Transactions of the Korean Nuclear Society Spring Meeting
Jeju, Korea, May 7-8, 2026

ESR Study on the N^+ Beam-Irradiated ZnO Thin Films on the Al_2O_3 Substrate

Jun Kue Park [a*], Junhyeok Seo [a], In Mok Yang[a], Gi Wan Jeon[a], Weon-Sik Chae[b], Jong-Soo Lee[c]
[a]Particle Beam Research Division, Korea Multi-purpose Accelerator Complex, Korea Atomic Energy Research Institute (KAERI), 181 Mirae-ro, Geoncheon-eup, Gyeongju-si 38180, Republic of Korea
[b] *Deagu Center, Korea Basic Science Institute, 80, Daehak-ro, Buk-gu, Deagu 41566, Republic of Korea*
[c] *Department of Energy Science and Engineering DGIST, 333 Techno Jungang-daero, Hyeonpung-eup, Dalseong-gun, Deagu 42988, Republic of Korea*
[*]*Corresponding author: jkuepark@kaeri.re.kr*

Keywords : ZnO thin films, beam irradiation, electron spin resonance, optoelectronic devices

1. Introduction

Ion beam irradiation is known as one of the novel doping methods for semiconductors, where dopants, irradiation dose, and the position of ions can be controlled as our demands. In particular, the beam irradiation for ZnO can be widely used for achieving p-type semiconductors.

Electron spin resonance (ESR) spectroscopy is one of the most sensitive methods for probing the local electronic structure, providing information about defects introduced in matter, because ESR can probe even the interaction between electron and nuclear spins. Especially, ESR is a bulk probe method, thus they detect the electronic structure of not only the films of interest but also the substrate.

In this work, we find the ESR spectra from the ZnO thin films as well as the Al_2O_3 substrates before and after beam irradiation. Unexpectedly, the ESR signal from the substrate turns out to be the Cr^{3+}(S=3/2) defect, which may be introduced in the process of synthesis.

2. Methods and Results

ZnO thin films were prepared by the magnetron sputtering method on the Al_2O_3 substrate which can be commercially obtained. The films obtained are ~100 nm-thick layer on the substrate. Beam irradiation is performed with the condition of N^+ beam with doses of 1×10^{14}, 1×10^{15}, and 3×10^{15} ions/cm^2 with the thermal annealing of 500°C during the beam irradiation.

We employed an ESR spectrometer for performing an angle-dependent measurements at 4 K with the resonance frequency of 9.38 GHz . The sample was placed in the center of the microwave cavity which resonates in the TE_{011} mode, where an alternating-current (ac) field is maximized. The ESR spectrum was measured by sweeping the magnitude of the external direct-current (dc) magnetic field H. The field H is rotated from the $[1\bar{1}0]$ direction (in the film plane) to the $[\bar{1}10]$ direction (in the film plane), passing through the [001] direction (perpendicular to the film plane).

2.1 Theory

The Cr^{3+} cation with an electron configuration of $3d^3$ has the ground level $^4F_{3/2}$ with effective spin S =3/2. When the cation is introduced in a crystal, the spin states are under the influence of the crystal field created by the neighboring ions. The experimental ESR resonance field data can be analyzed with the spin Hamiltonian in the conventional notation [1].

$$\mathcal{H} = \mathcal{H}_{\text{Zeeman}} + \mathcal{H}_{\text{ZFS}} = \mu_B \mathbf{B}\cdot\mathbf{g}\cdot\mathbf{S} + \mathbf{S}\cdot\mathbf{D}\cdot\mathbf{S}, \quad (1)$$

where μ_B denotes the Bohr magneton, **B** the applied magnetic field, **g** the spectroscopic splitting "tensor", **S** the electron spin operator, and **D** the zero-field splitting (ZFS) tensor.

The conventional ZFS D and E parameters, also represented as D_{ij}, are given as follows,

$$\mathrm{D} = \frac{3}{2}\mathrm{D}_{ZZ}, \quad \mathrm{E} = \frac{1}{2}(D_{XX} - D_{YY}) \quad (2)$$

2.2 Angle-dependent ESR spectra

Figure 1 shows the angle-dependent ESR spectra for pristine ZnO. The resonance peak at g=2.004 which shows no angle dependence may come from a zinc vacancy in ZnO films [2,3]. Before and after beam irradiation, the resonance peak remains unchanged, reflecting the defect intrinsically formed in the film. We confirmed the peak is from the ZnO layer by performing the ESR measurement for the Al_2O_3 substrate which shows no peak at g=2.004. For Al_2O_3 substrate, on the other hand, we find the angle-dependent ESR spectra whose resonance field spreads from low to high fields.

In Fig. 1, the solid lines exhibit the resonance fields obtained by EasySpin simulation code. The spin Hamiltonian as denoted by Eq. (1) with S=3/2 may well correspond to the experimental resonance lines. The simulation may give us the parameters of $g_\parallel = 2.1115, g_\perp = 2.8285$, $D = 2355$ MHz, and $E = -3233$ MHz.

