Electronic Supplementary Information

Exploring the feasibility and conduction mechanisms of P-type nitrogen-doped β-Ga_2O_3 with high hole mobility

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1. Formation energies of phase transition from GaN to β-Ga_2O_3

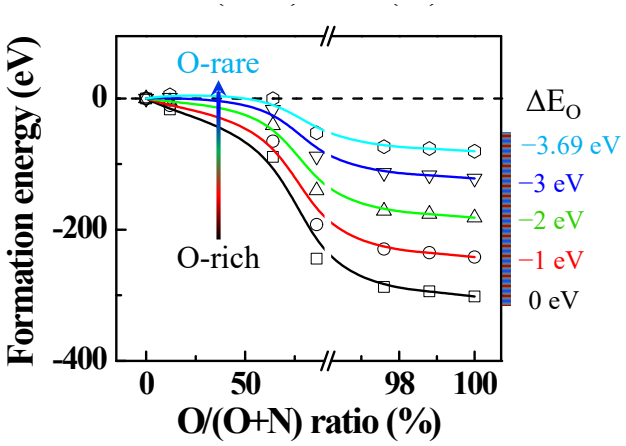

Fig. S1. Formation energy versus O/(O+N) ratio from 0 (GaN) to 1 (β-Ga_2O_3) under different O ambient conditions.

2. Band structure of $Ga_{48}O_{70}N_2$

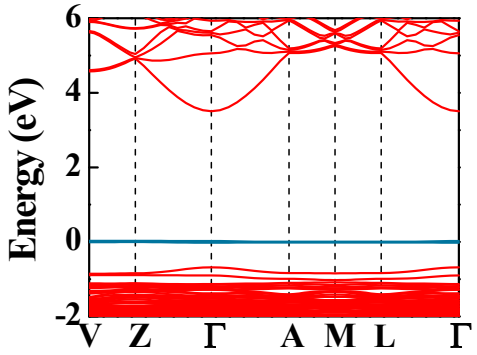

Fig. S2. Band structure of $Ga_{48}O_{70}N_2$.

The band structure of $Ga_{48}O_{70}N_2$ shows an impurity level (blue line) at 0.56 eV above VBM.

3. Ultraviolet-photoelectron-spectroscopy (UPS) valence band spectrum of N-doped β-Ga_2O_3

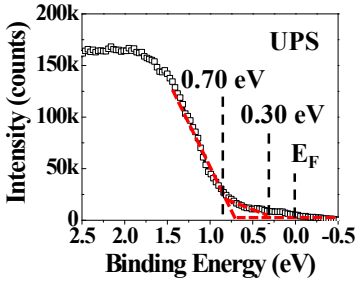

Fig. S3. UPS (21.22 eV He I radiation) valence band photoemission spectrum of the valence band edge.

4. Formation energies of neutral and charged $Ga_{48}O_{70}N_2$

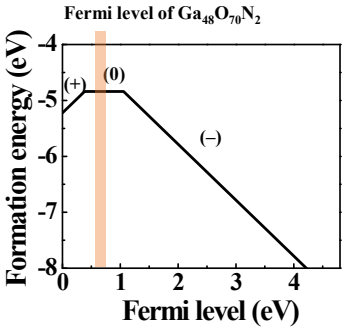

Fig. S4. Formation energies of neutral and charged $Ga_{48}O_{70}N_2$ versus Fermi level.

The relationship between formation energy of neutral $Ga_{48}O_{70}N_2$ and Fermi level is described by $E^f[^{N}_{O}{}^{0}(Ga_{48}O_{70}N_2), E_F = 0] = E_{tot}[^{N}_{O}{}^{0}(Ga_{48}O_{70}N_2)] - E_{tot}(Ga_{48}O_{69}N_3) + E_N - E_O$.

The relationship between formation energy of $Ga_{48}O_{70}N_2^-$ and Fermi level is described by $E^f[^{N}_{O}{}^{-}(Ga_{48}O_{70}N_2), E_F = 0] = E_{tot}[^{N}_{O}{}^{-}(Ga_{48}O_{70}N_2)] - E_{tot}(Ga_{48}O_{69}N_3) + E_N - E_O - (E_{VBM} + E_F + E_{corr})$.

