Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplemental Information

for

Local zincblende coordination in heteroepitaxial wurtzite $Zn_{1-x}Mg_xO$:Mn thin films with $0.01 \le x \le 0.04$ identified by electron paramagnetic resonance

by

Rolf Böttcher, Michael Lorenz*, Andreas Pöppl, Daniel Spemann and Marius Grundmann

* e-mail: mlorenz@physik.uni-leipzig.de

Table S1. Magnesium content in PLD target *x*, oxygen partial pressures p_{O2} during PLD, manganese concentrations in PLD target c_{MnO}, extrapolated HR-XRD *c*- and *a*-axis lattice parameters, *FWHM* of the ZnO(002) and ZnO(101) rocking curve, and ZFS parameter *D* with distribution width ΔD of Mn^{2+} species WZ of selected $Zn_{1-x}Mg_xO$:Mn thin films on *a*-plane sapphire. The FWHM of the rocking curves do not show a clear trend: For 0.016 mbar oxygen pressure there is no influence of *x*. However, for 0.16 mbar the FWHM increases, while for 0.002 mbar (not included in the table) a wide scattering was found. The table contains only data for samples on which EPR measurements were carried out, i.e. with manganese concentration in the PLD target c_{MnO} = 0.05%.

sample	Mg cont. *x*	p_{O2} (mbar)	*c* (Å)	*a* (Å)	*FWHM* ω(002) (°)	*FWHM* ω(101) (°)	*D* (MHz)	Δ*D* (MHz)
G5193	0	0.016	5.21377	3.24661	0.135	-	-644	20
G5191	0.005	0.016	5.21309	3.24524	0.175	0.247	-653	50
G5189	0.01	0.016	5.2106	3.24922	0.15	0.261	-665	70
G5187	0.02	0.016	5.20882	3.24808	0.148	0.249	-680	120
G5185	0.03	0.016	5.20724	3.23563	0.156	0.256	-695	140
G5183	0.04	0.016	5.20354	3.24425	0.147	0.249	-710	170
G5192	0	0.16	5.20299	3.24943	0.219	0.39	-695	90
G5190	0.005	0.16	5.20161	3.25222	0.19	0.361	-734	30
G5188	0.01	0.16	5.1992	3.25112	0.197	0.434	-749	60
G5186	0.02	0.16	5.19638	3.25349	0.275	0.441	-782	110
G5184	0.03	0.16	5.1935	3.25496	0.267	0.468	-818	130
G5182	0.04	0.16	5.19209	3.25512	0.284	0.446	-842	170

Table S2: Regression parameters for lattice parameters *c*, *a*, and *u* of $Mg_xZn_{1-x}O$:Mn thin film samples using the formulae $\boldsymbol{l = l_0 + l_1 x}$.

Data set	p_{O2} (mbar)	l_0 (x =0) (Å)	l_1 (Å)
c	0.002	5.22856	-0.38155
c	0.016	5.21337	-0.22645
c	0.16	5.20256	-0.28187
a	0.002	3.24839	0.03126
a	0.016	3.24555	0.06217
a	0.16	3.25037	0.13453
u	0.002	0.37866	0.02032
u	0.016	0.3792	0.01608
u	0.16	0.38011	0.02496

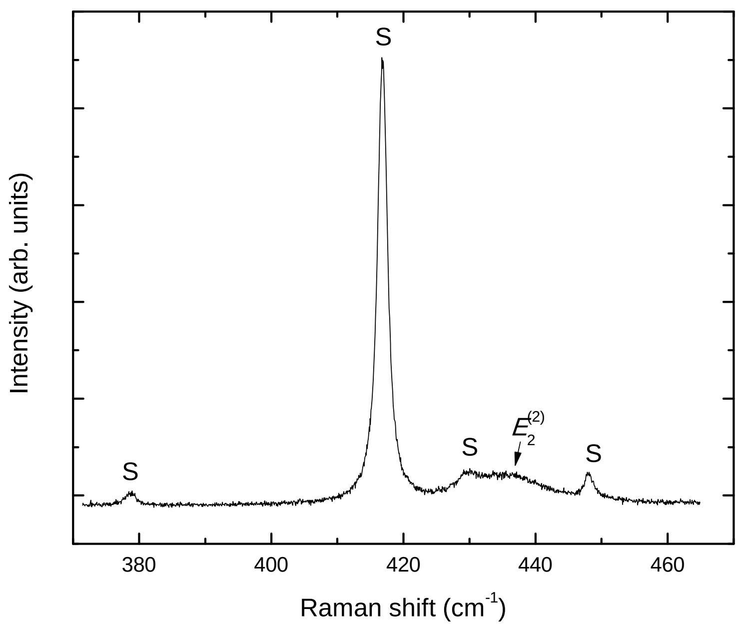

Figure S1. Micro-Raman spectrum of (Zn,Mg)O:Mn film No. G5182 with x=0.04, see Table S1. For zincblende ZnO, an additional peak at 400 cm^{-1} is expected, see Serrano et al, Phys. Rev. B 69, 094306 (2004). Because of the generally low intensity of the E2 peak from thin film, we cannot give a clear statement about zincblende ZnO phase. Substrate peaks from a-plane sapphire are marked with S.

