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Atomic-Scale Structure of Etch-Pit Sidewalls in Wet-Etched GaN Films Revealed by Scanning Transmission Electron Microscopy

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Abstract

Defect-selective wet etching is widely used to reveal crystallographic defects in gallium nitride (GaN) through the formation of etch pits. Although the surface morphology and size distribution of GaN etch pits have been extensively studied, the atomic-scale structure of their sidewalls remains insufficiently understood. In this study, etch pits were formed in a 100-nm-thick GaN epitaxial film using a molten KOH–NaOH eutectic mixture and characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Integrated differential phase-contrast scanning TEM (iDPC-STEM) was employed to resolve the relative positions of Ga and N atoms and determine the crystallographic polarity of the GaN film. SEM observations revealed hexagonal etch pits with a broad size distribution and cross-sectional TEM analysis showed that larger pits exhibited greater etching depths. The etched sidewalls consisted of atomic-scale steps and terraces rather than atomically flat facets. At several step and terrace segments, the outermost resolved atomic columns were identified as Ga, indicating local Ga termination of the wet-etched sidewalls. These results extend the characterization of GaN etch pits from morphology to polarity-resolved atomic structure.

Introduction

Defect-selective etching is an established technique for evaluating crystalline defects in semiconductor materials by exploiting differences in local chemical reactivity (Weyher et al. 2000; Zhuang and Edgar 2005). Among the available etching techniques, wet chemical etching is particularly useful for revealing crystallographic defects because dissolution occurs preferentially at structurally disturbed regions (Zhuang and Edgar 2005). Unlike plasma-based dry etching, which may introduce ion-induced damage, wet etching proceeds through chemical reactions between the etchant and the exposed materials. The resulting surface morphology depends on factors such as crystallographic orientation, surface polarity, and the local defect structure (Weyher et al. 2000; Zhuang and Edgar 2005). Gallium nitride (GaN) is a wurtzite semiconductor whose crystallographic polarity strongly influences its surface properties and chemical reactivity. In particular, the Ga-polar (0001) and N-polar $\left(000\bar{1}\right)$ surfaces exhibit different atomic configurations and etching characteristics (Weyher et al. 2000; Zhuang and Edgar 2005). Alkaline solutions, including KOH- and NaOH-based etchants, have therefore been extensively used for defect-selective etching of GaN (Weyher et al. 2000; Kamler et al. 2002; Zhuang and Edgar 2005). Local lattice distortions associated with dislocations can modify the reactivity of neighboring atomic sites, promoting preferential dissolution and the formation of etch pits (Weyher et al. 2007). Consequently, the morphology and distribution of etch pits provide useful information for assessing crystalline defects in GaN (Zhuang and Edgar 2005; Weyher et al. 2007). Scanning electron microscopy (SEM) and atomic force microscopy (AFM) are commonly used to examine the surface morphology, dimensions, and spatial distribution of etch pits, and to estimate etch pit density (Zhuang and Edgar 2005; Weyher et al. 2007). However, surface morphological observations provide limited information about the atomic configurations of the newly formed surfaces. Transmission electron microscopy (TEM) and scanning TEM (STEM) can resolve local crystal structures and atomic arrangements at etched boundaries. Among

STEM techniques, integrated differential phase-contrast STEM (iDPC-STEM) is particularly advantageous because it visualizes light and heavy atomic columns simultaneously (Lazić et al. 2016). Previous studies on defect-selective etching of GaN have primarily focused on the relationship between etch-pit morphology and dislocation characteristics in bulk crystals or relatively thick epitaxial layers (Weyher et al. 2000; Kamler et al. 2002; Weyher et al. 2007). However, the atomic structure of the etch-pit sidewalls, including their step configuration and the identity of the outermost atomic layer, has rarely been examined directly. This information is needed to link the etch-pit geometry to the polarity-dependent etching chemistry of GaN, and obtaining it requires a technique that resolves both Ga and N columns at the etched surface.

In this study, defect-selective wet etching was performed on a 100-nm-thick GaN epitaxial film using a molten KOH–NaOH eutectic mixture. The polarity of the as-grown film was first determined using high-angle annular dark-field STEM (HAADF-STEM) and iDPC-STEM. The surface morphology, size distribution, and cross-sectional geometry of the resulting etch pits were subsequently examined by SEM and cross-sectional TEM. Finally, atomic-resolution iDPC-STEM was used to determine the step structure of the etched sidewalls and to identify the outermost resolved atomic columns.

