

# Modification of the Electronic Structure and the Electrical Properties of ZnO Thin Films by Nickel-ion Irradiation at Room Temperature

Hyun-Woo PARK, Min-Jun CHOI and Kwun-Bum CHUNG\*

*Division of Physics and Semiconductor Science, Dongguk University, Seoul 04620, Korea*

Jonghan SONG and Keun Hwa CHAE

*Advanced Analysis Center, Korea Institute of Science and Technology, Seoul 02792, Korea*

Byung-Hyuk JUN

*Division of Neutron Utilization Technology, Korea Atomic Energy Research Institute, Daejeon 34057, Korea*

Byung Du AHN, Jong-moo HUH and Hyedong KIM

*Samsung Display Corporation, Yongin 17113, Korea*

(Received 15 June 2015, in final form 23 November 2015)

Radio-frequency (RF) sputtered ZnO films were investigated as a function of the Ni-ion irradiation dose at room temperature. The prepared ZnO films were irradiated with Ni-ions at an acceleration energy of 130 MeV in the dose range from  $5 \times 10^{11}$  ions/cm<sup>2</sup> to  $1 \times 10^{13}$  ions/cm<sup>2</sup>. The electrical properties of the irradiated ZnO films changed with changing Ni-ion irradiation dose. In order to explain the change in the electrical properties of ZnO films, we investigated the physical properties and the electronic structure, such as the physical structure, the molecular orbital in the conduction band, and the band edge state below the conduction band. The physical structure and the physical composition showed no changes, regardless of the Ni-ion irradiation dose. On the other hand, the electronic structure showed a drastic modification of the hybridized molecular orbital ordering of the Zn 4*sp* and the O 2*p* in the conduction band. In addition, two distinct band edge states below the conduction band were observed with increasing Ni-ion irradiation dose. These remarkable changes in the electronic structure could be correlated to changes in the electrical properties.

PACS numbers: 34.50.Bw, 34.50.Gb, 39.30.+w

Keywords: ZnO, Swift heavy-ion irradiation, Electronic structure

DOI: 10.3938/jkps.68.190

## I. INTRODUCTION

Zinc-oxide (ZnO) materials are the most promising candidates for fabricating optoelectronic devices, light emitting diodes, piezoelectronic transducers, biological sensors, and laser diodes with short wavelengths because of their unique characteristics, including wide bandgap ( $\sim 3.3$  eV) and significantly larger exciton binding energy ( $\sim 60$  meV) [1–3]. If these applications are to be realized, key issues related to the modulation method of ZnO electrical properties, such as the carrier concentration and the mobility at low temperature, should be considered. The modification methods of ZnO material properties include thermal annealing, impurity doping, ion implantation, and other treatments [4, 5]. Unfortunately, the thermal annealing process is performed at high temper-

atures above  $\sim 300$  °C, and ion implantation produces collision damage in the ZnO matrix, which can generate unnecessary and uncontrollable defect states; thus, a curing process such as post-annealing is required [6].

Very recently, several researchers have reported changes in the structural, optical, and electrical properties of ZnO films by using an ion irradiation method. Ion irradiation is a unique tool to modify the structural, electrical, and optical properties of a material at room temperature [7–10]. The irradiated ions lose their energy by elastic collisions with the target nuclei in the materials, as well as by inelastic collisions that result in electronic excitations of the target atoms in the materials. In addition, ion irradiation using a heavy ion is more suitable for manipulating the physical and electrical properties while causing smaller damage to the material [11, 12].

