Structural and Optical Properties of Nitrogen-Ion-Implanted ZnO Nanorods

S.-H. Park
New Materials & Components Research Center, Reach Institute of Industrial Science & Technology, Pohang 790-600

Department of Materials Science and Engineering, Pohang University of Science and Technology, Pohang 790-784

Yong-Dae Choi
Department of Optical & Electronic Physics, Mokwon University, Daejeon 302-729

S.-W. Han*
Institute of Fusion Science, Institute of Science Education and Division of Science Education, Chonbuk National University, Jeonju 561-756

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We present a study of the structural and the optical properties of nitrogen-ion-implanted ZnO nanorods. Vertically-aligned ZnO nanorods were synthesized on Al₂O₃ substrates by using a catalyst-free metal-organic chemical vapor deposition (MOCVD) procedure. Nitrogen ions with an energy of 120 keV and an ion flux of $1 \times 10^{16}$ particles/cm² were implanted on the vertically-aligned ZnO nanorods. The structural properties were studied by using various techniques, including field emission transmission electron microscopy (FE-TEM), X-ray diffraction (XRD), and X-ray absorption fine structure (XAFS) analyses. The XRD measurements revealed that the crystalline properties of the nitrogen-ion-implanted ZnO nanorods were comparable with those of the as-grown ZnO nanorods. However, the XAFS analysis demonstrated that the bonding lengths of atomic pairs on the c-axis were slightly elongated and that the ion implantation caused an extra structural disorder of Zn-O pairs. The FE-TEM revealed that the nanorods had structurally-damaged spots along the entire length of the nanorods. From the photoluminescence (PL) spectra, we observed a considerably weak main donor-acceptor transition peak at 3.02 eV in the temperature range of 5 – 300 K. The blue shift and the intensity decrease of the main transition peak strongly suggest that the implanted nitrogen ions play a role in the optical property changes of the nanorods.

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I. INTRODUCTION

ZnO nanorod arrays have attracted considerable attention because of their practical applications to nanoscale electronic, photonic, and biosensing devices [1-6]. ZnO nanorods have many advantages. Their band gap energy and exciton binding energy are 3.3 eV and 60 meV at room temperature (RT), respectively. The band gap energy can be expanded or reduced by alloying Mg or Cd with ZnO [7-9]. Vertically well-aligned ZnO nanorods are relatively easy to fabricate using various techniques [10]. ZnO devices operate under harsh environments such as high radiation areas and outer space. ZnO is reasonably harmless and is used as a skin care medicine, such as a diaper rash ointment. ZnO nanorods are relatively strong solids in comparison to carbon nanotubes. Therefore, ZnO nanorods can be widely used for practical applications of nano building-blocks as well as for fundamental academic research.

Single ZnO nanowires have been studied for their potential applications to atomic force microscopy (AFM) cantilevers [11], gas sensors [12, 13], nanotransistors [5], and logic gate devices [14]. Investigations have also been carried out on heterostructures of n-type ZnO nanorods, on p-type GaN for light-emitting diode (LED) applications [15-17], and on high power nanodevices [18]. Bundles of ZnO nanorods have also been investigated for their practical applications, including LEDs [16,19], ultraviolet sensors [20], piezoelectronics [21], and transistors [22]. However, there is still a limit to the applica-
tions of ZnO nanorods for practical devices because of $n$-type and $p$-type doping. ZnO nanorods are known to be natural $n$-type semiconductors because they are rich in zinc and deficient in oxygen. While there have been a few attempts to fabricate $p$-type ZnO nanorods, Lee and Lim reported that a hole-doping method, carried out by adding an impurity during the growth of ZnO nanorods, did not guarantee a sufficient level of thermal stability and concentration of doped holes [23]. Moreover, the ZnO nanorods deformed, transforming into a film, when impurities were added during their growth. A previous study demonstrated that an ion-implantation method could be a solution for the hole doping of nanostructures [24]. When the ions were implanted, they caused structural damages and affected the optical properties of the nanorods [24].

