Diffusivity of Hydrogen in ZnO Single Crystal

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Abstract. Hydrogen diffusivity in ZnO (0001) single crystal was investigated using electrical resistometry and nuclear reaction analysis (NRA). ZnO crystals were covered with a thin Pd over-layer and electrochemically charged with hydrogen. The net concentration of hydrogen determined by NRA was found to be in a reasonable agreement with the value estimated from the transported charge using the Faraday's law. The hydrogen diffusion coefficient in ZnO was estimated from in-situ electrical resistivity measurements. Moreover, NRA investigations revealed existence of a subsurface layer with very high concentration of hydrogen (up to 40 at.%). Typical surface modification observed on hydrogen loaded crystal by light microscope indicates hydrogen-induced plastic deformation realized by a slip in the c-direction. Open-volume defects introduced by hydrogen-induced plastic deformation trap diffusing hydrogen and cause an enhancement of hydrogen concentration in the deformed subsurface layer.

Introduction

ZnO is a wide band gap semiconductor with a variety of applications including UV light emitting diodes, optoelectronic devices, and gas sensors [1]. Due to a progress in crystal growth, high quality single crystals are nowadays available. Properties of ZnO crystals are strongly influenced by intrinsic point defects and impurities. Detailed investigations of hydrothermally grown ZnO single crystals revealed that hydrogen is the most important impurity in virgin crystals [2]. Moreover, it was shown that a high amount of hydrogen can be introduced into ZnO crystal by electrochemical loading [3]. Understanding of hydrogen behavior in ZnO crystals is very important since hydrogen may from complexes with intrinsic point defects and influence significantly electrical and optical properties of ZnO crystals [4]. In this work we performed detailed characterization hydrogen concentration profile in electrochemically loaded ZnO crystal and investigation of hydrogen diffusion 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. The crystal face (10 x 10 mm^2 area) was covered by a 20 nm thick Pd cap deposited by a cold cathode beam sputtering. The Pd over-layer acts as a catalyst for hydrogen permeation into ZnO and prevents hydrogen losses due to the formation of H$_2$ molecules on the surface [5]. The specimens were electrochemically doped with hydrogen in a cell filled with a 1:1 mixture of H$_3$PO$_4$ and glycerin. Hydrogen charging was performed at room temperature by constant current pulses using a Pt counter-electrode, while the loaded specimen was acting as cathode. The hydrogen concentration introduced into the sample can

be estimated from the transported charge using the Faraday's law $c_H = I\,t\,V_m / F\,V$, where I is the loading current, t is the duration of loading pulse, V_m is the ZnO molar volume, V is the volume of the sample and F is the Faraday's constant.

The hydrogen concentration introduced into the sample was determined by NRA using the resonant nuclear reaction $^{15}N + {}^{1}H \rightarrow {}^{12}C + {}^{4}He + \gamma$–rays [6]. Two kinds of NRA scans were performed: (i) constant energy scans where the studied sample was irradiated by ^{15}N ions with energy of 6.6 MeV (corresponding to the penetration depth of ≈ 60 nm in ZnO) and (ii) depth scans performed using ^{15}N ions with energy gradually increasing from 6.39 to 7.1 MeV, corresponding to the penetration depth into ZnO practically from the surface up to 260 nm. Energy transfer from bombarding ^{15}N ions to the crystal during NRA analysis can be sufficient to release a weekly bound hydrogen atom from its site. Such released hydrogen starts diffusion motion and is then no longer available at the point of the analysis. This is seen as a drop in the γ-ray yield with increasing ^{15}N fluence. Hence, constant energy scan enables to determine the concentration of "unbound" hydrogen $c_{H,u}$ (i.e. hydrogen which is diffusing during analysis) and the concentration of "tightly bound" hydrogen $c_{H,b}$, which is not released by the energy transfer from ^{15}N ions. Since penetration of ^{15}N ions increases with increasing energy depth scan provides information about the depth profile of hydrogen concentration.