In this study, we examine the effect of Ni-ion irradiation on ZnO films in terms of their physical and elec-

\*E-mail: kbchung@dongguk.edu; Fax: +82-2-2290-1467

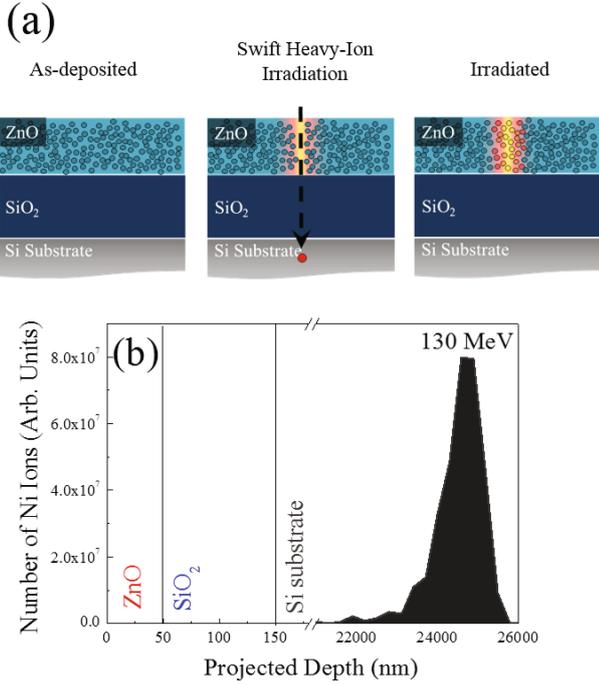


Fig. 1. (Color online) (a) Schematic illustrations of the swift heavy-ion irradiation process and (b) projected depth of Ni ions at an acceleration energy of 130 MeV.

trical properties. Moreover, the origins of the change in the electrical properties of the ZnO films are investigated and are analyzed by using the change in the electronic structure as a function of the irradiation dose of Ni ions.

## II. EXPERIMENTS AND DISCUSSION

ZnO films were deposited without substrate heating on thermally-grown SiO<sub>2</sub> (100 nm)/heavily-doped p-type Si wafers by using a RF sputtering system. The process pressure and the Ar gas flow rate were 10 mTorr and 50 sccm, respectively. The RF power of the ZnO target was fixed at 75 W, and the ZnO film thickness was 50 nm. The ZnO films were then irradiated with a 130-MeV Ni-ion beam (at room temperature) by using the 15UD Tandem Accelerator at the Inter University Accelerator Centre (IUAC), New Delhi, India, at different Ni-ion irradiation doses of  $5 \times 10^{11}$  ions/cm<sup>2</sup>,  $1 \times 10^{12}$  ions/cm<sup>2</sup>, and  $1 \times 10^{13}$  ions/cm<sup>2</sup>. The irradiation was performed under high vacuum conditions (base pressure:  $2 \times 10^{-6}$  Torr). The incident angle of the ion beam was kept slightly away from the surface normal of the sample to avoid the channeling effects. Figure 1(a) shows a schematic illustration of the as-deposited and the irradiated ZnO films by using the swift heavy-ion irradiation method. During swift heavy-ion irradiation, an energetic ion passing through a solid is well established to lose its energy via two nearly independent processes: (i) elec-

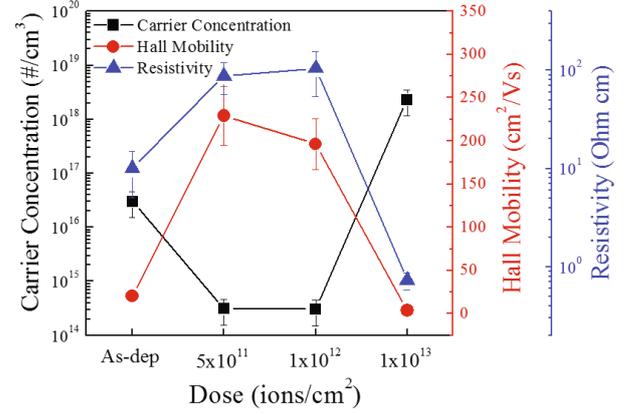


Fig. 2. (Color online) Electrical properties, including carrier concentration, mobility, and resistivity, for as-deposited and irradiated ZnO films.

tronic excitation and ionization (electronic energy loss:  $-(dE/dx)_e = S_e$ ) and (ii) elastic collisions with the nuclei of the target atoms (nuclear energy loss:  $-(dE/dx)_n = S_n$ ). In high-energy ion-solid interactions, the nuclear energy loss may be neglected as compared to the electronic energy loss [13]. Figure 1(b) shows simulated trajectories of Ni ions at an acceleration energy of 130 MeV that were obtained by using the stopping and range of ions in matter (SRIM) simulation code. From the simulation results, an acceleration energy of 130 MeV was shown to be adequate for Ni ions to pass completely through a 50-nm-thick ZnO film and not to become incorporated in the films.