A Cr^{3+}(S=3/2) ion with the electron configuration $3d^3$ has 3 resonance lines from the allowed transitions. However, we observed more than 3 resonance lines of Cr^{3+} impurity ion using a X-band ESR spectrometer as can be seen in Fig. 1. The 6 resonance lines of Cr^{3+} center obtained in our X-band experiments as shown in the crystallographic ab plane (Fig. 4) and bc-plane (Fig. 5) are composed of 3 resonance lines from the allowed transitions and another 3 from the forbidden transitions. The energy levels of Cr^{3+} impurity ion in Al_2O_3 crystal depending on the magnetic field applied along the major crystallographic axis are calculated with optimized spin Hamiltonian parameters (g_{ij} and D_{ij}) and are shown in Figs. 2. The arrows between the levels indicate the observed resonance transition at 9.38 GHz.

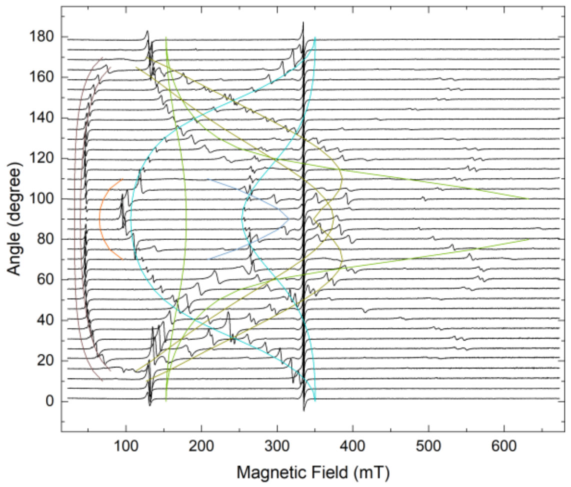

Fig. 1 ESR spectra of the pristine ZnO film on Al_2O_3 substrate. Stack plot for rotation of the magnetic field (5° step width) from B∥ c axis to B⊥c axis.

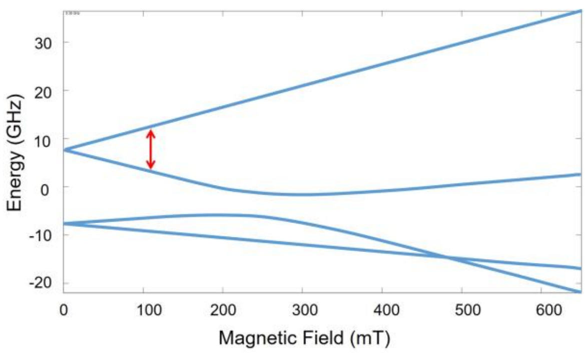

Fig. 2 Energy level diagram of Cr^{3+}-center in Al_2O_3 substrate depending on field B applied along the a-axis.

3. Conclusions

We have investigated N^+ beam-irradiated ZnO thin films on the Al_2O_3 substrate using ESR spectroscopy. Unexpectedly, the ESR signal from the substrate is found to be associated with the Cr^{3+}(S=3/2) defect. Furthermore, before and after beam irradiation, the resonance peak at g=2.004 remains unchanged, indicating that the defect is intrinsically formed in the ZnO layer and possibly assigned to a zinc vacancy. Consequently, ESR spectroscopy gives information on the thin film as well as the substrate.

REFERENCES

[1] T. H. Yeom, Electron Magnetic Resonance Study of Cr^{3+} Paramagnetic Impurity Ions in an Alexandrite Single Crystal, Journal of Magnetics, Vol.29, p. 179, 2024.

[2] H. Zeng, G. Duan, Y Li, S. Yang, X. Xu, and W. Cai, Blue Luminescence of ZnO Nanoparticles Based on Non-Equilibrium Processes: Defect Origins and Emission Controls, Adv. Funct. Mater., Vol.20, p.561, 2010.

[3] J. F. Ziegler, J. P. Biersack, "SRIM-2000, 40: The Stopping and Range of Ions in Matter", IBM-Research, Yorktown, NY 2000.

[4] B. Cao, W. Cai, and H. Zeng, Temperature-dependent shifts of three emission bands for ZnO nanoneedle arrays, Applied Physics Letters, Vol.88, p.161101, 2006.

[5] J.-H. Lin1,2, R. A. Patil, R. S. Devan, Z.-A. Liu, Y.-P. Wang, C.-H. Ho, Y. Liou, and Y.-R. Ma, Photoluminescence mechanisms of metallic Zn nanospheres, semiconducting ZnO nanoballoons, and metal-semiconductor Zn/ZnO nanospheres, Scientific Reports, Vol.4, p.6967, 2014.