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Detection of charge transition level of near-surface hydrogen interstitials introduced into Mg-ion-implanted GaN by annealing

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Excellent properties were obtained for metal-oxide-semiconductor (MOS) structures fabricated on n-type GaN after light Mg-ion implantation and subsequent ultrahigh-pressure annealing. However, a small bump caused by near-surface defects was detected in capacitance–voltage (C – V) characteristics. Nevertheless, conventional C – V methods for evaluating interface states cannot evaluate the charge transition of near-surface defect states. By analyzing the plot of dC/dV versus the surface Fermi level, we detected bulk defect states at 0.5 eV below the conduction band edge with the (+/–) charge transition. The defects were assigned to hydrogen interstitials.

Gallium nitride (GaN) grown on a GaN substrate has achieved excellent characteristics of metal-oxide-semiconductor (MOS) interfaces formed on GaN.^{1–5)} As a result, the development of high-efficiency MOS field-effect transistors (FETs) has been reported.^{6–11)} In fabricating MOSFETs, ion implantation is a useful technique for forming selectively doped n-type GaN (n-GaN) and p-type GaN (p-GaN) regions. However, realizing a method of fabricating high-quality p-GaN regions using ion-implantation technology is still a challenging issue. Although p-GaN regions have been realized by ion implantation with magnesium (Mg) ions,^{12–22)} the quality of the ion-implanted region is critically dependent on post-implantation annealing. As one of the promising annealing methods, ultrahigh-pressure annealing (UHPA) without using any cap layers has been proposed and intensively studied, achieving a high activation ratio of up to 100% with a reduction in the density of nitrogen-vacancy-related defects.^{20–27)} On the other hand, to realize a highly efficient MOSFET, the quality of the MOS interface should be excellent. Thus far, although excellent MOS interfaces on homoepitaxial GaN layers have been reported,^{1–5)} there are only a few reports on the MOS interfaces formed on Mg-ion-implanted GaN. In our previous study,²⁸⁾ we investigated interface states and near-surface defect states near the conduction band edge (E_C), which might affect the operation of inversion-type MOSFETs, for MOS diodes fabricated on Mg-ion-implanted GaN after UHPA at 1400 °C under a nitrogen pressure of 1 GPa for 5 min. We found that the interface state density can be suppressed to as low as $10^{11} - 10^{12} \text{ cm}^{-2}\text{eV}^{-1}$ near E_C . However, the measured capacitance–voltage ($C-V$) characteristics indicated bumps due to near-surface defect states. We discussed the possibility of assigning the defect states to hydrogen interstitials (H_i). Nevertheless, obtaining direct evidence was a residual issue. On the basis of recent research results, long-term UHPA under a reduced nitrogen pressure with the temperature decreased to 1300 °C is also effective for achieving a high activation ratio of Mg acceptors.²¹⁾ Here, using MOS structures fabricated on Mg-ion-implanted GaN after long-term UHPA with reduced temperature and pressure, we detected evidence of H_i in excellent $C-V$ characteristics which exclude the influence of the interface states. We propose an original analysis method for distinguishing the charge transition of near-surface defects.

The MOS structure was prepared as shown in **Fig. 1**. A 3- μm -thick Si-doped n-GaN epitaxial layer with a donor concentration N_D of $3.8 \times 10^{17} \text{ cm}^{-3}$ was grown by metalorganic vapor phase epitaxy on a freestanding n^+ -GaN (0001) substrate. Since it is difficult to evaluate gap states near the conduction band using a p-GaN MOS structure, we used a MOS structure with light Mg-ion implantation onto n-GaN, maintaining an n-type conduction. Mg

ions were implanted at an energy of 50 keV up to a dose of $1.5 \times 10^{12} \text{ cm}^{-2}$ with an incident angle of 7° tilted from the normal incidence and with a lateral rotation of 15° from the normal direction to the orientation flat. The Mg concentration [Mg] was controlled so as not to exceed N_D using the computer code of “stopping and range of ions in matter” (SRIM). The [Mg] distribution after UHPA detected by secondary ion mass spectrometry (SIMS) is shown in **Fig. 2** with the [H] distribution for the discussion described later. UHPA was performed without using a cap layer at 1300 °C for 60 min under a nitrogen pressure of 500 MPa. Subsequently, the sample was treated with a solution of HF:H₂O = 1:1 prior to the formation of the 30-nm-thick Al₂O₃ layer by atomic layer deposition at 300 °C. The MOS structure was formed with Ni/Au top circular electrodes (300 μm diameter) and a Ti/Au back ohmic contact. Finally, post-metallization annealing was carried out at 300 °C.^{1, 2)}

