

DIFFUSION AND THERMAL STABILITY OF IMPLANTED HYDROGEN IN ZnO NANORODS*

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Abstract

The 20-MeV proton-beam with a fluence of 10^{12} cm⁻² was irradiated on ZnO nanorods. The effects of proton-beam irradiation on ZnO nanorods are investigated by using ¹H nuclear magnetic resonance (NMR) spectroscopy. After irradiation, new and modified NMR resonance lines are observed in ¹H NMR spectra. The diffusion and thermal stability of each proton species are investigated from the laboratory- and rotating-frame spin-lattice relaxation data depending on temperature. Understanding the properties of thermally stable hydrogen species created by the beam irradiation may promise many possible applications, since the hydrogen stable up to high temperature only meets the device working conditions.

INTRODUCTION

Electronic and diffusion properties of hydrogen in ZnO have been extensively studied, since efficient defect engineering is essential to fabricate electronic, ferroelectric, and optical devices [1-3]. Furthermore, diffusion properties of H donors may help in understanding the mechanism responsible for ferromagnetic order triggered by proton implantation [4]. The electronic characteristics on ZnO can be modified by proton irradiation, as the physical origin is attributed to the hydrogen shallow donors [5]. Recently, it has also been reported that radiation-induced defects cause the threshold voltage shift and the electrical conductance modulation, making them potentially applicable in nanoelectronic devices [6]. Although previous works addressed effects of proton implantation on electrical properties, it is still far from being well understood from a microscopic point of view.

¹H NMR spectroscopy can be one of the best methods to identify hydrogen species and to observe their diffusion properties in ZnO. The dynamical properties of mobile protons in the lattice site of ZnO were previously investigated by ¹H NMR spectroscopy [7]. However, the assignment of interstitial H (H_i) and surface hydroxyl group on the NMR spectra is a matter of controversy [7,8]. Previously, Wang *et al.* attributed the NMR line at 4.8 ppm to the mobile proton in the lattice of ZnO [7]. In contrast, it has been recently reported that the resonance line is due

to the hydroxyl group on the surface of ZnO [8]. Thus, the identification of H_i and surface hydroxyl group on ZnO and their diffusion properties are still not clear.

Here we identify comprehensive hydrogen species in proton-implanted ZnO nanorods and investigate their dynamical properties by employing ¹H NMR spectroscopy. Our work demonstrates the rigid protons are attributed to the water molecules adsorbed on ZnO surface, which are still present after irradiation.

EXPERIMENTS

ZnO nanorods were synthesized via a sol-gel technique from zinc acetate, (CH₃COO)₂Zn·2H₂O, supplied by Aldrich. To prepare hydrogen doped ZnO, we used a water-soluble linear polymer polyvinyl pyrrolidone following previous works [9]. Unlike our previous synthesis temperature of 573 K, the samples in this work were synthesized at a higher temperature of 773 K to better remove organic compounds from the ZnO surfaces [9]. The obtained nanocrystalline powders were then pressed into pellet disks of ~1.5 mm thickness and 10 mm diameter for proton beam irradiation.

The samples were irradiated with 20 MeV proton beams under low fluence condition of 10^{12} cm⁻², corresponding to beam irradiation time of 600 s, at the Korean Multi-purpose Accelerator Complex. The penetration depth of 20 MeV protons in ZnO were obtained by using the code SRIM (stopping and range of ions in matter). The simulation result shows that most of H⁺ ions can penetrate and stop ~1.2 mm from the top surface. The ¹H magic-angle spinning (MAS) NMR measurements were made by using a 400-MHz ¹H pulsed NMR spectrometer (Bruker Avance II⁺) with a spinning rate of 7 kHz.

EXPERIMENTAL RESULTS

Figure 1(a) shows the Fourier-transformed ¹H NMR spectra at 300 K for ZnO nanorods before irradiation. Motionally narrowed NMR lines appear at ~1 ppm, exhibiting markedly increased intensity after irradiation. The origin of the peaks at ~1 ppm is still not clear, which was previously attributed to the surface OH group, hydrogen substituting to oxygen (H_O), or methyl group [7]. It is noted that thermal activation barrier of H_O in ZnO or the isomerization reaction in methyl group is greater than ~0.7 eV [2], whereas that of H atoms from OH group on ZnO surface was reported to be ~0.5 eV [2]. After irradiation, in Fig. 1(b), the peak at ~1 ppm is separated into

* This work has been supported through KOMAC operation fund of KAERI by Ministry of Science ICT and Future Planning of Korean Government.

