Supplementary data

P-type nitrogen-doped β-Ga_2O_3: the role of stable shallow acceptor N_O-V_{Ga} complexes

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3. Electronic band structures and DOS of undoped β-Ga_2O_3, β-Ga_2O_3:V_{Ga}, β-Ga_2O_3:N_O and β-Ga_2O_3: N_O-V_{Ga} complexes with spin-polarization.

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1. Crystal structures of calculated supercells

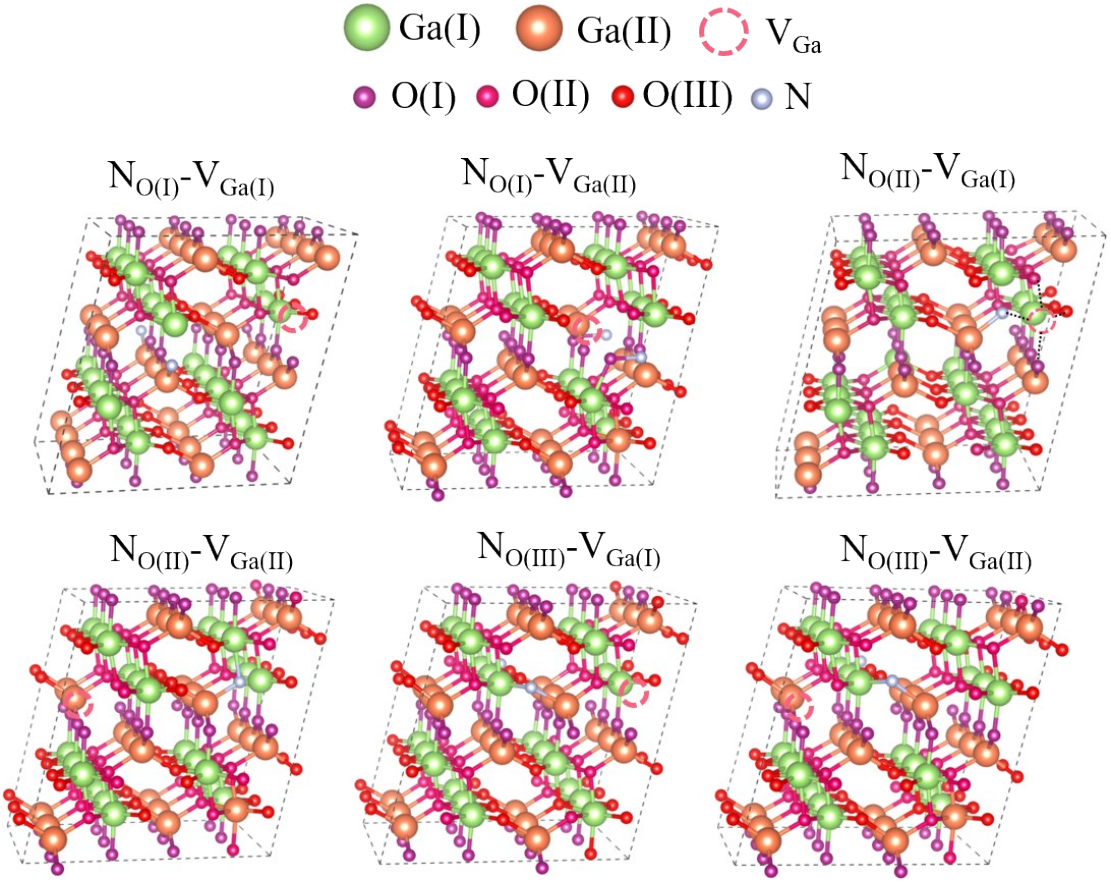

Fig. S1. Schematic crystal structures of calculated supercells β-Ga_2O_3:N_O-V_{Ga} complexes.

Fig. S1 shows schematic diagram for the crystal structures of six different β-Ga_2O_3:N_O-V_{Ga} complexes with V_{Ga} and N_O at different nonequivalent Ga and O sites.

