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Impact of surface treatment on metal-work-function dependence of barrier height of GaN-on-GaN Schottky barrier diode

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The impact of surface treatment on Schottky contacts on a GaN-on-GaN epitaxial layer was comprehensively investigated by combining X-ray photoelectron spectroscopy (XPS) at each step of the treatment process and electrical measurements on Schottky barrier diodes. XPS showed that a photolithography process on a GaN surface reduced the surface oxide and band bending and that the subsequent HCl-based treatment reduced them further. Electrical measurements indicated that HCl treatment after photolithography affected the metal-work-function, ϕ_M , dependence of the Schottky barrier height, ϕ_B , resulting in an increase in the slope factor compared with that of the samples without HCl treatment. It is highly likely that the reduction in interface disorder by the chemical treatment led to a reduction in the interface state density at the metal/GaN interface. On the basis of the obtained ϕ_B – ϕ_M plots, the charge neutrality level was measured experimentally to be 5.0 eV from the vacuum level and 0.9 eV from the conduction band edge, while the electron affinity was measured to be 4.1 eV. © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). <https://doi.org/10.1063/1.5057401>

For a sustainable society, electronic device technology that reduces the loss of power electric systems, communication systems, and car electronics is one of the key approaches. GaN is a promising material for constructing highly efficient power electronics devices^{1,2} because of its wide bandgap (3.4 eV), high breakdown field (3.3 MV/cm), high electron mobility (1,200 cm²/V·s), and high saturation electron velocity (2.6×10⁷ cm/s). Recently, it has become possible to obtain a high-quality GaN layer with a low dislocation density by epitaxial growth on GaN substrates, enhancing the advantageousness of this material. In the actual construction of electronic devices, a metal/GaN interface is an important building block. The Schottky barrier height, ϕ_B , is a key parameter in characterizing the metal/GaN interface. In actual fabrication processes and device design, knowledge of the dependence of ϕ_B on the metal work function, ϕ_M , is useful. Though the ϕ_M dependence of ϕ_B has been reported for GaN in the literature,^{3–10} the impact of a surface chemical treatment before metallization on the ϕ_B – ϕ_M relation at the metal/GaN interface has not been discussed except in a few studies on GaN on sapphire.^{6,7} Although the host semiconductor was different, a work has been reported on the effect of surface treatment on the ϕ_B – ϕ_M relation of SiC Schottky barrier diodes (SBDs).¹¹ The report showed that a difference in the surface treatment led to a change in the slope of the ϕ_B – ϕ_M plot, which enabled the electron affinity, χ , and charge neutrality level, E_{CNL} , relative to the vacuum level, E_{vac} , to be experimentally obtained.¹¹ Thus, it is worth investigating the impact of surface treatment on the ϕ_B – ϕ_M relation for GaN. A GaN epitaxial layer grown on a GaN substrate exhibits a low dislocation density and an excellent current–voltage (I – V) characteristic,^{12,13} where the latter is useful for investigating the surface pretreatment of Schottky contacts without suffering from a leakage current. Thus far, there have been no reports on the surface-treatment dependence of

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the $\phi_B - \phi_M$ relation for a GaN-on-GaN layer. In this work, the impact of surface treatment on the position of the surface Fermi level at a bare surface and the $\phi_B - \phi_M$ relation at the Schottky contact is investigated using a GaN-on-GaN epitaxial layer.

Sample preparation was carried out as follows. An n-type GaN epitaxial layer (2 μm thick, Si doped: $n = 5.0 \times 10^{16} \text{ cm}^{-3}$) was grown by metal-organic vapor phase epitaxy on a free-standing c-plane n-type GaN substrate (Si-doped: $n = 2.0 \times 10^{18} \text{ cm}^{-3}$). After organic cleaning, photolithography was performed, including the spin-coating of photoresist, prebaking at 90 °C, exposure to ultraviolet light, and development using a tetramethylammonium hydroxide (TMAH)-based solution. After lithography, a hydrochloric acid (HCl) treatment (HCl:H₂O = 1:3) was performed, followed by rinsing in deionized water. For comparison, a sample without HCl treatment after lithography was also prepared. Ag, Cu, Au, Ni, and Pt were deposited as electrode metals by electron-beam evaporation. The effect of the surface treatment on GaN was monitored by X-ray photoelectron spectroscopy (XPS) performed using a monochromatic Al-K α X-ray source (1486.6 eV) on a separate chip. The shift in the binding energy due to charging was corrected by setting the C-C bond component peak of C 1s core-level spectra to 285.0 eV.

