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Hydrogen interaction with defects in ZnO

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Abstract. In the present work hydrothermally grown ZnO single crystals were electrochemically charged with hydrogen. The influence of hydrogen on ZnO microstructure was investigated by positron annihilation spectroscopy (PAS) combined with X-ray diffraction (XRD) using synchrotron radiation. Hydrogen concentration in the samples was determined by nuclear reaction analysis (NRA). It was found that a high concentration of hydrogen can be introduced into ZnO by electrochemical loading. At low concentrations absorbed hydrogen causes elastic volume expansion of ZnO crystal. At higher concentration, hydrogen-induced stresses exceed the yield stress in ZnO and plastic deformation of the crystal takes place leading to formation a defected subsurface layer in the crystals.

Introduction

ZnO is a wide band gap semiconductor with a number of perspective applications in optoelectronics. Electrical and optical properties of ZnO are controlled by point lattice defects and complexes of these defects with impurities. It was found that hydrogen is one of the most important impurities in ZnO crystals [1]. It is always present in the crystal growth environment despite of the growth technique used. Hence, it is very important to investigate hydrogen interaction with defects in ZnO.

Experimental

Hydrothermally grown ZnO (0001) single crystal (MaTecK GmbH) with dimensions 10 x 10 x 0.5 mm^3 and with O-terminated optically polished surface was investigated. Palladium cap of 20 nm thickness was deposited by a cold cathode beam sputtering on one side. The Pd over-layer serves as a catalyst for hydrogen permeation into ZnO and prevents hydrogen losses due to the formation of H_2 molecules on the surface [2]. The specimens were electrochemically loaded with hydrogen in a cell filled with a 1:1 mixture of H_3PO_4 and glycerin. Hydrogen charging was performed at room temperature by constant current pulses of 0.6 mA using a Pt counter-electrode, while the loaded specimen was acting as cathode. The hydrogen concentration introduced into the sample was determined by NRA using the resonant nuclear reaction ^{15}N + ^{1}H → ^{12}C + ^{4}He + γ-rays [3]. Depth scans were performed using ^{15}N ions with energy gradually increasing from 6.39 to 7.1 MeV, corresponding to the penetration depth into ZnO from the surface up to 260 nm. Slow positron implantation spectroscopy (SPIS) investigations were performed on a magnetically guided variable energy slow positron beam SPONSOR [4]. Energy of incident positrons was varied in the range from 0.03 to 36 keV. Doppler broadening of annihilation profile was measured by HPGe detector with energy resolution of (1.09 ± 0.01) keV at 511 keV and analyzed using S and W line shape parameters. XRD was measured at the European Synchrotron Radiation Facility (ESRF) using synchrotron radiation with the wavelength $\lambda = 1.078$ Å on the beamline BM20 equipped with 4-axis Eulerian cradle goniometer.

Results and Discussion

Hydrogen concentration profiles measured by NRA and presented in Fig. 1 show a sharp increase of c_H at the surface due to weakly bounded adsorbed hydrogen molecules. With increasing depth c_H decreases to a bulk value. Fig. 1A testifies that deposition of Pd cap has no significant impact on hydrogen content in the sample. However, one can notice in Fig. 1 a discontinuity in c_H at the interface between Pd cap and ZnO crystal due to excess hydrogen trapped at open-volume misfit defects at the interface. In comparison with the virgin crystal (Fig. 1A), the crystals loaded with hydrogen exhibit significantly higher c_H which gradually increases with increasing time of hydrogen charging (see Figs. 1 B,C). The bulk hydrogen concentration in the loaded crystal is in a reasonable agreement with the value estimated from the transported charge using the Faraday's law (dashed lines in Figs. 1B,C).