Electrical resistivity of Pd over-layer was measured in-situ during hydrogen loading by DC four point method using source meter Keithley 2400-C.

Results and discussion

Virgin crystal. Fig. 1(A) shows depth profile of hydrogen concentration determined by NRA depth scan in the virgin ZnO crystal. Hydrogen concentration is enhanced in a narrow subsurface layer with thickness of ≈ 5 nm due to 'unbound' hydrogen adsorbed on the surface. With increasing depth hydrogen concentration reaches bulk value $c_H \approx 0.03$ at.%. Since no change in the bulk hydrogen concentration with increasing fluence was detected hydrogen in the crystal is tightly bound in the lattice. On the other hand, inside the subsurface layer hydrogen concentration decreases with fluence testifying presence of "unbound" hydrogen. From inspection of Fig. 1 one can conclude that deposition of Pd cap on the virgin crystal leads only to a minor changes in the depth profile of hydrogen concentration consisting of (i) an increase of the hydrogen concentration adsorbed on the surface, likely due to catalytic effect of Pd causing dissociation of H_2 molecules, and (ii) a small hump in hydrogen concentration close to the interface between Pd layer and ZnO bulk, see Fig. 1(A). This is most probably due to hydrogen trapped at open-volume defects at the interface.

Hydrogen loaded crystal. Fig. 1(B) shows results of NRA constant energy scan performed in depth of ≈ 60 nm in the ZnO crystal electrochemically loaded with hydrogen (t =3 h, I = 0.6 mA). NRA measurements were performed on both sides of the sample, i.e. on the loaded side covered with Pd cap and also on the opposite side without Pd cap. NRA results give clear evidence that hydrogen concentration in the loaded crystal is substantially enhanced compared to the virgin sample demonstrating that hydrogen was indeed introduced into ZnO by electrochemical charging. One can see in Fig. 1(B) that hydrogen concentration decreases with increasing ^{15}N fluence testifying that the loaded crystal contains some "unbound" hydrogen. With increasing fluence hydrogen concentration reaches a plateau corresponding to the 'tightly bound' hydrogen. The decrease of hydrogen concentration with fluence can be well described by exponential decay, see solid lines in Fig. 1(B). The concentration of "unbound" hydrogen was determined as the difference between the hydrogen concentration extrapolated to zero fluence and the steady-state plateau value approached at high fluences. On both sides of the sample the concentration of "unbound" hydrogen represents $\approx 50\%$ of the total hydrogen content.
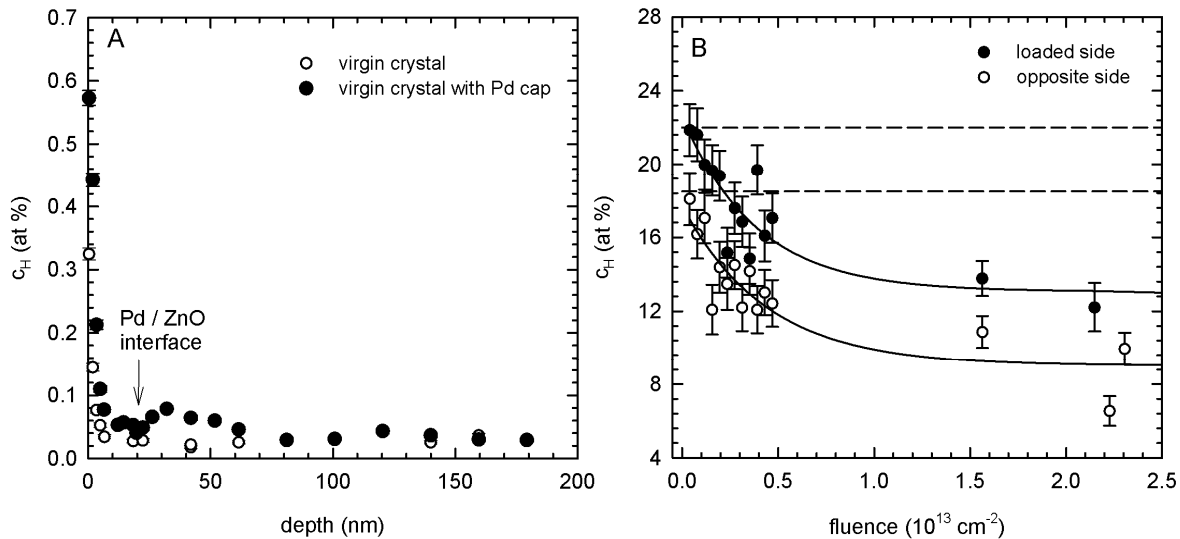
Figure 1 (A) Depth profile of hydrogen concentration determined by NRA depth scan on the virgin ZnO crystal (open points) and the virgin crystal with Pd cap (full points). The position of the Pd/ZnO interface is indicated by arrow. (B) Results of NRA constant energy scan performed on ZnO crystal loaded with hydrogen for 3 h. NRA investigations were performed at depth of $\approx$ 60 nm both on the loaded side (full points) and the opposite side (open points). Solid lines show fit by exponentially decaying function, dashed lines indicate extrapolated net hydrogen concentration $c_{H,u} + c_{H,b}$

