Current-driven hydrogen incorporation in zinc oxide

Min-Suk Oh, Dae-Kue Hwang, Jae-Hong Lim, Yong-Seok Choi, and Seong-Ju Park
Department of Materials Science and Engineering, Gwangju Institute of Science and Technology, Gwangju 500-712, Korea

(Received 12 July 2007; accepted 1 November 2007; published online 20 November 2007)

The effect of electrical current on the hydrogen incorporation into single crystalline ZnO was investigated. The current-voltage characteristics of single crystalline ZnO were measured as a function of the electrical conductivity of ZnO. The electrical current of ZnO was significantly increased at the second sweep of voltages when the electrical conductivity of ZnO was higher than 0.32 S/cm. A depth profiling analysis of ZnO by dynamic secondary ion mass spectrometry indicated that the hydrogen atoms were incorporated to form hydrogen-related donors, such as a substitutional hydrogen (H$_{s}$) and an interstitial hydrogen (H$_{i}$), which resulted in an increase in the donor concentration of ZnO. © 2007 American Institute of Physics. [DOI: 10.1063/1.2816119]

ZnO is a wide band gap semiconductor, and is one of the most widely investigated oxide materials due to its high electrical conductivity and its transparency. Low cost and the availability of a large area ZnO substrate, wet chemical etching, and low temperature growth also make it attractive for application to electronic devices.\(^{1}\) For example, fully transparent ZnO-based thin-film transistors were fabricated on either glass or flexible substrate\(^{21}\) and ultraviolet light-emitting diodes\(^{4,5}\) were fabricated as a result of realization of p-type ZnO doped with various elements.\(^{6,7}\) However, with ZnO, unestablished reliability and reproducibility issues remain unsolved. It has been reported that high electrical gate bias stress (\(V_{GS}>30\) V) results in a shift of the threshold voltage in the transfer characteristics as a consequence of defect state creation within the ZnO channel\(^{8}\) and the p-type conductivity of ZnO films are often converted to an insulating or n-type conductivity within a period of several days or months.\(^{9,10}\) Therefore, understanding the source of unintentional conductivity for undoped ZnO and type conversion of p-type ZnO is essential in order to control doping and develop reliable high-performance ZnO-based devices.

Atomic hydrogen is well known to behave as an exclusive shallow donor in bulk ZnO.\(^{11,12}\) Hydrogen is ubiquitous and can be easily incorporated in ZnO during the crystal growth.\(^{13}\) The intentional hydrogen doping of ZnO by plasma irradiation and remote plasma hydrogenation was found to affect the electrical and optical properties of ZnO.\(^{14,15}\) In this study, atomic hydrogen atoms were readily incorporated into the ZnO surface region through mediation of electrical current and this greatly affected the electrical properties of ZnO. Hydrogen atoms incorporated into ZnO by electrical current were found to form hydrogen-related shallow donors, resulting in an increase of the effective carrier concentration.

The single crystalline ZnO used in this work was oxygen-terminated ZnO(0001) substrate provided from CrysTech GmbH. The ZnO substrates were hydrothermally grown and showed n-type conductivity. The surface roughness measured by atomic force microscope (AFM) was typically less than 0.25 nm. The carrier concentration, mobility, and electrical conductivity of the as-received ZnO substrates were measured to be $5 \times 10^{15} \text{cm}^{-3}, 124 \text{cm}^2/\text{V s}$, and 0.11 S/cm, respectively. In an effort to control the conductivity of ZnO, the ZnO substrates were thermally annealed under various annealing conditions. Before the annealing treatment, all the samples were ultrasonically degreased using trichloroethylene, acetone, methanol, and de-ionized water for 5 min at each step, followed by N$_2$ blowing as a cleaning process. The annealing time was 20 min, the working pressure of the annealing chamber was $7 \times 10^{-7} \text{Torr}$, and the annealing temperature was varied from 100 to 900 °C to control the electrical conductivity of ZnO. The electrical properties of ZnO were characterized by Hall effect measurement with the Van der Pauw geometry using a nonalloyed Ti/Au (30/60 nm) metal scheme as contact layers. Current-voltage (\(I-V\)) measurements of ZnO were carried out using a parameter analyzer (HP 4155A). The first \(I-V\) measurement was performed by applying a voltage ranging from 0 to 5 V (referred to here as “the first voltage sweep”). The \(I-V\) curves of all ZnO samples were measured again by applying a voltage in the range of from 0 to 10 V (referred to here as “the second voltage sweep”) to observe the change in the currents at given voltages. In order to obtain the depth profiles of the hydrogen atoms, a secondary ion mass spectrometry (SIMS) (PHI 7200 TOF-SIMS/ALI) was employed by using a Cs$^+$