2. Electronic band structures and PDOS without spin-polarization.

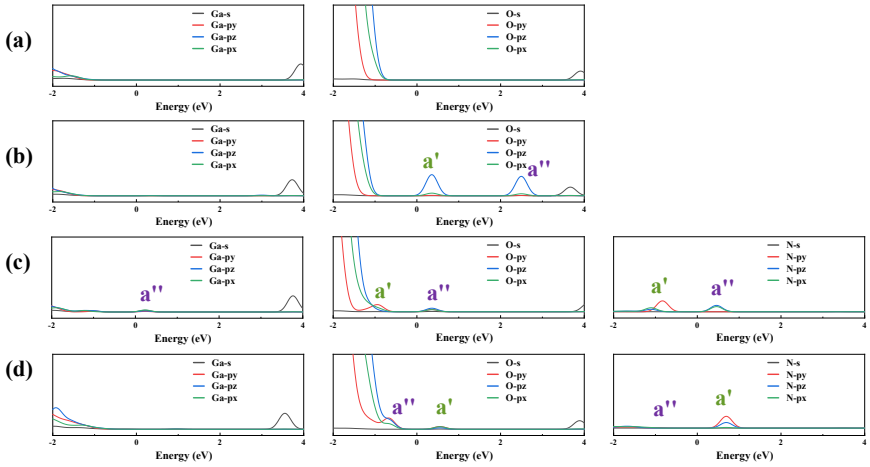

Fig. S2. PDOS of (a) undoped β-Ga_2O_3, (b) β-Ga_2O_3:$V_{Ga(I)}$, (c) β-Ga_2O_3:$N_{O(II)}$, (d) β-

Ga_2O_3:$N_{O(II)}$-$V_{Ga(I)}$. The PDOSs have been aligned with the O 1s core level of the host materials. The calculation has been performed using the HSE functional without spin-polarization.

Fig. S2 shows the partial DOS (PDOS) of undoped β-Ga_2O_3, β-Ga_2O_3:V_{Ga}, β-Ga_2O_3:N_O, and β-Ga_2O_3:N_O-V_{Ga} complexes. In the figure, a' and a" denote the doublet and singlet states, respectively, split from the p orbitals of Ga, O and N atoms.

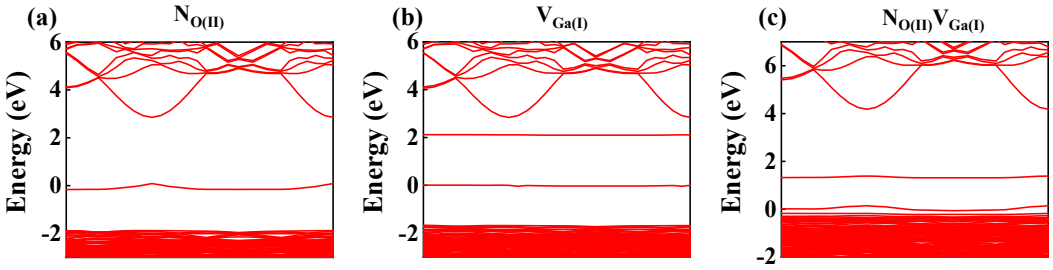

Fig. S3. Electronic band structures of (a) β-Ga_2O_3:$V_{Ga(I)}$, (b) β-Ga_2O_3:$N_{O(II)}$, (c) β-Ga_2O_3:$N_{O(II)}$-$V_{Ga(I)}$ without considering spin-polarization.

According to the previous studies, the difference between the minimum direct gap and the fundamental indirect band gap of β-Ga_2O_3 is only 29-50 meV. [1-2] Despite having an indirect fundamental gap, β-Ga_2O_3 is capable of light emission similar to direct-gap materials. Our calculated electronic band structures demonstrate that the doped structures investigated in the paper can also indeed be treated as a direct bandgap semiconductor.