In this article, we investigate the structural and the optical property changes of the ZnO nanorods due to nitrogen-ion implantation and compared them with their as-grown ZnO nanorods counterparts. X-ray diffraction (XRD) detected the crystalline structural properties of the nanorods. Field-emission tunneling electron microscopy (FE-TEM) measurements on various positions of the nanorods showed their position-dependent microstructural property changes. Polarization-dependent X-ray absorption fine structure (XAFS) measurements revealed orientation-dependent structural damages. The optical property changes due to the ion implantation were studied using photoluminescence (PL) measurements.

II. EXPERIMENTS

The vertically-well-aligned ZnO nanorod arrays were synthesized on $\alpha$-$\text{Al}_2\text{O}_3$ (0001) substrates by using a catalyst-free metal-organic chemical vapor deposition (MOCVD) [10,25,26]. Diethylzinc (DEZn, Zn(C$_2$H$_5$)$_2$) and high-purity oxygen (99.999 %) were used as the zinc and the oxygen precursors, respectively. The pressure of the growth chamber was maintained at 0.2 – 0.4 Torr, and the substrate temperature was sustained between 350 – 450 °C. The ratio of the oxygen to the DEZn precursor was accurately monitored with a flow-mass controller and an electric pressure controller, respectively, and was kept at approximately 300 : 1. The ZnO nanorod growth rate was approximately 10 nm per minute [10]. For the growth of nanorods with a uniform diameter, the growth-chamber pressure, the precursor ratio, and the substrate temperature were maintained at constant values during the growth of the ZnO nanorods. The ZnO nanorods had an average diameter of about 50 nm and an average length of about 1 $\mu$m [24].

For nitrogen-ion implantation [24, 27–29], the ZnO nanorods were uniformly grown on $1 \times 1$ cm$^2$ sapphire surfaces and were vertically exposed to a mixed beam of N$^+$ and N$_x^-$ ions with an energy of 120 keV for 0.5 – 1 hour under vacuum at room temperature. The total flux of the ions was approximately $1 \times 10^{16}$ particles/cm$^2$. High-resolution XRD measurements on the ZnO nanorods were performed with a conventional X-ray source of Cu K$_{\alpha}$ radiation in air. The position-dependent structural properties of the nanorods were determined by using field-emission transmission electron microscopy (FE-TEM) measurements. For the FE-TEM measurements, samples were carefully prepared, using a focused ion beam method in order to avoid any possible damage caused by ion bombardment during the ion-milling process. XAFS measurements at the Zn K-edge were carried out with a fluorescence mode at RT by selecting the incident X-ray energy with a three-quarters tuned Si(111) double monochromator at 3C1 beamline of Pohang Light Source. For the polarization-dependent XAFS measurements, the electric field vector of the incident X-rays was aligned parallel and perpendicular to the length direction of the ZnO nanorods. The details of the polarization-dependent XAFS measurements are described elsewhere [30]. The PL measurements on the nanorods were performed with a He-Cd laser ($\lambda = 442$ nm) and an $f = 0.85$ double monochromator with a liquid N$_2$-cooled, front-illuminated charge-coupled-device detector at 5, 10 and 300 K.

III. RESULTS AND DISCUSSION

The crystalline structural properties of the nitrogen-ion implanted ZnO nanorods were characterized by using XRD, as shown in Figure 1. The XRD revealed that the N$^+$-ion-implanted nanorods had wurtzite (WZ) structures without any extra phase and kept their orientations perpendicular to the substrate surface.
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Fig. 2. TEM images of nitrogen-ion-implanted ZnO nanorods with a total ion flux of $1 \times 10^{16}$ particles/cm$^2$. (a), (b) and (c) are for the upper, lower, and near bottom parts of the nanorod, respectively. The (') and ("') symbols indicate an expansion and the Fourier transformation of the expansion part, respectively.

constant and the full widths at half maximum (FWHM) of the $N^+$-ion-implanted ZnO nanorods were 5.210(2) Å and 0.19(1) degrees, respectively. The XRD from the as-grown ZnO nanorods determined the lattice constant and FWHM to be 5.219(2) Å and 0.22(1) degrees, respectively. These values of the two specimens agree with those obtained from previous studies [7]. From the XRD results, we noticed that the diffraction peak from the $N^+$-implanted sapphire substrate was distorted, as shown in Figure 1. This implied that the nitrogen ions reached the substrate and caused structural damages even on the substrate. XRD can detect only the average crystalline structure. Therefore, it cannot effectively describe the microstructures of the nanorods.

