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Author(s)	Takahashi, Masanobu; Jiao, Yining; Akazawa, Masamichi
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Effects of SiO₂ cap annealing at 800 °C on Ga-polar n-type and p-type GaN (0001) surfaces compared by X-ray photoelectron spectroscopy

Masanobu Takahashi¹, Yining Jiao¹, and Masamichi Akazawa^{1*}

¹Research Center for Integrated Quantum Electronics, Hokkaido University, Sapporo 060-0813, Japan

*E-mail: akazawa@rciqe.hokudai.ac.jp

The effects of SiO₂ cap annealing at 800 °C on Ga-polar n-type and p-type GaN (0001) surfaces were compared by X-ray photoelectron spectroscopy. We found that the native oxide thickness at the GaN surfaces is usually at the monolayer level regardless of the process step, except immediately after SiO₂ cap annealing for p-type GaN. Furthermore, for both conduction types, the surface Fermi level is located between the conduction band edge and the charge neutrality level regardless of the process step, which indicated that donor-like defects existed in the vicinity of the p-type GaN surfaces.

GaN has a wide bandgap,¹⁾ a high breakdown field,²⁾ a high electron mobility,¹⁾ a high electron saturation velocity,¹⁾ and a good thermal conductivity.¹⁾ There is a possibility that a highly efficient power device can be realized by utilizing these features of GaN in a meta-oxide-semiconductor field-effect transistor (MOSFET)^{3–6)}. For the excellent performance of MOSFETs, the properties of the oxide/GaN interface should be well controlled. In GaN MOS structures, however, there are distinct differences in the electrical interface properties between n-type GaN (n-GaN) and p-type GaN (p-GaN). Although n-GaN MOS interfaces exhibit excellent properties^{7–10)}, the properties of p-GaN MOS interfaces are usually affected by a high density of gap states.^{11–15)} The gap states include interface states due to interface disorders and defect states due to near-interface bulk defects. Since the charge neutrality level (E_{CNL}) of GaN is located near the conduction band edge (E_{C}),¹⁶⁾ the density of interface states near the valence band edge (E_{V}) can be high.^{17, 18)} On the other hand, according to first-principles calculation,^{19, 20)} the formation energy of a nitrogen vacancy (V_{N}) is as low as to be negative in p-GaN. Even though V_{N} defects cannot be easily generated in the p-GaN bulk, they might be generated in the vicinity of the GaN surface during device fabrication processes such as annealing and plasma etching. In particular, annealing at above 700 °C is required for p-GaN after growth to activate the Mg acceptors through dehydrogenation.²¹⁾ Recently, we have reported that the generation of midgap states at the MOS interface can be suppressed using a SiO₂ cap layer during annealing at 800 °C prior to the Al₂O₃/p-GaN interface formation.²²⁾ However, the resultant capacitance–voltage characteristics revealed the existence of a high density of positive fixed charges at the MOS interface or p-GaN surface. Since the origin of positive fixed charges is still unclear, further investigation is needed. In particular, a comparison between p-GaN and n-GaN might lead to a clue to the origin of such charges. In this paper, we present the results of monitoring the SiO₂ cap annealing step for n-GaN and p-GaN by X-ray photoelectron spectroscopy (XPS).

The process sequence monitored by XPS is schematically shown in Fig. 1. XPS was conducted after each process step, as follows:

- (1) after the epitaxial growth of n-GaN ([Si]= $5 \times 10^{17} \text{ cm}^{-3}$) and p-GaN ([Mg]= $1 \times 10^{17} \text{ cm}^{-3}$) layers with Ga-polar c-plane surfaces by metalorganic vapor phase epitaxy on free-standing n⁺-GaN (0001) substrates,
- (2) after the surface treatment with a diluted hydrofluoric acid (HF) solution (HF:H₂O=1:1),
- (3) after the 30-nm-thick SiO₂ layer deposition by RF sputtering followed by thinning the SiO₂ layer down to 3 nm by wet etching using buffered HF (BHF; HF:NH₄F=1:5),
- (4) after cap annealing at 800 °C for 20 min using a 30-nm-thick surface protection layer

followed by thinning the SiO₂ layer down to 2 nm by wet etching using BHF,
 (5) after the HF treatment to remove the SiO₂ cap layer, and
 (6) after the atomic layer deposition (ALD) of a 3-nm-thick Al₂O₃ layer at 300 °C.
 The AlK α X-ray source (1486.6 eV) was used for XPS. The binding energy was calibrated by setting the C–C component of the C 1s spectrum at 285.0 eV. The photoelectron exit angle (take-off angle) was set at 45° for all measurements.

