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Spin-Polarized Positron Annihilation Measurement on Ga Vacancies in p-type GaN*

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Nitrogen-implanted p-type GaN films have been investigated through the Doppler broadening of annihilation radiation (DBAR) measurements with spin-polarized positrons and magnetization (M–H) measurements. The DBAR spectra showed asymmetry upon magnetic-field reversal at 300 K, while no asymmetry appeared at 30 K. This result indicates that excess electron spins at Ga vacancies are aligned under the application of magnetic field at 300 K, but such spin ordering vanishes at low temperatures. No hysteresis was found in M–H curves both at 10 K and 300 K. This means that no macroscopic magnetism appears even though excess electron spins at Ga vacancies are introduced. [DOI: 10.1380/ejssnt.2018.347]

Keywords: Positron spectroscopy; Ion implantation methods; Gallium nitride

I. INTRODUCTION

After the first observation of the vacancy-induced magnetism (VIM) on a hafnium oxides in 2004 [1], appearance of VIM has been reported successively on zinc oxides (ZnO) [2–7], tin oxides (SnO_2) [8, 9] and cerium oxides (CeO_2) [10, 11]. Based on the *ab initio* studies, excess electron spins at cation vacancies are thought to be the origin of magnetism [12–16]. The degenerate energy levels associated with cation vacancies are exchange-splitted due to the interaction among unpaired electrons. One electrically-neutral cation vacancy in metal oxides possesses the magnetization of 2 μ_B (μ_B: Bohr magneton) of excess electron spins [16–21]. When the density of cation vacancies is high enough, collective magnetization appears as a result of the exchange interaction among excess electron spins at cation vacancies. This is an overview of VIM. In metal nitrides, the magnetization of cation vacancies is expected to be larger as compared to the case of metal oxides [20].

In spite of many extensive studies, the magnetization of cation vacancies had not yet been confirmed. One of the reasons is the lack of measurement methods that can detect excess electron spins at cation vacancies. Positron annihilation spectroscopy is a powerful tool to detect vacancy-type defects [22]. Furthermore, using spin-polarized positrons, excess electron spins at vacancy-type defects can also be detected [23]. Actually, the existence of excess electron spins at cation vacancies in ZnO after oxygen implantation was confirmed by this spin-polarized positron annihilation spectroscopy (SP-PAS) [24]. In this study, we explored VIM in p-type gallium nitride films by the SP-PAS.

II. EXPERIMENTAL

Samples used in this study were Mg-doped p-type GaN films of 2 μm thick on sapphire substrates with dimensions of 10 mm × 10 mm × 0.5 mm. The nominal carrier density was 3×10^{17} cm^{-3}. These samples were implanted with nitrogen ions at 100 keV to doses of 1×10^{15} cm^{-2}–1×10^{17} cm^{-2} at room temperature using a 400 keV ion implanter of our institute. By using a spin-polarized positron beam apparatus as shown in Fig. 1 [25], the Doppler-broadening annihilation radiation (DBAR) spectra were obtained in the magnetic fields of ±0.91 T at 30 K and 300 K. The beam spin polarization was 27%. Magnetization (M–H) curves were also obtained by a superconducting quantum interference device (SQUID) apparatus at 10 K and 300 K.

Figure 2 shows the depth profile of vacancies calculated by the Stopping and Range of Ions in Matter (SRIM) code [26]. To probe vacancies effectively, positrons were implanted at 6 keV (the positron implantation profile calculated by the Makovian function [27] is also shown in Fig. 2).

