Supporting Information

Polarity Control of an All-Sputtered Epitaxial GaN/AlN/Al Film on a Si(111) Substrate by Intermediate Oxidization

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[Effect of 2-cycle deposition: GaN/AlN/GaN/AlN/Si stack structure]

Multilayer and thicker films are known to reduce defects and improve crystallinity (Ponce et al., Appl. Phys. Lett. 65, 2303, 1994). Therefore, we prepared samples in which the GaN and AlN layers were deposited twice. This approach enabled clear observation of the improvement in crystallinity and the difference in polarity.

Figure S1. (a) Schematic of the structure of the sample. The first AlN layer for some samples was oxidized. (b) 2D-XRD, (c) AFM, and (d) TOFLAS pole-figure images for GaN/AlN/GaN on As- (left images), 10-Ox- (center images), and 3-Ox-AlN (right images).
In the Ref. 41, the polarity dependence of the shape of valence band of polar materials used results of hard x-ray photoelectron spectroscopy ($h \nu = 5.95$ kV) on GaN crystals. Owning to the difference in the photoionization cross section, the shapes of valance band is different from our results. To better compare the shape changes, XPS measurements were also performed on free-standing GaN substrates (Shinyo co. ltd, : dislocation density $< 5 \times 10^5$, RMS $<0.2$ nm), as shown in Fig. S2. The peaks, especially on the low-energy side, are sensitive to the change in measurement angle to the plane in the case of Ga surfaces.

Figure S2. Valence-band spectra for $+c$, $-c$, and m-plane free-standing GaN substrate obtained by XPS at various take off angles (TOAs). The inset showed the measurements setup. The TOA=54.7° for $-c$-$\mathrm{GaN}$ corresponds to angle 35.3° for $+c$-$\mathrm{GaN}$ relative to the normal of $+c$-$\mathrm{GaN}$ in the direction of the C axis.
[Characteristic of polar AlN films on c-sapphire substrates]

We found that the +c-AlN film could be obtained by changing the electric floating condition between the sputtering cathode and the substrate. Figure S3 shows valence-band spectra and TOFLAS images for +c and mixed AlN films. Compared with the GaN film, the +c-AlN film shows a smaller difference in the ratio between P1 and P2.

Figure S3. (a) Valence-band spectra for +c and −c-/mixed polar AlN films on a c-sapphire substrate. TOFLAS pole-figure images for (b) +c-AlN and (c) −c-/mixed polar AlN films. Bottom images show the simulated TOFLAS pole-figure images for the (d) (001) and (e) (00−1) planes of wurtzite-structured AlN.
[+c-GaN growth of thick AlN layer]

To identify the effects of the thickness of the initial AlN film, thin GaN and AlN films were deposited onto thick AlN films after the thick AlN films were air-exposed. Figure S4 shows valence-band spectra for the 7 nm GaN film on an oxidized 46 nm AlN film, where the AlN film was oxidized after reaching a thickness of 46 nm (46-Ox-AlN), and for the 3 nm AlN film on a 43 nm-thick AlN film oxidized after reaching a thickness of 43 nm (43-Ox-AlN). The spectra of the GaN film showed an increase in the intensity of the P1 peak, suggesting the formation of +c-GaN. By contrast, the AlN film was not a +c structure.

Figure S4. Valence-band spectra for 7 nm-thick GaN and 3 nm-thick AlN films on 46- and 43-Ox-AlN films.
Oxynitridation of Si substrates

The oxidization of the Si substrate was verified. After the substrate was cleaned, the naturally oxidized surface layer was removed. For the 3-Ox and 10-Ox films, the oxidization of Si was confirmed after air exposure. Both samples showed SiO$_x$N$_y$ bonding states, indicating that the Si surface was nitrided during deposition of the film. The Si substrate could not be detected when the film thickness was greater than 13 nm; however, this result suggests that the Si interface side contained more oxygen.

Figure S5. Si 2$p$ spectra for the Si (111) substrate after the HF cleaning process, 3-Ox-AlN, 10-Ox-AlN, and a 13 nm-thick AlN film on 10-Ox-AlN.