The electrical properties, such as the carrier concentration, mobility, and resistivity of the as-deposited and the irradiated ZnO films, were assessed by using a Hall measurement system with a 0.55-Tesla permanent magnet at room temperature. The modifications of the physical properties, including the crystallization and the physical composition, were measured by using X-ray diffraction (XRD) and Rutherford backscattering (RBS). The detailed electronic structures, related to changes in the band edge state below the conduction band and the ordering of the Zn *4sp* and O *2p* hybridized molecular orbital in the conduction band, were investigated by using X-ray absorption spectroscopy (XAS). In particular, the XAS spectra were measured at the facility of the 10D beam line, Pohang Accelerator Laboratory (PAL), Pohang, Korea.

Figure 2 shows the carrier concentration, mobility, and resistivity of the irradiated ZnO films as a function of the Ni-ion irradiation dose. In the as-deposited ZnO film, the carrier concentration and mobility were  $3.11 \times 10^{16}$  /cm<sup>3</sup> and  $20.67$  cm<sup>2</sup>/V·s, respectively, and the films displayed n-type semiconductor characteristics. When the Ni-ion irradiation dose was increased to  $5 \times 10^{11}$  ions/cm<sup>2</sup>, the carrier concentration decreased to  $3.09 \times 10^{14}$  /cm<sup>3</sup> and the mobility increased to  $229$  cm<sup>2</sup>/V·s. As the Ni-ion irradiation dose was increased to  $1 \times 10^{12}$

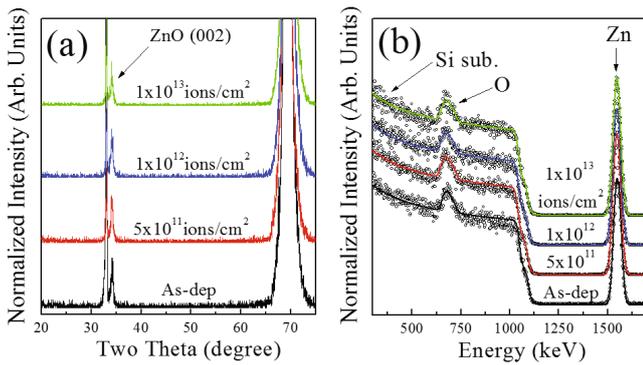


Fig. 3. (Color online) (a) X-ray diffraction patterns and (b) Rutherford backscattering spectra for ZnO films deposited on silicon substrates for various value of the Ni-ion irradiation does.

ions/cm<sup>2</sup>, the carrier concentration showed small variations of less than  $\sim 10^{14}$  /cm<sup>3</sup> and the mobility showed a similar trend. However, at a Ni-ion irradiation dose of  $1 \times 10^{13}$  ions/cm<sup>2</sup>, the carrier concentration and mobility were drastically changed to  $2.31 \times 10^{18}$  /cm<sup>3</sup> and  $3.74$  cm<sup>2</sup>/V·s, respectively, which indicate a parabolic behavior as a function of the Ni-ion irradiation dose. These remarkable changes in the electrical properties could be associated with the changes in the hybridized molecular orbital in the conduction band and the band edge states below the conduction band such as oxygen vacancies, which are affected by the Ni-ion irradiation dose. More information has been provided below and the physical and electronic structures have been considered.

