

Nitrogen-Vacancy-Related States in Ga- and N-Polar GaN by XPS and First-Principles Calculations

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N-polar InGaN/GaN heterostructures are attractive for optoelectronic and energy-conversion devices because the reversed polarization field can facilitate the separation and extraction of photogenerated carriers[1]. However, point defects may limit their optical and electronic properties through nonradiative recombination[2]. The photothermal deflection spectroscopy signal intensity in the bandgap was higher for N-polar GaN than for Ga-polar GaN, suggesting a larger contribution from defect-related states. In this context, experimental characterization of nitrogen vacancies (V_N) remains a crucial issue. We investigated the valence-band states of Ga- and N-polar GaN by X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) calculations. The measured spectra were compared with calculated densities of states (DOS) for pristine GaN and GaN containing V_N . The pristine GaN DOS reproduced the Ga-polar spectrum well, whereas the N-polar sample showed a tail-like feature near the valence-band maximum that was not reproduced by the pristine calculation. Figure 1 shows the discrepancy between the experimental spectrum and the pristine-GaN DOS. Calculations including V_N produced additional states in the corresponding energy region. To evaluate V_N , the difference DOS, $DOS_{V_N} - DOS_{pristine}$, was compared with the residual XPS spectrum obtained by subtracting the scaled defect-free DFT spectrum from the experimental XPS spectrum. Figure 2 shows the broadened difference DOS scaled to reproduce the experimental residual spectrum. From the scaling factor, the near-surface V_N concentration in the N-polar sample was estimated to be approximately $6 \times 10^{19} \text{ cm}^{-3}$. These results suggest that valence-band XPS combined with first-principles calculations can provide an approach for evaluating V_N -related electronic states in GaN.

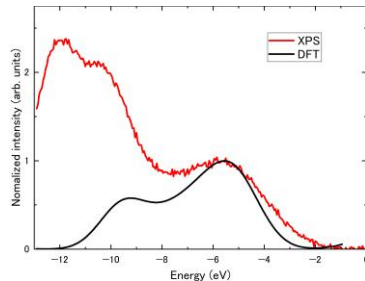


Figure 1 Comparison of the experimental valence-band XPS spectrum of N-polar GaN with the Gaussian-broadened DOS calculated for pristine GaN.

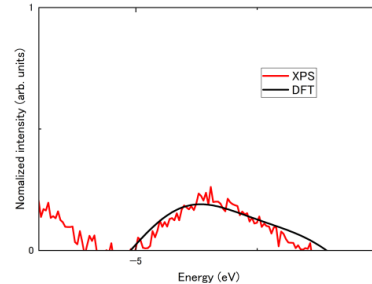


Figure 2 Comparison of the residual XPS spectrum with the Gaussian-broadened and scaled V_N -induced difference DOS for N-polar GaN.

[1] J.-Y. Chang *et al.* J. Appl. Phys. **112**, 033109 (2012). [2] S. F. Chichibu *et al.* Nat. Mater. **5**, 810–816 (2006).

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Supplementary Pages (Optional)

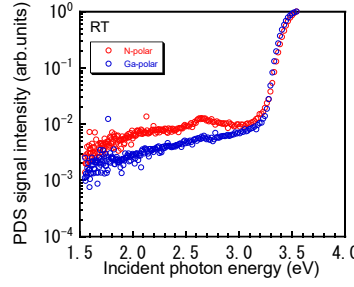


Figure S1 Room-temperature PDS spectra of Ga- and N-polar GaN.

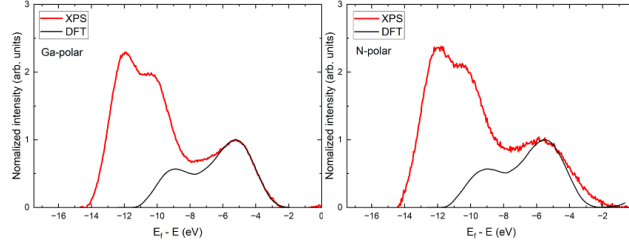


Figure S2 Comparison of the experimental XPS valence-band spectra with the broadened DFT density of states for Ga-polar GaN and N-polar GaN.

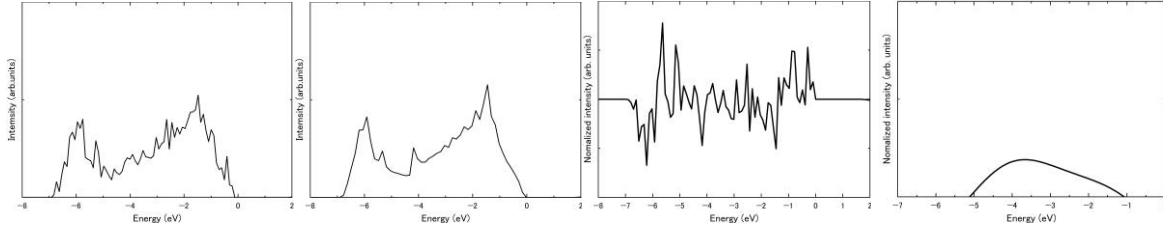


Figure S3 Calculated density of states used for the nitrogen-vacancy analysis. From left to right: DOS of GaN containing one nitrogen vacancy, DOS of defect-free GaN, the difference DOS defined as $DOS_{V_N} - DOS_{pristine}$, and the broadened difference DOS used for comparison with the experimental residual spectrum.

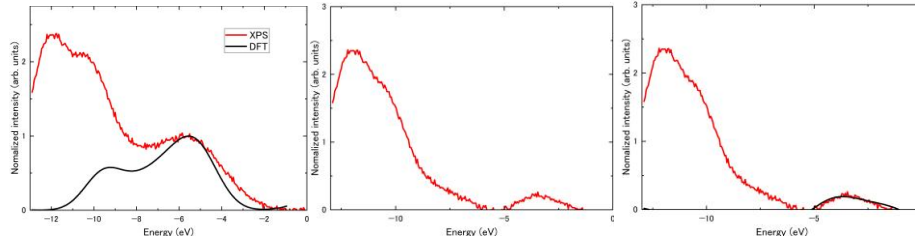


Figure S4 Extraction and comparison of the residual electronic-state contribution in N-polar GaN. Left: comparison of the experimental XPS valence-band spectrum with the defect-free DFT spectrum. Center: residual spectrum obtained by subtracting the scaled defect-free DFT spectrum from the experimental XPS spectrum. Right: comparison of the experimental residual spectrum with the broadened V_N -induced difference DOS scaled by a factor of 0.067.

The V_N -induced difference DOS was scaled by a factor of 0.067 to reproduce the residual XPS spectrum. Since the DFT model contains one V_N per 54 N sites, the corresponding vacancy fraction was estimated as $0.067 \times \left(\frac{1}{54}\right)$. Using an N-site density of $4.45 \times 10^{22} \text{ cm}^{-3}$, the near-surface V_N concentration was estimated to be approximately $6 \times 10^{19} \text{ cm}^{-3}$.