Figure 3 shows the C - V characteristics of the fabricated MOS sample. The solid lines represent the C - V characteristics in a bias sweep direction from the negative to positive voltage side (forward direction). Although the 1 MHz curve measured under the voltage sweep in the opposite direction (backward direction) is plotted by a fine line in Fig. 3, it is not distinct because of a negligible hysteresis except at around $1 \times 10^{-7} \text{ Fcm}^{-2}$ (see supplementary data Fig. S-1 for an enlarged illustration). In addition, no significant frequency dispersion was observed. The flat band voltage V_{FB} was 1.07 V, which was derived from the backward direction of the measured 1 MHz C - V curve as a voltage that achieves the flat band capacitance of $2.04 \times 10^{-7} \text{ F/cm}^2$ calculated without assuming unknown parameters, *i.e.*, the work function difference between metal and semiconductor, the oxide fixed charge, and the surface charge due to spontaneous polarization likely reduced by surface passivation. Without considering the aforementioned parameters, we cannot discuss the quality of the MOS interface on the basis of V_{FB} at this stage. The dashed line shows the ideal curve shifted to overlap with the measured curves in the deep depletion region, which was calculated assuming that N_D is constant at $3.8 \times 10^{17} \text{ cm}^{-3}$ according to the doping profile derived from the backward-direction 1 MHz C - V curve in the deep depletion region²⁹⁾ as shown in the inset in Fig. 3. The profile at a depth smaller than 50 nm is omitted because it cannot be appropriately evaluated owing to the short electron emission time constant of interface states at the corresponding surface Fermi level (within $\sim 1 \text{ eV}$ below E_C) compared with the bias sweep rate of 50 mV/s.^{30, 31)} The doping profile is almost constant, indicating that it is not affected by defect charges. The obtained C - V characteristics show that UHPA under the present conditions leads to an excellent MOS interface on Mg-ion-implanted GaN.

The high-low-frequency method³⁰⁾ was applied to the forward-direction C - V

characteristics to derive the distribution of gap state density (D_T). Here, gap states include interface states and near-surface-defect states. The results are shown in **Fig. 4**. A detailed discussion of the detection range is provided in our previous study.³²⁾ No marked discrete level was detected within the range of 0.15–0.45 eV below E_C , resulting in part of a U-shaped interface state density distribution.^{33, 34)} Although we also applied the Terman method to the forward-direction 1 MHz C – V curve, D_T cannot be calculated above $E_C - 0.45$ eV because the dC/dV of the measured C – V curve was larger than that of the ideal curve, as shown at around 1 V in Fig. 3. Basically, dC/dV increases as the doping concentration decreases, whereas dC/dV decreases as D_T increases. Therefore, the doping density was lower than $3.8 \times 10^{17} \text{ cm}^{-3}$ in the corresponding range of depletion widths ($< \sim 40$ nm). There is a possibility that this nonuniformity was caused by the charge compensation by the near-surface defects. Indeed, the Terman method revealed a D_T peak indicating defect states at 0.7 eV below E_C . However, there is a possibility that this method cannot determine the exact energy positions of the defect states in the band gap for the case where the defects distribute in bulk GaN. In addition, conventional C – V methods cannot distinguish the donor/acceptor nature of defect states.

Figure 5 shows a comparison of dC/dV as a function of surface Fermi level (E_{FS}) location, *i.e.*, $E_{FS} - E_C$, between the measured and ideal C – V curves. It can be seen that the measured dC/dV is larger than the ideal one above $E_{FS} - E_C = -0.5$ eV, as described above. On the other hand, it can also be seen that the measured dC/dV is smaller than the ideal one below $E_{FS} - E_C = -0.5$ eV. Generally, dC/dV decreases as D_T increases. According to the results in Fig. 4, the U-shaped interface density distribution below $E_C - 0.5$ eV seems to be very low. Thus, there is a possibility that the near-surface defects mainly affected the observed behavior of dC/dV . If we assume the defect states at $E_C - 0.5$ eV with a charge transition (+/–), the obtained result can be explained. In Fig. 5, the band bending with near-surface defects at $E_T = E_C - 0.5$ eV is also illustrated schematically for four regions A–D indicated in the dC/dV plot. In region A, the near-surface defect states are above the Fermi level E_F and charged positively similarly to donors, which only shift the C – V curves toward the negative bias direction while maintaining the same dC/dV as that of the ideal C – V curve. In region B, the charges of near-surface defect states below E_F change partially according to the bias voltage change, which is similar to the behavior of interface states to decrease dC/dV . Around region C, or the boundary between regions B and D, the topmost part of the near-surface defects crosses E_{FS} , where the Fermi–Dirac distribution function becomes 1/2 at $E_C - 0.5$ eV, roughly resulting in the neutrality of the defect charge if the defect density peaks

