Bistability of Hydrogen in ZnO: Origin of Doping Limit and Persistent Photoconductivity

Ho-Hyun Nahm1,2,3, C. H. Park1 & Yong-Sung Kim4,5

Substitutional hydrogen at oxygen site (H_O) is well-known to be a robust source of n-type conductivity in ZnO, but a puzzling aspect is that the doping limit by hydrogen is only about 10^{18} cm^{-3}, even if solubility limit is much higher. Another puzzling aspect of ZnO is persistent photoconductivity, which prevents the wide applications of the ZnO-based thin film transistor. Up to now, there is no satisfactory theory about two puzzles. We report the bistability of H_O in ZnO through first-principles electronic structure calculations. We find that as Fermi level is close to conduction bands, the HO can undergo a large lattice relaxation, capturing electrons at a deep level can be induced, capturing electrons and the deep state can be transformed into shallow donor state by a photon absorption. We suggest that the bistability can give explanations to two puzzling aspects.
level which is created by the LLR. It is shown that the bistability can give clear explanations to the microscopic mechanisms of long-term puzzling phenomena in ZnO: the persistent photo-conductivity in ZnO and the low doping limit of H-rich ZnO.

**Results**

In ZnO, a H atom is suggested to be strongly captured by an O-vacancy, which is a substitutional impurity at O-site (H$_0$), as shown in Fig. 1(a). The H$_0$ state is known to be a robust state, and normally positively charged, as suggested by Janotti et al., since the highest occupied state from the hydrogen state is located above the CBM. However, here we find that H$_0$ can be negatively charged and capture electrons through a large lattice relaxation (LLR). We find that in the negative charge state, the H atom can be significantly displaced into an interstitial hollow (H*)-site. The LLR structure is described by Fig. 1(b).

Through the LLR, the H is separated from O-vacancy site, and thus the LLR structure can be considered as a pair of H$_0^-$ and V$_{O^0}$, that is a Frenkel defect. In this respect, it is similar to the well-known DX center in AlGaAs. Thus, we call the LLR structure as "H-DX". The present H-DX is slightly different from DX center. In the former, two H-O bonds are broken by LLR [see Fig. 1(b)], while in the latter, only one bond is broken. In the H-DX, as shown in Fig. 1(b), the H couples with three Zn atoms which are located altogether at a same layer of ab-plane. Electronic structure calculations indicate that a deep level within gap is created by the LLR and it captures two electrons, as shown in Fig. 2(a). The more detail will be discussed below. We examined another metastable LLR structure, which is described as H-DX* in Fig. 1(c), where the displaced H is located between two ab-layers. This state is less stable by 0.26 eV than H-DX, and the H-DX* is less probable to be formed, compared to the H-DX. We also examined another LLR: only one Zn atom is separated from the H, similarly to conventional DX center, but we find that these states are unstable, the deep level is not formed by the LLR.

As shown by Figs. 2(a) and 2(b), electronic structure calculations indicate that two deep levels are created by H-DX*. The lower α level is located at 0.49 eV above the VBM, and the upper α* level is located at 1.06 eV below the CBM. As shown by Fig. 2(d), the α level is found to come mainly from the H atom and the nearby H-coupled Zn atoms ([Zn(1), Zn(4), Zn(5) in Fig. 1(b)], and, as shown by Fig. 2(e), the upper α* level comes mainly from the O-vacancy site, i.e., from the Zn(2) and Zn(3) atoms separated from H. The two defect levels are fully occupied. The electronic energy reduction by the capture of two electrons at α* level contributes to the stabilization of the H-DX.

In the isolated point defect V$_O$, four nearby Zn atoms are relaxed inward by the electron capture of V$_O$. In the V$_O^+$, the Zn atoms are relaxed inward by about 0.24 Å from ideal positions (ideal Zn-O bond lengths: $d_{Zn-O} = 1.97$ and 1.99 Å). Similarly, in the H-DX*, Zn(2) and Zn(3) atoms are inward relaxed by 0.28 Å and 0.32 Å, respectively. Three Zn host cations coupled to the H move towards the H by about 0.12 Å (0.10 Å for Zn(5)), from ideal locations. For the H-DX' LLR structure, the H atom is largely displaced by 1.92 Å from the original location of H$_0$.