HCl treatment has been reported to be effective for reducing the native oxide on the surface of GaN on sapphire.^{7,14,15} This surface treatment may also be effective for GaN on GaN. To investigate this, XPS measurement was carried out. The observed XPS O 1s core-level spectra are summarized in Fig. 1. The component around 531 eV is assigned to be O-Ga bond, whereas that around 533 eV to be O-H bond.¹⁶ At the as-grown surface, the intensity of the O-Ga bond is much higher than the O-H bond as shown in Fig. 1(a). The O-Ga bond is considered to have resulted from the surface oxide, whereas the O-H bond is considered to have resulted from the absorbed molecules, most probably from absorbed water. After photolithography, the intensity of the O-Ga bond decreased, as shown in Fig. 1(b), which is likely caused by the TMAH-based solution used for developing. Although complete removal of the surface oxide was not achieved, the subsequent HCl treatment reduced the O-Ga bond further as shown in Fig. 1(c). The thickness of the residual oxide layer was estimated to be less than 0.1 nm, which indicated that the oxide did not form a layer but was scattered on the surface.

The position of the surface Fermi level, E_{FS} , was measured by XPS at each step of the fabrication process using valence band maximum (VBM) spectra. The core-level spectra, even the surface-sensitive Ga 2p spectra, did not show any oxide component for every sample because the surface oxide layer was very thin. Thus, E_{FS} can be extracted from the VBM spectra by ignoring the oxide

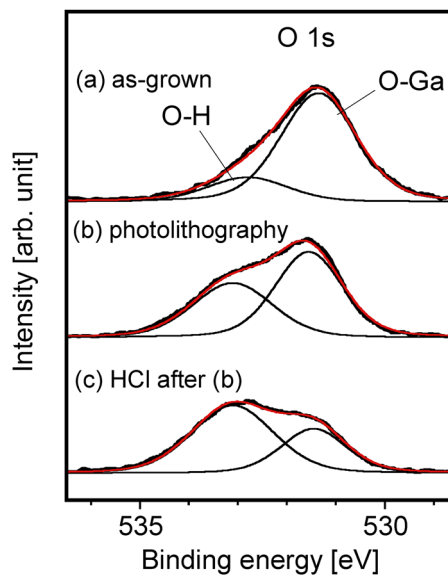


FIG. 1. XPS O 1s spectra for (a) as-grown surface, (b) surface after photolithography, and (c) surface treated by HCl after photolithography.

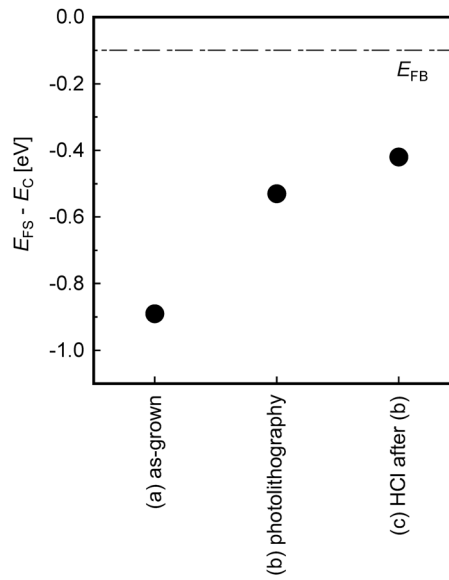


FIG. 2. E_{FS} measured by XPS for (a) as-grown surface, (b) surface after photolithography, and (c) surface treated by HCl after photolithography.

layer. The results are plotted in Fig. 2. Although E_{FS} was located at a deep point in the as-grown sample, a shift toward the conduction band edge, E_C , was observed after photolithography. After the subsequent HCl treatment, a further shift was observed. Consequently, E_{FS} shifted toward the position of the bulk Fermi level, E_{FB} . This result shows that surface band bending was reduced by the surface treatment, which indicated that the surface-localized charge was reduced. There is a possibility that the surface state charge was reduced.

This surface treatment, which reduced the surface oxide and band bending at the bare GaN surface, may affect the properties of the metal/GaN interface. To investigate this, I - V measurement was carried out at room temperature for fabricated SBDs. Examples of results are shown in Fig. 3 for (a) Ag and (b) Ni electrodes, where excellent rectifying characteristics can be seen. The current density seems to be changed roughly according to the metal work function, ϕ_M , because Ag has the lower ϕ_M than that of Ni. However, it can be seen that the impact of the surface treatment on the current density-voltage (J - V) characteristics is dependent on the electrode metal. The current density was increased by HCl treatment after photolithography for the SBD with Ag electrodes, while it was decreased by HCl treatment for the SBD with Ni electrodes. ϕ_B and the ideality factor, n , were obtained for each sample by fitting the forward-bias characteristics to the thermionic emission model

