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Role of diatomic hydrogen in the electronic structure of ZnO

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According to the traditional point of view, interstitial H in ZnO is a shallow donor. We report that the feature can be inhibited by another interstitial H. Although there is a chemical bonding between the two H atoms, they cannot necessarily be considered as a H_2 molecule: one of the H atoms is tightly bonded into the nearest O and forms the O-H complex, the other H atom forms a chemical bond with the nearest Zn and these bonds are stronger than the H-H bond. The defect molecule can be called a H_2^* complex and it forms a deep energy level in the band gap. At Fermi levels closer to the conduction-band minimum, the complex is found to be more stable than the two distant H atoms. We discuss the role of H_2^* in electronic structure, optical, and electrical properties of ZnO. In particular, formation of the H_2^* complex provides a natural limitation for the *n*-type doping of ZnO by H.

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I. INTRODUCTION

Hydrogen is one of the commonly used impurities in wide band-gap semiconductors.[1–7] Distinct from its amphoteric behavior in other semiconductors, in ZnO, H possesses a unique feature such as always being a shallow donor and enhance electrical conductivity when it is at the interstitial site around O atom[1–3,8,9] and at the O vacancy site[1,10,11]—being an acceptor when it substitutes Zn site—a passivator of shallow acceptors of Li (Ref. 12) and N.[13] H is also found to exist in hidden form, which cannot be detected by infrared (IR) spectroscopy and does not give rise to free carriers at room temperature.[14–16] Several other experimental findings are suggested to be caused by the "hidden H." Some of them are: (i) decrease in the concentration of the O-H complex responsible for shallow donor level and bimolecular character of the decrease,[14,16] (ii) discrepancy in concentration of H determined by secondary-ion mass spectroscopy (SIMS) from that of free electrons measured by Hall method,[17] and (iii) a flat region in the dependence of concentration of free electrons on the pressure of the H_2 gas.[17] The reason why electron concentration is larger in the near-surface regions of the H plasma-treated thin films and of crystalline ZnO (Ref. 18) than that in the bulk crystalline ZnO is not clear. Although it was shown recently that H diffuses from ZnO at temperatures ≥ 600 °C,[19] the I_4 line exits at the elevated temperatures and the result has been ascribed to thermally stable H or H trapped at secondary defect.[7]

It should be noted that H_2 molecule is suggested to be the candidate for the "hidden H."[15,16] However, in IR spectroscopy, no line near 4000 cm^{-1} corresponding to the H_2 was observed.[15,20] Furthermore, the formation energy of both H_2^* complex[21] and H_2 (Ref. 3) in ZnO is shown to be large and, therefore, unstable. The diatomic H complexes have also been studied before in other semiconductors, such as, e.g., Si,[22–25] GaP,[26] and GaAs (Ref. 27) and it is found to be unstable in the latter two compounds. Incorporation of N into GaAs and GaP is predicted to increase stability in H_2^* and H_2.[26,27] Experimental and theoretical results suggest (see, e.g., Refs. 23, 25, 28, and 29 and references therein) that in hydrogenated amorphous (*a*-Si:H) and crystalline Si H predominantly bonds to the Si network in diatomic pairs. The H_2^* configuration, consisting of a bond-centered H and a H located at an adjacent antibonding site, is found to be low in energy and plays an important role in electronic structure of Si by forming the Si{111} platelet structures and is responsible for metastability of *a*-Si:H. It should be noted that at Fermi levels close to conduction-band (CB) minimum, the diatomic H complex in ZnO can be even more stable than positively charged H.[3,21] For this particular case, the role of the H complex in electronic structure and electrical and optical properties of ZnO was not studied. In this paper, we explore this problem. We found that: (i) although there is a chemical bonding between two H atoms, they cannot necessarily be considered as a H_2 molecule because the Zn-H and O-H chemical bonding is stronger than the H-H bond; (ii) the defect molecule can be called as H_2^* complex, which can form a deep trap level; (iii) at Fermi levels closer to CB minimum, formation of the H_2^* complex is energetically more preferable than two distant H atoms; and (iv) in strained part of ZnO, e.g., around voids and grain boundaries, the distant H is energetically more preferable than H_2^*.

II. COMPUTATIONAL DETAILS

The computations have been performed using the Vienna *ab initio* simulation package (VASP).[30,31] We used the generalized-gradient approximation (GGA), following the Perdew-Bueke-Ernzerhof scheme (PBE),[32] for the exchange-correlation functional and with the multiorbital mean-field Hubbard potential GGA+*U*. Non-norm-conserving pseudopotentials, generated in accordance to the projector augmented-wave (PAW) method,[33,34] have been used. It allowed us to construct orthonormalized all-electronlike wave functions for the Zn-3*d*, −4*s*, O-2*s*, and −2*p*, H-1*s* valence electrons.

