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Hydrogen absorption and diffusivity in ZnO single crystals

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ABSTRACT

ZnO single crystals electrochemically charged with hydrogen were characterized. The concentration of hydrogen introduced into the crystals was determined by nuclear reaction analysis and was found to be in a reasonable agreement with the value estimated from the Faraday's law. Moreover, a sub-surface layer with very high concentration of hydrogen and very high density of open-volume defects was formed by plastic deformation caused by hydrogen-induced stress. Specific surface modification caused by hydrogen-induced slip in the *c*-direction was observed on hydrogen loaded crystals. Hydrogen diffusion coefficient in ZnO was estimated by *in situ* electrical resistivity measurement. It was found that hydrogen diffusion in the *c*-direction is faster than in the *a*-direction most probably due to open channels existing in the wurtzite structure along the *c*-axis.

1. Introduction

ZnO is a wide band gap (3.37 eV) semiconductor with a large free exciton binding energy of 60 meV. Due to its unique properties ZnO takes great attention as a material for UV light emitting diodes, optoelectronic devices, gas sensors and transparent electrodes for solar cells [1]. Progress in crystal growth techniques made high quality ZnO single crystals available [2]. Most of ZnO crystals exhibit *n*-type conductivity [1]. On the other hand, acceptor doping leading to stable and reproducible *p*-type conductivity in ZnO has not been found so far despite a large effort focused on this problem. Using *ab inito* theoretical calculations Van de Walle [3] predicted that hydrogen is easily incorporated into ZnO lattice and can form a shallow donor state. Later experimental studies revealed that hydrogen is indeed the most important impurity in high quality ZnO crystals and its concentration exceeds the concentration of other impurities by at least one order of magnitude [4]. Moreover, recently it has been demonstrated that very high concentration of hydrogen can be introduced into ZnO by electrochemical charging [5]. For these reasons it is very important to understand hydrogen behaviour in ZnO lattice. In particular, hydrogen motion in ZnO lattice is an important issue. Hydrogen diffusion in ZnO was investigated using secondary ion mass spectroscopy (SIMS) [6–9], optical methods [10] and first principles theoretical calculations [11–13]. However the results obtained by various approaches are controversial and the diffusion activation energies ranging from 0.17 up to 1.12 eV have been reported. This discrepancy could be caused by different concentration of defects in particular in sub-surface region. In the present work hydrogen absorption and hydrogen diffusivity in ZnO single crystals were studied by nuclear reaction analysis (NRA) and *in situ* measurement of electrical resistivity which represents a simple technique for investigation of hydrogen diffusion in bulk.

2. Experimental

Hydrothermally grown ZnO single crystals (MaTecK GmbH) with (0001) and (10–10) orientation were investigated. Each ZnO crystal has dimensions 10 × 10 × 0.5 mm^3 and O-terminated optically polished surface. The crystal faces (10 × 10 mm^2 area) were covered by a 20 nm thick Pd cap deposited by sputtering. The Pd over-layer makes the surface conductive and facilitates hydrogen permeation into ZnO [14]. Hydrogen was introduced into ZnO crystals by electrochemical cathodic charging using Pt counter electrode and constant current pulses. Hydrogen charging was performed at room temperature in a cell filled with a 1:2 mixture of H_3PO_4 and glycerine. Charged ZnO sample was deluged by electrolyte only from the side covered by Pd (called here 'loaded side'), while the opposite side was on air without any contact with electrolyte.

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 [15]. NRA studies were performed by ^{15}N ions with energy adjustable in range from 6.39 to 7.2 MeV. Penetration of ^{15}N ions into ZnO increases with increasing energy from the surface up to depth of 300 nm. Hence using ^{15}N ions with adjustable energy depth profile of hydrogen concentration in the sample can be determined.

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

3. Results and discussion

Fig. 1a shows depth profile of hydrogen concentration c_H determined by NRA in the virgin ZnO (0001) crystal. Hydrogen concentration is enhanced on the surface due to weakly bound adsorbed hydrogen atoms. With increasing depth hydrogen