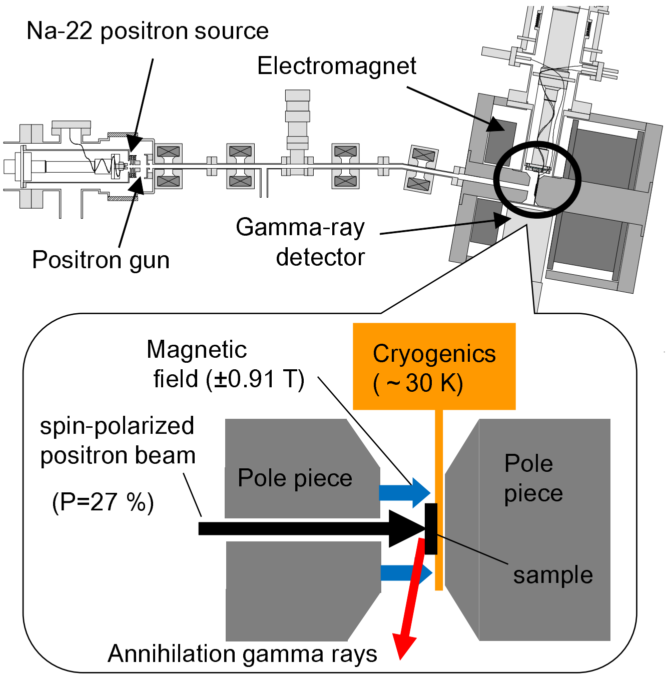

FIG. 1. Schematic of the spin-polarized positron beam apparatus. Longitudinally spin-polarized positrons are injected into the sample mounted between the electromagnet pole pieces. The DBAR measurements are possible with a maximum magnetic field of ±0.91 T.

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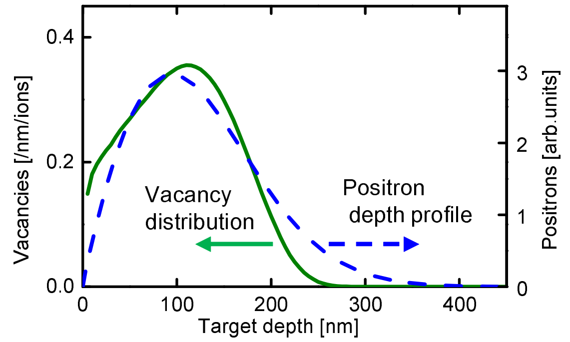

FIG. 2. Solid line is the SRIM calculation of vacancy distribution in 100 keV-nitrogen implanted GaN. Broken line is the positron implantation profile at 6 keV calculated by the Makovian function.

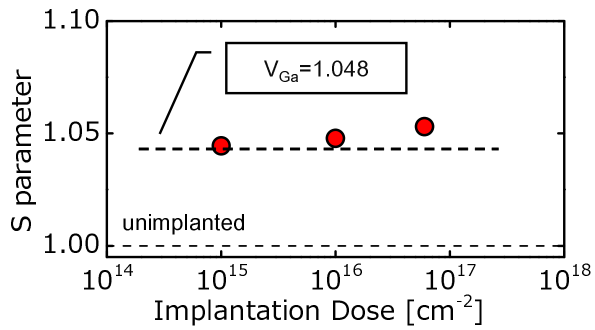

FIG. 4. Dose dependence of S parameters before and after nitrogen implantation. S parameter for the Ga vacancy from literature (S = 1.048) obtained by Hautakangas is also indicated.

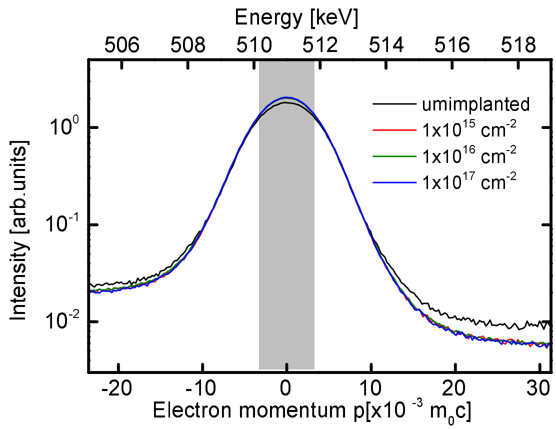

FIG. 3. The Doppler-broadening annihilation radiation (DBAR) spectra obtained before and after nitrogen implantation. The area intensity is normalized to unity.

