Magnetic Resonance Spectroscopy for N^+ beam-irradiated ZnAlO

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***Keywords :** N^+ beam irradiation, magnetic resonance spectroscopy, ZnAlO

1. Introduction

In Korea multi-purpose accelerator complex (KOMAC), there are versitile ion beam implanters, whose ion species cover many kinds of elements from hydrogen to transition metals with an energy range of 20 keV to 200 keV [1]. Among various ion species that the implanter may emit, we applied nitrogen ion beams to the Al-doped ZnO (ZnAlO) to introduce bi-component dopants which is a possible way to obtain *p*-type ZnO [2]. Al was introduced in the process of sample fabrication prior to the beam irradiation on the sample.

There are some efforts to realize *p*-type ZnO which may act as a good hole transport layer in optoelectronic conversion devices [2-4]. Thus, the key to manufacturing ZnO-based LEDs is to achieve stable *p*-type doping of ZnO [2]. In previous works, ZnO may readily have a hydrogen defect which acts only as a donor in the fabrication process. Although ZnO may have intrinsic *n*-type characteristics, some suggestions to obtain the stable *p*-type ZnO have been reported [3-6]. In this work, we study on some magnetic resonance spectroscopy for ZnO co-doped with Al and N, and discuss the local electronic structure that the dopants can induce.

2. Methods and Results

In this section, the detailed methods for experiments and simulation for N^+ beam-irradiated ZnAlO. We exhibit electron spin resonance (ESR) spectroscopy and ^{27}Al nuclear magnetic resonance (NMR) spectroscopy for as-grown ZnAlO and the irradiated ZnAlO.

2.1 Sample preparation

The Al-doped ZnO thin films were fabricated as follows. First, 200 nm-thick SiO_2 was deposited on *p*-type silicon substrates. Then, 30 nm-thick ZnAlO films were deposited by atomic layer deposition at 80 °C. The diethylzinc ($Zn(C_2H_5)_2$) was used as a zinc precursor. The ZnAlO samples prepared were followed by the N^+ beam irradiation experiments.

2.2 N^+ beam irradiation

The N^+ beam irradiation was performed by using the gaseous ion beam implanter which are widely being used such as material science and condensed matter physics. The N^+ beam with the energy of 40 keV was irradiated on the samples as much as 1×10^{14}, 1×10^{15}, and 1×10^{16} cm^{-2}. The beam irradiation was performed after simulation using the SRIM package to ensure how the beam can be penetrated and straggled into the samples. According to the SRIM data, 40 keV N^+ beam may penetrate down to ~180 nm in depth.

2.3 Electron spin resonance spectroscopy

ESR measurements were performed on an X-band (~9.4 GHz) Bruker spectrometer equipped with a continuous He-flow cryostat, allowing the regulation of the sample temperature from 4 K to room temperature.

Figure 1 shows the ESR spectra for the unirradiated and the irradiated ZnAlO thin films. As shown in Fig. 1, the unirradiated film does not show any noticeable signal, but the irradiated samples unambiguously show the resonance signals. Further, the irradiated sample with a fluence of 1×10^{16} cm^{-2} exhibits the resonance shift compared with the samples with fluences of 10^{14} cm^{-2} and 10^{15} cm^{-2}, as well as some smaller peaks at 351.7 mT and 352.1 mT.

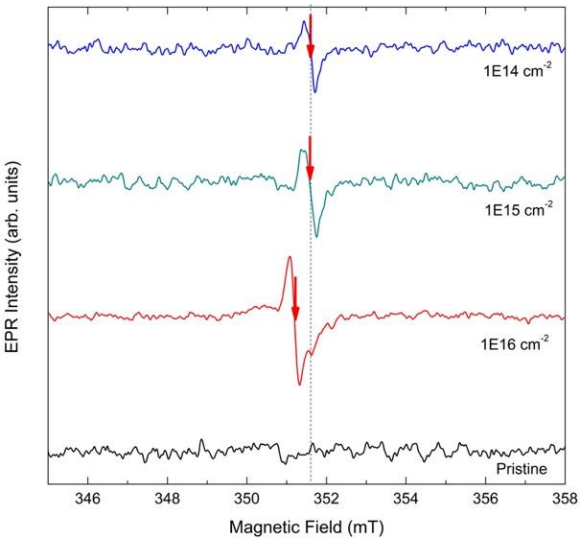

Fig. 1. ESR data measured at room temperature for the unirradiated and the irradiated ZnAlO. Vertical red arrows denote the resonance fields for the irradiated samples.

To understand how the peaks are observed in the ESR data, we simulated the data with the EasySpin package.

In Fig. 2(a), the spectrum of the irradiated sample with a fluence of 10^{16} cm^{-2} is displayed. In Fig. 2(b), the simulated spectrum is shown, in which three components are introduced. First, an isotropic broad line at 350.8 mT (g=2.007) may be assigned to the spin coupled with Zn or Al on the surface. Second, the spectrum at 351.2 mT ($g_{\perp}$=2.005, $g_{\parallel}$=2.002) exhibits an anisotropic shape due to the axial crystal structure.

The last spectrum at 351.6 mT (g=2.002) gives a smaller contribution to the convoluted spectrum with three hyperfine lines. This spectrum can be analyzed using the following spin-Hamiltonian that includes an electron Zeeman term and a central hyperfine interaction term:

$$\mathcal{H} = \mu_B \mathrm{BgS} + \mathrm{S} \cdot \mathrm{A} \cdot \mathrm{I}, \quad (1)$$

where, S denotes an effective electron spin, I the nuclear spin and B is an external magnetic field, g and A are the electron g-tensor and the hyperfine interaction tensor, respectively, and μ_B is the Bohr magneton.

Nitrogen is the only element that fulfills these criteria, since the ^{14}N isotope has I=1 and 99.6% natural abundance [7]. As expected, the sample with the greatest fluence of 1×10^{16} cm^{-2} clearly exhibits these hyperfine lines.

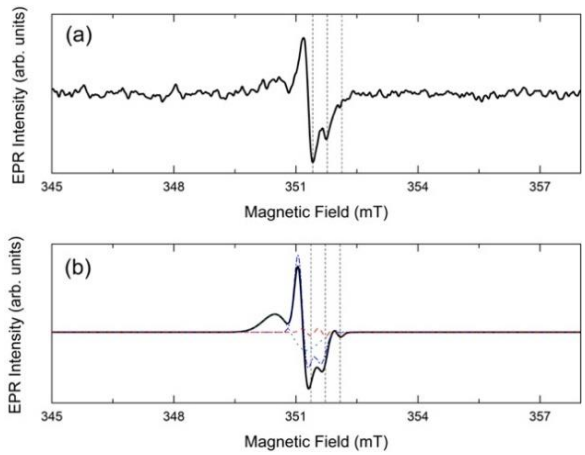

Fig. 2. (a) ESR data for the irradiated ZnAlO with a fluence of 10^{16} cm^{-2} measured at room temperature. (b) Simulated ESR data with three deconvoluted components for the irradiated ZnAlO with a fluence of 10^{16} cm^{-2}. Three dotted black lines denote resonance fields of N-center.

3. Conclusions

We have studied the magnetic resonance spectroscopy for N^+ beam-irradiated ZnAlO using the ion implanter operating at KOMAC. In EPR spectra, we found the resonance spectra for the irradiated samples, unlike in the unirradiated sample. The N^+ beam-irradiated ZnAlO thin film with a fluence of 1×10^{16} cm^{-2} clearly exhibits a hyperfine signal coming from the nitrogen introduced by the implanter. We will further discuss the ^{27}Al NMR data.

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