As an example, Figs. 2(a) and 2(b) show the Ga 3d and O 1s spectra obtained for the as-grown surface of p-GaN, respectively. As can be seen, the Ga–O component in the Ga 3d spectrum was faint compared with the Ga–N component, which indicated that the native oxide layer was very thin at the as-grown surface for both conduction types. Indeed, the intensity of the O–Ga component in the O 1s spectrum was as weak as that of the O–H component observed in a separate experiment for the HF-treated Au foil surface where only the absorbed water was a possible source of this spectrum. Therefore, the thickness of the native oxide layer should have been at the monolayer level.

A straightforward analysis resulted in the following equation for the thickness of the Ga oxide layer $d_{\text{Ga oxide}}$.²³⁾

$$d_{\text{Ga oxide}} = \lambda \ln \left(1 + \frac{I_{\text{Ga-O}}/I_{\text{Ga-N}}}{I_{\text{Ga-O},\infty}/I_{\text{Ga-N},\infty}} \right), \quad (1)$$

where λ is the escape depth of photoelectrons at the binding energy of the Ga–O component, which is assumed to be common in Ga oxide and GaN layers. $I_{\text{Ga-O}}$ is the observed intensity of the Ga–O component, $I_{\text{Ga-N}}$ is the observed intensity of the Ga–N component, $I_{\text{Ga-O},\infty}$ is the intensity of the Ga–O component for a sufficiently thick Ga oxide layer, and $I_{\text{Ga-N},\infty}$ is the intensity of the Ga–N component for a sufficiently thick GaN layer. Here, λ was assumed to be 1.8 nm for the photoelectron exit angle of 45° calculated according to the theory reported in Refs. 24 and 25, whereas the $I_{\text{Ga-O},\infty}/I_{\text{Ga-N},\infty}$ ratio was assumed to be 1.09 which is the ratio of the atomic density of Ga₂O₃ to that of GaN. On the basis of Eq. (1), $d_{\text{Ga oxide}}$ was calculated using the intensity ratio of the Ga–O component to the Ga–N component in the Ga 3d spectra as shown in Fig. 3. At all process steps except the step right after cap annealing for p-GaN, $d_{\text{Ga oxide}}$ was in the range of 0.05–0.1 nm. There is a possibility that the native oxide layer thickness was around one monolayer at these process steps. However, the length of a surface Ga–O bond does not necessarily coincide with that of a Ga–N bond in the GaN bulk. In addition, the Ga–O bond length should be affected by the O-coverage, the bond structure, and the disorder. Thus, strictly speaking, a precise determination of the

number of monolayers is difficult. Nevertheless, a rough estimation might be possible as follows. According to the previous report on a first-principles calculation,²⁶⁾ the distance between O and Ga atoms is estimated to be 0.179 nm for the (0001) surface covered with one monolayer of oxygen. On the other hand, the growth rate of amorphous Ga₂O₃ films formed by ALD has been reported to be 0.052 nm/cycle.²⁷⁾ Since the measured thickness was between these values, the native oxide layer thickness was presumably around one monolayer at each process step. Indeed, an abrupt interface structure has been confirmed by high resolution transmission electron microscopy for an Al₂O₃/GaN interface formed by ALD after HF treatment, which indicated that the native oxide layer thickness was at a monolayer level and supports the present results.²⁾ However, after cap annealing at 800 °C, the p-GaN sample showed an approximately twofold larger $d_{\text{Ga oxide}}$, which indicated that the oxidation proceeded during annealing. Because there was no such further oxidation for n-GaN, this result is peculiar to p-GaN, which should be taken into account for the oxide/GaN interface formation including postdeposition annealing. Nevertheless, the HF treatment after SiO₂ cap annealing led to the thinning of the oxide layer. After the subsequent Al₂O₃ ALD, the oxide thickness did not increase. Therefore, there is a possibility that an abrupt interface can be formed in a completed MOS structure.