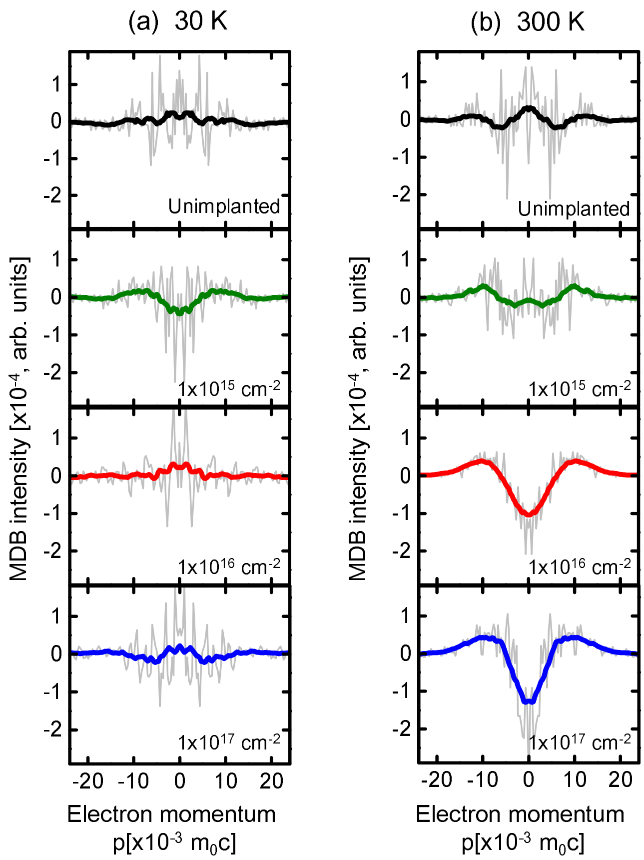

FIG. 5. MDB spectra of the GaN sample measured at (a) 30 K and (b) 300 K. Narrow gray lines are raw experimental data and bold lines are smoothed data.

III. RESULTS AND DISCUSSION

Figure 3 shows the results of the DBAR measurements before and after nitrogen implantation. The energy shift from 511 keV (= m_0c^2, where m_0 is the electron rest mass and c is the speed of light) corresponds to an electron momentum of $p = 3.92 \times 10^{-3} m_0 c$ per 1 keV. After nitrogen implantation, the central area intensity of the DBAR spectrum increases. This means that positrons are trapped at vacancy-type defects introduced by nitrogen implantation, since positrons tend to annihilate with valence electrons having lower momenta than core electrons. The central area intensity of 511 $\pm$ 0.8 keV (the dark area in Fig. 3) is characterized as 'S parameter', which increases with the size and the density of vacancy-type defects [28]. Figure 4 shows the ion dose dependence of S parameter. All the S parameters were normalized to the value of the unimplanted sample. After nitrogen implantation, S parameter increases to around 1.05 and shows no significant dose dependence. This means that positrons are fully trapped at one kind of vacancies. The obtained S parameter agrees with that for the Ga vacancies in GaN (S = 1.048) [29–31]. From this result, it is confirmed that Ga vacancies are the major positron trapping centers.

Figure 5 shows the differential DBAR spectra in positive and negative magnetic fields at 30 K and 300 K. We call such differential DBAR spectra 'magnetic Doppler-broadening (MDB)' spectra. Narrow gray lines are raw experimental data and bold lines are 10-points smoothed data. At 30 K, MDB spectra are almost flat for all the dose conditions. On the contrary, at 300 K MDB intensity increases for doses of 1×10^{16} cm^{-2} and 1×10^{17} cm^{-2}. This indicates that excess electron spins exist at Ga vacancies, as follows. Figure 6 shows the schematic explanation of MDB spectra, when excess electron spins at vacancies are ferromagnetically aligned in magnetic field [24]. If positron and electron spins are parallel (antiparallel), two-gamma annihilation is prohibited (permitted). Con-