More information about the depth profile of hydrogen concentration can be obtained from depth NRA scans which were performed again on both sides of the hydrogen loaded ZnO crystal and results are plotted in Fig. 2(A). On both sides hydrogen concentration is substantially enhanced in a subsurface region. On the loaded side a high hydrogen concentration was found in the Pd over-layer. With increasing depth it readily decreases and one can notice a step in c_H at the interface between Pd layer and ZnO crystal caused likely by hydrogen trapped in open-volume defects at the interface. Inside ZnO crystal c_H decreases further with depth but slope of this dependence becomes significantly lower, see Fig. 2(A). On the opposite side without Pd cap hydrogen concentration also decreases with depth but more rapidly than on the loaded side. The depth dependence of hydrogen concentration can be well described by exponential decay, see solid and dashed lines in Fig. 2(A). Note that on the loaded side fitting was performed separately inside the Pd cap and inside ZnO bulk. From fitting of data in Fig. 2(A) and extrapolation of model functions the depth profile of hydrogen concentration across the whole sample was constructed and is plotted Fig. 2(B). One can see in the figure that going from the loaded side up to depth of $\approx$ 2 μm there is a region with very high hydrogen concentration which exponentially decreases with depth and approaches a bulk value. Hydrogen enhanced region on the opposite side is significantly narrower and extends to depths of $\approx$ 0.2 μm only. Enhanced hydrogen concentration on the opposite side is most probably due to hydrogen adsorbed on ZnO surface during loading. Interestingly, fitting of NRA data measured on both the loaded side and the opposite gave virtually the same plateau value $c_H = (4 \pm 1)$ at.% which is in very reasonable agreement with the net hydrogen concentration of 4.2 at.% estimated from the Faraday's law, see dashed line in Fig. 2(B).
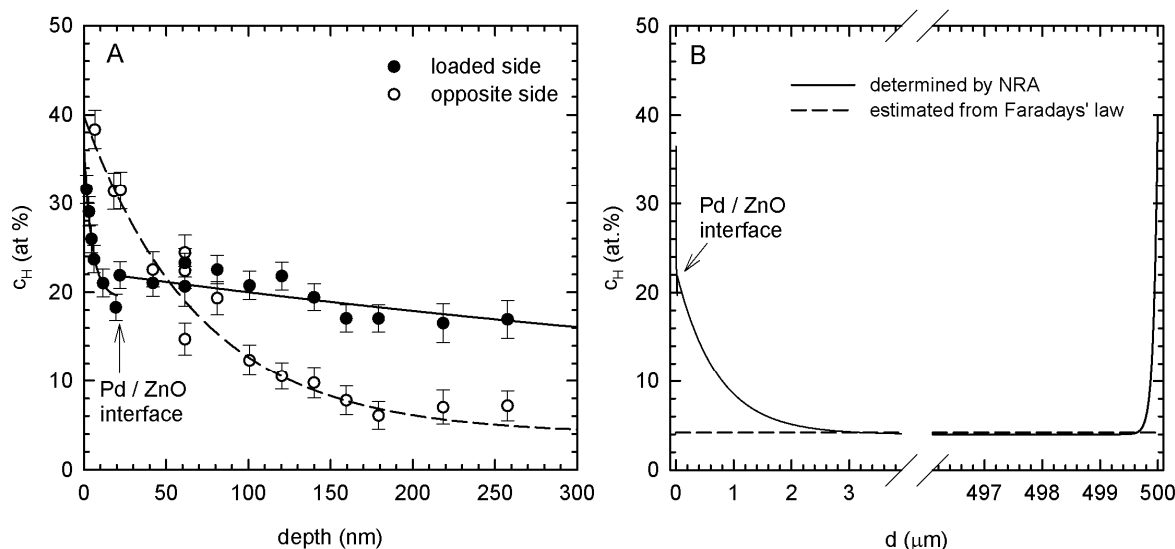
Figure 2 (A) Depth profile of hydrogen concentration determined by NRA on ZnO crystal loaded with hydrogen for 3 h. NRA depth scan was performed both on the loaded side (full points) and the opposite side (open points). Solid and dashed lines show fit of experimental data by exponentially decaying function on the loaded and the opposite side, respectively. Position of the interface between Pd cap and ZnO crystal is indicated by arrow. (B) Estimated depth profile of hydrogen concentration across the whole sample thickness obtained from fitting of NRA data. For comparison, the total hydrogen concentration estimated from the Faraday's law is shown by dashed line.
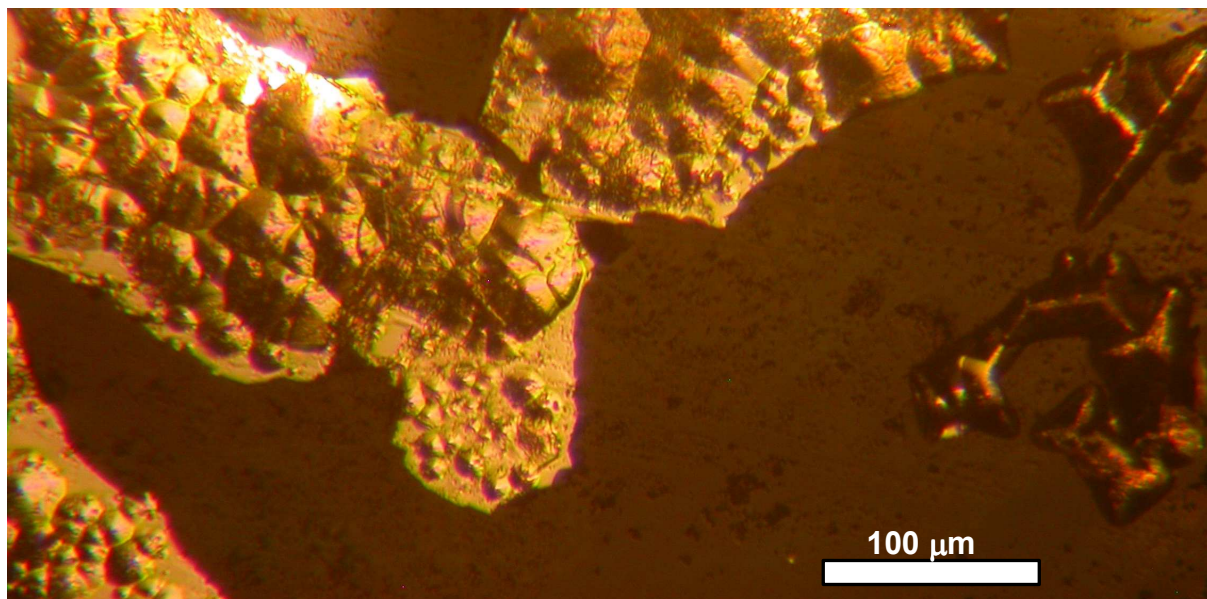
Figure 3 Light microscopy image of surface of ZnO crystal covered with Pd cap and electrochemically loaded with hydrogen for 7 h. The image was taken on the loaded side.