Results and discussion

The crystallographic structure and polarity of the GaN epitaxial film were first examined to provide a reference for interpreting the etched surfaces. Figure 1a schematically illustrates the wurtzite crystal structure of GaN, including the a-, m-, and c-planes. Owing to the non-centrosymmetric arrangement of Ga and N atoms along the c-axis, wurtzite GaN exhibits two distinct polar orientations, referred to as Ga-polar and N-polar structures (Fig. 1b; Zhuang and Edgar 2005). The polarity of GaN plays an important role in determining its surface properties and chemical etching behavior (Weyher et al. 2000; Zhuang and Edgar 2005). Figure 1c presents a cross-sectional high-angle annular dark-field STEM (HAADF-STEM) image and the corresponding energy-dispersive X-ray spectroscopy (EDS) elemental maps of the GaN epitaxial film. The GaN layer, approximately 100 nm thick, was grown on a SiC substrate with an intermediate AlN buffer layer approximately 10 nm thick. The elemental distributions of Ga, N, Al, Si, and C are consistent with this layer sequence. Atomic-resolution HAADF-STEM and iDPC-STEM images acquired from the selected region are shown in Figs. 1d and 1e, respectively. In the HAADF-STEM image, Ga atomic columns exhibit relatively high intensity owing to the strong dependence of electron scattering intensity on atomic number, whereas the lighter N atomic columns are not clearly resolved (Pennycook and Jesson 1991). However, iDPC-STEM provides enhanced sensitivity to light elements, enabling the simultaneous visualization of Ga and N atomic columns (Lazić et al. 2016). In the iDPC-STEM image, each N column lies below its neighboring Ga column within the projected Ga–N dumbbell, which matches the $\left[11\bar{2}0\right]$ projection of Ga-polar wurtzite GaN. The epitaxial film is therefore Ga-polar, with the [0001] direction pointing toward the film surface. This identification provides a crystallographic reference for examining the atomic configurations of the etched GaN surfaces.

Defect-selective wet etching was subsequently performed using a molten KOH–NaOH eutectic mixture to investigate the formation and morphological characteristics of GaN etch pits. Preliminary experiments indicated that increasing the etching temperature or extending the etching duration promoted pit enlargement and overlap between adjacent etch pits. Accordingly, an etching condition of 290°C for 10 min was selected to preserve individual etch-pit morphologies for subsequent structural characterization. Figure 2a shows the FE-SEM image of the GaN surface after etching under this condition. Hexagonal etch pits with various lateral dimensions were observed across the surface. The diameter histogram (Fig. 2e) shows a trimodal distribution, and the etch pits were accordingly classified into three groups: small etch pits (S-EPs, < 120 nm), medium etch pits (M-EPs, 120–220 nm), and large etch pits (L-EPs, > 220 nm). S-EPs dominated the population, whereas M-EPs and L-EPs were rare. Similar size-dependent groups of etch pits in GaN have been associated with threading dislocations of different types (Weyher et al. 2007), suggesting that the three groups observed here may also originate from different dislocation types; this correlation was not examined in the present work.

The variation in etch-pit size indicates that the wet etching process produced localized surface features with different lateral dimensions. To further investigate the relationship between lateral pit dimensions and etching depth, representative etch pits from each size group were examined by cross-sectional TEM. Figures 2b–d shows the cross-sectional morphologies of S-EPs, M-EPs, and L-EPs, respectively. The measured depths were approximately 14.5 nm for S-EPs, 25.5 nm for M-EPs, and 77 nm for L-EPs, indicating that the larger pits were also deeper. These observations demonstrate that KOH–NaOH wet chemical etching produces morphological changes in both the lateral and depth directions. Because S-EPs accounted for the largest proportion of the observed etch-pit population, they were selected for subsequent atomic-resolution structural analysis.

