9. Observation of the distortion around Ga lattice sites due to the residual hydrogen in GaN single crystal wafer

Kazuki Sato*, Tomoaki Nishimura*, Kazuo Kuriyama*, Tohru Nakamura*

1. Introduction

The high-quality GaN films can be achieved by using the substrate with small lattice mismatch and small difference in thermal expansion coefficients between GaN and substrate. Therefore the growth of GaN single crystal wafers that can be used as substrate materials is essential. However hydrogen is often introduced into GaN during growth by metalorganic chemical vapor deposition. An evaluation of the residual hydrogen in GaN is important because the formation of H complex defect such as H-Mg complex defect affects its electrical activity[1]. Slight displacement around Ga lattice sites due to H-Ga interaction has been also proposed by Myers *et al.*[2]. Also hydrogen passivation during growth facilitates p-type doping by diminishing the driving forces for formation of electrically compensating defect such as the N vacancy[3,4]. In the present study, the disturbance of Ga lattice due to the residual hydrogen is evaluated by Rutherford backscattering spectrometry (RBS) and Elastic recoil detection analysis (ERDA).

2. Experimental

GaN single crystal wafer of about 370 μm in thickness grown by the hydride vapor phase epitaxy (HVPE) method was used in this study. Samples were annealed at 400, 700 and 900℃ for 10 min under N_2 flow. The distortion around Ga lattice sites was evaluated by means of Rutherford backscattering spectrometry in channeling mode (RBS/C) using a 1.5 MeV H^+ beam. The backscattered H^+ was detected with a solid-state detector (SSD) located at 150°. The residual hydrogen in GaN was evaluated by ERDA using 1.8 MeV $^4He^+$ ion beam[5,6]. The recoiled H-ions were detected with the SSD located at 25 ～ 35° for recoil angle. An aluminum film with 7.5 μm in thickness was placed in front of the ERDA detector in order to stop all the recoiled atoms heavier than hydrogen. ERDA measured using 1.8 MeV - $^4He^+$ ion beam can evaluate hydrogen until about 90 nm in depth. The similar beam energy has been used for evaluating hydrogen in proton implanted ZnO bulk single crystals[7].

3. Results and Discussion

Figures 1 and 2 show the random and aligned RBS spectra and an enlarged figure from 350 ～ 500 nm, respectively. The minimum yield χ_{min} (the ratio of aligned and random yields) was evaluated using a width of 40 channels (100 – 200 nm) from the crystal surface. Based on the χ_{min} value of the 900℃ annealed sample, the number of Ga atoms

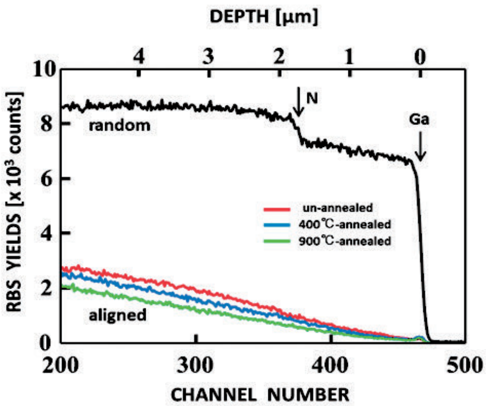

Fig. 1 Random and aligned RBS spectra for un-annealed, 400 and 900℃-annealed GaN obtained by using 1.5 MeV H^+ beam.

*Research Center of Ion Beam Technology, Hosei University

displaced into channels near the surface was estimated by

$$N_D = N_{Ga} (\chi_{min} - \chi_{min\,(900)}) / (1 - \chi_{min\,(900)}),$$

where N_{Ga} is the Ga density (4.38×10^{22} cm^{-3}) in GaN. Figure 2 shows an enlarged figure from 350 to 500 nm along the c-axis of un-annealed and annealed samples. χ_{min} values for un-annealed, 400 and 900℃ annealed samples were 1.97%, 1.91%, and 1.70%, respectively. The χ_{min} value for GaN annealed at 900℃ is close to the previously reported value (1.61%[6]) for as-grown GaN single crystals. The displaced Ga atom concentrations estimated from the χ_{min} values were 1.11 x 10^{20} cm^{-3} for the un-annealed GaN and 0.94 x 10^{20} cm^{-3} for the 400℃ annealed ones.