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three peaks at 1.0, 1.4, and 1.7 ppm with increasing temperatures, reflecting slightly different chemical environments around this hydrogen species.

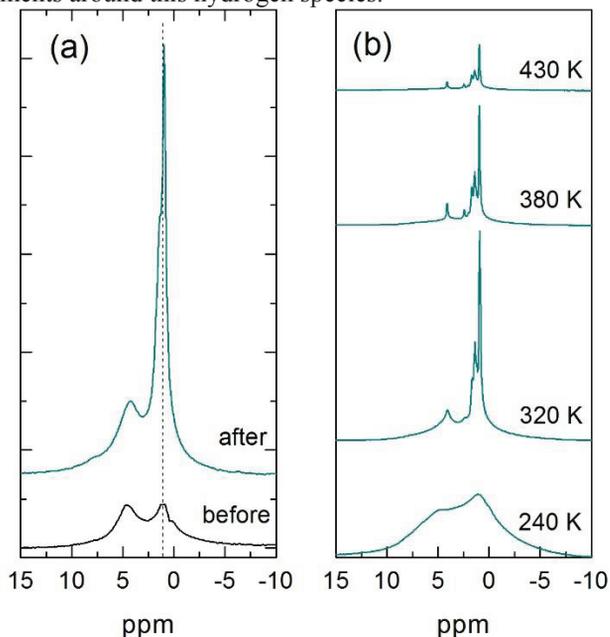


Figure 1: ¹H MAS NMR spectra for the samples before and after irradiation at 300 K (a), and for those after irradiation at various temperatures (b).

Figure 2 shows the temperature evolution of proton NMR spectra before irradiation. The spectra exhibit the multiple lines at ~1 ppm, which are motionally narrowed with increasing temperature. After irradiation, in Fig. 3, an apparent narrow NMR line at 4.1 ppm as well as a smaller peak at 2.4 ppm appears with increasing temperatures. It is a clear evidence that the narrow line at 4.1 ppm after irradiation arises from the implanted protons, superimposing the broad one before irradiation. Interestingly, the narrower line at 4.1 ppm with increasing temperature appear up to the highest temperature, indicating obviously distinct hydrogen species with distinct dynamical features compared to the broad line.

The temperature dependence of the linewidth and chemical shift of the broad line is displayed in Fig. 4. This proton species exhibits relatively broad lines ($\Delta\nu \sim 1.1$ kHz) up to the highest temperature, indicating thermally stable species unlike the other proton species undergoing motional narrowing. Larger ¹H NMR line shifts (~1 ppm) of this line to lower ppm values with increasing temperature are shown in the range of around 300 to 400 K (up-field). The chemical shifts of the other protons, on the other hand, are less than 0.3 ppm in all the samples.

DISCUSSION

The H_i^+ introduced by proton beam irradiation in ZnO causes the resonance line at 4.1 ppm. The resonance line is consistent with the proton in the lattice in terms of the resonance shift for the sample synthesized at low temperature followed by thermal annealing, thus conclusively ascribed to H_i . In Fig. 4 the greater resonance shifts may

be due to a greater change in the bond length and/or strength compared to that of the other resonance lines.