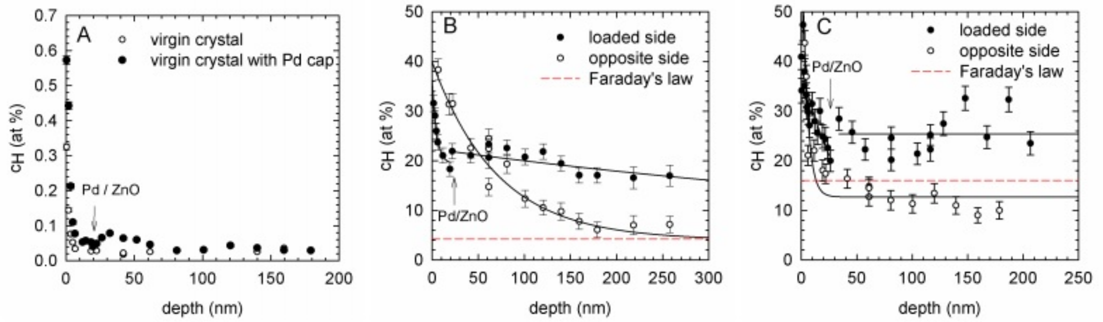

Fig. 1: Depth profile of hydrogen concentration c_H determined by NRA: (A) the virgin ZnO crystal (open points) and the virgin crystal covered with 20 nm Pd cap (full points), (B) the ZnO crystal loaded with hydrogen for 3 hours and (C) ZnO crystal loaded for 24 hours. NRA investigations were performed on the loaded side covered with Pd cap (full points) and on the opposite side (open points). Solid lines show fit by exponentially decaying function, dashed lines indicate hydrogen concentration estimated from the transported charge using Faraday's law.

One can see in Figs. 1B,C that a subsurface region with enhanced hydrogen concentration was formed on the loaded side and is further extended deeper into the crystal with increasing loading time. Formation of such subsurface region can be explained by hydrogen-induced plastic deformation which introduces open volume defects into the subsurface region. Enhanced c_H detected in the subsurface region by NRA is due to excess hydrogen atoms trapped at deformation-induced open volume defects. Indeed, plastic deformation in the sub-surface region is observed by appearance of hexagonally shaped pyramids on the surface created by hydrogen-induced slip in the c-direction (see Fig. 2A). The open points in Figs. 1B,C show that the sub-surface region with enhanced hydrogen concentration was formed not only on the loaded side covered with Pd cap but also on the opposite side without Pd overlayer. Since ZnO is a semiconductor the negative charge introduced on the Pd cap flows through ZnO and electrochemical hydrogen charging takes place also on the opposite side. However, substantially smaller thickness of the defected region on the opposite side testifies that the amount of hydrogen introduced through the opposite side is much lower compared to that introduced through the loaded side covered with Pd cap.

Fig. 2A shows XRD profile of peak (0002), i.e. diffraction from the planes parallel with the sample surface. With increasing hydrogen content in the crystal the (0002) peak is firstly shifted to lower diffraction angles due to lattice expansion in the c-direction. Subsequently in the sample loaded for 8.4 h the peak is split due to formation of hydrogen enhanced defected subsurface layer (see Fig. 1 B) characterized by higher lattice parameter while the rest of the crystal exhibits lower hydrogen content and, thereby, also a lower lattice expansion. With increasing loading time, the defected layer with enhanced hydrogen concentration propagates deeper and deeper into the crystal. Finally, in the sample loaded for 37 h, the thickness of the defected region with enhanced hydrogen content becomes so high that it exceeds the penetration depth of synchrotron radiation and the diffraction pattern in Fig. 2B becomes a single peak which comes from the defected region only.

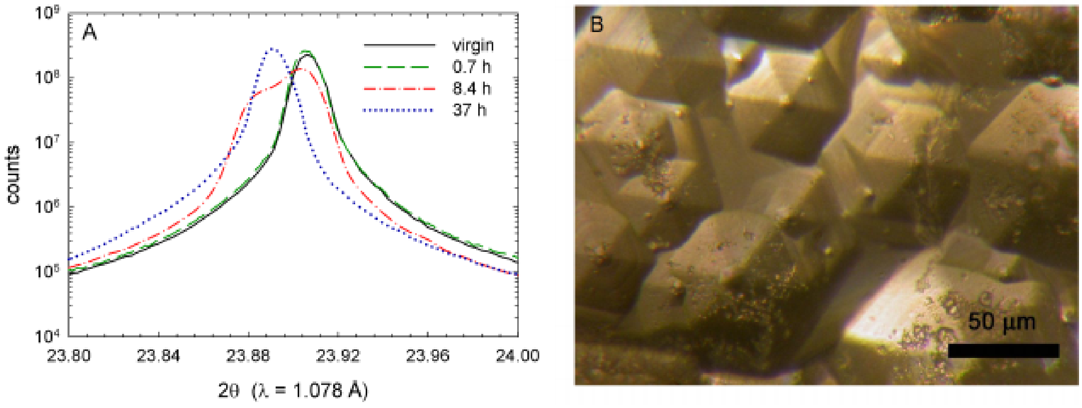

Fig. 2: (A) XRD profile of peak (0002) measured after various loading times. (B) Hexagonally shaped pyramids on the surface after hydrogen loading are observed by optical microscope.

