

Enhancement of the Hall Mobility in Hydrogen-ion-irradiated ZnO Films

C. S. YEO and K. B. CHUNG*

Department of Physics, Dankook University, Cheonan 330-714, Korea

J. S. PARK

Material Science and Engineering, Dankook University, Cheonan 330-714, Korea

J. H. SONG

Nano Analysis Center, Korea Institute of Science and Technology, Seoul 136-791, Korea

(Received 18 November 2011)

RF-sputtered ZnO films were irradiated with hydrogen ions by using an ion accelerator at 110 keV. The physical and the electrical characteristics of the irradiated ZnO films were studied as functions of the hydrogen-ion irradiation dose. The Hall measurement indicated that the carrier concentration had small changes regardless of irradiated hydrogen amount, but the mobility was dramatically enhanced after irradiation of 10^{15} atoms/cm². Even when the irradiated hydrogen dose was increased, the crystalline structure had no transformation and the composition was preserved. On the other hand, the electronic structure, measured by using X-ray absorption spectroscopy, exhibited a modification of the molecular orbital structure in the ZnO films irradiated at doses above 10^{15} atoms/cm². These distortions of the molecular orbital in the conduction band could lead to a mobility enhancement without a structural transformation.

PACS numbers: 71.20.Nr, 72.20.-I, 73.50.-h, 73.61.-r

Keywords: ZnO film, Hydrogen, Ion irradiation, Hall mobility, Electronic structure

DOI: 10.3938/jkps.60.307

I. INTRODUCTION

Oxide thin film transistors (TFTs) have been the subject of intensive research in the last 10 years because of their potential for flexible, lightweight, mechanically robust electronics for displays and other devices on plastic substrates [1,2]. The most common oxide semiconductor materials such as indium-gallium-zinc-oxide (InGaZnO) have good TFT characteristics with a high field effect mobility (μ_{FE}) and large on/off ratio [2]. Despite the excellent performances, the complex quaternary oxide, which includes the expensive indium element, is the drawback to realizing practical applications. One possible solution to overcome such a problem is the utilization of a simple binary oxide with efficient and reliable properties.

An intrinsic ZnO semiconductor is a wide band gap (~ 3.3 eV), *n*-type semiconductor with a hexagonal wurtzite structure and a high melting temperature. As a result, ZnO has been considered to be a material of interest for high-quality optoelectronics application [3]. Several research groups have recently reported transpar-

ent TFTs using binary stoichiometric zinc oxide (ZnO) semiconductor [4–6]. Particularly, ZnO TFTs are attractive because good quality polycrystalline ZnO films with moderate Hall mobility (>1 cm²/V^s) can be made at room temperature, so there is good compatibility with flexible substrate [4].

The major issue for various applications of ZnO semiconductors is control of the ZnO semiconductor properties, such as the carrier concentration and the mobility, at low processing temperature under ~ 150 °C, which is typically a limitation of plastic substrate. The properties of ZnO have been modified by using annealing, ion implantation, and other treatments [7–9]. Unfortunately, the annealing process is achieved at high temperatures above ~ 400 °C, and ion implantation physically induces structural damage into the grown film, thus requiring a curing process such as post-annealing. The purpose of this work is to modify the electrical properties of ZnO films without structural transformation and at room temperature, by using ion irradiation. Ion irradiation is an interesting way to change the material properties by introducing structural disorder, defects, and amorphization through variations in the ionic element and the ion's mass and acceleration energy [10,11]. In this study, the physical and the electrical characteris-

