Study of defects in high energy ion implanted ZnO crystals

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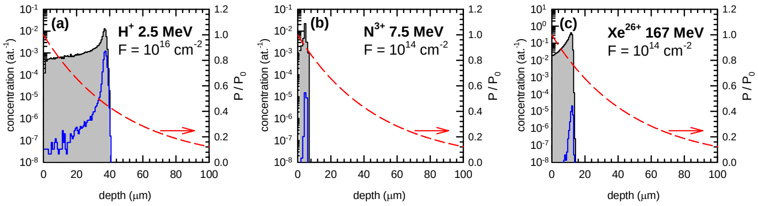
Introduction. Zinc oxide is a wide band gap (3.4 keV) semiconductor with high exciton binding energy (60 meV). Nowadays ZnO attracts interest as a promising material for blue/UV light emitters, detectors and optoelectronic devices. Point defects strongly influence optical and electrical properties of ZnO crystals and their characterization is therefore very important. By electron and ion irradiation point defects can be introduced into ZnO crystals in a controlled way. Investigation of irradiation-induced defects is important also because ZnO is known as radiation hard material with lower sensitivity to irradiation-induced damage than other semiconductors like Si, GaAs and GaN.

In the present work positron annihilation spectroscopy (PAS) combined with optical methods was employed for characterization of defects in the hydrothermally (HT) grown ZnO single crystals irradiated by high energy ions.

Samples. HT grown (0001) ZnO single crystals (10 x 10 x 0.5 mm^3), MaTecK GmbH (Jülich).
Three sets of samples were prepared:
(1) implanted by **2.5 MeV protons** up to fluences 10^{14}, 10^{15}, 6×10^{15}, 10^{16} cm^{-2};
(2) implanted by **7.5 MeV N^{3+}** ions up to fluences 10^{13} and 10^{14} cm^{-2};
(3) implanted by **167 MeV Xe^{26+}** ions up to fluences 3×10^{12}, 3×10^{13}, 1×10^{14}, 6×10^{14}, 1×10^{15} cm^{-2}.
During implantation the samples were kept at temperature not exceeding 100°C.

Results

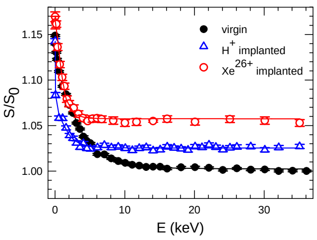


***Ion implantation into ZnO simulated using the SRIM code** [4]: Simulated depth profiles of ions implanted into ZnO (blue solid lines) and vacancies produced by implantation (filled gray areas): (a) 2.5 MeV protons, fluence 10^{16} cm^{-2}; (b) 7.5 MeV N^{3+} ions, fluence 10^{14} cm^{-2}; (c) 167 MeV Xe^{26+} ions, fluence 10^{14} cm^{-2}. Dashed line shows the implantation profile P of positrons emitted by ^{22}Na radioisotope related to its surface value P_0.*

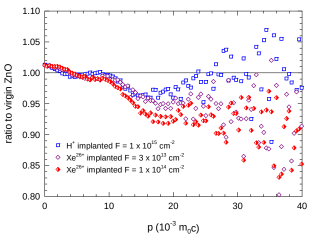
***Summary of SRIM simulations and PAS studies**: z_{stop} – the stopping depth of implanted ions, f – the fraction of positrons annihilated in the region modified by ion implantation, τ_2 – the characteristic lifetime of radiation-induced defects, L_+ – the mean positron diffusion length, c_v – the concentration of radiation-induced defects. The average number of created vacancies per ion and the estimated number of vacancies per ion survived in the sample are given in table as well.*

ion	energy (MeV)	z_{stop} (μm)	f	created vacancies/ion	τ_2 (ps)	L_+ (nm)	c_v (ppm)	survived vacancies/ion
H^+	2.5	41	0.57	26	246-260	19(2)[a]	650(100)[a]	20
N^{3+}	7.5	6	0.12	1370	365			
Xe^{26+}	167	14	0.25	56668	365-425	47(2)[b]	40(10)[b]	50

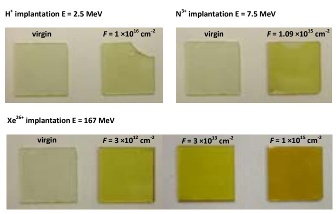
[a]for fluence of H^+ ions $F = 1\times10^{16}$ cm^{-2}, [b]for fluence of Xe^{26+} ions $F = 1\times10^{14}$ cm^{-2}

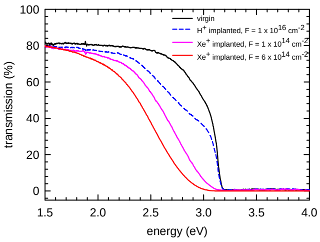


***SPIS results**: The S(E) curves for the virgin ZnO crystal, proton irradiated sample (F = 10^{16} cm^{-2}) and the sample implanted by Xe ions (F = 10^{14} cm^{-2}).*

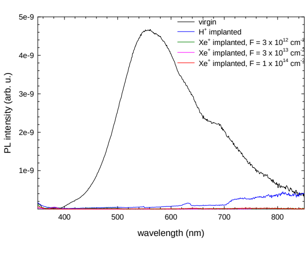


***CDB results**: CDB ratio curves (with respect to virgin ZnO) for implanted ZnO crystals*





***↑OT results**: Measured transmittance as a function of photon energy for virgin and implanted ZnO crystals.*



***←PL results**: PL intensity as a function of photon wavelength for virgin and implanted ZnO crystals.*

Methods of characterization.