The lattice was fully relaxed using the conjugate gradient method. Plane-wave cutoff of 500 eV is employed to ensure the convergence in our calculations, which is found to be sufficient to reproduce ground-state and high-pressure structural properties. The convergence was achieved when the

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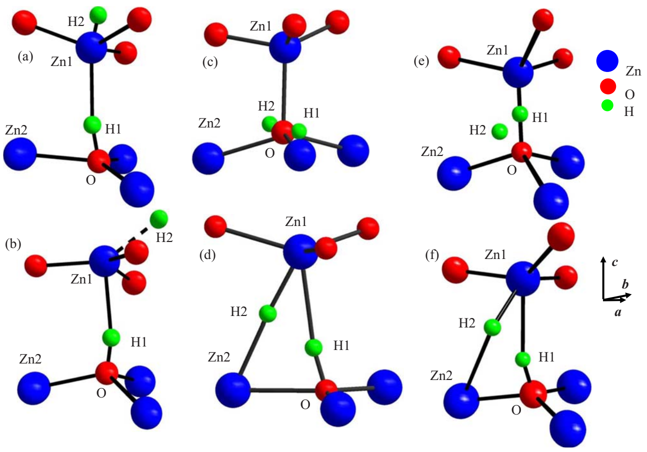

FIG. 1. (Color online) Schematic presentation of (a), (c), (e) unrelaxed and (b), (d), (f) relaxed lattices of ZnO with two H atoms for (a)–(d) $2\times2\times2$ and (e) and (f) $3\times3\times2$ supercells.

forces acting on the atoms were smaller than 10 meV $Å^{-1}$ and the total-energy difference between two consecutive iterations was $<10^{-6}$ eV.

It is well known that in the calculations by density-functional theory (DFT) within GGA, the Zn 3d bands are located inappropriately close to the topmost valence band (VB) of ZnO, hybridizing with the O 2p band, falsifying the band dispersion, reducing the band gap, modifying the spin-splitting and crystal-field energies, and changing the order of states at the topmost valence band. The problem has partially been solved[35–37] by using the GGA+U,[33,34] which requires explicit values of the parameters U and J as input. Analysis of literature (see, e.g., Refs. 35–37) shows that the calculated band parameters can be more within reasonable limit for U $=6$ eV and $J=1$ eV.

The changes in energy levels of the H_2^* in the band gaps E_t^{GGA} and $E_t^{\text{GGA}+U}$, coming out from GGA and GGA+U, reflect their character relative to VB and CB. Therefore, to estimate the correct value of energy level E_t of H_2^*, we use the following extrapolation:

$$E_t = E_t^{\text{GGA}+U} + \frac{E_t^{\text{GGA}+U} - E_t^{\text{GGA}}}{E_g^{\text{GGA}+U} - E_g^{\text{GGA}}} \times (E_g^{\text{Expt}} - E_g^{\text{GGA}+U}). \quad (1)$$

Here E_g^{GGA} and $E_g^{\text{GGA}+U}$ are the band gaps obtained from calculations within GGA and GGA+U, whereas E_g^{Expt} is the experimental band gap of ZnO. Equation (1) has previously been used by many authors (see, e.g., Ref. 38) for calculating the defect transition level. The computations have been performed for $2\times2\times2$, $3\times3\times2$ (Fig. 1), $3\times3\times3$, and $4\times3\times2$ supercells, which correspond to H concentrations of 4.9×10^{21}, 2.2×10^{21}, 1.5×10^{21}, and 1.7×10^{21} cm^{-3}, respectively.

Formation energy of H_2^* in ZnO has been calculated as[38]

$$E^f(D^q) = E_{\text{tot}}(D^q) - E_{\text{tot}}(\text{ZnO,bulk}) - n_H\mu_H + qE_F. \quad (2)$$

Here $E_{\text{tot}}(D^q)$ and $E_{\text{tot}}(\text{ZnO,bulk})$ are the total energies of the lattice with an impurity D in charge state q and of the perfect ZnO, respectively. E_F is the Fermi energy. μ_{H} is the chemical potential of H and n_{H} is the number of H atoms in the supercell. Dissociation energy for H_2^* has been calculated as difference of $E_{\text{tot}}(D^q)$ for ZnO with H_2^* from that with two distant H atoms.

III. RESULTS

We have performed structural study for the following three models with two H atoms (H1 and H2) in a unit cell. One of them, to be called hereafter as two distant H, H1, and H2, has been located at two different Zn-O bonds aligned with the c axis and located from each other at a distance of 9.98 Å. Electronic studies show that the two distant H atoms form shallow donor level in the band gap, in agreement with the theoretically and experimentally established result (see, e.g., Ref. 39).