3. Electronic band structures and DOS spin-polarization.

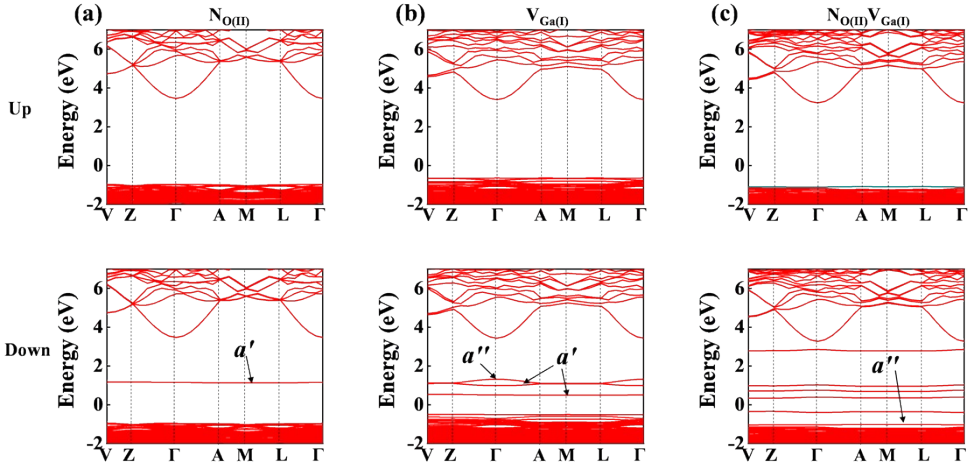

Fig. S4. Electronic band structures of (a) β-Ga_2O_3:$V_{Ga(I)}$, (b) β-Ga_2O_3:$N_{O(II)}$, (c) β-Ga_2O_3:$N_{O(II)}$-$V_{Ga(I)}$ with spin-polarization.

The calculated electronic band structures with spin-polarization still show that the doped structures investigated in the paper can indeed be treated as a direct bandgap semiconductor.

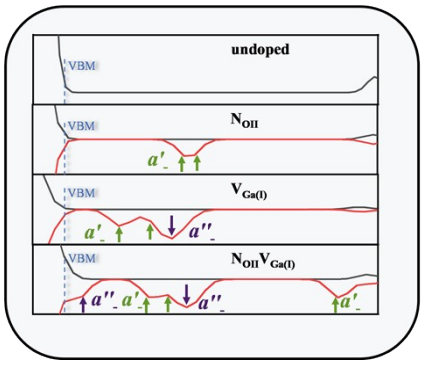

Fig. S5. DOS of (a) β-Ga_2O_3:$V_{Ga(I)}$, (b) β-Ga_2O_3:$N_{O(II)}$, (c) β-Ga_2O_3:$N_{O(II)}$-$V_{Ga(I)}$ with spin-polarization.

The states in DOS are labeled as + (spin up) or – (spin down). The a' doublet state splits into two separate states in β-Ga_2O_3:$V_{Ga(I)}$, with no degeneracy between them. In β-Ga_2O_3:$N_{O(II)}$, the a' doublet state splits into two nearly degenerated states. When the neighboring $N_{O(II)}$ and $V_{Ga(I)}$ defects in β-Ga_2O_3 combine to form $N_{O(II)}$-$V_{Ga(I)}$ complexes, the lowest a" state occurs at about 0.23 eV above VBM due to the level repulsion between $N_{O(II)}$ and $V_{Ga(I)}$. Without considering spin polarization, the lowest a" state is 0.22 eV, which is only slightly different from the value when spin polarization is taken into account. This indicates that, regardless of whether spin polarization is considered, the formation of a shallow acceptor level arises from the formation of $N_{O(II)}$-$V_{Ga(I)}$ complexes, thus contributing to the p-type conductivity.

Reference:

1. Y. Kang, H. Peelaers, K. Krishnaswamy and C. G. Van de Walle, *Appl. Phys. Lett*., 2018, **112**, 062106.
2. K. A. Mengle and E. Kioupakis, *AIP Adv*., 2019, **9**, 015313.