![FIG. 1. (Color online) Carrier concentration, Hall mobility, and conductivity of the ZnO samples as a function of annealing temperature.](image)

---

*Electronic mail: sjpark@gist.ac.kr*
The conductivity of ZnO was observed to increase and decrease with the application of electrical current, as shown in Figs. 2 and 3. The inset of Fig. 2(b) shows the current-driven hydrogen incorporation into ZnO, confirming the current-driven hydrogen incorporation into ZnO. The inset of Fig. 3 shows the relative change of the current in-situ ion implanted ZnO, with the electrical current recovered to the initial value.

The distribution of elements in ZnO was determined by using SIMS analysis before and after applying an electrical bias to ZnO. The ZnO annealed at 900 °C was chosen for SIMS analysis, because it showed the highest I/I_0 after the voltage sweep. Figure 4 shows the SIMS depth profiles for hydrogen (a) and OH radicals (b). The distribution of hydrogen was quantified by using a hydrogen ion implanted ZnO standard, as shown in Fig. 4(a). However, the quantification of OH radical was not performed due to the difficulties in obtaining the implanted standard for OH radicals. Figure 4(a) shows that the hydrogen atoms are present in the as-received ZnO at a concentration in the range of (2–5) × 10^{15}/cm^2. It should be emphasized that not all of the initial hydrogen atoms are in a donor state because Hall effect measurement showed that the carrier concentration of as-received ZnO is only 5 × 10^{15}/cm^3. This indicates that most of the hydrogen atoms are in an inactive state in as-received ZnO. Most of the hydrogen atoms and OH radicals diffused out of ZnO at 900 °C, showing hydrogen concentration of 1 × 10^{10}/cm^3. After the first voltage sweep, however, hydrogen atoms and OH radicals were detected in large quantities near the surface region of ZnO. The maximum concentration of incorporated hydrogen was measured to be 6.5 × 10^{15}/cm^3 for the first voltage-swept ZnO. The penetration depth of hydrogen-related species was estimated to be 0.29 μm. In order to confirm the current-driven hydrogen incorporation into ZnO, the ZnO subjected to the first voltage sweep was subsequently annealed at 500 °C for 5 min. As shown in Fig. 4, the hydrogen atoms were removed from ZnO (2 × 10^{10}/cm^3) and electrical current was recovered to the initial value.
In summary, the change of current-voltage characteristics of single crystalline ZnO by voltage sweeps has been measured as a function of the conductivity of ZnO. The electrical current of ZnO was significantly increased by voltage sweeps when the conductivity of ZnO was higher than 0.32 S/cm. A SIMS depth profiling of ZnO indicated that the applied electrical current can induce the incorporation of the hydrogen atoms down to the 0.29 μm depth of ZnO, resulting in an increase of the effective carrier concentration. The I-V and SIMS measurements also suggested that the hydrogen atoms are incorporated into ZnO to form hydrogen-related donors, such as the substitutional hydrogen bound to zinc atoms and the interstitial hydrogen bound to oxygen atoms.

This work was partially supported by the IT R&D program of MIC/IITA (2006-S079-01), Smart window with transparent electronic devices, the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korea government (MOST) (No. R17-2007-078-01000-0), the Grant from the Ministry of Commerce, Industry and Energy (No. 10024859-2007-12).