

Supplementary Information for ‘Bistability of Hydrogen in ZnO: Origin of Doping Limit and Persistent Photoconductivity’

Ho-Hyun Nahm,^{1,2,3,4} C. H. Park,^{1,*} and Yong-Sung Kim^{4,5,†}

¹Research Center for Dielectric and Advanced Matter Physics,

Department of Physics Education, Pusan National University, Pusan 609-735, Korea

²Center for Correlated Electron Systems, Institute for Basic Science (IBS), Seoul 151-747, Korea

³Department of Physics and Astronomy, Seoul National University, Seoul 151-747, Korea

⁴Korea Research Institute of Standards and Science, Yuseong, Daejeon 305-340, Korea

⁵Department of Nano Science, University of Science and Technology, Daejeon 305-350, Korea

(Dated: January 2, 2014)

We performed first-principles calculations with the projector augmented wave (PAW) pseudopotentials [1] using the Vienna *ab initio* simulation package (VASP) code [2]. In order to overcome the problem of band-gap underestimation by normal density functional theory (DFT) calculation, we applied the hybrid functional of Heyd-Scuseria-Ernzerhof (HSE) [3], that is an advanced and highly-accurate approach mixing the Hartree-Fock exchange and the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [4]. We set the mixing parameter $\alpha=0.375$, indicating that 37.5% of Hartree-Fock exchange is used, since it leads to the calculations of the structural parameters, band gap of ZnO, and heat of formation in good agreements with the experimental data [5] and the other HSE-calculational results [6, 7]. Some HSE calculated results for the pure ZnO are shown in Table I. The screening parameter in the HSE was fixed at a value of 0.2 \AA^{-1} [3]. We used the standard PAW potentials for Zn, O, and H in the VASP distribution. A cut-off of 400 eV was used for the plane wave expansion of wave functions. To simulate the impurities and defects, we mostly used a hexagonal-shaped supercell geometry including 96 atoms. The k -space was integrated by using $(2 \times 2 \times 2)$ mesh points including Γ . All atomic positions were fully relaxed until the Hellmann-Feynman force on each atom was reduced to 0.01 eV/\AA . We corrected the effect of the small supercell size through the LDA+U calculations using several bigger supercells, to be discussed below.

We modified total energies by including the corrections of the artificial size effect of constructed supercell for $H\text{-DX}^-$ and $H\text{-O}^+$ [8–10]. Three supercells, including 96, 288, and 576 atoms, were constructed in order to estimate the trend of the size effect of supercell. The size effect was tested only by PBE+U calculations to reduce heavy com-

putations. Since the electronic structure of $H\text{-DX}^-$ is not well described by normal PBE+U calculation, due to the problem of the underestimation of band-gap, in which a U parameter for Zn_d is usually considered. Instead, we performed PBE+U calculations with a large U of 34.6 eV for Zn_s by following the suggestions of ref[11], by which the band gap of ZnO is well described. We focus on the modifications of formation enthalpies (Ω_s) with respect to the 96-atom supercell calculations, with which the HSE calculations were performed. We modified calculated total energies by considering the band-gap, the band filling effect [8], and the potential alignment effect and the image

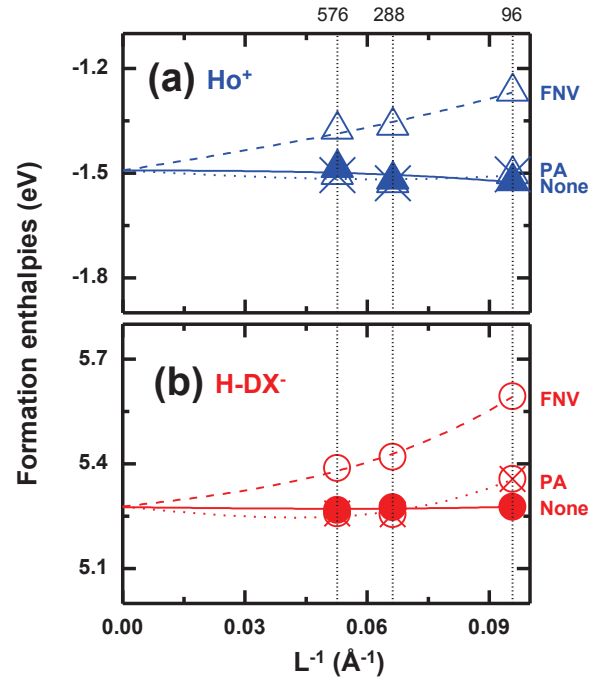


TABLE I. For wurtzite ZnO, calculated structural parameters (a and c), band-gap (E_g) at Γ -point, and the heat of formation per chemical unit are compared with experiments (Expt.) [5] and other HSE calculations [6, 7].