The relationship between formation energy of $Ga_{48}O_{70}N_2^+$ and Fermi level is described by $E^f[^{N}_{O}{}^{+}(Ga_{48}O_{70}N_2), E_F = 0] = E_{tot}[^{N}_{O}{}^{+}(Ga_{48}O_{70}N_2)] - E_{tot}(Ga_{48}O_{69}N_3) + E_N - E_O + (E_{VBM} + E_F$

$+ E_{corr}$).

5. Numerical method and computational details of scattering characteristics

The hole mobility and scattering characteristics are predicted based on the Boltzmann transport theory using the Ab *initio* Scattering and Transport package. The scattering rate from initial state $|nk>$ to final state $|mk+q>$ is defined using Fermi's gold rule as $\tau^{-1}_{nk\to mk+q} = \frac{2\pi}{\hbar}|g_{mn}(k,q)|^2\delta(\varepsilon_{nk} - \varepsilon_{mk+q})$, where ε_{nk} denotes the energy of state $|nk>$, ε_{mk+q} the energy of state $|mk+q>$, $g_{mn}(k,q)$ the coupling matrix element for scattering from state $|nk>$ to state $|mk+q>$, k the wave vector, n and m the band index. Acoustic deformation potential scattering (ADP), optical phonon scattering (OPP) and ionized impurity scattering (IOI) are addressed. The impact of various scatterings on hole mobility is expressed via the coupling matrix element.

The matrix element of ADP is given by: $g^{ADP}_{nm} = \sqrt{K_B T}\sum_{G\neq -q}\left[\frac{\mathcal{D}_{nk}:\hat{\mathcal{S}}_l}{C_l\sqrt{\rho_m}} + \frac{\mathcal{D}_{nk}:\hat{\mathcal{S}}_{t_1}}{C_{t_1}\sqrt{\rho_m}} + \frac{\mathcal{D}_{nk}:\hat{\mathcal{S}}_{t_2}}{C_{t_2}\sqrt{\rho_m}}\right] < mk+q|e^{i(q+G)\cdot r}|nk>$, where $\mathcal{D}_{nk}$ denotes the deformation potential tensor, $\hat{\mathcal{S}}$ the unit strain associated with an acoustic mode, ρ_m the density of materials, c the wave velocity, and subscripts l, t_1 and t_2 indicate properties belonging to longitudinal and transverse modes. The deformation potential tensor $\mathcal{D}_{nk}$ is obtained by $D_{nk} + V_{nk} \otimes V_{nk}$, where D_{nk} denotes the second rank deformation potential tensor, V_{nk} the group velocity. The unit strain associated with an acoustic mode ($\hat{\mathcal{S}}$) is obtained by $\hat{q} \otimes \hat{u}$, where $\hat{u}$ denotes the unit vector of phonon polarization. The matrix element of OPP is described by: $g^{OPP}_{nm} = \left[\frac{\hbar\omega_{op}}{2}\right]^{\frac{1}{2}}\sum_{G\neq -q}\left(\frac{1}{\hat{n}\cdot\varepsilon_\infty\cdot\hat{n}} - \frac{1}{\hat{n}\cdot\varepsilon_s\cdot\hat{n}}\right)\frac{<mk+q|e^{i(q+G)\cdot r}|nk>}{|q+G|}$, where ω_{op} denotes the optical phonon frequency, $\hat{n} = (q+G)|q+G|$ a unit vector in the direction of

scattering, ε_s the static dielectric tensor, ε_∞ the high-frequency dielectric tensor. The matrix element of IOI is given by: $g_{nm}^{IOI} = \sum_{G \neq -q} \frac{n_{ii}^{1/2} Ze}{2\hat{n} \cdot \varepsilon_s \cdot \hat{n}} \frac{< mk+q | e^{i(q+G)\cdot r} | nk >}{|q+G|^2 + \beta^2}$, where Z denotes the charge state of the impurity center, $n_{ii} = C_{self} \times (p - n)/Z$ the concentration of ionized impurities, C_{self} the amount of charge compensation, and β the inverse screening length. The β^2 is obtained by $\frac{e^2}{\varepsilon_s KT} \int \frac{D(\varepsilon) f(1-f)}{V} d\varepsilon$, where V denotes the unit cell volume, $D(\varepsilon)$ the density of states, and f Fermi-Dirac distribution.