at the topmost surface. In region D, all the near-surface defect states are below E_F and negatively charged similarly to acceptors to compensate for the donor charge, which makes the measured dC/dV larger than the ideal one. To confirm this model, a simulation using the computer code we developed was conducted. The fitting result is shown in Fig. 5 as a broken line. An excellent fitting was achieved. The assumed defect concentration N_T distribution is also shown in the inset in Fig. 5, where the complementary error function (broken line) and the Gaussian distribution function (dotted line) are used in combination by adding them (solid line). From the 1 MHz C - V curve, we derived the total sheet-charge change N_{total} and depletion-layer-sheet-charge change N_{depl} in region B by calculating the following:

$$N_{\text{total}} = \frac{1}{q} \int_{-1.1 \text{ V}}^{-0.33 \text{ V}} C dV, \quad (1)$$

$$N_{\text{depl}} = \int_{E_{FS}-E_C=-0.86 \text{ eV}}^{E_{FS}-E_C=-0.50 \text{ eV}} C_D d\psi_S, \quad (2)$$

$$C_D = \sqrt{\frac{q\epsilon N_D}{2\psi_S}}, \quad (3)$$

where C_D is the depletion layer capacitance, ψ_S is the surface potential, q is the elemental charge, and ϵ is the dielectric constant. Region B corresponds to ψ_{FS} ranging from -0.50 eV to -0.86 eV and V ranging from -0.33 V to -1.1 V . The calculation results are $N_{\text{total}} = 5.5 \times 10^{11} \text{ cm}^{-2}$ and $N_{\text{depl}} = 4.8 \times 10^{11} \text{ cm}^{-2}$. Therefore, the sheet charge with a density of $7 \times 10^{10} \text{ cm}^{-2}$ should have been provided by the near-surface defect states. On the other hand, the integration of total N_T versus depth in the inset of Fig. 5 results in $8 \times 10^{10} \text{ cm}^{-2}$, which is in good agreement with the defect sheet charge calculated from the C - V curve.

It is highly likely that the detected near-surface defect states are assigned to H_i with a (+/-) charge transition state at approximately $E_C - 0.5 \text{ eV}$ as shown in Fig. 2(a) of Ref. 35 and in Fig. 1 of Ref. 36 based on the first-principles calculation using Heyd-Scuseria-Ernzerhof hybrid function methods. The (+/-) charge transition is unusual for interface states. A hydrogen radical (H^*) with a single electron in the 1s orbital is unstable and reactive. The nature of H_i without a charge (H_i^0) can be similar to that of H^* . Indeed, the calculated formation energy of H_i^0 never becomes the lowest among H_i^0 , H_i^+ , and H_i^- at any positions of E_F in the band gap.³⁷⁾ Consequently, the charge of H_i changes between H_i^+ and H_i^- . (The energy position of the H_i (+/-) charge transition level in Ref. 37 is different from that in Refs. 35 and 36, which may be due to the difference in the calculation method used. We adopted

the more recent result in Refs. 35 and 36.) In Fig. 2, the SIMS results of the [H] distribution are also plotted with those of the [Mg] distribution. (Note that the SIMS results in the near-surface region within ~ 30 nm are uncertain because of surface contamination.) Hydrogen atoms should have been introduced through the moisture in the high-pressure nitrogen atmosphere.²⁵⁾ Therefore, this phenomenon is specific to UHPA. The sheet density of hydrogen atoms detected by SIMS was higher than that of near surface H_i defects and that of Mg atoms detected by SIMS as shown in Fig. 2. Hydrogen atoms may have been mainly trapped by defects. There is a possibility that a small portion of these trapped hydrogen atoms were released upon the recovery of the defects during long-term UHPA, although the detailed mechanism is unclear at this stage. The Gaussian N_T distribution may have originated from the released hydrogen atoms, whereas the complementary error function distribution may have originated from the hydrogen atoms introduced from the moisture in the ultrahigh-pressure ambience through the surface regardless of Mg-ion implantation. Since the Mg atoms at Ga sites with a density lower than H_i density should have been passivated by H according to the lower formation energy of Mg–H than of H_i ,³⁵⁾ it is highly likely that they did not contribute to electrical measurement results. It is worth comparing a sample with UHPA without Mg-ion implantation, even though the same dC/dV behavior may not be observed because H atoms should be mainly trapped by Mg atoms²²⁾ and implantation-induced defects, which is a future issue.