The other model is similar to β-H_2^* modification of diatomic H in GaP.[26] In the model, H1 is located at Zn-O bond center whereas H2 is at antibonding site near to Zn [Fig. 1(a)]. Upon relaxation, H1 has been shifted closer to nearest O thus forming O-H complex while H2 has been moved toward nearest Zn atoms [Fig. 1(b)]. Total energy for β-H_2^* is smaller than that for two distant H to ~0.06 eV and is also a donor.

In the third model, to be called hereafter as H_2^* complex, both H1 and H2 of the unrelaxed lattice are located in the close vicinity of the same O atom [Figs. 1(c) and 1(e)]. Upon relaxation H1 has been moved to the Zn-O bond along c axis, whereas H2 has been shifted to antibonding site closer to H1 [Figs. 1(d) and 1(f)]. Total energy of the system is smaller than that with two distant H atoms to ~0.5 eV. In the configuration H1 and H2 remind a H_2 molecule. However, as we show later, it can be called a H_2^* complex rather than H_2 molecule. The nearby Zn and O atoms have been shifted drastically out of their positions in the equilibrium lattice. The displacements of the O, Zn1, and Zn2 atoms from their positions corresponding to ideal lattice, as well as bond lengths for Zn1-H2, H2-Zn2, H1-O, and H1-H2, have been presented in Table I. Analysis of Table I shows that the H1-H2 bond calculated in the present work is larger than 0.798 Å,[3] 0.770 Å,[20] and 0.782 Å for the free H_2 molecule. Also, in all the supercells considered, the Zn1-H2, O-H1, and H1-H2 bond lengths are almost the same. As we demonstrate later, the calculated energy band of the diatomic H complex is also almost the same for all the supercells considered. This indicates that the Zn1-H2, O-H1, and H1-H2 bonds can be responsible for the H diatomic complex bands.

To know the influence of the H_2^* complex in electronic structure of ZnO, we have studied total density of states (DOS) (Fig. 2). It is seen that a deep well-localized band has been formed. From computations within GGA and GGA+U, it is found [using Eq. (1)] that the band is located at 0.75 eV above the VB of ZnO. Width of the band is 0.70 eV and it is completed by electrons. Analysis of orbital and site projected DOS shows that H1, H2, and the O atom located near to H1 are responsible for the deep trap derived band. The above result can be consistent by several experimental findings. One of them is the result related to H-related deep trap[39] (located at 0.90 eV) found from deep level transient spectroscopy (DLTS) measurements and wide defect green

TABLE I. Calculated displacements Δ (in Å) of Zn and O atoms located in close vicinity of the diatomic H complex as well as bond lengths d (in Å) for Zn1-H2, Zn2-H2, O-H1, and H1-H2.

	O	Δ_{Zn1}	Δ_{Zn2}	$d_{\mathrm{Zn1\text{-}H2}}$	$d_{\mathrm{Zn2\text{-}H2}}$	$d_{\mathrm{O\text{-}H1}}$	$d_{\mathrm{H1\text{-}H2}}$
$2\times2\times2$	0.70	0.47	0.19	1.625	1.939	1.009	1.280
$3\times3\times2$	0.58	0.52	0.22	1.652	2.674	1.029	1.258
$4\times3\times2$	0.49	0.49	0.22	1.675	2.727	1.028	1.271
$3\times3\times3$	0.62	0.45	0.11	1.645	2.240	1.012	1.301

band located in the energy range from 2.0–2.8 eV determined from microcathodoluminescence studies. The other one is the reduction in the intensity of near-gap emission by more than three orders of magnitude in room-temperature cathodoluminescence of ZnO, even for a dose of 10^{15} cm^{-2} ^{1}H^{+} ions.[40] The increase in electrical resistance by about seven orders of magnitude was experimentally observed in Refs. 41 and 42, which has been explained by generation of ion irradiation-induced traps. The H_2^* complex can be a candidate for the traps.

Although the spatially well-separated H atoms are shallow donors, those located very close to each other in pure stoichiometic ZnO can passivate each other and form deep energy levels in the band gap. So, such a H_2^* complex can—probably—be one of the candidates for the "hidden H." It can also explain the reason of the experimental results as to: (i) why the concentration of H atoms determined from SIMS is larger than that of free electrons found by Hall measurements[17] and (ii) why the concentration of the O-H shallow donor complexes decreases with increasing the time.[16]