In the neutral state, the H-DX structure becomes unstable, since the electronic energy reduction by one electron trap is not enough to stabilize it. Similarly, in the positive charge state, the H-DX structure is unstable. The H-DX' structure is stable only in the negative charge state, having two electrons at α* level, and it is more stable than the H$_0$ in the negative charge state, which is actually H$_0^0 + 2e$ (at CBM), since the donor level of H$_0$ is located much higher than CBM.

Now, we examine the stability of H-DX state relative to the normal H$_0^-$, depending on Fermi level ($\varepsilon_F$), by calculating the formation enthalpies. Since two structures have different charge states, the relative stability should depend on Fermi level. The calculated results of $\varepsilon_F$-dependent formation enthalpies of these states are shown in Fig. 3. Here, we assumed O-poor and H-rich conditions (simulating the O-deficient and H-rich case). Since H$_0$ is shallow-donor-like, only the positive charge state is stable when Fermi level is inside the band gap. The calculation results indicate that as Fermi level is located above 0.05 eV below the CBM, electron-capturing H-DX' becomes more stable than H$_0^-$. We did not consider the interstitial H (H$_i$) state, assuming that substitutional H$_0$ is much more abundant than interstitial hydrogenic H$_i$ state, since the H$_i$ is suggested to be easily removed through thermal annealing due to its high mobility. These results indicate that when Fermi level is close to the 0.05 eV below CBM, the concentration of the H-DX states becomes comparable to that of H$_0$. These indicate that the pinning position of the Fermi level is located at about 0.05 eV below CBM.

The results indicate that H$_0$ state can be self-compensated through LLR transition. An electron can be generated by a shallow donor such as H$_0$, and the electron is captured by other H$_0$.

$$H_0^- \rightarrow H_0^+ + e \tag{1}$$
The overall process is found to be exothermic by 0.10 eV, when Fermi level is located at CBM. We estimated total energy profile for the structural transformation between HO and H-DX. The charge states of H-DX in the neutral or (1-) charge state is unstable. When the high concentration of electron carriers is present at conduction band, two electrons can be captured by the HO through the deformation toward H-DX structure, and the H-DX^2 state can be more stable than the HO^1 (at CB). We calculated the variation of the total energy according to the structural deformation, as shown in Fig. 4, and we find that there is the energy barrier for the structural recovery: HO^1 + 2e \rightarrow H-DX^−. It is estimated to be 0.36 eV.

We examined the binding energies of HO^+ and H-DX^− with respect to well-separated H, and V_0. The binding energies of HO^+ and H-DX^− were estimated by comparing two states, i.e., by using [E(H^+) + E(V_0^0)] - [E(HO^+) + E(pure)] and using [E(H^+) + E(V_0^0) + 2e (at CBM)] - [E(H-DX^−) + E(pure)], respectively. As shown by (gray)-dashed lines in Fig. 3, the binding energy of HO^+ is estimated to be 0.97 eV, which is largely exothermic, which is comparable to the previous large values of 0.80 eV (in LDA) and 3.8 eV (in LDA + U) in other calculations. The binding energy of H-DX^− is also estimated to be largely exothermic by 1.27 eV. Thus, this indicates that substitutional H-DX^− is a thermally-stable complex defect.

**Discussion**

The electronic structure of H-DX, as schematically described by Fig. 2(c), can be understood with respect to interaction between H_i and V_0. As Takenaka and Singh suggested, H itself in HO^+ is anion-like, capturing two electrons, indicating that HO^+ is rather a complex defect composed of the H_i^− and V_0^++. The anionic behavior is not a surprising one, since H electronegativity (\(\zeta\)) is between those of Zn and O [\(\zeta(H) = 2.2, \zeta(Zn) = 1.65, \) and \(\zeta(O) = 3.44\)]. The V_0^++ in...
complex defect $H_O$ cannot trap the electron, since the Zn-$s$-levels around the H atom are pushed upward above the CBM by the strong interaction between the upper Zn-$s$-level and the lower H-$s$-level. Therefore, the electronic property of the H atom is anionic either at $H_O^{2-}$ or at $H$-DX state and the level of H-$s$-orbital is located lower than that of Zn-$s$-orbital.