*E-mail: kbchung@dankook.ac.kr

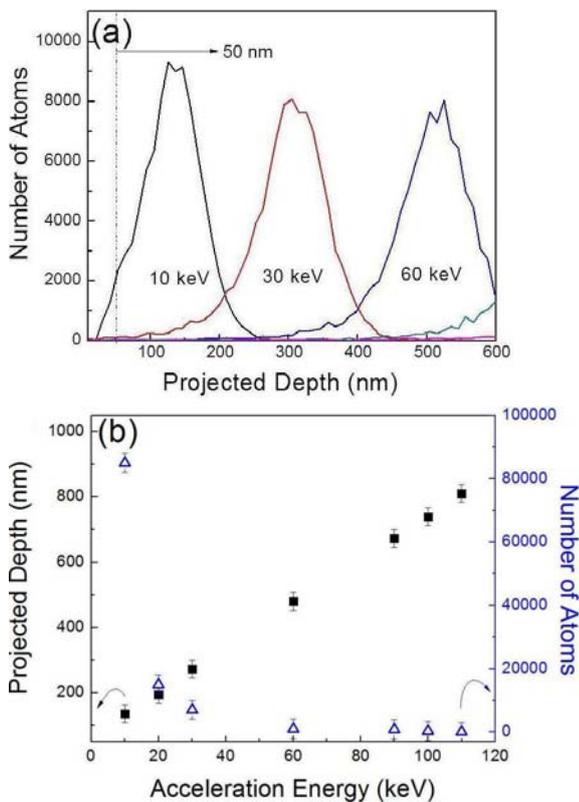


Fig. 1. (Color online) (a) Simulation of the dependence of the trajectory of a hydrogen ion in the depth direction of ZnO films on the ion acceleration energy and (b) the calculated results for the projected depth and number of hydrogen atoms as functions of the acceleration energy. In order to determine the acceleration energy of the hydrogen ion that can minimize the incorporation of hydrogen ions into ZnO (50 nm) films and damage, we performed the simulation by using the stopping and range of ions in matter (SRIM) code.

tics of hydrogen-ion-irradiated ZnO films were examined, and the associated electronic structures were analyzed.

II. EXPERIMENT

P-type Si wafers with thermally grown SiO₂ (100 nm) were employed as substrates onto which ZnO films (50 nm) were deposited by using a radio-frequency (RF) sputtering system. The RF power and the process pressure were 75 W and 10 mTorr, respectively, which was controlled by using an Ar gas flow rate of 50 sccm. Then, hydrogen ions were irradiated onto the ZnO films at 110 keV by using a 2-MeV tandem accelerator.

In order to examine the effect of the amount of irradiated hydrogen, we adjusted the dose of hydrogen ion, using 10¹⁴ atoms/cm² and 10¹⁵ atoms/cm². Figure 1(a) show a simulation of the dependence of the trajectory of a hydrogen ion in the depth direction of a ZnO film on the ion acceleration energy. The simulations of the

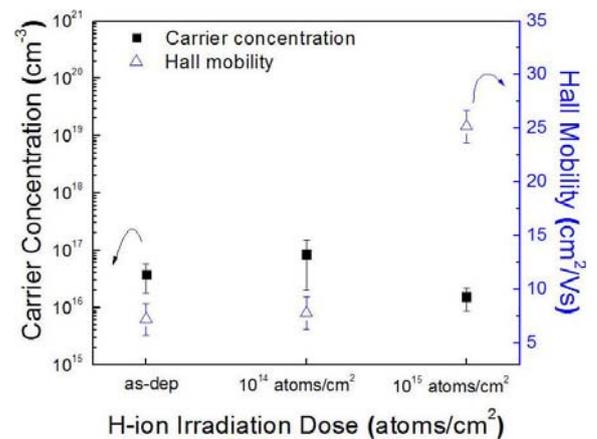


Fig. 2. Carrier concentration and mobility of as-deposited and hydrogen-ion-irradiated ZnO films as functions of irradiation dose.

projected depth (range) and number of atoms were performed by using the stopping and range of ions in matter (SRIM) code. The dotted line at 50 nm shown in Fig. 1(a) indicates the thickness of the ZnO film. From the calculation based on the simulation results, Fig. 1(b) represent the projected depth and number of hydrogen atoms as functions of the acceleration energy. The determined acceleration energy of 110 keV was adequate for hydrogen ions to pass completely through the entire ZnO film (50 nm). After irradiation with hydrogen ions, the remnant hydrogen ions in the ZnO films were very low, with densities less than $\sim 10^8$ atoms/cm². Consequently, hydrogen ions are not incorporated into the ZnO films, and the damage due to accelerated ions is minimized due to the light mass of hydrogen.