Because iDPC-STEM resolves both Ga and N atomic columns (Fig. 1e), it was employed to investigate the atomic configurations of the etched GaN sidewalls along the $\left[11\bar{2}0\right]$ zone axis. Figure 3 presents cross-sectional iDPC-STEM images of the etched sidewalls and magnified images of selected regions. As shown in Figs. 3a and 3d, the etched boundaries exhibit locally irregular profiles at the atomic scale. The magnified images in Figs. 3b, 3c, 3e, and 3f reveal that the sidewalls consist of a series of atomic-scale steps and terraces rather than atomically flat surfaces, so the local surface structure varies along the etched boundaries. The atomic arrangements of Ga and N at the etched sidewalls were further examined to identify the outermost atomic configurations. At selected step and terrace regions, the outermost resolved atomic columns were identified as Ga, and similar configurations were observed at different locations along the etched sidewalls. On the c-plane terraces (Figs. 3e and 3f), this Ga-outermost configuration is consistent with the Ga polarity of the film, because terminating a Ga-polar (0001) surface at the Ga layer breaks only one Ga–N bond per surface atom. The stepped structures suggest that the local atomic coordination and the relative chemical stability of exposed atomic sites vary along the sidewalls. However, iDPC-STEM observations do not directly establish the sequence of atomic removal or the kinetics of step formation. The observations indicate local Ga termination at selected boundary segments rather than uniform Ga termination of the entire etched surface.

Nevertheless, these findings demonstrate that iDPC-STEM enables direct examination of both Ga and N atomic arrangements at etched boundaries, extending the characterization of GaN etch pits from their morphology and dimensions to their local atomic structures.

Conclusions

In this study, the morphology and atomic-scale structure of etch pits formed in a Ga-polar GaN epitaxial film by KOH–NaOH defect-selective wet etching were investigated using electron microscopy. iDPC-STEM resolved both Ga and N atomic columns, which are not simultaneously resolved by HAADF-STEM, and identified the Ga polarity of the 100-nm-thick GaN film grown on SiC with a 10-nm-thick AlN buffer layer. Wet etching at 290°C for 10 min produced hexagonal etch pits with a trimodal size distribution dominated by small pits (S-EPs), and representative small, medium, and large pits showed depths of approximately 14.5, 25.5, and 77 nm, respectively. Atomic-resolution iDPC-STEM further revealed that the etched GaN sidewalls consisted of atomic-scale steps and terraces, and that the outermost resolved atomic columns at several of these segments were Ga, indicating local Ga termination. These results demonstrate that iDPC-STEM can directly determine the atomic structure of wet-etched GaN surfaces and provide a structural basis for understanding the polarity-dependent mechanism of defect-selective etching.

Experimental section

GaN thin-film growth

GaN epitaxial films were grown on 4-inch SiC substrates using molecular beam epitaxy (MBE). A 10 nm thick AlN buffer layer was first deposited on the SiC substrate, followed by the growth of a 100 nm thick GaN epitaxial layer. Nitrogen was supplied using a radio-frequency (RF) plasma source and an ammonia cracker. High-purity NH_3 (99.99995%) was supplied through a getter purification system, and GaN growth was performed under nitrogen-rich conditions.

Defect-selective wet etching

Defect-selective wet etching of GaN films was performed using a molten KOH–NaOH eutectic mixture with a molar ratio of 48.5:51.5 (Kamler et al. 2002; Zhuang and Edgar 2005). The KOH and NaOH mixture was placed in a nickel crucible and heated to 410°C for 30 min to obtain a homogeneous molten etchant. The temperature was subsequently reduced to 290°C for wet etching. Prior to etching, the specimens were sequentially cleaned in acetone, isopropyl alcohol (IPA), and deionized (DI) water for 3–5 min each, followed by drying with nitrogen gas. The specimens were then immersed in a 1:1 HCl–DI water solution for 30 s. Wet etching was performed at 290°C for 10, 20, and 30 min. Specimens etched for 10 min were selected for detailed electron microscopy characterization. After etching, the specimens were briefly cooled under nitrogen gas and immersed in DI water maintained at approximately 50°C for 5 min. The

specimens were subsequently rinsed two to three times with DI water, immersed in a 5% acetic acid solution for 1 min, and rinsed again with DI water. Finally, the specimens were ultrasonically cleaned in IPA for 5 min and dried with nitrogen gas.

Surface morphology characterization

The surface morphologies of the etched GaN films were examined using field-emission scanning electron microscopy (FE-SEM, JSM-7610F, JEOL). Prior to SEM observation, the specimens were dried on a hot plate at 120°C for 10 min and coated with Pt using a sputter coater (JEC-3000FC, JEOL) operated at a current of 30 mA and a chamber pressure of 1.9 Pa for 30 s. Silver paste was applied to provide electrical grounding during SEM observation. SEM imaging was performed at an accelerating voltage of 10 kV, a working distance of 8 mm, and a probe-current setting of 6. The diameters of the hexagonal etch pits were measured between opposite vertices and classified into three groups: small etch pits (S-EPs, 0–120 nm), medium etch pits (M-EPs, 120–220 nm), and large etch pits (L-EPs, > 220 nm).