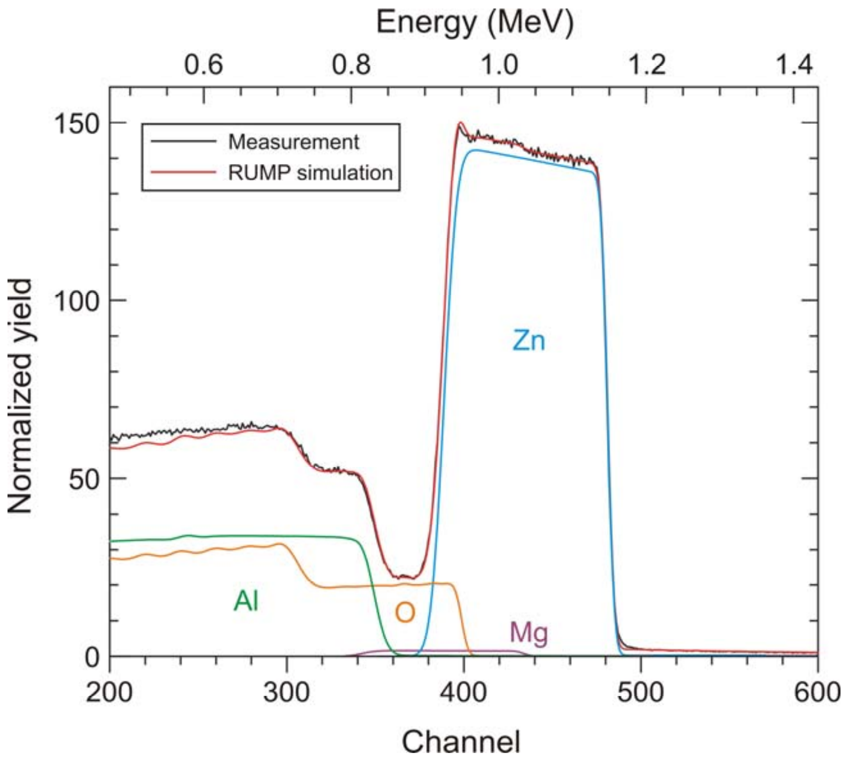

Figure S2. Ion backscattering spectrum of (Zn,Mg)O:Mn film No. G5187 with x = 0.02, see Table S1, recorded using a 1.2 MeV proton beam. From the XRUMP simulation the film thickness was determined to (0.82 ± 0.03) mg/cm^2. The contributions of the different elements of film and substrate to the backscattering yield are indicated.

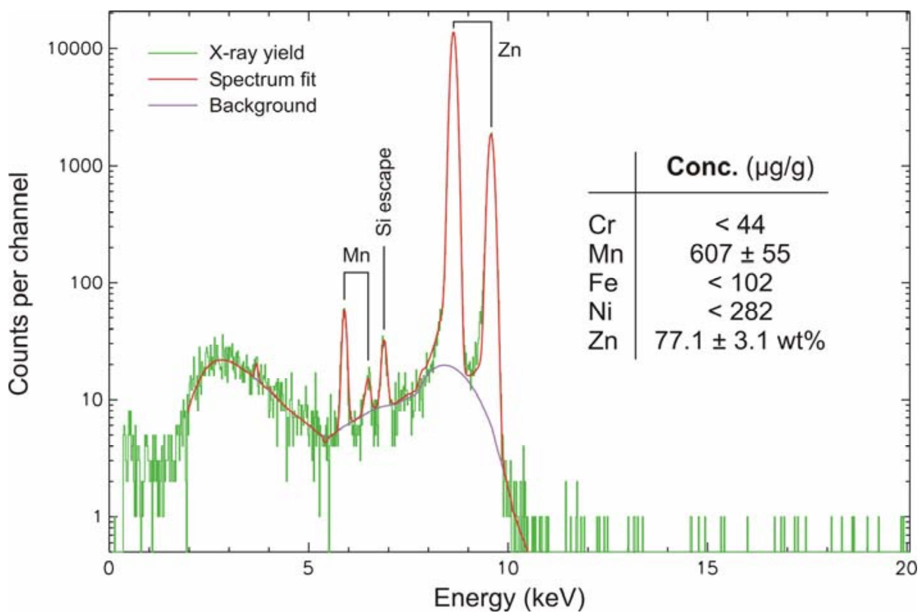

Figure S3. PIXE spectrum of (Zn,Mg)O:Mn film No. G5185 with x = 0.03, see Table S1, recorded using a 1.2 MeV proton beam. For elements with $Z > 12$ concentrations can be obtained from a GeoPIXE II analysis of the spectrum (red curve). The X-ray lines of Mn and Zn are indicated and concentrations of Mn and Zn as well as the minimum detection limits of typical impurities are given in the table. The Si escape line is a typical artefact for Si(Li) detectors as used here.