FE-TEM measurements were employed in order to investigate the position-dependent micro-structural properties of the ZnO nanorods. Figure 2 demonstrates the FE-TEM images of the $N^+$-ion-implanted ZnO nanorods. The TEM images demonstrated that the $N^+$-implanted ZnO nanorods maintain a sound shape and have small, damaged spots on their upper and lower parts. The spot size was approximately 3 – 5 nm, and the density of the spots was approximately 1000 per nanorod (50 nm x 1 μm). The spots were somewhat uniformly spread through the nanorod, but did not follow any regularity. The TEM images indicated that the nitrogen ions were implanted through the entire length of the nanorod. This is somewhat surprising because a model calculation, assuming an exponential decay, predicted that the penetration depth of the 120-keV nitrogen ions on a ZnO film would be approximately 0.25 μm. Our observation of a 1-μm penetration of the nitrogen ions suggests that this ion implantation technique is very useful for electron- or hole-doping of nanostructured semiconductors. While the ion implantation technique has been applied for the doping, it is limited in its practical application to film and bulk semiconductors because of its short penetration depth and structural damage. For the vertically-aligned ZnO nanorods, the thickness of the nanorods is less than a few hundred nanometers with some space between them. The ion beam is able to reach the bottom of the nanorods through the space between the nanorods. However, if the ion beam is perfectly aligned in the nanorod length direction, the beam may not penetrate through the entire nanorod. Because of the angular diversion of the ion beam and the variation of the nanorod direction, the incident ions penetrate the nanorods with an angle from the nanorod length direction. The TEM measurements demonstrated the presence of local structural damage caused by the ion beam. However, TEM could not accurately determine the local distortion of the atomic bonds.

The orientation-dependent local structural properties of the $N^+$-implanted ZnO nanorods were investigated using polarization-dependent XAFS. XAFS data were analyzed using the UWXAFS package [31] and standard procedures [30, 32]. Figure 3 shows the Fourier-transformed XAFS with $k^3$-weight as a function of the distance from a Zn atom. The two sets of polarization-
dependent XAFS data were simultaneously fitted to the XAFS theory [33]. The fit was initiated with a fully occupied WZ structure and included single- and multi-scattering paths. In the fit, the atomic bonding lengths, the Debye-Waller factor ($\sigma^2$ including thermal vibration and static disorder), and the coordination numbers were varied. The first and the second peaks in Figures 3 (a) and (c) correspond to one O(1) atom, located directly below the Zn atom in the c-axis and 6 Zn(1) atoms located at approximately 55 degrees off from the Zn ab-plane. In addition, the first and the second peaks in Figures 3 (b) and (d) correspond to 3 O(2) atoms near the a-plane and 6 Zn(2) atoms in the ab-plane. From the simultaneous fits of the two sets of data, the bonding length of each atomic pair was independently determined. The fit results are summarized in Table 1. The XAFS analysis of as-grown ZnO nanorods demonstrated that the bonding lengths of the Zn-O(1) and the Zn-Zn(1) pairs were elongated while that of Zn-O(2) pairs shrank in comparison to the ZnO powder. This result agrees well with results from previous studies [25, 34]. We did not observe any vacancy in either the zinc or the oxygen sites of the as-grown ZnO nanorods. The analysis of the N$^+$-ion-implanted ZnO nanorods revealed that the bonding lengths of the Zn-O(1) and the Zn-Zn(1) pairs were further expanded by about 0.02 Å in comparison to that of the as-grown ZnO nanorod counterpart. We also observed that there was a substantial amount of extra structural disorder existing in the N$^+$-ion-implanted ZnO nanorods in comparison to the as-grown ZnO nanorods. This agrees with the FE-TEM results. The extra disorder was only observed in the Zn-O(1) pairs. The oxygen coordination number of the ZnO nanorods slightly decreased as the N$^+$ ions were implanted. These results strongly suggest that the N$^+$ ions effectively affect the oxygen site. The implanted N$^+$ ions might be substituted for oxygen atoms. However, the XAFS analysis was unsuccessful for the location of the implanted N$^+$ ions because XAFS is limited in distinguishing oxygen and nitrogen atoms.