TEM specimen preparation

Cross-sectional TEM specimens were prepared using a focused ion beam (FIB) system (Helios G4, Thermo Fisher Scientific). Protective carbon and Pt layers were deposited over the regions of interest prior to ion milling. The selected regions were subsequently milled using a Ga^+ ion beam, followed by specimen extraction using the lift-out technique. Final thinning was performed to obtain electron-transparent lamellae with thicknesses below approximately 50 nm.

Atomic-resolution STEM characterization

Cross-sectional microstructural and atomic-resolution analyses were performed using a spherical aberration-corrected scanning transmission electron microscope (Themis Z, Thermo Fisher Scientific) operated at an accelerating voltage of 300 kV. High-angle annular dark-field STEM (HAADF-STEM) and integrated differential phase-contrast STEM (iDPC-STEM) imaging were conducted to characterize the crystal structure, polarity, and atomic arrangements of the as-grown and etched GaN films. Energy-dispersive X-ray spectroscopy (EDS) elemental mapping was performed to examine the elemental distributions across the GaN/AlN/SiC multilayer structure.

Declarations

Competing interests

The authors declare that they have no competing interests.

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Author Contributions

J.M.P. performed defect-selective wet etching of GaN thin films, conducted SEM characterization, analyzed the HRTEM and iDPC-STEM data, and wrote the original draft of the manuscript. E.H.K. prepared cross-sectional TEM specimens using focused ion beam (FIB) milling. C.S.K. reviewed the manuscript and provided guidance on the experimental procedures and data interpretation. H.Y.J. conceived the research idea and supervised the overall project.

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Data availability

The datasets generated during the current study are available from the corresponding author on reasonable request.