We can investigate the position of the surface Fermi level (E_{FS}) or the amount of band bending by XPS. Here, the E_{FS} position relative to the valence band maximum (VBM) E_{V} was derived from the binding energy of the Ga–N component in Ga 3d spectra at each step of the surface treatment by using the following equation:²⁸⁾

$$E_{\text{F}} - E_{\text{V}} = E_{\text{F}} - E_{\text{Ga3d}} - (E_{\text{V}} - E_{\text{Ga3d}}) = B_{\text{Ga3d}} - (B_{\text{Ga3d}} - B_{\text{VBM}}), \quad (2)$$

where E_{Ga3d} is the Ga 3d core level energy, and B_{Ga3d} and B_{VBM} are the binding energies of Ga 3d and VBM, respectively. Here, $(B_{\text{Ga3d}} - B_{\text{VBM}})$ is a material constant of GaN and measured to be 17.2 eV.²⁸⁾ The results are shown in Figs. 4(a) and 4(b) for n-GaN and p-GaN, respectively. In the n-GaN sample, E_{FS} located between E_{C} and E_{CNL} , which can be explained by the fact that the negative charge of the acceptor-like surface states above E_{CNL} balanced with the positive charge of the ionized donor impurities in the depletion region of n-GaN. We found that E_{FS} located very close to E_{C} right after the SiO₂ cap annealing. This result indicates that the surface state density decreased upon SiO₂ cap annealing, resulting in a decrease in the density of negative charges due to the ionized acceptor-like surface states above E_{CNL} . On the other hand, results for p-GaN in Fig. 4(b) also show that E_{FS} was located

near E_C above E_{CNL} despite the p-type conduction, which indicates that a large band bending occurred regardless of the process step. Indeed, right after the SiO_2 cap annealing, E_{FS} located nearest E_C . This result indicates that a positive charge existed at the p-GaN surface to balance with the negative charge of the ionized acceptors in the depletion region. However, surface states above E_{CNL} are acceptor-like states that generate negative charges at the surface.^{29, 30)} Therefore, it is highly likely that defects generating positive charges existed in the vicinity of the p-GaN surface. As described above, V_N defects are characterized with very low formation energy in p-GaN and forms the (+/0) level at $E_C - 0.2$ eV.¹⁹⁾ Therefore, they can be positively charged up as long as E_{FS} locates below $E_C - 0.2$ eV. Thus, V_N defects might have been the main cause of the large band bending at the p-GaN surface. Upon SiO_2 cap annealing, the decrease in surface state density, as indicated by n-GaN, led to a decrease in the density of surface negative charges that compensated for the positive charges of V_N defects, resulting in a slight increase in band bending compared with other process steps. This situation of band bending at the p-GaN surface is illustrated in Fig. 5. An example of the estimation of defect density is as follows. The surface space charge density N_{SC} generated by the surface band bending can be estimated using the following equation:²⁹⁾

$$N_{SC} = \sqrt{\frac{2\varepsilon N_A \psi_s}{q}}, \quad (3)$$

where ε is the dielectric constant of GaN, N_A is the acceptor concentration, ψ_s is the surface potential, and q is the elemental charge. For the p-GaN surface right after SiO_2 cap annealing, N_{SC} is estimated to be $1.8 \times 10^{12} \text{ cm}^{-2}$ with ψ_s of 2.8 eV as derived from Fig. 4(b). From the results for the n-GaN surface at the same process step, a negligible band bending was observed in Fig. 4(a), which indicated that the interface state density at the SiO_2/GaN interface can be negligible. Therefore, the charge by N_{SC} in p-GaN should have been balanced with the charge by the V_N (+/0) defect level. Since the V_N (+/0) defect level locates around $E_C - 0.2$ eV, it is fully ionized with the observed E_{FS} position of $E_C - 0.4$ eV. If we assume V_N defects were distributed within 10 nm from the GaN topmost surface, the density of V_N can be estimated to be $1.8 \times 10^{18} \text{ cm}^{-3}$.

