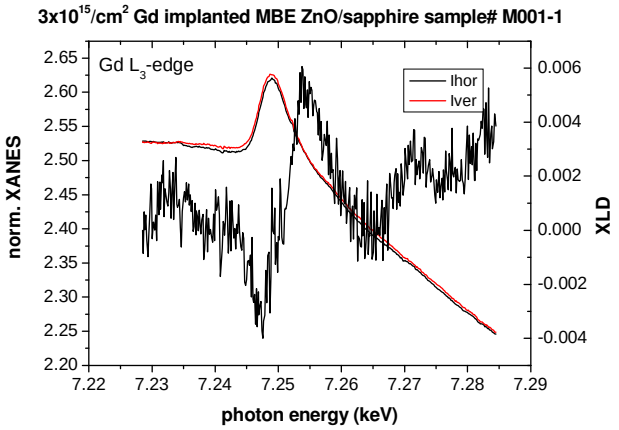

Figure 2: XANES and respective XLD spectra recorded on a Gd ion implanted ZnO epitaxial film. Obviously the absorption signal is small compared to the background so that proper normalization was not possible. The information derived from XLD is thun only of qualitative rather than quantitative character.

grown by reactive magnetron sputtering on sapphire substrates. A small reduction of the XLD signal for higher Gd concentrations is visible indicating reduced local structural quality. Ths is corroborated by a decrease of the XLD signal at the Zn K-edge which also reduced with increasing Gd concentration from 0.40 to 0.28 (not shown). The 16% and the 4% Gd-doped ZnO samples were investigated with respect to their magnetic properties. Both samples show a clear x-ray magnetic circular dichroism (XMCD) signal at the Gd L_3-edge which is slightly smaller for the 16% sample which can indicate the onset of phase separation. However, both element specific M(H)-curves are purely paramangetic which was corroborated later-on by intergral SQUID magnetometry (not shown). Therefore, all experimental efforts have failed to demonstrate ferromagnetic order in any of the RE-doped ZnO samples. Where XLD and XMCD investigations were possible, paramagnetism has been found.

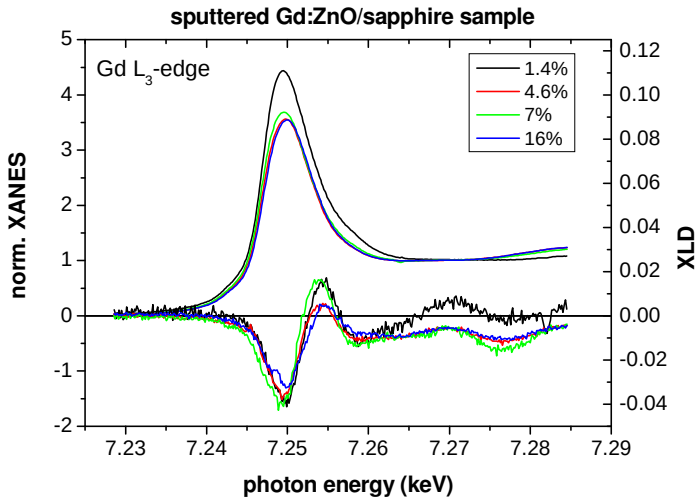

Figure 3: XANES and respective XLD spectra of four different concentrations of Gd in ZnO epitaxial films fabricated by reactive magnetron sputtering.

A smaller fraction of the beamtime has therefore been used to augment prior studies on Co-doped ZnO films using backup samples where the preparation conditions were altered compared to previous studies. These investigations can be combined with earlier findings (HE-2399 and HE-2714) for a comprehensive understanding of the Co:ZnO system. We were able to identify phase separation of metallic Co clusters in few samples by means of reduced XLD and respective alteres fine structure of the XANES. Element specific M(H)-curves could be recorded at different photon energies showing either a superposition of paramagnetic and superparamagnetic behavior or pure superparamagnetism when characteristic spectral features of the XMCD of Co metal were probed (not shown). We could corroborate metallic Co precipitates in the Co:ZnO sample reported in PRB **77**, 201303(R) (2008) as well as in the clustered sample reported in EPJB **63**, 437 (2008). Further we have found metallic Co signatures in samples comparable to those reported in New J. Phys. **10**, 055009 (2008), where soft x-rays failed to probe the entire bulk of the Co:ZnO film. Further Al-codoped Co:ZnO samples comparable to those studied in New J. Phys. **10**, 055010 (2008) have been studied and no phase separation has been found by means of XLD as well as pure paramagnetism by means of XMCD and element specific M(H)-curves. Since these measurements were not the initial focus of the current beamtime, and the attempts to measure the small RE absorption signals have consumed the majority of this beamtime, the results are not reported here. Nevertheless, we plan to prepare a comprehensive manuscript which will comprise some of the data of the Co:ZnO films measured during this beamtime as backup samples. In case of acceptance of such a manuscript, credit will be given to this beamtime as well and the report may be eventually updated.

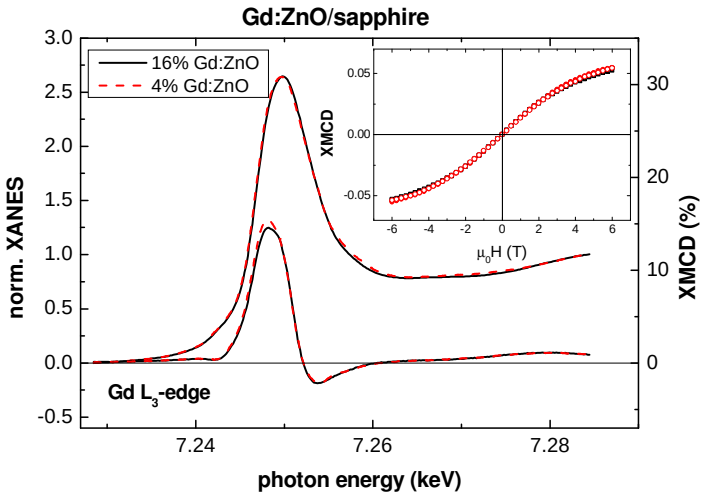

Figure 4:. XANES, XMCD and element specific hysteresis at the Gd L_3-edge of two Gd-doped ZnO epitaxial films. The highest Gd concentration of 16% exhibits a slightly smaller XMCD that the 4% sample. Both samples behave paramagnetic as seen from the M(H)-curves.