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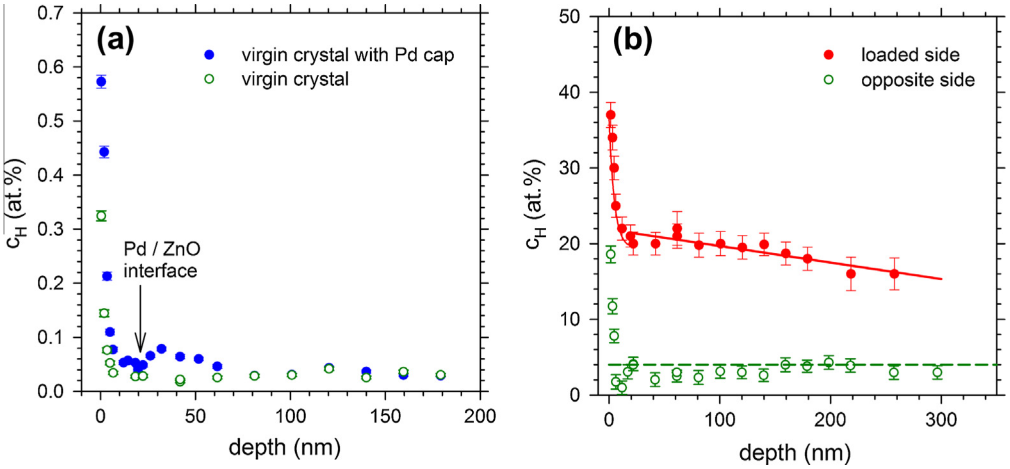

Fig. 1. Depth profile of hydrogen concentration c_H determined by NRA in ZnO (0001) crystal: (a) comparison of virgin crystal and the virgin crystal covered with Pd cap; (b) comparison of loaded and opposite side of the crystal charged electrochemically with hydrogen (t = 3 h, I = 0.5 mA).

concentration quickly reaches the bulk value $c_H \approx 0.03$ at.% representing hydrogen which has been introduced into ZnO lattice *unintentionally* during the crystal growth. Full points in Fig. 1a show the depth profile of hydrogen concentration in the virgin ZnO crystal covered by Pd over-layer. From inspection of the figure one can conclude that deposition of Pd cap on the virgin crystal leads to (i) an increase of the hydrogen concentration adsorbed on the surface, likely due to catalytic effect of Pd causing dissociation of H_2 molecules [6], and (ii) a slight increase of c_H close to the interface between Pd layer and ZnO crystal indicated in Fig. 1a by an arrow. This is most probably due to excess hydrogen trapped at open-volume defects at the interface.

Fig. 1b shows results of NRA characterization of ZnO (0001) crystal electrochemically loaded with hydrogen for the period t = 3 h using the current I = 0.5 mA. Obviously hydrogen concentration in the loaded sample is strongly increased compared to the virgin crystal. On the loaded side hydrogen concentration is very high ($c_H \approx 40$ at.%) on the surface covered by Pd over-layer. This testifies that Pd over-layer was transformed into the hydride phase (PdH). High concentration of hydrogen was detected also inside the ZnO crystal. With increasing depth c_H readily decreases and its depth dependence can be well described by an exponential decay function, see solid line in Fig. 1b. In Pd over-layer c_H decreases faster than in the ZnO crystal. Therefore, the depth dependences of c_H in Pd cap and in the ZnO crystal were fitted separately by exponential decay functions with different decay constants. A step in the depth dependence of hydrogen concentration can be again observed at the interface between the Pd cap and the ZnO crystal at the depth of 20 nm, see Fig. 1b. Hydrogen concentration at the interface is enhanced due to hydrogen trapped at open volume misfit defects at the interface. Hydrogen concentration is significantly enhanced also on the opposite side which was not exposed to electrolyte; see open points in Fig. 1b. This indicates that hydrogen introduced into the crystal through the loaded side diffuses across the sample towards the opposite side.

The total concentration of hydrogen introduced into the sample estimated from the transported charge by the Faraday's law is 4.2 at.% and this value is shown in Fig. 1b by a dashed line. This concentration is in a good agreement with c_H determined by NRA on the opposite side of the crystal. From extrapolation of the exponential decay function describing depth profile of c_H on the loaded side the bulk hydrogen concentration of (4 ± 1) at.% was obtained which also agrees with the value estimated from the Faraday's law. Hence, we can conclude that the bulk hydrogen concentration in the ZnO crystal charged with hydrogen is ≈4 at.%, i.e. more than two orders of magnitude higher than c_H in the virgin crystal.