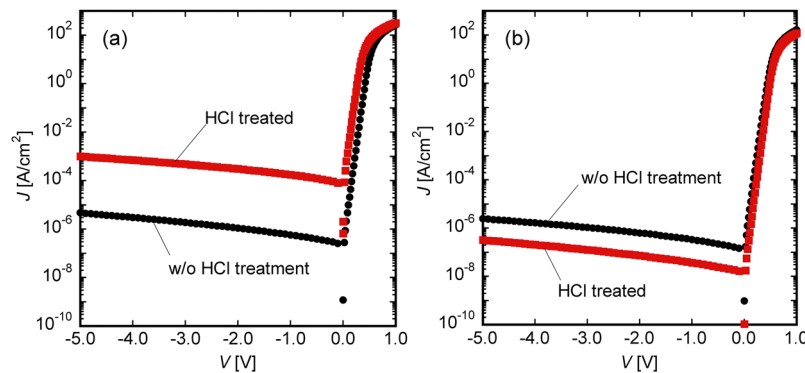


FIG. 3. Examples of I - V characteristics of Schottky contacts with and without HCl treatment after photolithography having (a) Ag and (b) Ni electrodes.

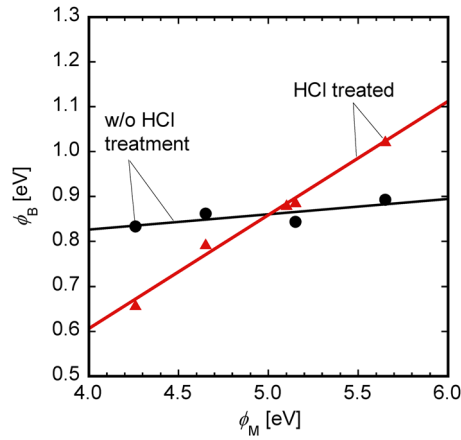


FIG. 4. Summary of ϕ_B - ϕ_M plots for the samples with and without HCl treatment after photolithography. Solid lines are fitting lines.

expressed by the equation

$$J = A^* T^2 \exp\left(-\frac{q\phi_{Bn}}{kT}\right) \exp\left(\frac{qV}{nkT} - 1\right), \quad (1)$$

where

$$\phi_B = \phi_{Bn} + \Delta\phi \quad (2)$$

and

$$\Delta\phi = \left(\frac{q^3 N_D |\psi_S|}{8\pi^2 \epsilon_S^3}\right)^{\frac{1}{4}}. \quad (3)$$

Here, A^* is the Richardson constant, T is the temperature, q is the elemental charge, ϕ_{Bn} is the Schottky barrier height lowered by the image force, k is the Boltzmann constant, $\Delta\phi$ is the lowering of the barrier height due to the image force, N_D is the doping density, ψ_S is the surface potential, and ϵ_S is the dielectric constant of GaN. The obtained ϕ_B and n are plotted as a function of ϕ_M in Figs. 4 and 5, respectively. In Fig. 4, it can be seen that ϕ_B changes with ϕ_M for the HCl-treated samples, whereas much less change in ϕ_B with ϕ_M is seen for the sample without HCl treatment. As shown in Fig. 5, excellent ideality factors were obtained for all the samples, which reflects the high quality of the GaN-on-GaN epitaxial layer. Nevertheless, the slope of each ϕ_B - ϕ_M plot is dependent on the surface treatment, which implies that the slope factor is related to the interface quality.

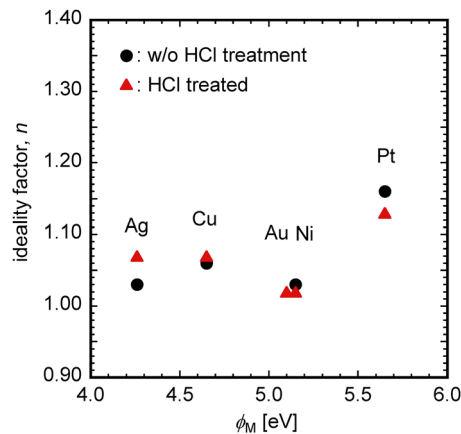


FIG. 5. Ideality factor versus ϕ_M for the samples with and without HCl treatment after photolithography.