In summary, we studied the MOS structures fabricated on n-type GaN after modest-dose Mg-ion implantation and subsequent UHPA at 1300 °C for 60 min under a nitrogen pressure of 500 MPa. From the C – V measurements of MOS structures, the oxide/GaN interface was excellent with a low D_T on the order of 10^{11} cm^{−2}eV^{−1} or lower near the conduction band edge despite the Mg-ion implantation into GaN. We examined the origin of the bump of the C – V curve by analyzing a plot of dC/dV versus the E_{FS} position, which resulted in the detection of near-surface defect states at $E_C - 0.5$ eV with the (+/−) charge transition. The defects were assigned to H_i with a sheet density of less than 10^{11} cm^{−2}. The simulated dC/dV – E_{FS} curve was fitted to the measured one, assuming a H_i density profile composed of a combination of a complementary error function and a Gaussian function. A possible generation mechanism of H_i in the near-surface region has been discussed.

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Figures

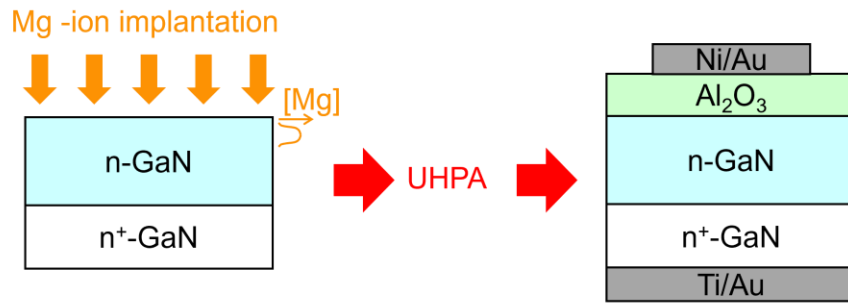


Fig. 1. Schematic of sample fabrication sequence.

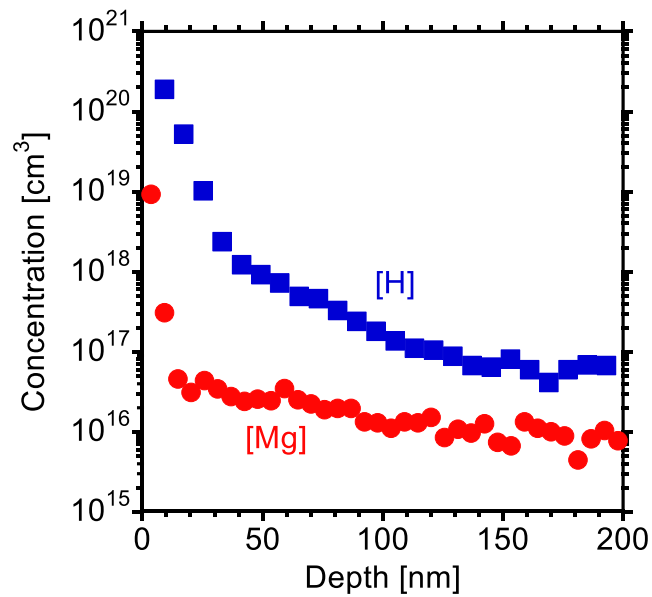


Fig. 2. SIMS results of [Mg] and [H] distributions for Mg-ion-implanted GaN after UHPA.

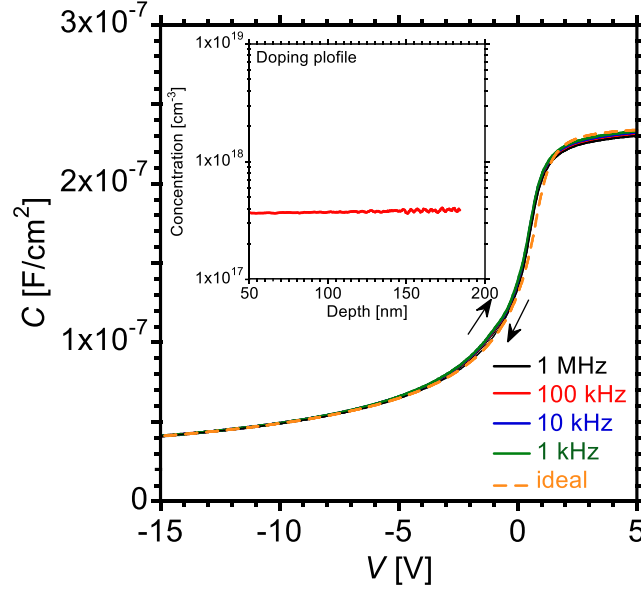


Fig. 3. C – V characteristics of Mg-implanted n-GaN MOS diode formed after UHPA at 1300 °C for 60 min under 500 MPa. The inset shows the doping profile calculated from the 1 MHz C – V curve.