Changes in the physical structure and the physical composition of the ZnO film as a function of the Ni-ion irradiation dose were investigated by using XRD and RBS measurements, as shown in Fig. 3(a), (b). The preferred orientations and their qualitative comparison were comparable because all XRD spectra were measured with a theta–2theta X-ray diffractometer and were normalized to the Si (400) peak from the Si (100) substrate. In the as-deposited and irradiated ZnO films, the preferred orientation of the hexagonal ZnO (002) phase was observed, regardless of the Ni-ion irradiation dose. These findings indicate that different Ni-ion irradiation doses had no effects on the physical structure. Similarly, the physical compositions of Zn and O showed no changes with changing Ni-ion irradiation dose within the detection limit of the RBS. These results indicate that an acceleration energy of 130 MeV was adequate for the Ni ions to pass completely through the ZnO film and not to be incorporated in the films and are similar to the simulation results presented in Fig. 1(b). Therefore, this remarkable change in the electrical properties of irradiated ZnO films could be associated with changes in other properties, not with the changes in the physical structure and the physical composition of the ZnO films.

The XAS analytical data, which show changes in the hybridized molecular orbital structures in the conduc-

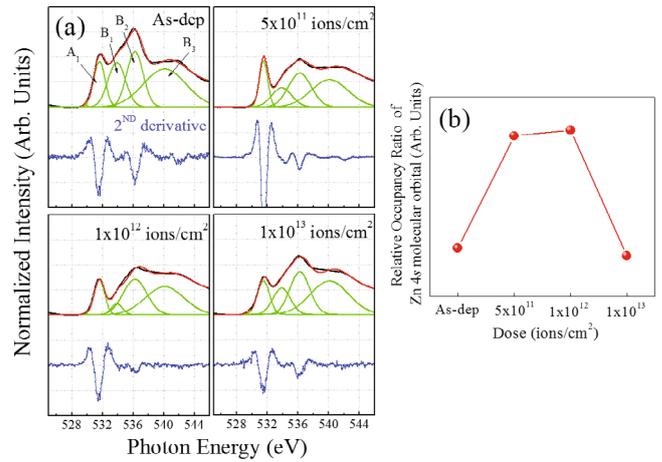


Fig. 4. (Color online) (a) Deconvoluted Oxygen *K*-edge XAS spectra for various value of the Ni-ion irradiation does and (b) relative occupancy ratio of the 4s molecular orbital of ZnO films as a function of Ni-ion irradiation dose.

tion band of the ZnO films as a function of the Ni-ion irradiation dose, are shown in Fig. 4(a). The normalized intensities of the O *K*-edge spectra of ZnO directly reflect the molecular orbital hybridization between the Zn 4s, 4sp, and the O with 2p states based on the local atomic bonding symmetry [14]. After normalization, the relative intensity can explain the transition of an electron from the O 1s orbital to the unoccupied Zn 4s and 4sp molecular orbitals of ZnO based on empirical symmetry-determined models [15], especially for the second derivative of the O-*K* spectra to determine the energy level of the molecular orbital states, as shown in Fig. 4(a) (blue line). The O *K*-edge spectra of as-deposited and irradiated ZnO films could be deconvoluted into 4 distinct absorption Gaussian peaks, which were denoted as A<sub>1</sub> and B<sub>1</sub>, B<sub>2</sub>, B<sub>3</sub> states associated with Zn 4s, Zn 4sp, and O 2p hybridized states. In the photon energy region of 530 – 535 eV, O *K*-edge spectra of transition-metal oxides can be mainly assigned to the O 2p orbital hybridized with Zn 4s states [16,17], and the region of 536 – 550 eV in the spectra can be attributed to the O 2p orbital hybridized with Zn 4sp states [18,19]. The relative occupancy ratio of Zn 4s molecular orbital was calculated by using the relative area ( $A_1/(B_1 + B_2 + B_3)$ ) of the deconvoluted Gaussian peaks, determined as in Fig. 4(a). As can be seen, the relative occupancy ratio of Zn 4s–O 2p was enhanced when the Ni-ion irradiation dose was increased to  $1 \times 10^{12}$  ions/cm<sup>2</sup>. However, at a Ni-ion irradiation dose of  $1 \times 10^{13}$  ions/cm<sup>2</sup>, the relative occupancy ratio of Zn 4s–O 2p was drastically decreased. This tendency can be clearly seen in Fig. 4(b), displaying the relative occupancy ratio of Zn 4s–O 2p hybridized molecular orbital. Based on the XAS results, the origin of the dependence of the changes in the electrical properties, such as mobility, on the Ni-ion irradiation dose may be attributed to a modification of the