As can be seen in Fig. 4, the ϕ_M -dependence of ϕ_B is affected by the surface treatment. The slope factor defined by

$$S = \frac{d\phi_B}{d\phi_M} \quad (4)$$

was found to be 0.034 for the sample without HCl treatment and 0.25 for the HCl-treated sample. According to the interfacial-layer model,¹⁷ the interface state density, D_{it} , can be estimated by

$$D_{it} = \frac{(1-S)\varepsilon_i}{S\delta q^2}, \quad (5)$$

where ε_i is the permittivity of the interlayer and δ is its thickness. Assuming ε_i to be equal to the permittivity of vacuum, ε_0 , and δ to be 0.3 nm in accordance with Ref. 17, D_{it} is calculated to be $5.2 \times 10^{14} \text{ cm}^{-2}\text{eV}^{-1}$ for the untreated sample and $5.5 \times 10^{13} \text{ cm}^{-2}\text{eV}^{-1}$ for the HCl-treated sample. However, considering the slight dispersion of the ideality factor for the same surface treatment as shown in Fig. 5, D_{it} may also be dependent on the condition of metal evaporation. The slightly high ideality factor for the Pt electrode might have resulted from the high melting temperature, which raised the temperature of the GaN surface during the metal evaporation. Nevertheless, as a first approximation, we can roughly comprehend the effect of the surface treatment on D_{it} derived from Eq. (5) as described above. It is highly likely that the reduction of the O-Ga bond in the XPS O 1s spectra led to a reduction of D_{it} and large S values. The detected surface oxide was formed in an uncontrolled manner. Since the oxide can be a source of interface disorder even after metallization, the origin of the Fermi level pinning at the metal/GaN interface seems to be the disorder at the interface. Therefore, the obtained results likely support the disorder-induced gap state model¹⁸ concerning the origin of the interface states and Fermi level pinning.

Based on the ϕ_B - ϕ_M plot in Fig. 4, the energy position of E_{CNL} and χ can be experimentally determined as follows. From the experimental data in Fig. 4, we can obtain the relation between ϕ_B and ϕ_M for each surface treatment as

$$\phi_B = S\phi_M + \phi_{M0}, \quad (6)$$

where ϕ_{M0} is the intercept with the ϕ_M axis. According to a textbook,¹⁷ the value of $(E_C - E_{CNL})$ is related to χ by

$$E_C - E_{CNL} = \frac{S\chi + \phi_{M0}}{1-S}. \quad (7)$$

Thus, we can determine the experimental values of $(E_C - E_{CNL})$ and χ by plotting Eq. (6) for two cases, with and without HCl treatment after photolithography, on the same $(E_C - E_{CNL}) - \chi$ coordinate space as shown in Fig. 6. From this plot, $(E_C - E_{CNL})$ is estimated to be 0.86 eV and χ is estimated to be 4.14 eV. The sum of $(E_C - E_{CNL})$ and χ is 5.00 eV, which indicates the energy difference between

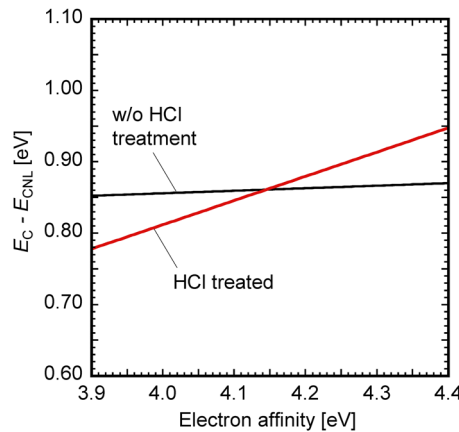
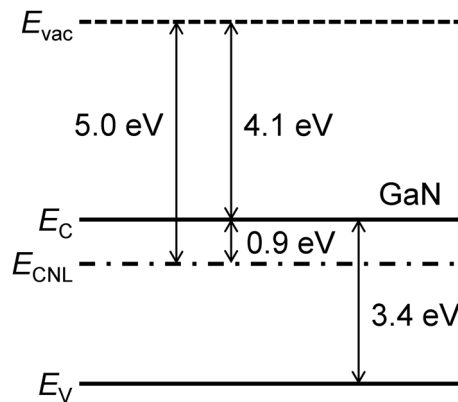


FIG. 6. Plots of $(E_C - E_{CNL})$ as a function of χ obtained from Eq. (7) using the measured S and ϕ_{M0} for the samples with and without HCl treatment after photolithography. We can obtain the measured values of $(E_C - E_{CNL})$ and χ at the cross point.

FIG. 7. Summary of measured $(E_C - E_{CNL})$, χ , and $(E_{vac} - E_{CNL})$.