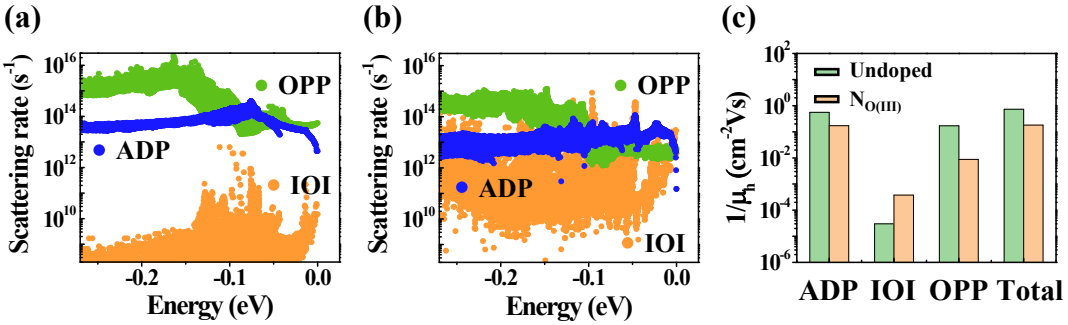

Fig. S5. Scattering rates of ADP, IOI, and OPP for (a) undoped β-Ga_2O_3 and (b) β-Ga_2O_3:$N_{O(III)}$ obtained by the spin-polarized calculations. (c) Calculated $1/\mu_{ADP}$, $1/\mu_{IOI}$, $1/\mu_{OPP}$, and $1/\mu_{Total}$ of undoped β-Ga_2O_3 and β-Ga_2O_3:$N_{O(III)}$, where μ_{Total} is the total hole mobility, μ_{ADP}, μ_{IOI}, and μ_{OPP} the hole mobilities related to the ADP, IOI and OPP, respectively.

Material	p (cm^{-3})	Temperature (K)	ADP (s^{-1})	IOI (s^{-1})	OPP (s^{-1})
Undoped β-Ga_2O_3					
	10^{10}	300	4.4×10^{12}	1.4×10^{10}	5.5×10^{13}
β-Ga_2O_3: $N_{O(III)}$					
Nonspin	10^{15}	300	4.3×10^{10}	4.8×10^{13}	3.3×10^{13}
Spin polarization	10^{15}	300	1.5×10^{11}	3.6×10^{12}	5.8×10^{12}

Table S1. Summary of room-temperature scattering rates of ADP, IOI, and OPP at VBM for undoped β-Ga_2O_3 and β-Ga_2O_3:$N_{O(III)}$ obtained by the nonspin and spin-polarized calculations.

Material	p (cm^{-3})	Temperature (K)	μ_{Total} ($cm^2V^{-1}s^{-1}$)	μ_{ADP} ($cm^2V^{-1}s^{-1}$)	μ_{IOI} ($cm^2V^{-1}s^{-1}$)	μ_{OPP} ($cm^2V^{-1}s^{-1}$)
Undoped β-Ga_2O_3						
	10^{10}	300	1.3	1.8	33300	5.8
β-Ga_2O_3: $N_{O(III)}$						
Nonspin	10^{15}	300	8.8	300.0	354.3	9.0
Spin polarization	10^{15}	300	5.5	5.8	2643.2	114.0

Table S2. Summary of room-temperature hole mobilities μ_{Total}, μ_{ADP}, μ_{IOI}, and μ_{OPP} for undoped β-Ga_2O_3 and β-Ga_2O_3:$N_{O(III)}$ obtained by the nonspin and spin-polarized calculations.

6. Growth and Materials characterization of N-doped β-Ga_2O_3 films

Growth of N-doped β-Ga_2O_3 films

The β-Ga_2O_3 films were prepared by thermal oxidation of GaN/sapphire substrates at 1000−1100 ^oC using a modified chemical vapor deposition system. The GaN surface was cleaned by acetone, ethanol, and deionized water for 10 mins in turn. After then the cleaned GaN films were placed in a quartz boat and inserted in a quartz tube furnace, followed by annealing of the GaN films under oxygen ambient. During the thermal oxidation process, the oxygen pressure, high-purity Ar gas purge, and pumping rate are well controlled. The growth rate and crystalline quality were maintained by well control of oxygen pressure and Ar gas purge for efficient N doping within the β-Ga_2O_3 films.

Materials characterization

Ultraviolet photoelectron spectroscopy (UPS, 21.22 eV He I radiation) was used to investigate the VB photoemission. The Fermi level (E_F) was calibrated by referring the Au energy. Temperature-dependent Van der Pauw Hall effect measurements were performed to analyze the p-type properties of the β-Ga_2O_3 films.