	a (\AA)	c (\AA)	E_g (eV)	ΔH_f (eV)
present	3.24	5.23	3.42	-3.13
HSE($\alpha=0.375$)	3.25	5.20	3.43	-3.13
Expt.	3.25	5.21	3.40	-3.64

FIG. 1. (Color online) The formation enthalpies of (a) $H\text{-O}^+$ and (b) $H\text{-DX}^-$ are shown as a function of $1/L=1/V^{1/3}$ (V =supercell volume) at $\epsilon_F=\epsilon_{VBM}$ under H-rich and O-poor condition. The correction schemes for the supercell size of charged H-related impurities were used by potential alignment (PA) and Freysoldt, Neugebauer, and Van de Walle (FNV). The solid, dot, and dash lines indicate fitting results for None (no correction), PA, and FNV with respect to $a + \frac{b}{L} + \frac{c}{L^3}$, respectively.

charge effect of the charged defect by using the Freysoldt, Neugebauer, and Van de Walle (FNV) finite-size correction scheme [9, 10]. The estimated formation enthalpies are shown in Fig. 1, depending on the supercell size, where the Fermi level is assumed to be at the valence band maximum (VBM). Here, the dielectric constant of ZnO was assumed to be 8.31 [12]. The correction of the total energy of H_O^+ for infinite size supercell was calculated to be 0.04 eV, 0.02 eV, and -0.22 eV, respectively, by considering (i) only atomic relaxation effect by the bigger supercell (None), (ii) by furthermore including the potential alignment effect (PA), and (iii) by the fully corrected scheme based on the FNV scheme (FNV), relative to the 96-atom supercell calculations without any correction. For $H-DX^-$, it was calculated to be 0.01 eV, 0.08 eV, and -0.32 eV for None, PA, and FNV cases, respectively, relative to the 96 atoms supercell calculations without any correction. The results indicated that the $H-DX^-$ becomes equally stable to H_O^+ , as the Fermi level is located at 0.05 eV below the conduction band minimum (CBM), where the electron concentration is estimated to be $4.25 \times 10^{17} \text{ cm}^{-3}$ at room-T.

We would like to note that we initially identified the bistability of the H-related DX through the calculations based on the conventional DFT methods such as GGA. The stability of the $H-DX$ center was calculated to be more enhanced by the hybrid functional HSE calculations than the former GGA calculations. The estimation for the doping limit becomes in a good agreement with experimental data through the hybrid functional HSE calculations. Compared with the HSE calculation, the deep level α^* by the $H-DX$ is located around the CBM due to the significant underestimation of the band-gap (E_g) by the GGA method, and therefore, the electronic energy gain by the capture of the electrons at the deep level is not enough to stabilize the large lattice relaxed $H-DX$ structure when the GGA method is used.

We also tested the relative energies of both H_O and $H-DX$ (a complex of H_i and V_O) structures for dependency of mixing parameter (α) in the HSE calculations by using a smaller 72-atom rhombohedral supercell. By using HSE($\alpha=0.37$) method, in the (-)-charge state, $H-DX^-$ structure is calculated to be more stable by 0.31 eV than the H_O^- , while by using the PBE($\alpha=0$) method, the former is calculated to be less stable by 0.39 eV than the latter. However, the $H-DX$ structure is still metastable. These indicate that the hybrid HSE calculation is more reliable in estimating the stability of the $H-DX$.