The Hall measurement was used to investigate the electrical characteristics such as the carrier concentration and the mobility of hydrogen-ion-irradiated ZnO films. The physical structure was observed using X-ray diffraction (XRD) with a monochromatic CuK α X-ray source. The composition and the chemical bonding states were examined by using X-ray photoelectron spectroscopy (XPS) with a monochromatic AlK α (1486.6 eV) source at a pass energy of 20 eV. In order to analyze the electronic structure, we carried out X-ray absorption spectroscopy (XAS) measurement with the coherent X-ray beam source at the Pohang Accelerator Laboratory (PAL) on beamline 7B1.

III. RESULTS AND DISCUSSION

Hall measurements were accomplished at room temperature to examine the electrical properties of ZnO films as a function of hydrogen ion irradiation dose, as shown in Fig. 2. In the case of the as-deposited ZnO film, the carrier concentration and the mobility were 3.7×10^{16} cm⁻³ and 7.25 cm²V⁻¹s⁻¹, respectively. When hy-

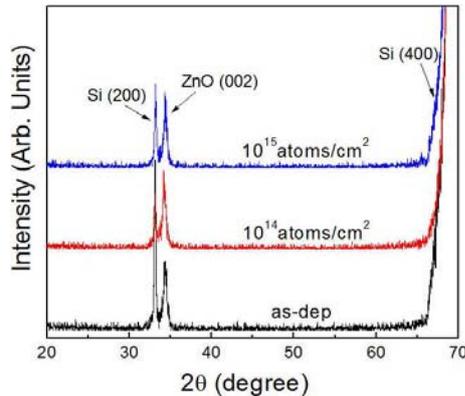


Fig. 3. (Color online) XRD data collected from as-deposited and hydrogen-ion-irradiated ZnO films as functions of irradiation dose.

drogen ions irradiated the ZnO film, the carrier concentration had small variation within $\sim 10^{16} \text{ cm}^{-3}$ order, regardless of the irradiated hydrogen ion dose. On the other hand, the mobility after irradiation with hydrogen ions was dramatically enhanced to $\sim 25 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at $10^{15} \text{ atoms/cm}^2$. These remarkable changes in the mobility could be associated with the irradiation of the ZnO film by hydrogen ions and with the amount of the irradiated hydrogen ions. More discussion is provided below in conjunction with an interpretation of the physical and the electronic structures.

Figure 3 shows XRD data collected from as-deposited and hydrogen-ion-irradiated ZnO films as functions of the irradiation dose. The evolution of the preferred orientations and a qualitative comparison are possible because all XRD spectra were measured by using a theta-2theta X-ray diffractometer and were normalized to the Si (400) peak from the Si (100) substrate. In as-deposited and hydrogen-irradiated ZnO films, the hexagonal ZnO (002) phase is revealed [12]. The crystalline ZnO (002) peak is preserved without structural transformation up to an irradiation of $10^{15} \text{ atoms/cm}^2$, as seen by the relative change in the ZnO (002) peak. In addition, even though not shown here, the stoichiometry and the chemical bonding states of ZnO films did not change, regardless of hydrogen-ion irradiation dose. These imply that hydrogen irradiation at a 110-keV ion energy has no effect on the physical structure and the composition of ZnO films.

XAS analyses were tried to examine the electronic structure and the orbital ordering upon hydrogen irradiation of ZnO films. Normalizations of the XAS spectra were carefully performed by subtracting an X-ray beam background from the raw data and subsequently scaling the difference between pre- and post-edge levels to an arbitrary, but uniform, value. Through the normalizations of XAS spectra, the qualitative changes and comparison of molecular orbital bonding symmetries could be analyzed [13]. Figure 4(a) presents the normalized oxygen (O) K_1 edge spectra caused by the molecular orbital hy-

