SUPPLEMENTARY MATERIAL

Fig. S1 shows the initial and optimized structures of F-terminated $3 \times 3 \times 3$ GaN supercell models with one to four F atoms placed around the N vacancy. Models are labeled according to the number of F atoms placed around the N vacancy (F*n*). The F2 and F3 models have two types of patterns that are distinguished by their symmetry: p1 and p2. The total energies of the F-terminated models, defects (V_N), and ideal GaN model (which was used as a reference) were calculated with considering various charged states of GaN models.

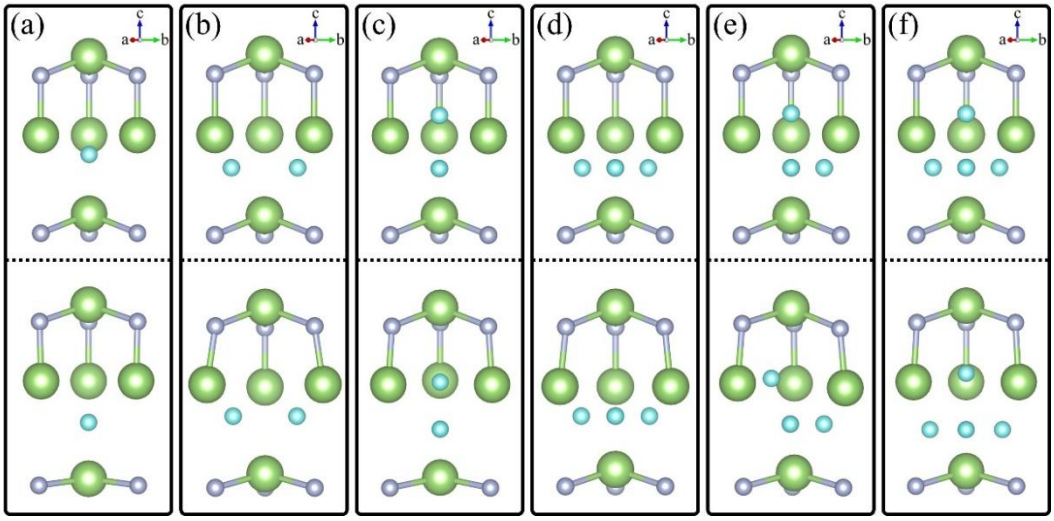

Fig. S1. Enlarged views of F-terminated models with one to four F atoms placed around the N vacancy: (a) F1, (b) F2p1, (c) F2p2, (d) F3p1, (e) F3p2, and (f) F4. The top row shows the initial structures, and the bottom row shows the optimized structures.

The formation energy ΔE_{form} is expressed as

$$\Delta E_{\mathrm{form}} = E_{\mathrm{term}} - E_{\mathrm{ideal}} + n_{\mathrm{N}}\mu_{\mathrm{N}} - n_{\mathrm{F}}\mu_{\mathrm{F}} + q(E_{\mathrm{F}} + \varepsilon_{\mathrm{V}}) + \Delta v \quad (1)$$

where E_{term} and E_{ideal} are the total energies of a F-terminated model and of the ideal GaN model, respectively. n_{N} is the number of missing N atoms, and $n_{\mathrm{N}} = 1$ in this study. μ_{N} is the chemical potential of N and calculated using the total energy difference between a Ga–N atom pair $(\mu_{\mathrm{GaN}}/2)$ and a Ga atom (μ_{Ga}) in the GaN crystal. n_{F} is the number of adsorbed F atoms, and μ_{F} is the chemical potential of a F atom in the GaN crystal. μ_{F} is given by the sum of the chemical potential of F in the molecular state F_2 ($\mu^{\mathrm{F_2}}_{\mathrm{molecule}}/2$) and the chemical potential parameter $\Delta\mu_{\mathrm{F}}$:

$$\mu^{\mathrm{F}}_{\mathrm{crystal}} = \frac{\mu^{\mathrm{F_2}}_{\mathrm{molecule}}}{2} + \Delta\mu_{\mathrm{F}}. \quad (2)$$