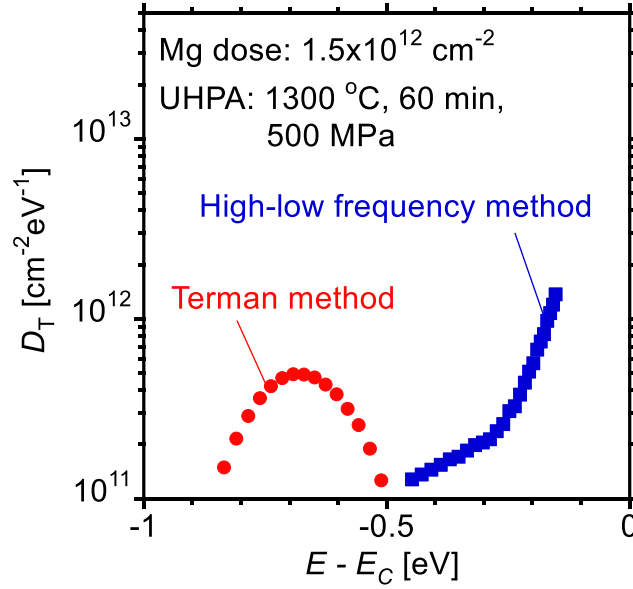


Fig. 4. D_T distributions at the ALD Al_2O_3 /n-GaN interface derived from C – V characteristics in Fig. 3 by high–low-frequency (solid rectangles) and Terman (solid circles) methods.

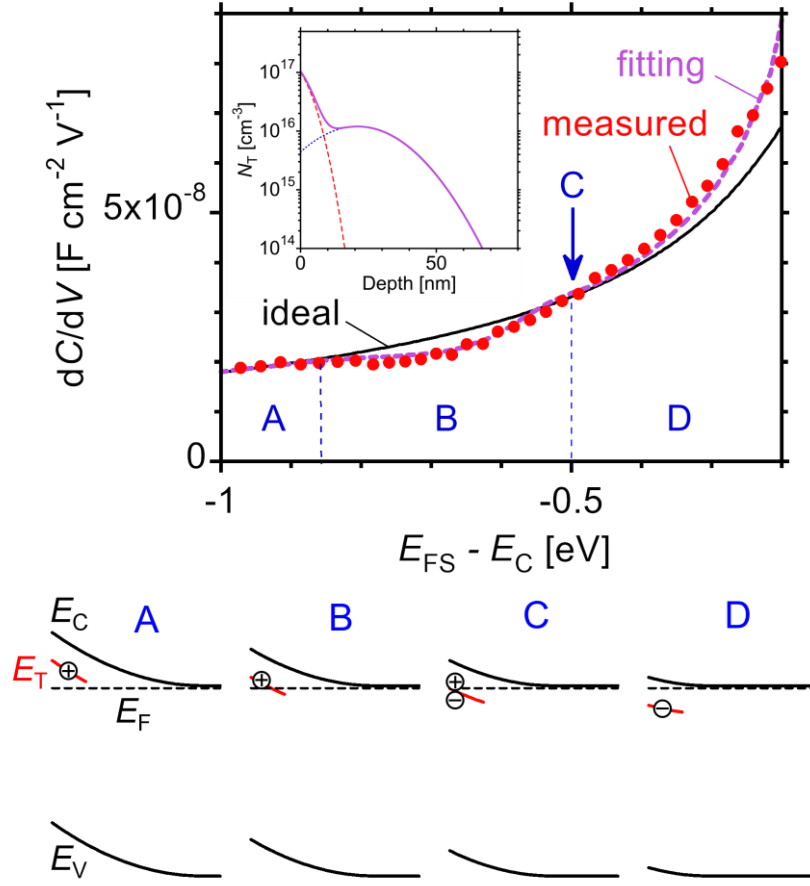


Fig. 5. Measured, ideal, and simulated dC/dV plotted versus $E_{\text{FS}} - E_{\text{C}}$ and schematic band diagram for regions A–D. The inset shows the assumed defect state density distribution for fitting.