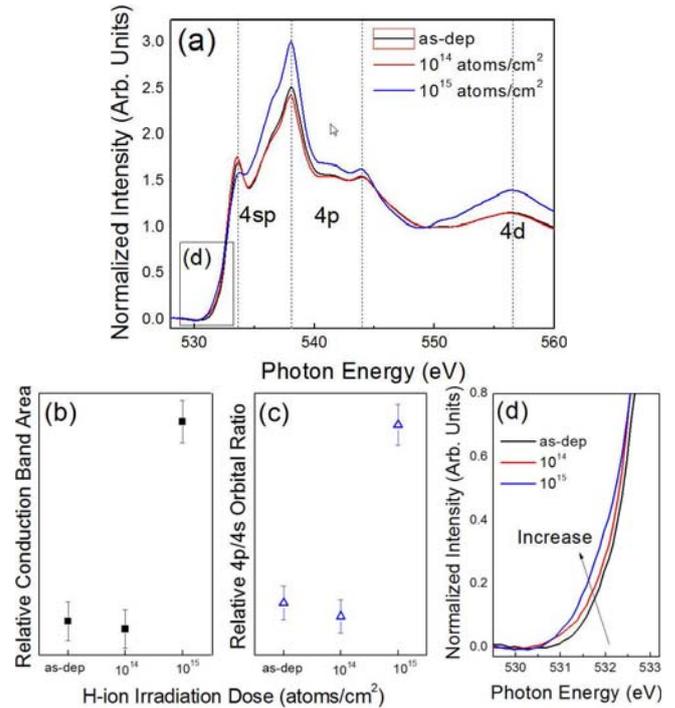


Fig. 4. (Color online) (a) Normalized XAS O K_1 edge spectra, (b) relative conduction band area including $4s$, $4p$, and $4d$ orbitals from 530 eV to 560 eV, (c) relative $4p/4s$ orbital ratio, and (d) the enlargement of band edge states near ~ 530 eV for as-deposited and hydrogen-ion-irradiated ZnO films.

bridization between Zn and O in the conduction band. The O K_1 edge spectra of ZnO are directly related to the oxygen p -projected states of the conduction band, which consists of unoccupied hybridized orbitals for Zn $4sp + O 2p$, Zn $4p + O 2p$, and Zn $4d + O 2p$ from 530 eV to 560 eV [14]. After hydrogen ion irradiation of $10^{15} \text{ atoms/cm}^2$, considerable changes in molecular orbital structure occur in the $4sp$ and the $4d$ orbitals. Detailed examinations of orbital modification are achieved by using relative comparisons of the conduction band area and the $4p/4s$ orbital ratio, as shown in Figs. 4(b) and (c). Similar to the normalized O K_1 edge spectra, drastic increases in the conduction band area and the $4p/4s$ orbital ratio are produced after hydrogen ion irradiation of $10^{15} \text{ atoms/cm}^2$. Moreover, Fig. 4(d) shows that the band edge states below the conduction band increase with increasing irradiated hydrogen ion dose.

Based on the XAS results, the most compelling origin of the dependence of the changes in the electrical properties such as mobility on the hydrogen irradiation may be attributed to a modification of electronic structure. An alternation of molecular orbitals and the dominance of the p orbital caused by a distortion of the electronic structure of ZnO film lead to an increase in the possibility of carrier transport in terms of an extension of the unoccupied conduction band and an enhancement of the directional p orbital ordering rather than the spherically

symmetric s orbital. In addition, the increase in the mobility after hydrogen irradiation could be explained by an increase in band edge states related to O vacancies [15–17]. The physical significance is obtained by using the Einstein relation, which states that the correlation between the mobility (μ) and the O vacancies (q) is given by $kT\mu = qD$ (k : Boltzmann's constant, T : temperature, D : diffusivity) [18]. From the above interpretations, the changes in the molecular orbital structure and the generation of O vacancies caused by hydrogen irradiation contribute to the enhanced electronic charge transport in ZnO films.