After the 3-nm-thick Al_2O_3 layer deposition, E_{FS} was pinned at E_{CNL} for both p-GaN and n-GaN, which indicated that the density of the interface states was very high. This result is in good agreement with the strong Fermi level pinning observed for GaN Schottky barrier diodes with an ultrathin Al_2O_3 interlayer.³¹⁾ There is possibility that the gap states at the

Al_2O_3 surface affected this pinning. Although further study is needed to clarify the mechanism of this phenomenon, it is beyond the scope of this work.

In summary, XPS investigation was conducted throughout the $\text{Al}_2\text{O}_3/\text{GaN}$ interface formation process including SiO_2 cap pre-annealing. The Ga oxide thickness is typically in the range of 0.05–0.1 nm, except the process step right after the SiO_2 cap annealing for p-GaN. E_{FS} position analysis indicated the existence of near-surface donor-like defects possibly assigned to V_{N} . There is a possibility that these defects degrade the channel mobility of MOSFETs. Consequently, it is necessary to remove or exclude near-surface donor defects in the vicinity of the insulator/p-GaN interface in addition to the decrease in the surface/interface state density to realize high-performance n-channel GaN MOSFETs.

Acknowledgments

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Figure captions

Fig. 1. Sample preparation sequence. XPS was conducted at each process step.

Fig. 2. XPS (a) Ga 3d and (b) O 1s spectra obtained for as-grown p-GaN surface.

Fig. 3. Ga oxide thickness derived from Ga 3d spectra at each process step.

Fig. 4. E_{FS} position derived from Ga 3d spectra at each process step for (a) n-GaN and (b) p-GaN.

Fig. 5. Schematic diagram for change in E_{FS} and band bending according to decrease in surface state density at p-GaN surface.

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Figures

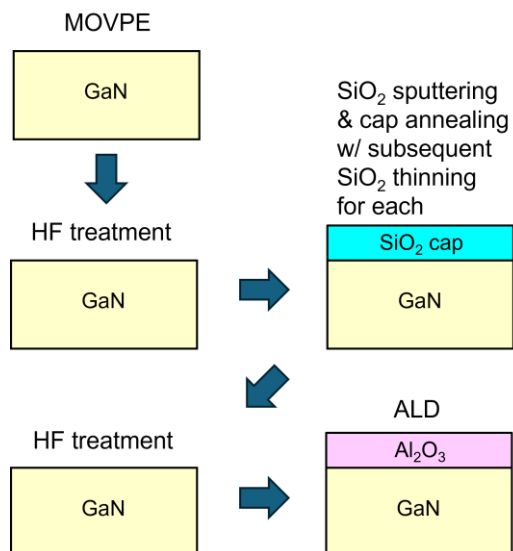


Fig. 1. Sample preparation sequence. XPS was conducted at each process step.

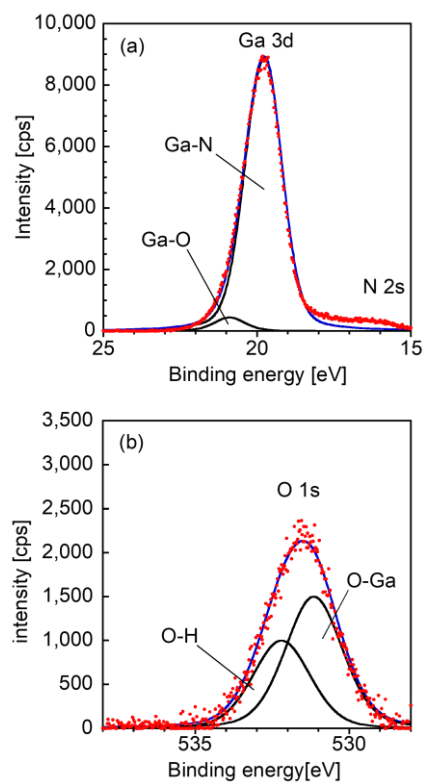


Fig. 2. XPS (a) Ga 3d and (b) O 1s spectra obtained for as-grown p-GaN surface.