Moreover, NRA studies revealed that a sub-surface region with enhanced hydrogen concentration was formed on the loaded side. During electrochemical charging hydrogen is firstly absorbed in Pd over-layer which is quickly transformed into the hydride phase. Subsequently hydrogen penetrates into the ZnO crystal and diffuses from the loaded side towards the opposite side due to the concentration gradient. Hydrogen over-pressure on the loaded side is responsible for the formation of a sub-surface region with enhanced hydrogen concentration below the Pd cap. Theoretical calculations performed in Ref. [3] revealed that hydrogen occupies bond-centred (BC) sites between O and Zn atoms and causes a significant outward relaxation of neighbouring atoms. One can distinguish two kinds of BC sites which differ by orientation of the O–H bond: (i) $BC_{||}$ sites, where O–H bond is parallel with c-axis and $BC_{\perp}$ sites, where it is not parallel. Extended calculations with increased convergence and additional relaxation [16] indicated that the lowest energy sites are the $BC_{||}$ positions. However, the energy difference between the $BC_{||}$ and $BC_{\perp}$ is very small (~0.1 eV). Hence, hydrogen absorbed in ZnO and occupying $BC_{||}$ sites causes a significant lattice expansion in the c-direction. In the sub-surface region on the loaded side hydrogen-induced lattice expansion is higher than in the rest of the crystal. Absorbed hydrogen introduces stress into the loaded crystal and when this stress exceeds the yield stress in ZnO plastic deformation of the crystal takes place. Excess hydrogen in the sub-surface region is trapped at open volume defects (dislocations and vacancies) introduced by hydrogen-induced plastic deformation. This picture is supported by variable energy positron annihilation spectroscopy which revealed very high defect density in the sub-surface region in hydrogen loaded ZnO crystal [17].

Hydrogen-induced plastic deformation causes a typical surface modification of ZnO crystal. Fig. 2a shows light microscopy image of the surface of hydrogen loaded ZnO (0001) crystal which contains a lot of hexagonally shaped pyramids growing out of the sample. All these pyramids have the same orientation with respect to the crystal and were formed by hydrogen-induced slip in the c-direction. Surface modification of hydrogen loaded ZnO (10–10) crystal is shown in Fig. 2b. Again hydrogen-induced slip takes place in the c-direction which now lies in the plane of the surface. As a consequence the pyramids are now rotated by 90° with respect to Fig. 2a. Careful examination of surface of the hydrogen-loaded ZnO crystals by light microscopy and AFM did not reveal any

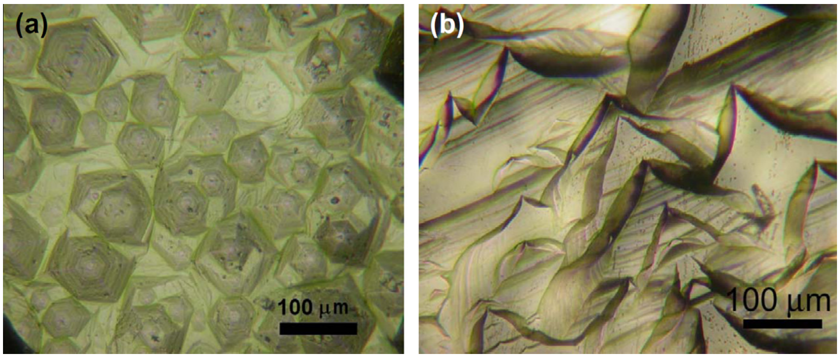

Fig. 2. Optical microscopy image of surface modification of hydrogen loaded ZnO crystal (t = 3 h, I = 0.5 mA): (a) crystal with (0001) orientation, (b) crystal with (10–10) orientation.

cracks. This is most probably due to hydrogen-induced slip in the c-direction, which enables relaxation of stresses introduced by hydrogen and prevents pile up of dislocations.