Positron annihilation investigations revealed that subsurface layer with high density of open-volume defects was formed in hydrogen loaded ZnO crystal [7]. Thickness of this defected layer is comparable with thickness of the region with enhanced hydrogen concentration obtained from NRA characterization. Fig. 3 shows light microscopy image of surface of ZnO crystal electrochemically loaded with hydrogen (t = 7 h, I = 0.5 mA). Absorbed hydrogen causes expansion of ZnO lattice. Since ZnO is relatively soft material high hydrogen over-pressure created on the loaded side by electrochemical charging introduces stresses exceeding ZnO yield stress and causing plastic deformation in the subsurface layer. This leads to typical surface modification visible in Fig. 3 as pyramids formed by slip in the c-direction, i.e. growing perpendicularly on the crystal surface and

breaking the Pd cap. Hydrogen-induced plastic deformation in the subsurface layer introduces high density of open-volume defects (dislocations, vacancies, vacancy clusters) which were detected by positron annihilation [7] and which act as trapping sites for hydrogen enhancing hydrogen concentration in the subsurface region.
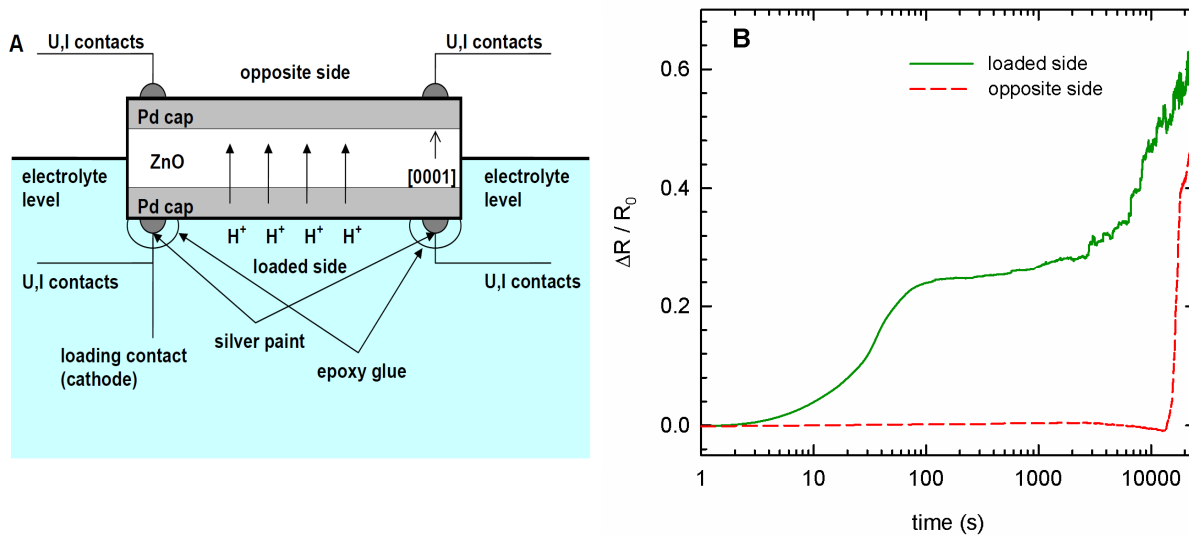
Figure 4 (A) Schematic depiction of configuration used in in-situ electrical resistivity measurement, (B) relative change of electrical resistivity of Pd cap during electrochemical hydrogen loading (current I = 0.1 mA). Resistivity was measured both on the loaded side (immersed in electrolyte, solid line) and on the opposite side (on air, dashed line)