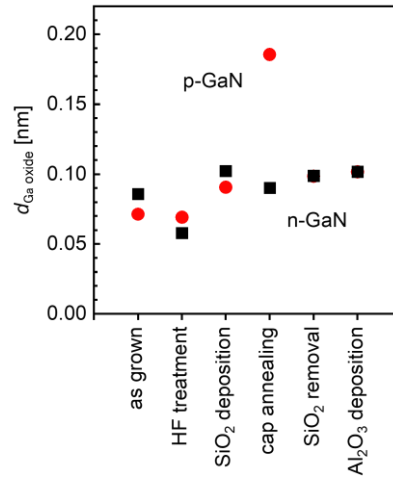


Fig. 3. Ga oxide thickness derived from Ga 3d spectra at each process step.

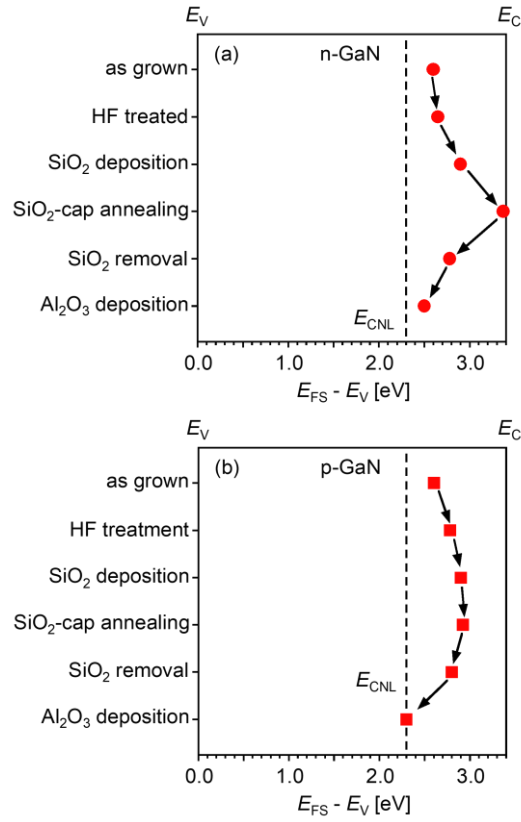


Fig. 4. E_{FS} position derived from Ga 3d spectra at each process step for (a) n-GaN and (b) p-GaN.

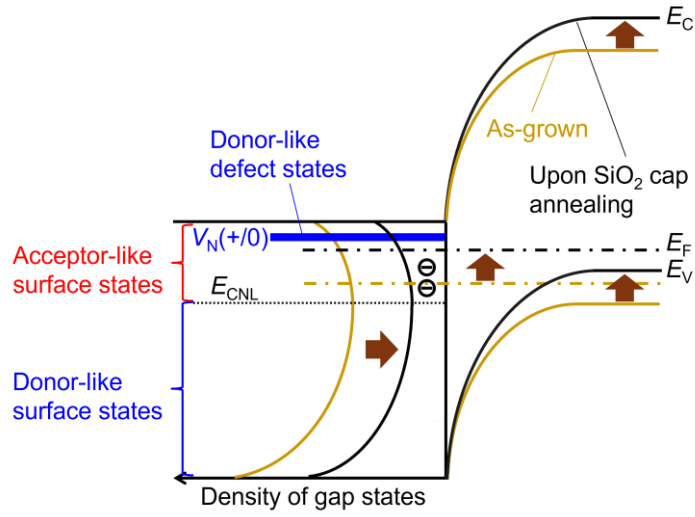


Fig. 5. Schematic diagram for change in E_{FS} and band bending according to decrease in surface state density at p-GaN surface.