IV. CONCLUSION

ZnO films were sputter-deposited and irradiated by hydrogen ions at an acceleration energy of 110 keV for various irradiation doses. The carrier concentration had small changes regardless of the amount irradiated hydrogen, but the hall mobility was dramatically enhanced to $\sim 25 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ after a hydrogen ion irradiation of $10^{15} \text{ atoms/cm}^2$. Regardless of the amount of irradiated hydrogen, the physical structural transition was preserved with the crystallinity oriented by the hexagonal ZnO (002) phase. However, changes in electronic structure were observed from hydrogen-ion-irradiated ZnO films for hydrogen ion doses above $10^{15} \text{ atoms/cm}^2$. The unoccupied states in the conduction band were increased due to a distortion of $4sp$ molecular orbitals; the band edge states below conduction band were also increased. The enhanced mobility with small change in carrier concentration and without structural transformation may be interpreted in terms of a modification of the $4sp$ orbitals and an increase in the number of O vacancies near conduction band edge induced by hydrogen irradiation.

ACKNOWLEDGMENTS

The present research was conducted by the research fund of Dankook University in 2010.

REFERENCES

- [1] J. F. Wager, *Science* **300**, 1245 (2003).
- [2] K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano and H. Hosono, *Nature* **432**, 488 (2004).
- [3] Ü. Özgür, Ya. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho and H. Morkoç, *J. Appl. Phys.* **98**, 041301 (2005).
- [4] P. F. Carcia, R. S. McLean, M. H. Reilly and G. Nunes, Jr., *Appl. Phys. Lett.* **82**, 1117 (2003).
- [5] E. M. C. Fortunato, P. M. C. Barquinha, A. C. M. B. G. Pimentel, A. M. F. Goncalves, A. J. S. Marques, R. F. P. Martins and L. M. N. Pereira, *Appl. Phys. Lett.* **85**, 2541 (2004).
- [6] S-H. Park, C-S. Hwang, M. Ryu, S. Yang, C. Byun, J. Shin, J-I. Lee, K. Lee, M. S. Oh and S. Im, *Adv. Mater.* **21**, 678, (2009).
- [7] D. C. Look, D. C. Reynolds, J. W. Hemsky, R. L. Jones and J. R. Sizelove, *Appl. Phys. Lett.* **75**, 811 (1999).
- [8] M. K. Puchert, P. Y. Timbrell and R. N. Lamb, *J. Vac. Sci. Technol., A* **14**, 2220 (1996).
- [9] H. S. Kang, J. S. Kang, J. W. Kim and S. Y. Lee, *J. Appl. Phys.* **95**, 1246 (2004).
- [10] C. Chappert, H. Bernas, J. Ferré, V. Kottler, J.-P. Jamet, Y. Chen, E. Cambril, T. Devolder, F. Rousseaux, V. Mathet and H. Launois, *Science* **280**, 1919 (1998).
- [11] K. Nordlund, J. Keinonen and T. Mattila, *Phys. Rev. Lett.* **77**, 699 (1996).
- [12] G. Bruno, M. M. Giangregorio, G. Malandrino, P. Capezuto, I. L. Fragalà and M. Losurdo, *Adv. Mater.* **21**, 1700 (2009).
- [13] K. B. Chung, J. P. Long, H. Seo, G. Lucovsky and D. Nordlund, *J. Appl. Phys.* **106**, 074102 (2009).
- [14] C. L. Dong, C. Persson, L. Vayssieres, A. Augustsson, T. Schmitt, M. Mattesini, R. Ahuja, C. L. Chang and J-H. Guo, *Phys. Rev. B* **70**, 195325 (2004).
- [15] G. Lucovsky *et al.*, *IEEE Trans. Device Mater. Reliab.* **5**, 65 (2005).
- [16] T. Kamiya, K. Nomura and H. Hosono, *J. Disp. Tech.* **5**, 273 (2009).
- [17] G. Lucovsky, *Jpn. J. Appl. Phys.* **50**, 04DC09 (2011).
- [18] S. Zafar, R. E. Jones, B. Jiang, B. White, P. Chu, D. Taylor and S. Gillespie, *Appl. Phys. Lett.* **73**, 175 (1998).