E_{CNL} and the vacuum level, E_{vac} , and is in agreement with the calculated value.¹⁹ The extracted χ is in good agreement with the value measured in a previous photoemission study.²⁰ Furthermore, E_{FS} observed by XPS for the as-served GaN surface is located 0.89 eV from E_C as shown in Fig. 2. This value is in agreement with the extracted $(E_C - E_{CNL})$ within the experimental error, which may indicate that strong pinning of the surface Fermi level at the as-grown bare surface occurs at E_{CNL} . Considering the experimental error should be ± 0.1 eV for the measured energy positions, we should conclude that $(E_C - E_{CNL}) = 0.9$ eV, $\chi = 4.1$ eV and $(E_{vac} - E_{CNL}) = 5.0$ eV. The results are summarized in Fig. 7.

In summary, the impact of a surface treatment on surface oxide, band bending and the ϕ_B -dependence of ϕ_B was comprehensively investigated for a GaN-on-GaN epitaxial layer by combining XPS and electrical measurements. XPS measurement showed that the surface oxide and the band bending of the bare GaN surface were reduced after photolithography and that they were reduced further by the subsequent HCl treatment. On the other hand, electrical measurements of GaN-on-GaN SBDs indicated that the slope factor of the ϕ_B - ϕ_M plot was increased by HCl treatment after photolithography. It is highly likely that the reduction in interface disorder by the chemical treatment led to a reduction of D_{it} at the metal/GaN interface. On the basis of the measured dependence of the ϕ_B - ϕ_M plot on the surface treatment, $(E_C - E_{CNL})$ was measured to be 0.9 eV, χ was measured to be 4.1 eV, and $(E_{vac} - E_{CNL})$ was measured to be 5.0 eV.

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- ¹ T. Kachi, *Jpn. J. Appl. Phys.* **53**, 100210 (2014).
- ² H. Amano *et al.*, *J. Phys. D: Appl. Phys.* **51**, 163001 (2018).
- ³ E. V. Kalinina, N. I. Kuznetsov, V. A. Dmitriev, K. G. Irvine, and C. H. Carte, Jr., *J. Electron. Mater.* **25**, 831 (1996).
- ⁴ A. C. Schmitz, A. T. Ping, M. Asif Khan, Q. Chen, J. W. Yang, and I. Adesida, *J. Electron. Mater.* **27**, 255 (1998).
- ⁵ V. M. Bermudez, *J. Appl. Phys.* **86**, 1170 (1999).
- ⁶ H. Hasegawa, Y. Koyama, and T. Hashizume, *Jpn. J. Appl. Phys.* **38**, 2634 (1999).
- ⁷ J. K. Kim and J.-L. Lee, *J. Electrochemical Soc.* **150**, G209 (2003).
- ⁸ W. Mönch, *J. Appl. Phys.* **109**, 113724 (2011).
- ⁹ H. Imadate, T. Mishima, and K. Shiojima, *Jpn. J. Appl. Phys.* **57**, 04FG13 (2018).
- ¹⁰ M. Akazawa and T. Hasezaki, *Phys. Status Solidi B* **255**, 1700381 (2018).
- ¹¹ T. Teraji and S. Hara, *Phys. Rev. B* **70**, 035312 (2004).
- ¹² J. Suda, K. Yamaji, Y. Hayashi, T. Kimoto, K. Shimoyama, H. Namita, and S. Nagao, *Appl. Phys. Express* **3**, 101003 (2010).
- ¹³ T. Maeda, M. Okada, M. Ueno, Y. Yamamoto, T. Kimoto, M. Horita, and J. Suda, *Appl. Phys. Express* **10**, 051002 (2017).
- ¹⁴ I. Waki, H. Fujioka, K. Ono, M. Oshima, H. Miki, and A. Fukizawa, *Jpn. J. Appl. Phys.* **39**, 4451 (2000).
- ¹⁵ I. Shalish, Y. Shapira, L. Burstein, and J. Salzman, *J. Appl. Phys.* **89**, 390 (2001).
- ¹⁶ Y.-J. Lin and C.-T. Lee, *Appl. Phys. Lett.* **77**, 3986 (2000).
- ¹⁷ S. M. Sze and K. K. Ng, *Physics of Semiconductor Devices* (Wiley, Hoboken, NJ, 2007) 3rd ed., Chap. 3.
- ¹⁸ H. Hasegawa and H. Ohno, *J. Vac. Sci. Technol. B* **4**, 1130 (1986).
- ¹⁹ C. G. Van de Walle and J. Neugebauer, *Nature* **423**, 626 (2003).
- ²⁰ J. I. Pankove and H. Schade, *Appl. Phys. Lett.* **25**, 53 (1974).