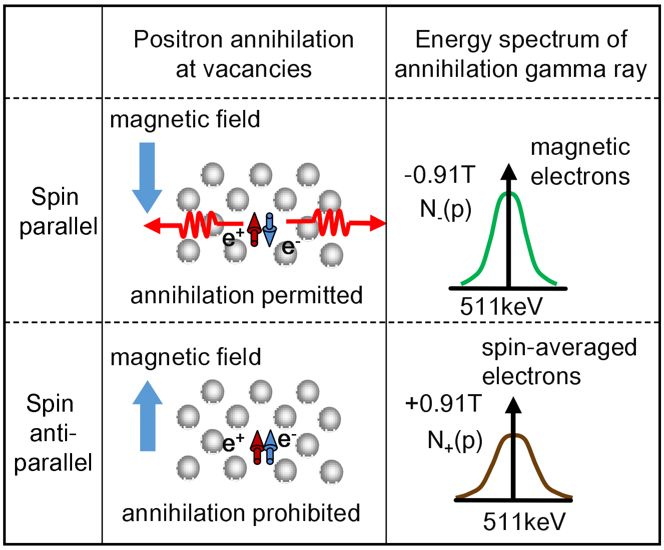

FIG. 6. The principle of the SP-PAS method. When positron and electron spins are parallel (antiparallel), two-gamma annihilation is prohibited (permitted). As the result, DBAR spectra shows the difference intensity for the positive and negative fields, which indicates the existence of excess electron spins at vacancies.

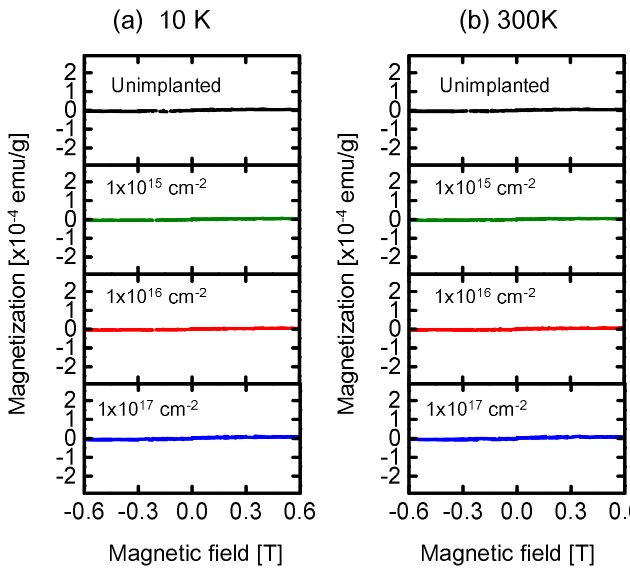

FIG. 7. *M–H* curves obtained before and after the nitrogen implantation at (a) 10 K and (b) 300 K.

sequently, the shape of the DBAR spectrum shows the difference between positive and negative fields.

The reason for the absence of MDB intensities at 30 K is not clear at present. It may be due to the change in magnetic coupling among excess electron spins at vacancies. As for this, Dev *et al.* proposed the appearances both ferromagnetic and antiferromagnetic phases depending on the charge state of Ga vacancies [32]. For more detailed discussions, the further experimental studies are under progress.

To confirm whether VIM appears or not, *M–H* measurements were carried out. Figure 7 shows the *M–H* curves obtained before and after nitrogen implantation at 10 K and 300 K. Practically no magnetizations are observed in any conditions. This is in contrast to the increases of the MDB intensities shown in Fig. 5(b). One possible reason for this contradiction may be because of different sensitivities of MDB and SQUID. In the case of nitrogen implantation for a shallow region, the total number of spins may not be sufficient for the SQUID measurement, while the MDB measurement can selectively detect excess electron spins at vacancies in the ion implanted region.

IV. CONCLUSION

In conclusion, we observed that excess electron spins at Ga vacancies in nitrogen-implanted p-type GaN films are aligned under the application of magnetic field at 300 K. However, such spin ordering vanishes at low temperatures. It may be due to the change in magnetic coupling among excess electron spins at vacancies. No hysteresis was found in *M–H* curves, showing that macroscopic magnetism appears even though excess electron spins at Ga vacancies are introduced.

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