Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information for:

Atomic-scale origin of piezoelectricity in wurtzite ZnO

Jung-Hoon Lee,*[a] Woo-Jin Lee,[b] Sung-Hoon Lee,[c] SeongMin Kim,[b] Sungjin Kim[b]

and Hyun Myung Jang*[a,d]

[a]*Division of Advanced Materials Science (AMS) and Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Republic of Korea.*

[b]*Samsung Advanced Institute of Technology (SAIT), Suwon 443-803, Republic of Korea.*

[c]*Center for Artificial Low Dimensional Electronic Systems, Institute for Basic Science, Pohang 790-784, Republic of Korea.*

[d]*Department of Physics, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Republic of Korea.*

* To whom correspondence should be addressed. E-mail: jhlee.david@gmail.com and hmjang@postech.ac.kr

(A) Atomic Positions

Table SI. Comparison of the calculated ground-state atomic positions of the polar $P6_3mc$ structure with the nonpolar $P6_3/mmc$ structure of hexagonal ZnO. The unit-cell parameters obtained from the experiment are a = 3.2418 Å and c = 5.1877 Å.[S1]

Space Group	Ion Type	Wyckoff Position	*x*	*y*	*z*
$P6_3mc$	Zn	2*b*	0.3333	0.6667	0.0016
	O	2*b*	0.3333	0.6667	0.3804
$P6_3/mmc$	Zn	2*b*	0.3333	0.6667	0.8804
	O	2*b*	0.3333	0.6667	0.3804

(B) Hybrid functional calculations

(1) Total density of states (DOS)

We have carefully examined the total DOS using the hybrid functionals of HSE.[S2] In order to reproduce the experimental band gap of wurtzite ZnO, the fraction of Hartree-Fock (α) is set to 0.35. At this value, the wurtzite ZnO has a direct band gap of 3.38 eV which is in good agreement with the experimental value.[S3] As shown in **Fig. S1**, the hybrid functionals significantly improve the band-gap prediction: 1.96 eV for the GGA+U method and 3.38 eV for the hybrid functionals.

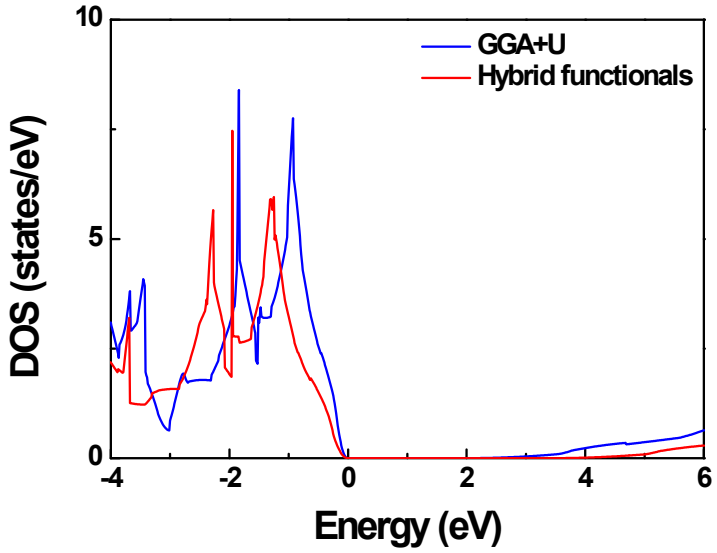

Fig. S1 A comparison of the total DOS by the GGA+U method with the PDOS obtained by the hybrid functionals.

(2) Oribital-resolved partial density of states (PDOS)

We have further examined the PDOS for various atomic orbitals using the hybrid functionals. In **Fig. S2**, we compare the orbital-resolved PDOS for O_A $2p_z$, Zn $4p_z$, and Zn $3d_{z^2}$ of the *P6₃/mmc* structure with those of the polar *P6₃mc* structure. According to the PDOS results shown in **Fig. S2**, the hybrid functionals also indicate a strong overlapping of the Zn $4p_z$ orbital PDOS with the Zn $3d_z^2$ orbital PDOS (for the energy range between -2 and 0 eV below the valence-band top) in the polar *P6₃mc* phase.

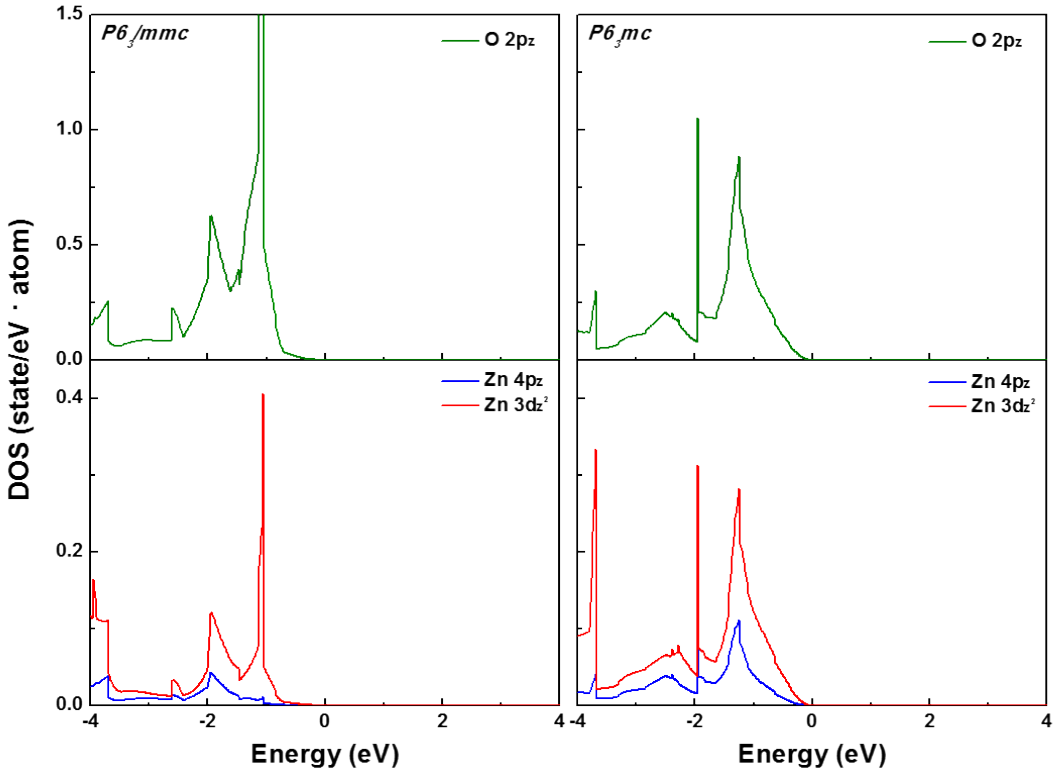

Fig. S2 Orbital-resolved PDOS for Zn $4p_z$, $3d_{z^2}$, and O_A $2p_z$ orbitals of the nonpolar $P6_3/mmc$ structure with those of the polar $P6_3mc$ structure.

* References

S1 J. Albertsson, S. C. Abrahams and Å. Kvick, *Acta Cryst. B* 1989, **45**, 34-40.

S2 J. Heyd, G. E. Scuseria and M. Ernzerhof, *J. Chem. Phys.*, 2006, **118**, 8207-8215.

S3 Ü. Özgür, Ya. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho and H. A. Morkoç, *J. Appl. Phys.*, 2005, **98**, 041301-1-041301-103.