The *in situ* electrical resistivity measurements of hydrogen loaded ZnO crystals were performed in the configuration shown in Fig. 3a. Both the loaded side and the opposite side were covered by 20 nm Pd cap. The loaded side was deluged by electrolyte while the opposite side was on air without any contact with the electrolyte. This configuration enables resistivity to be measured independently on the loaded side and also on the opposite side. Fig. 3b shows the relative change of electrical resistivity $\Delta R/R_0$ measured on the loaded side and on the opposite side. ZnO crystals with c-orientation (0001) and a-orientation (10–10) were compared in order to examine possible anisotropy of hydrogen diffusivity on ZnO. Both crystals have the same thickness of 0.5 mm and were loaded using the current of 0.1 mA. Behaviour of electrical resistivity measured on the loaded side is very similar in both crystals: the Pd layer is firstly hydrogenated and transforms into the hydride phase (PdH) which is reflected by an increase of the resistivity. Continuous flux of incoming hydrogen during further loading keeps the Pd cap in the hydride phase (i.e. its electrical resistivity remains approximately constant) and hydrogen penetrates into the ZnO crystal. Additional increase of electrical resistivity accompanied with increased scatter of data occurs at longer loading times ($t > 2000$ s), see Fig. 3b. This is due to hydrogen-induced plastic deformation taking place in ZnO sub-surface layer and causing local destruction of Pd cap [18]. On the opposite side the rise of electrical resistivity is postponed and occurs after extended loading period of ≈14,000 s in the c-oriented crystal and after even longer period of ≈33,000 s in the a-oriented crystal, see Fig. 3b. Postponed response of electrical resistivity on the opposite side is due to diffusion of hydrogen from the loaded side across the sample thickness towards the opposite side. Hence, the room temperature hydrogen diffusion coefficient D_H in ZnO crystal can be estimated from the time lag t_{lag} between the resistivity response on the loaded side and on the opposite side $D_H \approx d^2/6t_{lag}$. The hydrogen diffusion coefficient $D_H = (3.0 \pm 1.0) \times 10^{-12}$ m^2 s^{-1} and $(1.3 \pm 0.6) \times 10^{-12}$ m^2 s^{-1} was obtained for the ZnO crystal with the c-orientation and the a-orientation, respectively. This result testifies that hydrogen diffusion in ZnO in the c-direction [0001] is significantly faster than in the a-direction [10–10]. Anisotropy of hydrogen diffusion in ZnO lattice is most probably due to open channels exiting in the ZnO wurtzite structure along the c-axis which facilitates hydrogen diffusion in the [0001] direction. Interestingly, the hydrogen diffusion coefficients determined here by electrical resistometry are roughly 3 orders of magnitude higher than the values extrapolated to room temperature from SIMS results [7,8]. It is possible that diffusivity of hydrogen determined by SIMS in a sub-surface region with depth of a few µm only, might be reduced by hydrogen trapping at defects, while bulk measurement by electrical resistometry is only slightly influenced by defected sub-surface region. Obviously, more detailed investigations are needed to resolve this question. However, it seems to be clear that concentration of defects is important parameter which has to be considered in study of hydrogen diffusion in ZnO.

4. Conclusions

Hydrothermally grown ZnO crystals were electrochemically doped with hydrogen. Bulk hydrogen concentration introduced

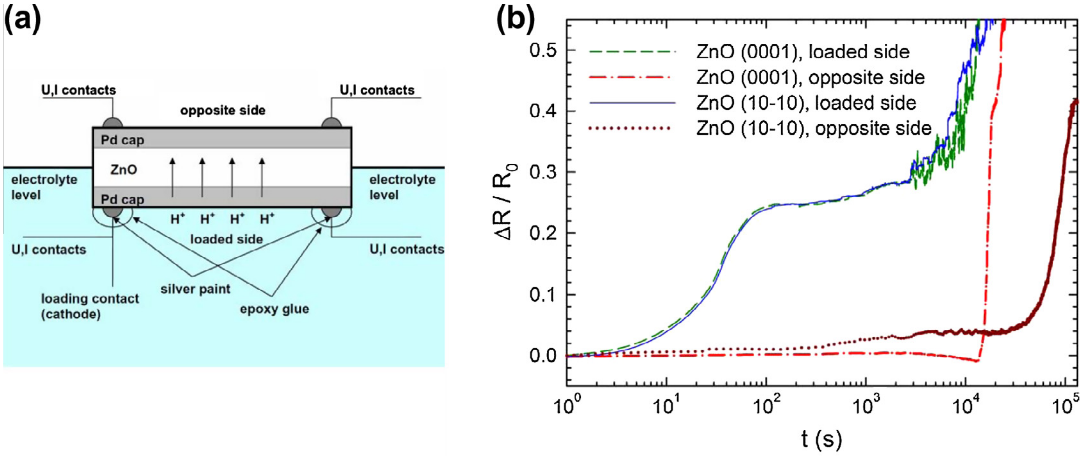

Fig. 3. (a) Schematic depiction of the arrangement used for *in situ* electrical resistivity measurement during hydrogen loading; (b) the relative increase of electrical resistivity in ZnO crystals with (0001) and (10–10) orientation charged with hydrogen using the current of 0.1 mA.

into the crystal agrees with that estimated from the Faraday's law. Excess hydrogen concentration on the loaded side initiates plastic deformation which introduces open volume defects into a sub-surface region and causes a specific surface modification created by hydrogen-induced slip in the c-direction. *In situ* electrical resistometry enabled hydrogen diffusion coefficient in ZnO to be determined and revealed that hydrogen diffusion in the c-direction is faster than in the a-direction due to open channels existing in the ZnO wurtzite structure along the c-axis and facilitating hydrogen diffusion.

Acknowledgements

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