In the $H_O$, a H atom interacts strongly with four Zn atoms, while a Zn atom with one H atom, and thus, the H-level is largely pushed down to below the valence band maximum (VBM) and all of Zn-$s$-levels are located above the CBM, as described in Fig. 2(c). On the other hand, in the $H$-DX, the H atom at H-site interacts with just three Zn atoms, so the hydrogenic level is less pushed-down and becomes located above VBM ($\varepsilon$ level in Fig. 2b). Through the LLR from $H_O$ to $H$-DX, the interaction between the H and the $V_O$ becomes weaker and the $V_O$ level becomes deeper below the CBM (see Fig. 2(a)). Two Zn atoms (Zn(2) and Zn(3)) in Fig. 2(b) are separated from H by the LLR, and the generated Zn dangling bonds can induce a deep level (\(\varepsilon\) level), which becomes deeper through the interaction between two Zn-dangling bonds, described by red lines in Fig. 2(c). We, thus, suggest that the electronic energy reduction by the capture of electrons at the deep $\varepsilon$ level stabilizes the displaced H-DX structure.

The fact that the $H$-DX structure is more stable than $H_O$ structure in the negative charge state indicates that as $\varepsilon$ becomes close to the CBM, the $H_O$ can undergo a shallow-to-deep transition through a LLR. Figure 3 indicates that $H$-DX structure can be stable only for the $\varepsilon$ close to CBM ($\varepsilon > 0.05$ eV below CBM). From the estimated pinning position of Fermi-level, we can estimate maximum electron concentration (\(n_{\varepsilon, \text{max}}\)) in H-rich ZnO, assuming the high concentration of $H_O$ to be about $10^{20}$ cm$^{-3}$ at room temperature, which is surprisingly in a good agreement with the experimental data. Therefore, we suggest that the present bistability can give an explanation to the doping limit puzzle for H-rich ZnO. As the $\varepsilon$ is close to the CBM, $H_O$ can undergo the large lattice relaxation into H-DX, and the electrons generated by $H_O$ are trapped in the deep H-DX $\varepsilon$ level, i.e., the $H_O$’s are self-compensated.

We find that the bistability of $H_O$ gives information on the persistent photo-induced conductivity (PPC) reported for ZnO. ZnO is well-known to be easily H-contaminated due to strong bonding between H and O atoms. In the H-rich and O-deficient ZnO, the concentrations of $H_O$ and H-DX states can be comparable due to the above-discussed self-compensation. The PPC effect can be explained by next process: (i) Since the H-DX structure is stable only in the negative charge state, the H-DX can be transformed into the $H_O$ structure, when an electron at H-DX state is excited by light illumination, and (ii) next it becomes spontaneously transformed into the $H_O$. The process is described as H-DX $\rightarrow$ H-DX + e $\rightarrow$ $H_O$ + 2e (\(\rightarrow\) indicates photo-excitation). Overall the deep H-DX state can be transformed into the shallow donor-like $H_O^+$ structure under light. By these processes, the concentration of free electrons can be increased, that describes the photo-induced conductivity. (iii) A larger energy barrier between $H_O$ and H-DX should prevent the structural recovery transformation from $H_O$ to H-DX at room-temperature. Thus, the photo-excited $H_O^+$ state is metastable but persistent, even in the presence of the high concentration of electron carriers at CBM. These results can give a good explanation to the metastable and persistent formation of shallow donor $H_O^+$ (PPC). The metastable $H_O^+$ state can be transformed into the stable H-DX state at a temperature high enough to overcome the energy barrier of 0.36 eV. It can describe the thermal recovery process of the photo-excited $H_O^+$ state. The estimated energy barrier for the transition from $H_O$ to H-DX is in a good agreement with the experimental value of 0.3 eV for the energy barrier for thermal recovery of PPC state.