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Figures

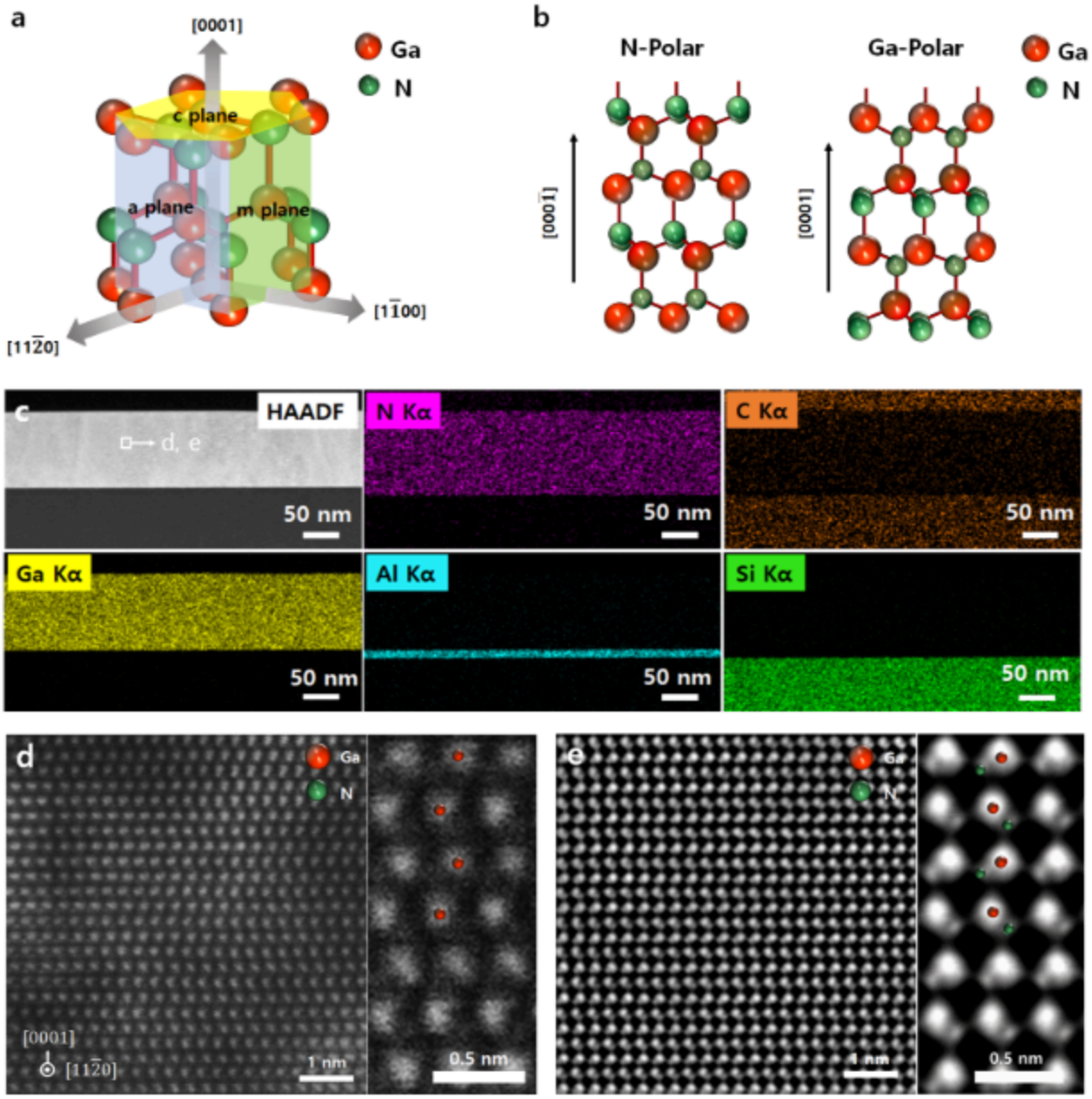


Figure 1

Crystal structure, polarity, and atomic-scale characterization of GaN thin films. a, Schematic representation of the wurtzite GaN crystal structure, illustrating the crystallographic a-, m-, and c-planes and their corresponding orientations. **b,** Schematic atomic configurations of N-polar and Ga-polar GaN, illustrating the differences in the stacking sequences of Ga and N atoms along the [0001] crystallographic direction. **c,**Cross-sectional high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and corresponding energy-dispersive X-ray spectroscopy (EDS) elemental maps of N, C, Ga, Al, and Si, showing a 100-nm-thick GaN layer grown on a SiC substrate with a 10-nm-thick AlN buffer layer. **d,** Atomic-resolution HAADF-STEM image obtained from the white-boxed region in (c), in which only the Ga columns are resolved. **e,**Atomic-resolution integrated differential phase-contrast STEM (iDPC-STEM) image obtained from the same region, clearly resolving both Ga and

N atoms and confirming the Ga-polar structure of the GaN thin film. Ga and N atomic positions are indicated in red and green, respectively, in the schematic illustrations and atomic-resolution images.

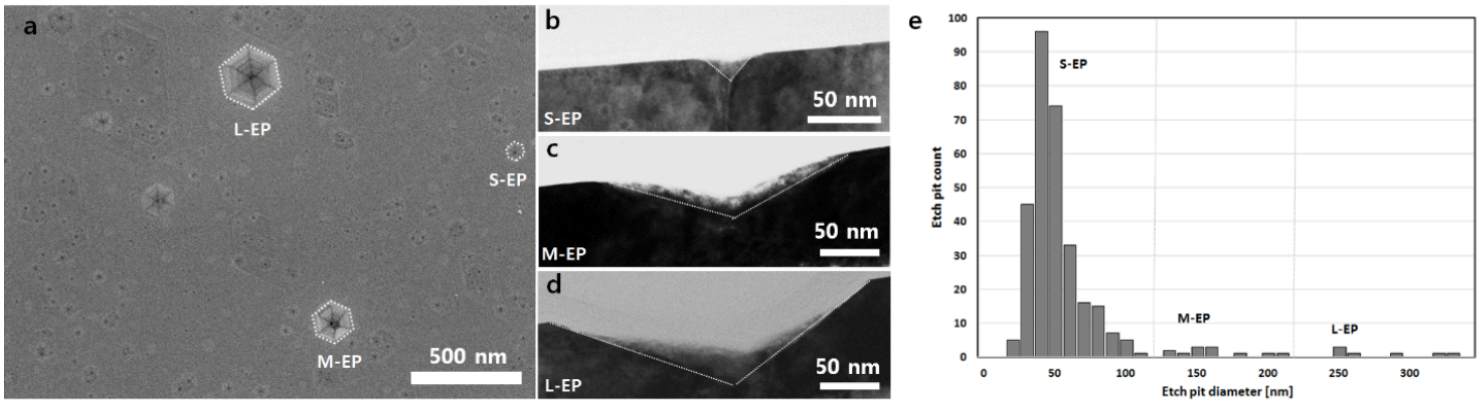


Figure 2

Surface and cross-sectional morphologies and size distribution of etch pits formed in GaN by defect-selective wet etching. a, Scanning electron microscopy (SEM) image showing the surface morphology of etched GaN with small (S-EP), medium (M-EP), and large (L-EP) etch pits. **b–d,** Cross-sectional bright-field transmission electron microscopy (BF-TEM) images of (b) S-EP, (c) M-EP, and (d) L-EP, showing their characteristic morphologies. **e,** Histogram of etch pit diameters measured from SEM images, showing the size distribution of S-EP, M-EP, and L-EP.