The in-situ electrical resistivity measurement of hydrogen loaded ZnO crystal was performed in the configuration shown schematically in Fig. 4(A). Contrary to NRA investigations, where the loaded crystal was completely immersed in electrolyte, here only the loaded side was deluged by electrolyte while the opposite side was on air. Moreover, not only the loaded side but also the opposite side was covered by 20 nm Pd cap. This configuration enables to measure resistivity independently on the loaded side and also on the opposite side. As shown schematically in Fig. 4(A) hydrogen comes into the crystal from the loaded side through Pd cap and diffuses due concentration gradient towards the opposite side, i.e. diffusion takes place in the c-direction [0001]. Fig. 4(B) shows relative change of electrical resistivity measured on the loaded side and on the opposite side during electrochemical loading with hydrogen using current I = 0.1 mA. On the loaded side the Pd layer is firstly hydrogenated and transforms into palladium hydride (PdH) which is reflected by a significant increase of its resistivity clearly visible in Fig. 4(B). The Pd cap transformed completely into the hydride phase exhibits relative increase of resistivity $\Delta R/R_0 \approx 0.25$, which is in reasonable agreement with the values determined in Ref. [8] for very thin Pd films deposited on Si substrate. The Pd cap is then kept in the hydride phase during loading due to continuous hydrogen flux, i.e. its resistivity remains unchanged, and hydrogen penetrates through Pd cap into ZnO crystal. Further increase of resistivity at longer loading times (t > 1000 s), see Fig. 4(B), is due to hydrogen-induced plastic deformation taking place in ZnO subsurface layer and causing local destruction of Pd cap, see Fig. 3. On the opposite side of the loaded crystal, resistivity remains firstly virtually unchanged and rises only when the crystal is loaded for period $t_0 \approx 14000$ s, see Fig. 4(B). Obviously, the resistivity response on the opposite side is postponed due to diffusion of hydrogen from the loaded side across the sample thickness d = 0.5 mm. The room temperature hydrogen diffusion coefficient D_H in ZnO crystal in the c-direction can be estimated from the time lag t_0 between the resistivity response on the loaded side and on the opposite side $D_H \approx d^2 / t_0 = (1.8 \pm 0.8) \times 10^{-11}$ m^{2}s^{-1}. This result testifies that hydrogen diffusion in ZnO in the c-direction is rather fast since D_H obtained here for ZnO crystal is comparable with the room temperature hydrogen diffusion coefficient in Pd of 4×10^{-11} m^{2}s^{-1} [9]. Hydrogen diffusion in the c-direction in ZnO

crystal is facilitated by open channels exiting in the ZnO wurtzite structure along the c-axis. However, it has to be mentioned that diffusion of hydrogen across the loaded ZnO sample is limited by trapping in open-volume defects created by hydrogen-induced plastic deformation.

Summary

Characterization of depth profile of hydrogen concentration in electrochemically loaded ZnO crystal revealed that the bulk value of hydrogen concentration agrees well the concentration estimated from the Farady's law. In addition, a subsurface region with enhanced hydrogen concentration was found in the loaded crystal. Typical surface modifications due to hydrogen-induced plastic deformation were observed on the loaded crystal by light microscopy. Enhanced hydrogen concentration in the subsurface region is due to excess hydrogen trapped at open-volume defects created by plastic deformation. The hydrogen diffusion coefficient in ZnO crystal in the c-direction of $(1.8 \pm 0.8) \times 10^{-11}$ $m^2 s^{-1}$ estimated by in-situ electrical resistometry testifies that hydrogen diffusion in the c-direction is rather fast.

Acknowledgement

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