The slight de-channeling phenomenon was observed from the depth of about 250 nm behind the surface peak in un-annealed GaN (see Fig. 2), suggesting the existence of the minute displacement of Ga. This result would be attributed to the Ga displacement arising from the complex defect of the residual hydrogen and Ga. In the case of H^-, there is the appreciable relaxation of Ga atoms toward H proposed by Myer et al. [2]. In aligned RBS spectra of annealed samples, the slight de-

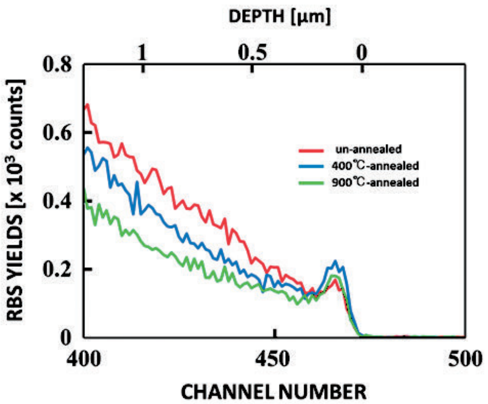

Fig. 2 The magnified figure of aligned RBS spectra from 400 to 500 channel for 400 and 900℃ -annealed GaN. De-channeling phenomena of Ga is observed from near 250 nm in depth in un-annealed single crystal wafers.

channeling phenomenon decreases. It is suggested that the distortion around Ga lattice sites of the H-Ga complex defects disappeared by the hydrogen out-diffusion as discussed later.

Figure 3 shows the result of ERDA measurements. The hydrogen concentration near the surface was calculated by the following equation[8],

$$N = Y \sin \theta / [Q (d\sigma / d\Omega) \Delta\Omega],$$

where N is the hydrogen concentration, Y is the yield of recoiled hydrogen, Q the number of incident $^4He^+$ ions, $(d\sigma / d\Omega)$ the differential scattering cross-section (cm^{-2}), $\Delta\Omega$ solid angle of the detector, and θ the recoil angle (15°). The hydrogen concentration in un-annealed, 400℃, 700℃, and 900℃ annealed samples were about 4.8 x 10^{14} cm^{-2}, 3.4 x 10^{14} cm^{-2}, 2.8 x 10^{14} cm^{-2}, and 2.8 x 10^{14} cm^{-2}, respectively. The hydrogen concentration at about 90 nm in depth in un-annealed GaN is about the twice of those in 700℃ and 900℃-annealed ones, suggesting that part of the residual hydrogen was out diffused by annealing. This result corresponds to a decrease in the minimum yield (χ_{min}) of the

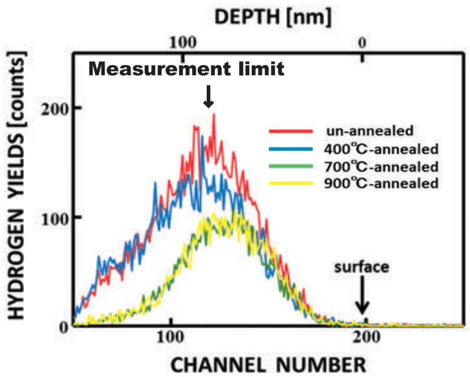

Fig. 3 The residual hydrogen in un-annealed, 400, 700 and 900℃-annealed GaN evaluated by ERDA using 1.8 MeV $^4He^+$ beam. ERDA measured using 1.8 MeV - $^4He^+$ ion beam can evaluate hydrogen until about 90 nm in depth due to the energy loss of the analytical beam in the solid. The arrow above the ERDA peak indicates the limit of the quantitative calculation of the hydrogen concentrations.

RBS/C experiment due to the out-diffusion of hydrogen by annealing.

4. Conclusion

In RBS channeling experiments, the slight de-channeling phenomenon of Ga was observed from the depth of about 250 nm in depth behind the surface peak in un-annealed GaN single crystal wafers. In ERDA experiments using 1.8 MeV He^{4+} beam, the hydrogen concentration $(4.8 \times 10^{14}\ cm^{-2})$ in un-annealed GaN was about the twice of that in 900℃ annealed one, suggesting that part of the residual hydrogen was out diffused by annealing. The existence of the minute displacement of Ga in un-annealed GaN was associated with the Ga displacement arising from the complex defect of the residual hydrogen and Ga. This phenomenon corresponds to the appreciable relaxation of Ga atoms toward H proposed by Myer *et al* [2]. The slight de-channeling phenomena of the Ga atom observed in the RBS channeling experiment disappeared in association with the reduction of hydrogen due to out diffusion of hydrogen in the annealed wafer.

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