The formation of the hydrogen enhanced defected subsurface layer after hydrogen charging is confirmed also by SPIS measurements. Fig. 3A shows dependence of the S parameter on energy of incident positrons for the virgin crystal and the crystal loaded with hydrogen. At very low energies, virtually all positrons annihilate on the surface. With increasing energy, positrons penetrate deeper and deeper into the sample and the S parameter approaches the bulk value. One can see in Fig. 3A that the virgin crystal and the crystal covered with Pd cap exhibit virtually the same bulk S parameter. The deposition of Pd cap modified the S(E) curve in the low energy range $1 - 5$ keV only due to a contribution of positrons annihilated in the Pd layer. Hence, one can conclude that deposition of Pd cap does not introduce additional defects to ZnO crystals. The samples loaded with hydrogen exhibit a huge increase of tee S parameter in the sub-surface region and also an increase in the bulk S parameter (see Fig. 3A). This gives clear evidence to that a lot of defects was created in the subsurface region in hydrogen loaded crystals by hydrogen-induced plastic deformation. One can see in Fig. 3A that the loaded side contains more defects than the opposite side which is in accordance with NRA results.

Fig. 3B shows S-W plot constructed from S and W parameters measured in the virgin crystal, the crystal covered with Pd cap and the crystal loaded with hydrogen for 24 h. In the virgin crystal, the S-W plot is a straight line going from the point corresponding to ZnO surface to the point representing the ZnO bulk. Deposition of Pd cap changed S-W plot at low energies because after surface of the sample was covered by Pd while the position of the bulk ZnO values remains unchanged. Hydrogen loading causes two prominent changes in the S-W plot (indicated in Fig. 3B by arrows): (i) an increase of the S parameter at the surface due to surface roughening and (ii) a shift of the point for ZnO bulk to higher S and lower W values due to defects created in ZnO by hydrogen loading.

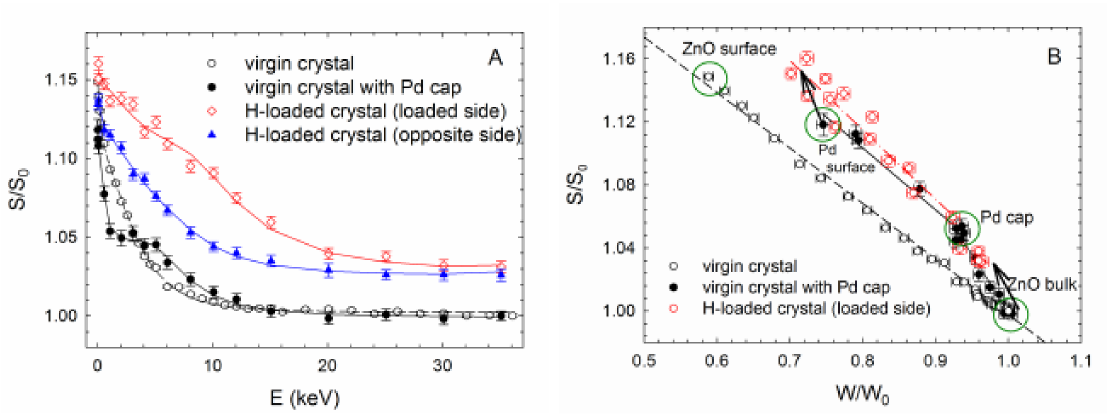

Fig. 3: Results of SPIS measurements (A) dependence of the S parameter on positron energy, (B) S-W plot. Important points in the plot are circled, namely ZnO (or Pd) surface, ZnO bulk and Pd layer. Arrows indicate changes in ZnO bulk and Pd surface after hydrogen loading for 24 h.

Conclusions

Precise measurements of hydrogen concentration by NRA confirmed that hydrogen is introduced into ZnO crystals by electrochemical charging. A defected sub-surface region with enhanced hydrogen concentration is formed in the hydrogen loaded crystals due to hydrogen-induced plastic deformation. With increasing loading time, this hydrogen enhanced sub-surface region extends gradually deeper and deeper into the crystal.

Acknowledgements

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