In order to understand the optical properties of N$^+$-ion-implanted ZnO nanorods, we carried out PL measurements on the nanorods. Figure 4 demonstrates the PL spectra from the N$^+$-ion-implanted ZnO nanorods. The PL spectra demonstrated that the optical properties of the N$^+$-ion-implanted ZnO nanorods were very different from those of as-grown ZnO nanorods shown in the inset. The donor-acceptor transition peak was observed at 3.02 eV in the temperature range of 5 – 300 K. The band gap energies of as-grown ZnO nanorods were 3.37 and 3.30 eV for 10 and 300 K, respectively. The intensity of the main transition peak was dramatically decreased as the N$^+$ ions were implanted. A massive deep impurity level around 2.2 – 2.4 eV was observed for the N$^+$-ion-implanted ZnO nanorods. The deep impurity level can be understood in terms of ion damage and impurity of the N$^+$ ions. However, the red shift and the intensity decrease of the main transition peak cannot be explained by the ion damage only. The results of the XRD, FE-TEM, and XAFS analyses consistently demonstrated that the N$^+$-ion implantation did not seriously damage the crystalline structure of the ZnO nanorods, although it caused a partial structural disorder in small areas. Therefore, the main peak intensity change in the PL spectra can be related to the effect of N$^+$-ion doping. As-grown ZnO nanorods are known to be naturally n-type due to their extra zinc atoms. When N$^+$ ions were implanted, the holes attracted the extra electrons. This reduced the charge carrier density in the nanorods and likely caused a weakening of the donor-acceptor transition. The peak shift should be related to the structural change. Previous studies reported that the band-gap energy of ZnO could be expanded and reduced by alloying...
Ion implantation technique can be widely applied for electron- and hole-doping of nanostructured semiconductors. Therefore, this technique has potential to be a unique tool for doping nanostructures, in particular, with Mg and Cd ions. The elongation of the bonding lengths of the Zn-O pairs along the c-axis are expanded and that the ion implantation causes extra structural disorder of ZnO atomic pairs. From the PL spectra, the donor-acceptor transition peak was observed at 3.02 eV in the temperature range of 5 - 300 K, and the peak intensity was considerably weak. The red shift can be attributed to a bonding-length change of the atomic pairs due to the ion implantation. The weakening peak intensity is caused by hole doping and structural disorders. The ion beam partially caused extra structural disorder of the ZnO nanorods. However, the nanorods still maintained a sound shape and a high crystalline quality. These results strongly suggest that the ion-implantation technique can be widely applied for electron- and hole-doping of nanostructured semiconductors.

IV. CONCLUSION

We investigated the structural and the optical properties of nitrogen-ion-implanted ZnO nanorods. The vertically-aligned ZnO nanorods were fabricated using a catalyst-free MOCVD system and were exposed to a nitrogen-ion beam with an energy of 120 keV and a total flux of $10^{16}$ particles/cm². XRD, XAFS, and FE-TEM measurements were carried out in order to characterize the structural properties of N⁺-ion-implanted ZnO nanorods. These were then compared with the measurements of as-grown ZnO nanorods. The XRD measurements revealed that the crystalline structure is only marginally affected by the ion implantation while the FE-TEM images demonstrated that the ions are implanted over the entire length of the nanorod and that there are small, clear ion-damaged parts. The XAFS analysis revealed that the bonding lengths of atomic pairs along the c-axis are expanded and that the ion implantation causes extra structural disorder of ZnO atomic pairs. From the PL spectra, the donor-acceptor transition peak was observed at 3.02 eV in the temperature range of 5 - 300 K, and the peak intensity was considerably weak. The red shift can be attributed to a bonding-length change of the atomic pairs due to the ion implantation. The weakening peak intensity is caused by hole doping and structural disorders. The ion beam partially caused extra structural disorder of the ZnO nanorods. However, the nanorods still maintained a sound shape and a high crystalline quality. These results strongly suggest that the ion-implantation technique can be widely applied for electron- and hole-doping of nanostructured semiconductors.

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REFERENCES