$\Delta\mu_{\mathrm{F}}$ is a correction term that is defined as the difference between $\mu^{\mathrm{F}}_{\mathrm{crystal}}$ and $\mu^{\mathrm{F_2}}_{\mathrm{molecule}}/2$:

$$\Delta\mu_{\mathrm{F}} = \mu^{\mathrm{F}}_{\mathrm{crystal}} - \frac{\mu^{\mathrm{F_2}}_{\mathrm{molecule}}}{2} \leq 0. \tag{3}$$

q denotes the charged states. Electrons added or removed from the supercell are expressed by the Fermi level (E_F) of the semiconductor host, which is in reference to the valence band maximum (VBM) (εv). In this study, any potential correction is not employed; therefore, $\Delta v = 0$. Based on Eqs. (2) and (3), Eq. (1) reduces to Eq. (4). Here, the case in which F is incorporated into the solid phase corresponds to $\mu^{\mathrm{F}}_{\mathrm{crystal}} - \mu^{\mathrm{F_2}}_{\mathrm{molecule}}/2 \leq 0$. $\Delta\mu_{\mathrm{F}} \to 0$ corresponds to an F-rich environment. In this environment, $\mu^{\mathrm{F}}_{\mathrm{crystal}}$ and $\mu^{\mathrm{F_2}}_{\mathrm{molecule}}/2$ are identical.

$$\Delta E_{\mathrm{form}} = E_{\mathrm{term}} - E_{\mathrm{ideal}} + n_{\mathrm{N}}\left(\frac{1}{2}\mu_{\mathrm{GaN}} - \mu_{\mathrm{Ga}}\right) - n_{\mathrm{F}}\frac{1}{2}\mu^{\mathrm{F_2}}_{\mathrm{molecule}} - n_{\mathrm{F}}\Delta\mu_{\mathrm{F}} + q(E_{\mathrm{F}} + \varepsilon_{\mathrm{V}}) \tag{4}$$

Fig. S2 shows the formation energy as a function of E_F for various $\Delta\mu_{\mathrm{F}}$. The black lines indicate the formation energies of V_N with various charged states. The results show good agreement with Ref. 32 at the GGA-PBE level. In an F-rich limit environment ($\Delta\mu_{\mathrm{F}} = 0$), F4(0) and F4(−) are thermodynamically stable. Eventually, the F4(−1), F3p2(0), and F2(+) configurations emerge as stable phases depending on the fluorine concentration. These results are reasonable because they satisfy the electron counting rule except for F4(0). Consequently, the F3p2 structure, which is the focus of this paper, is considered a realistic configuration that can exist stably. In addition, the tendency of fluorine atoms to be incorporated near the defect is revealed.

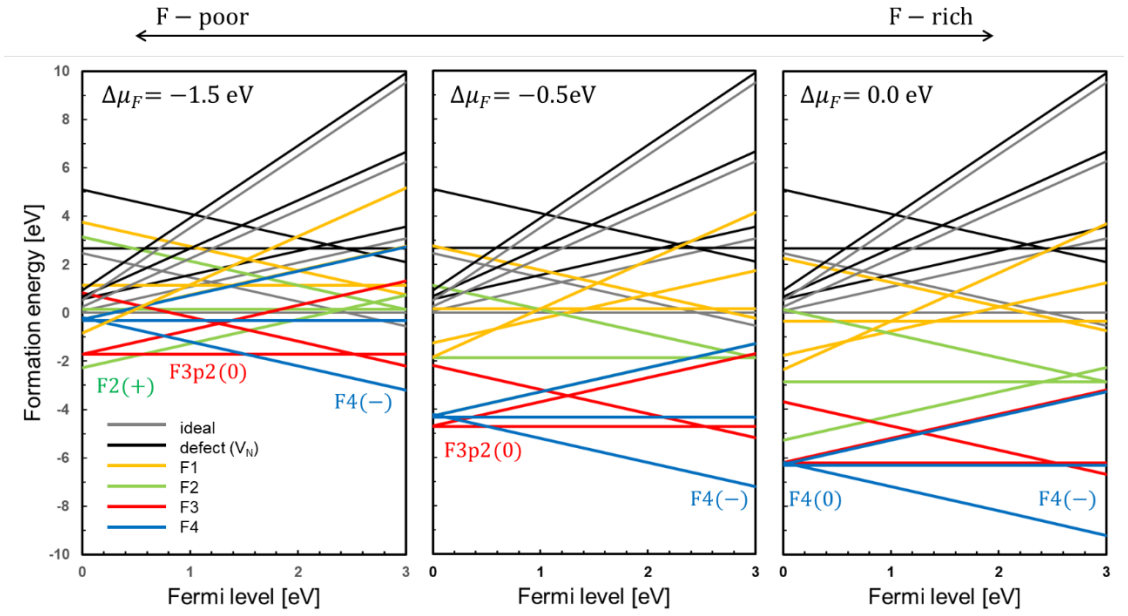

Fig. S2. The formation energy ΔE_{form} as a function of E_F with various $\Delta\mu_{\mathrm{F}}$ conditions.