Segerh and Gislason measured the photon energy spectrum for PPC$^{27}$. The calculated optical absorption spectrum for H-DX state is found to be in a good agreement with the measured optical data$^{27}$. The peak in the calculated optical absorption spectrum of H-DX around 2.3 eV agrees with measured peak in the photon excitation spectrum for PPC effect at 2.15 eV. The minimum optical excitation energy (\(E_{\text{opt}}\)) of H-DX at about 1.06 eV, which comes from the electron excitation from $\varepsilon$ level to CBM, also agrees with the measurement indicating $\sim 1.3$ eV. Therefore, we suggest that the bistability of $H_O$ should be an important source of persistent photoconductivity in ZnO. These propose that in order to prevent the light-induced instability of the ZnO-based devices, either hydrogen contamination or O-deficiency should be reduced. We would note that the scenario of the PPC by metastable $V_O^{2-}$ suggested by Lany and Zunger works in the $V_O$ coupled by an H atom, which is $H_O$.

In conclusion, we identify a bistability of shallow donor $H_O$ center in ZnO. We find that when Fermi level is close to CBM, the $H_O$ can undergo a large lattice relaxation and create a deep level, trapping electrons. It gives an explanation to the low doping limit in H-rich n-type ZnO. We find that H-DX is unstable against shallow-donor state $H_O$ by light-induced electron ionization, and there is a large energy barrier between $H_O$ and H-DX states. Thus, we suggest that the bistability of $H_O$ gives also a microscopic explanation for persistent photo-conductivity in ZnO. The bistability of the H donor will
provide a new way to consider the physics of hydrogen in oxide materials.

**Methods**

We performed DFT calculations as implemented in the Vienna ab initio simulation package (VASP) code. The projector augmented wave (PAW) pseudopotentials, the plane wave basis set with a kinetic energy cutoff of 400 eV, and the hybrid functional of Heyd-Scuseria-Ernzerhof (HSE) with a mixing parameter of 0.375 and a screening parameter of 0.2 Å⁻¹ were used. The calculated lattice constants (\(a = 3.24\) Å and \(c = 5.23\) Å), the band gap (\(E_g = 3.42\) eV), and the heat of formation (\(\Delta H_f = -3.13\) eV) of ZnO were in good agreement with the other HSE calculations and the experiments. With a hexagonal 96-atom supercell, a \(2 \times 2 \times 2\) k-point mesh including \(\Gamma\) was mainly used. All the atomic positions were fully optimized until the Hellmann-Feynman forces were less than 0.01 eV/Å.