By using the estimated formation enthalpies of H_O^+ and $H-DX^-$, we examined the carrier concentrations as a function of temperature (K) in Fig. 2(a). The various cases of Fermi-pinning levels were examined. We would note that since the density of states around the CBM is low in ZnO, the calculated Fermi-pinning-level of 50 meV is not so critical to explain the low doping limit of about 10^{17} - 10^{18} cm^{-3} . We tested the various pinning positions of the Fermi-level between 0.0 eV and -0.08 eV relative to

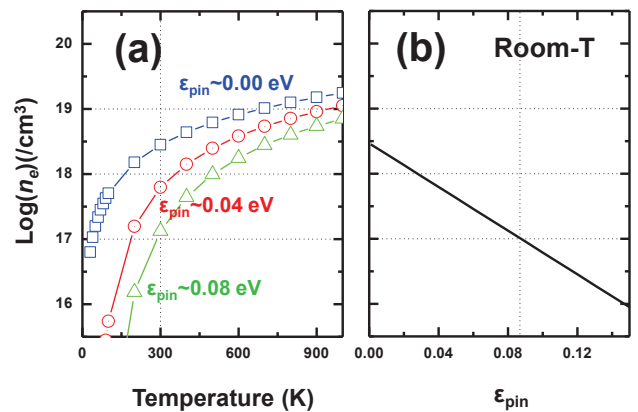


FIG. 2. (Color online) (a) Carrier concentration orders, $\log(n_e)$ (cm^{-3}), are shown as a function of temperature (K) for three Fermi pinning levels (ϵ_{pin} s) located at 0.00 eV, 0.04, and 0.08 eV below CBM. (b) Carrier concentration order is also shown at $T=300 \text{ K}$ as a function of ϵ_{pin} below CBM.

the CBM, and the estimated carrier concentration is varied around 10^{17} - 10^{18} cm^{-3} , as shown in Fig. 2(b). The results are consistent with experimental data for the maximum carrier concentration of about 10^{17} - 10^{18} cm^{-3} . An important thing is the formation of the deep trap level by the large lattice relaxation, when the Fermi level is around CBM.

Finally, we would note a similarity of the present $H-DX$ to a well-known orthorhombic C_{2V} -type DX center formed at the anion-like donor S atom in GaSb and AlGaAs [13]. In both case, the impurities are located at an anion site. Furthermore, the formation mechanism of deep level α^* in the $H-DX$ is similar with that in the C_{2v} -type DX . The deep level comes from the cation-cation coupling state. However, the crystal structure of ZnO is hexagonal, and therefore, the atomic structure of the $H-DX$ is slightly different from the C_{2V} -type DX center and the atomic displacement of the impurity is much larger in $H-DX$.

* cpark@pusan.ac.kr

† yongsung.kim@kriss.re.kr

- [1] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994); G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
- [2] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996); G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
- [3] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003); **124**, 219906 (2006).
- [4] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
- [5] *Semiconductors-Basic Data*, 2nd revised ed., edited by O. Madelung (Springer, Berlin, 1996).
- [6] J. L. Lyons, A. Janotti, and C. G. Van de Walle, Appl. Phys. Lett. **95**, 252105 (2009).
- [7] F. Oba, A. Togo, I. Tanaka, J. Paier, and G. Kresse, Phys.

- Rev. B **77**, 245202 (2008).
- [8] S. Lany and A. Zunger, Phys. Rev. B **78**, 235104 (2008).
- [9] C. Freysoldt, J. Neugebauer, and C. G. Van de Walle, Phys. Rev. Lett. **102**, 016402 (2009).
- [10] C. Freysoldt, J. Neugebauer, and C. G. Van de Walle, Phys. Status Solidi B **248**, 1067 (2011).
- [11] T. R. Paudel and W. R. L. Lambrecht, Phys. Rev. B **77**, 205202 (2008); A. Boonchun and W. R. L. Lambrecht, Phys. Status Solidi B **248**, 1043 (2011).
- [12] V. A. Coleman and C. Jagadish, *Basic Properties and Applications of ZnO* in Zinc Oxide: Bulk, Thin Films and Nanostructures, edited by C. Jagadish and S. J. Pearton. Chap. 1 (pp. 15), Elsevier, Oxford, (2006).
- [13] C. H. Park and D. J. Chadi, Phys. Rev. B **55**, 12995 (1997).