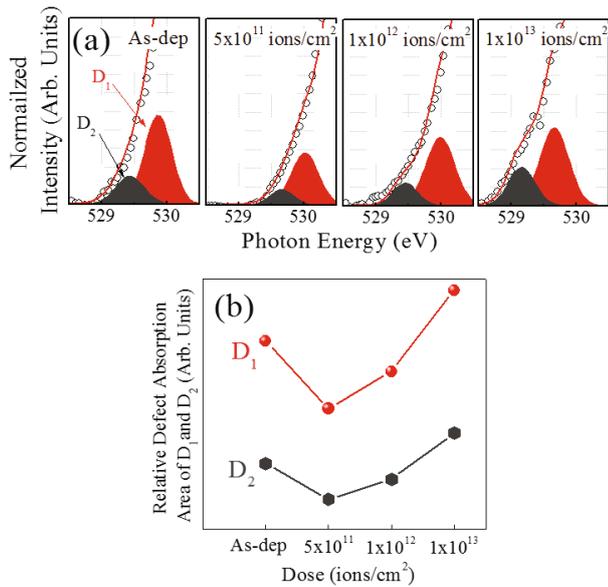


Fig. 5. (Color online) (a) Enlargements of the XAS spectra for band edge states below the conduction band edge of as-deposited and irradiated ZnO films. (b) Relative defect absorption area of two distinct band edge states ( $D_1$  and  $D_2$ ), calculated by using the Gaussian fits in Fig. 5(a).

electronic structure. The enhancement of the relative occupancy ratio of the  $s$ -orbital caused by changes in the electronic structure of the ZnO film led to an increase in the possibility of carrier transport in terms of an enhanced spherically-symmetric  $s$ -orbital compared to the directional  $p$ -molecular orbital. In addition, the change in the band edge state below the conduction band corresponded to the electrical results shown in Fig. 2.

Figure 5(a) shows XAS O  $K$ -edge spectra over a narrow energy region below the conduction band edge states for as-deposited and irradiated ZnO films. The conduction band edge state was fitted with two Gaussian peaks, are representing the shallow band edge state ( $D_1$ ) and the other representing deep band edge state ( $D_2$ ). The ZnO films showed decreased band edge states for  $D_1$  and  $D_2$  when the Ni-ion irradiation dose was  $5 \times 10^{11}$  ions/cm<sup>2</sup>. On the other hand, the ZnO films showed a sequential increase in the band edge states for  $D_1$  and  $D_2$  when the Ni-ion irradiation dose was increased to  $1 \times 10^{13}$  ions/cm<sup>2</sup>. The quantitative amount of band edge states ( $D_1$  and  $D_2$ ) changed as a function of the Ni-ion irradiation dose, as shown in the relative defect absorption area of the band edge states in Fig. 5(b). If the previous electrical data are considered, the variations of  $D_1$  and  $D_2$  states are strongly correlated with the increase in the carrier concentration and the degradation of the mobility at a Ni-ion irradiation dose of  $1 \times 10^{13}$  ions/cm<sup>2</sup> [20]. Based on the above results, the most plausible origin of the change in the electrical properties of the ZnO film as a function of the Ni-ion irradiation dose may be a modification of the electronic structure, such as an enhance-

ment of the relative occupancy ratio of the  $s$ -orbital and a change in the band edge state below the conduction band.