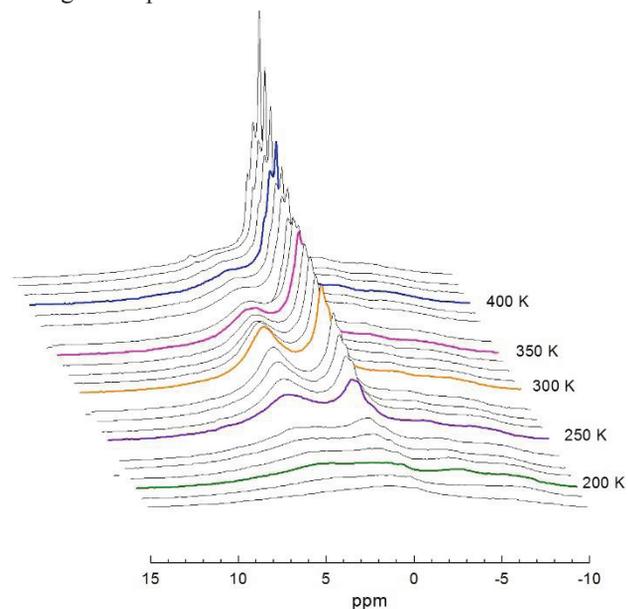


Figure 2: Temperature evolution of ¹H MAS NMR spectra for the sample before irradiation.

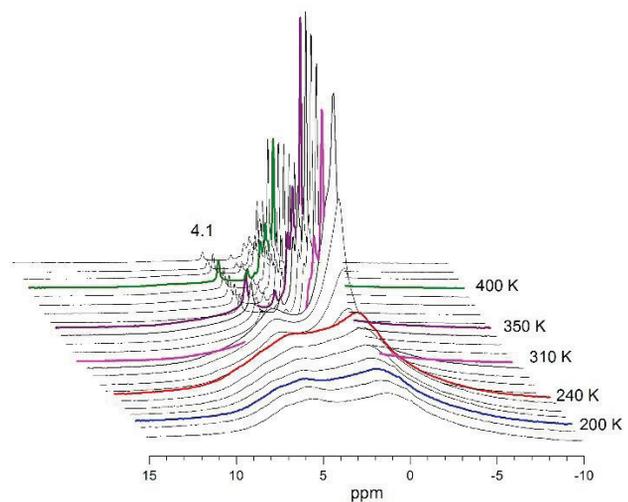


Figure 3: Temperature evolution of ¹H MAS NMR spectra for the sample after irradiation.

Water molecules adsorbed on ZnO surface can form hydrogen bonds showing greater temperature dependence on chemical shift, as well as can be static. They can be introduced into the lattice during synthesis, exhibiting a broad resonance line due to effective proton-proton dipolar interactions of static single water molecules.

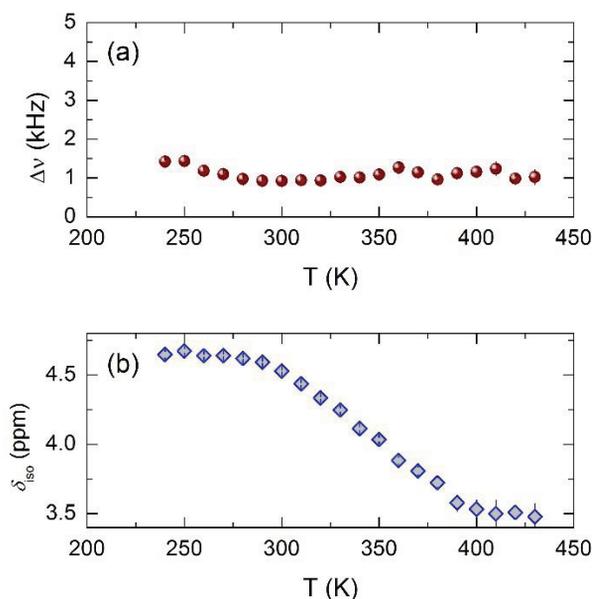


Figure 4: Temperature dependence of the linewidth, $\Delta\nu$ (a) and isotropic chemical shift, δ_{iso} (b) of the broad line before irradiation.

CONCLUSION

We employed proton NMR spectroscopy to identify comprehensive hydrogen species in proton-implanted ZnO nanorods. Our work identified the rigid protons as the water molecules adsorbed on ZnO surface, which are still present after proton-beam irradiation.

ACKNOWLEDGEMENT

This work has been supported through KOMAC operation fund of KAERI by Ministry of Science ICT and Future Planning of Korean Government. The measurements at the Korean Basic Science Institute (KBSI) are acknowledged.

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