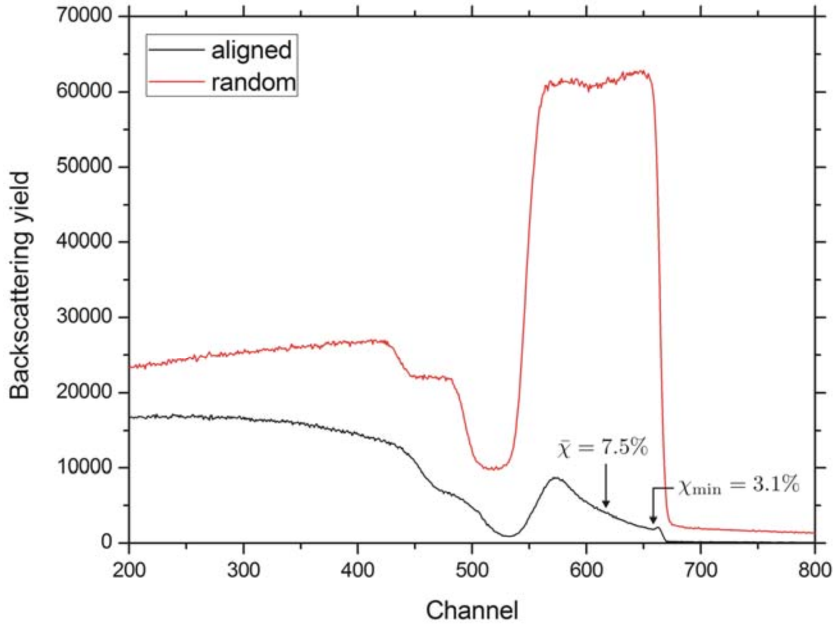

Figure S4. Ion backscattering spectrum of (Zn,Mg)O:Mn film No. G5185 with x = 0.03, see Table S1, recorded using a 1.2 MeV proton beam for two different orientations of the crystalline film. Whereas the red curve corresponds to a random alignment, i.e. the ion beam was not aligned with any major crystal axis or plane, the black curve was obtained under ion channeling into the *c*-axis of the film. Here, the backscattering yield drops to $\chi_{\mathrm{min}} = 3.1\%$ of the random yield close to the film surface, demonstrating a very good crystal quality of the film. The average reduction in backscattering yield across the film thickness amounts to $\overline{\chi} = 7.5\%$.

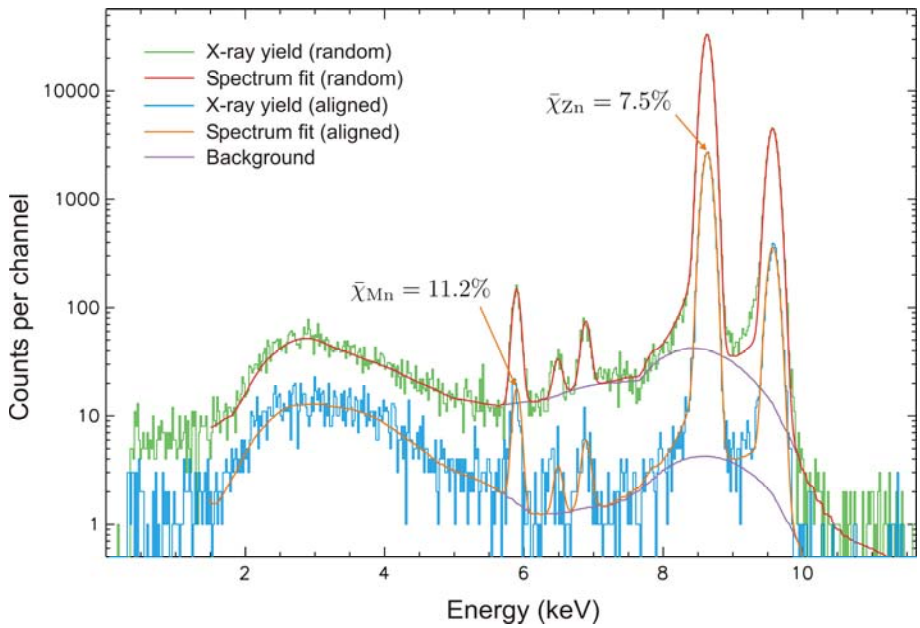

Figure S5. PIXE spectra recorded simultaneously to the backscattering spectra shown in Figure S4 for random and channeled alignment. Similar to ion backscattering, the X-ray yield is reduced under channeled alignment, because the ionization of the K-shell requires a close encounter collision between ion and target atom. As PIXE provides no inherent depth resolution the normalized yield is an average over the whole film thickness. The reduction of the Zn X-ray yield amounts to $\overline{\chi}_{Zn}$= 7.5% in excellent agreement to ion backscattering. From the slightly less pronounced drop in Mn X-ray yield of $\overline{\chi}_{Mn}$= 11.2% can be concluded that no more than 4% of all Mn atoms in the film reside on interstitial lattice sites when viewed along the *c*-axis of the film, whereas the remaining 96% appear substitutional.