### III. CONCLUSION

In summary, the electrical properties of ZnO films were evaluated as a function of the Ni-ion irradiation dose at room temperature. As the Ni-ion irradiation dose was increased up to  $1 \times 10^{12}$  ions/cm<sup>2</sup>, the electrical properties were changed with a carrier concentration and mobility of  $\sim 10^{14}$  cm<sup>-3</sup> and 196 cm<sup>2</sup>/V·s, respectively. However, when the Ni-ion irradiation dose was increased up to  $1 \times 10^{13}$  ions/cm<sup>2</sup>, the carrier concentration and mobility were drastically changed to  $2.31 \times 10^{18}$  /cm<sup>3</sup> and 3.74 cm<sup>2</sup>/V·s, respectively. The structural transition and modification were preserved, with the crystalline oriented by the hexagonal ZnO (002) phase, regardless of the Ni-ion irradiation dose, and had no relation with the electrical properties. The electronic structure showed a drastic change in the relative occupancy of the Zn 4s, 4sp and O 2p hybridized molecular orbitals in the conduction band. In addition, two distinct band edge states as a function of the Ni-ion irradiation dose were observed below the conduction band and interpreted as oxygen vacancies, are correlated to the changes in the carrier concentration and the mobility. The change in the carrier concentration when the Ni-ion irradiation dose was increased up to  $1 \times 10^{13}$  ions/cm<sup>2</sup> could be related to the increase in the shallow band edge state ( $D_1$ ), and the degradation of mobility could be associated with the increase in the deep band edge state ( $D_2$ ).

### ACKNOWLEDGMENTS

This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (NRF-2013R1A1A2A10005186) and a National Research Foundation grant (NRF-2013M2A8A1035822) from Ministry of Science, ICT and Future Planning (MSIP) of Republic of Korea. This work was also supported by Samsung Display Co., Ltd.

### REFERENCES

- [1] A. Tsukazaki *et al.*, Nat. Mater. **4**, 42 (2005).
- [2] M. G. Kim, M. G. Kanatzidis, A. Facchetti and T. J. Marks, Nat. Mater. **10**, 382 (2011).
- [3] D. C. Look, Mater. Sci. Eng. B **80**, 383 (2001).
- [4] S. Kohiki, M. Nishitani, T. Wada and T. Hirao, Appl. Phys. Lett. **64**, 2876 (1994).

- [5] H. S. Kang, J. S. Kang, J. W. Kim, and S. Y. Lee, *J. Appl. Phys.* **95**, 1246 (2004).
- [6] M. Schmidt, M. Ellguth and F. Schmidt, *Phys. Status Solidi B* **247**, 1220 (2010).
- [7] H. W. Park, M. J. Choi, Y. C. Jo and K. B. Chung, *Appl. Surf. Sci.* **321**, 520 (2014).
- [8] N. Matsunami, J. Fukushima, M. Sataka, S. Okayasu, H. Sugai and H. Kakiuchida, *Nucl. Instrum. Methods. B* **268**, 3071 (2010).
- [9] S. Pal *et al.*, *Nucl. Instrum. Methods. B* **311**, 20 (2013).
- [10] C. S. Yeo, J. S. Park, J. H. Song and K. B. Chung, *J. Korean Phys. Soc.* **60**, 307 (2012).
- [11] C. Chappert *et al.*, *Science* **280**, 1919 (1998).
- [12] K. Nordlund, J. Keinonen and T. Mattila, *Phys. Rev. Lett.* **77**, 699 (1996).
- [13] Z. G. Wang, C. Dufour, E. Paumier and M. Toulemonde, *J. Phys. Condens. Matter* **6**, 6733 (1994).
- [14] C. Y. Kim, K. S. Jeong, Y. S. Kang, S. W. Cho, M.-H. Cho, K. B. Chung, D.-H. Ko, Y. Yi and H. Kim, *J. Appl. Phys.* **109**, 114112 (2011).
- [15] K. C. Ok, Y. S. Park, K. B. Chung and J. S. Park, *Appl. Phys. Lett.* **103**, 213501 (2013).
- [16] V. Vaithianathan, K. Asokan, J. Y. Park and S. S. Kim, *Appl. Phys. A* **94**, 995 (2009).
- [17] J. W. Chiou *et al.*, *Appl. Phys. Lett.* **84**, 3462 (2005).
- [18] K. Asokan *et al.*, *J. Phys. Condens. Matter* **13**, 11087 (2001).
- [19] 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).
- [20] H. W. Park, J. S. Park, J. H. Lee and K. B. Chung, *Electrochem. Solid-State Lett.* **15**, 133 (2012).