1. Janotti, A. & Van de Walle, C. G. Fundamentals of zinc oxide as a semiconductor. *Rep. Prog. Phys.* 72, 126501 (2009).
2. Özgüür, Ü. et al. A comprehensive review of ZnO materials and devices. *J. Appl. Phys.* 98, 41301 (2005).
3. Van de Walle, C. G. & Neugebauer, J. Universal alignment of hydrogen levels in semiconductors, insulators and solutions. *Nature* 423, 626–628 (2003).
4. Van de Walle, C. G. Hydrogen as a Cause of Doping in Zinc Oxide. *Phys. Rev. Lett.* 85, 1012–1015 (2000).
5. Wardle, M. G., Goss, J. P. & Briddono, P. R. First-principles study of the diffusion of hydrogen in ZnO. *Phys. Rev. Lett.* 96, 205504 (2006).
6. Shi, G. A. et al. Hydrogen local modes and shallow donors in ZnO. *Phys. Rev. B* 72, 195211 (2005).
7. Jokela, S. J. & McCluskey, M. D. Structure and stability of O−H donors in ZnO from high-pressure and infrared spectroscopy. *Phys. Rev. B* 72, 113201 (2005).
8. Janotti, A. & Van de Walle, C. G. Hydrogen multi-centre bonds. *Nature Mater.* 6, 44–47 (2007).
9. Strzhemechny, Y. M. et al. Remote hydrogen plasma doping of single crystal ZnO. *Appl. Phys. Lett.* 84, 2545 (2004).
10. Li, Y. J. et al. Electronic properties of H and D doped ZnO epitaxial films. *Appl. Phys. Lett.* 92, 152105 (2008).
11. Ohashi, N. et al. Lowered stimulated emission threshold of zinc oxide by hydrogen doping with pulsed argon–hydrogen plasma. *J. Cryst. Growth* 306, 316–320 (2007).
12. Brauer, G. et al. Identification of Zn-vacancy–hydrogen complexes in ZnO single crystals: A challenge to positron annihilation spectroscopy. *Phys. Rev. B* 79, 115212 (2009).
13. Halliburton, L. E. et al. Production of native donors in ZnO by annealing at high temperature in Zn vapor. *Appl. Phys. Lett.* 87, 172108 (2005).
14. Minami, T., Nanto, H. & Takata, S. Highly Conductive and Transparent Aluminum Doped Zinc Oxide Thin Films Prepared by RF Magnetron Sputtering. *Jpn. J. Appl. Phys.* 23, L280 (1984).
15. Noh, J.-Y., Kim, H., Kim, Y.-S. & Park, C. H. Electron doping limit in Al-doped ZnO by donor-acceptor interactions. *J. Appl. Phys.* 113, 153703 (2013).
16. T-Thienprasert, J. et al. Compensation in Al-Doped ZnO by Al-Related Acceptor Complexes: Synchrotron X-Ray Absorption Spectroscopy and Theory. *Phys. Rev. Lett.* 110, 055502 (2013).
17. Seghier, D. & Gislasen, H. P. Characterization of donor states in ZnO. *Physica B* 401–402, 404–407 (2007).
18. Hoffman, R. L., Norris, B. J. & Wagner, J. F. ZnO-based transparent thin-film transistors. *Appl. Phys. Lett.* 82, 733–735 (2003).
19. Chadi, D. J. & Chang, K. J. Theory of the Atomic and Electronic Structure of DX Centers in GaAs and AlGaAs. *Phys. Rev. Lett.* 61, 873–876 (1988).
20. Lany, S. & Zunger, A. Anion vacancies as a source of persistent photoconductivity in II–VI and chalcopyrite semiconductors. *Phys. Rev. B* 72, 035215 (2005).
21. Janotti, A. & Van de Walle, C. G. Oxygen vacancies in ZnO. *Appl. Phys. Lett.* 87, 122102 (2005).
22. Du, M.-H. & Biswas, K. Anionic and Hidden Hydrogen in ZnO. *Phys. Rev. Lett.* 106, 115502 (2011).
23. Park, C. H. & Chadi, D. J. Hydrogen-Mediated Spin–Spin Interaction in ZnCoO. *Phys. Rev. Lett.* 94, 127204 (2005).
24. Adolph, B., Furthmüller, J. & Bechstedt, F. Optical properties of semiconductors using projector-augmented waves. *Phys. Rev. B* 63, 125108 (2001).
25. Takenaka, H. & Singh, D. J. Bonding of H in O vacancies of ZnO: Density functional calculations. *Phys. Rev. B* 75, 241102(R) (2007).
26. Kresse, G. & Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* 6, 15–50 (1996).
27. Blochl, P. E. Projector augmented-wave method. *Phys. Rev. B* 50, 17953–17979 (1994).
28. Kresse, G. & Joubert, J. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* 59, 1758–1775 (1999).
29. Heyd, J., Scuseria, G. E. & Ernzerhof, M. Hybrid functionals based on a screened Coulomb potential. *J. Chem. Phys.* 118, 8207–8215 (2003).
30. Oba, F., Togo, A., Tanaka, I., Paier, J. & Kresse, G. Defect energetics in ZnO: A hybrid Hartree-Fock density functional study. *Phys. Rev. B* 77, 245202 (2008).
31. Lyons, J. L., Janotti, A. & Van de Walle, C. G. Why nitrogen cannot lead to p-type conductivity in ZnO. *Appl. Phys. Lett.* 95, 252105 (2009).
32. Madelung, O. *Semiconductors- Basic Data* (Springer, Berlin, 1996).

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**Author contributions**

H.N. suggested the original main idea of this work and performed all calculations. C.P. and H.N. wrote the main manuscript text and Y.K. provided some ideas and wrote some manuscript parts. All authors reviewed the manuscript.

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