• <u>Positron lifetime (LT) measurement</u>: A digital spectrometer [1] with a time resolution of 145 ps (FWHM ^{22}Na) was employed for LT measurement. At least 10^7 positron annihilation events were collected in each LT spectrum. A ^{22}Na positron source with activity of 1 MBq deposited on 2 μm thick mylar foil was sealed between two pieces of measured sample. The source contribution consisted of two components with lifetimes of ≈368 ps and ≈1.5 ns and relative intensities ≈8% and ≈1% .

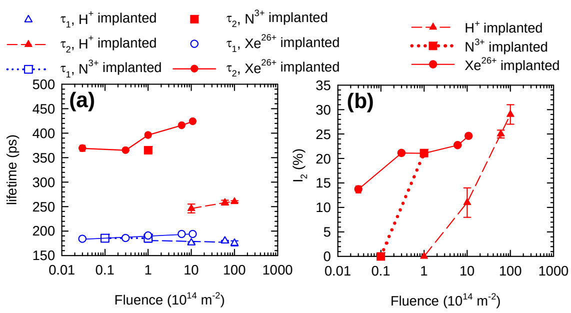
•<u>Coincidence Doppler broadening (CDB)</u> investigations were carried out using a digital spectrometer [2] equipped with two HPGe detectors. At least 10^8 positron annihilation events were accumulated in each CDB spectra.

•<u>Slow-positron implantation spectroscopy (SPIS)</u>: A magnetically guided slow positron beam SPONSOR [3] with positron energy adjustable from 0.03 to 36 keV was employed for measurement of defect depth profiles. The Doppler broadening (DB) of the annihilation photopeak was measured by a HPGe detector with an energy resolution of (1.06 ± 0.01) keV at 511 keV. The DB of the peak was characterized by the ordinary sharpness (S) parameter. The S values were normalized to the bulk S parameter S_0 of the virgin ZnO crystal.

•<u>Measurements of optical trasmittance (OT)</u>: An UV-VIS spectrometer (Ocean Optics) equipped with a deuterium and tungsten halogen light source and a grating monochromator was employed in measurements of OT within a wavelength interval 340 - 880 nm. To a first approximation, the reflectivity of each crystal was considered to be independent of wavelength so that no corrections of the transmitted light intensity for reflectivity variations with wavelength were applied.

•<u>Photoluminescence (PL)</u>: Steady state PL spectra were excited by 325 nm photons and detected by a photomultiplier equipped with a monochromator. All PL spectra were corrected for the spectrometer response.

All measurements were performed at room temperature.



***LT results**: The lifetimes resolved in LT spectra of ion implanted crystals (a) and the relative intensity I_2 of positrons trapped at radiation-induced defects (b) plotted as a function of fluence.*

Summary

• Positron annihilation spectroscopy (PAS) combined with optical methods was employed for characterisation of radiation induced defects in HT grown ZnO single crystals implanted by high energy protons, N^{3+} and Xe^{26+} ions.

• Defects created in ZnO crystals by 2.5 MeV protons, 7.5 MeV N^{3+} and 167 MeV Xe^{26+} ions were compared. The virgin ZnO crystals contain Zn-vacancies associated with hydrogen. Ion implantation introduced additional defects, namely Zn+O di-vacancies in crystals irradiated by protons and small vacancy clusters in samples implanted by N and Xe ions.

•The crystals were irradiated up to various fluences and the development of irradiation-induced defects with the fluence was examined. The virgin ZnO crystal exhibited a single component LT spectrum with a lifetime of 182 ps which is attributed to saturated positron trapping in Zn vacancies associated with hydrogen atoms unintentionally introduced into the crystal during the crystal growth. The H^+ irradiation introduced zinc-oxygen di-vacancies (V_{Zn}+V_O) characterized by a positron lifetime of 260 ps. The Xe ion irradiated ZnO crystals exhibit defect component with a longer positron lifetime of ≈ 360 ps which comes from clusters consisting of ≈ 10 to 12 vacancies.

•The concentration of radiation-induced vacancies was estimated by back-diffusion measurement of slow positrons.

•The ion implantation changed the colour of ZnO crystals from colourless to dark yellow. The green emission band which is well-seen in the virgin ZnO crystal was completely destroyed in the both H^+ and Xe^+ implanted crystals.

Acknowledgement

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References

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