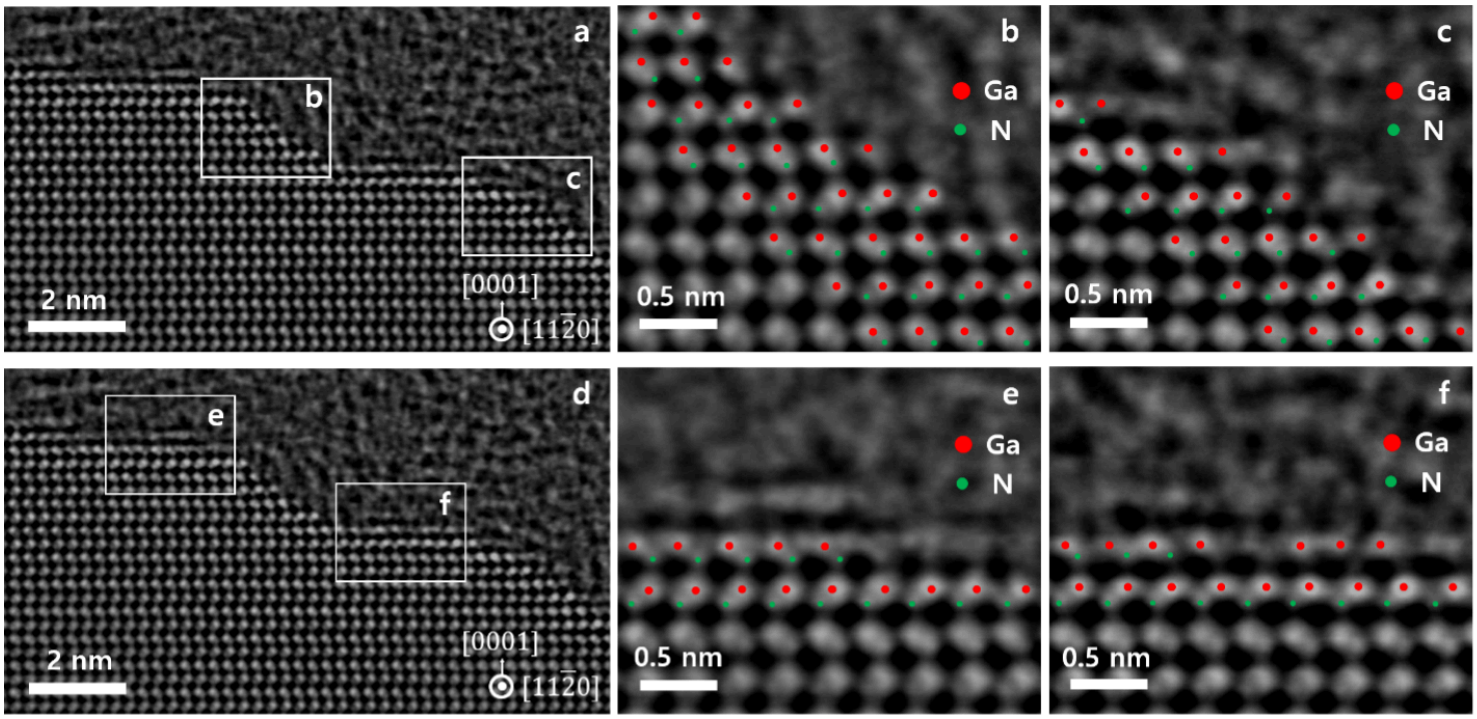


Figure 3

Atomic-scale structural characterization of etched GaN sidewall using iDPC-STEM. a, d,Cross-sectional atomic-resolution iDPC-STEM images of etched GaN sidewalls viewed along the [11^{-}2 0] zone axis. **b, c,** Magnified atomic-resolution images of the white-boxed regions in (a), showing the atomic arrangements of Ga and N at different positions along the etched sidewall. **e, f,** Magnified atomic-resolution images of the white-boxed regions in (d), showing the atomic arrangements of Ga and N at different positions along the etched sidewall. Ga and N atomic positions are indicated by red and green dots, respectively.