To clarify whether H1 and H2 in Fig. 1(d) is a molecule or not, we have analyzed charge density and electron localization function (ELF) [Figs. 3(a) and 3(b)]. It is seen that chemical bonding of ZnO in close vicinity of H1 and H2 has been basically reconstructed. The Zn1-O bond has been broken and the strong H1-O complex has been formed [Fig. 3(a)], thus, weakened the Zn2-O bond. The H2 atom forms chemical bond with the nearest Zn atom and these bonds are stronger than the H1-H2 bond. Analysis of Fig. 3(a) shows that both H1 and H2 are negatively charged. ELF analysis [Fig. 3(b)] confirms this point and is in agreement with orbital and site projected DOS analysis. In Figs. 3(a) and 3(b) one can see Zn1-H2-Zn2, H1-H2, Zn2-O, and H2-O bonds. In the $3\times3\times2$ supercell only one Zn1-H2 bond has been formed. These analyses show that the defect molecule in Figs. 1(d) and 1(f) can be called as H_2^* complex rather than H_2 molecule. For quantitative analysis, we have calculated the charge around the atoms incorporated into the H_2^* complex. We found that the charge is equal to +1.16 for Zn1, +1.20 for Zn2, −0.57 for H1, −0.68 for H2 as well as −0.23 for O atoms.

For the analysis of stability, we have studied dependence of total energy E_{tot} on volume V [Fig. 4(a)] for ZnO with H_2^* complex and two distant H atoms. It is seen that the former is more stable than the latter. Consequently, the H_2^* complex is the energetically preferable state for H atoms. This result explains the reason of experimental findings of Ref. 16, regarding why concentration of the O-H complex decreases according to bimolecular model.

Analysis of Fig. 4(a) shows that at large volumes, the two dependencies $E_{\mathrm{tot}}(V)$ intersect each other. It indicates that when ZnO is well strained, the H-related complex can become less stable than the distant ones. Consequently, one can expect that the H_2^* complex can exist only in that part of ZnO, which is not strained well. Around voids, grain boundaries, dislocations, etc., which can be the source of the strained ZnO with elongated Zn-O bonds, the formation of the H_2^* complex is less probable. In such places for H, the preferable configuration is existence separate from each

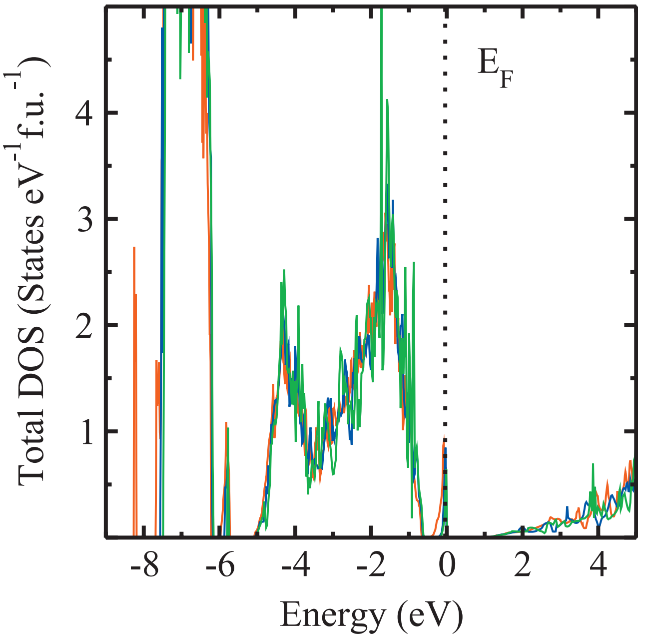

FIG. 2. (Color) Total DOS for optimized ZnO unit cells with two H atoms located closely to each other for the $2\times2\times2$ (red color), $3\times3\times2$ (blue color), and $3\times3\times3$ (green color) supercells.

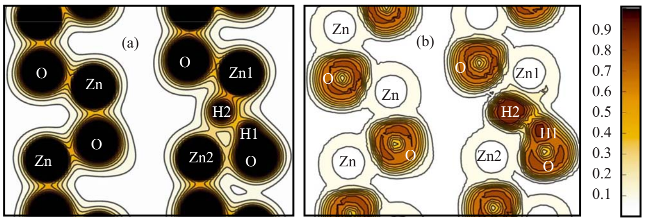

FIG. 3. (Color online) (a) Charge density and (b) ELF for $2\times2\times2$ supercell of ZnO with two H atoms located closely to each other.

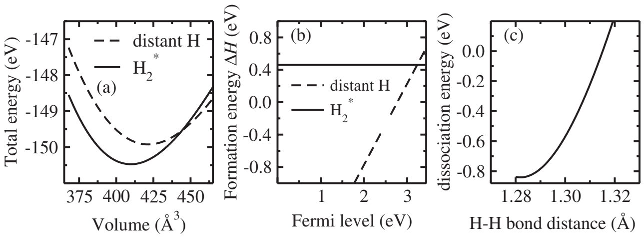

FIG. 4. (a) Dependence of total energy on volume for two types of unit cells of ZnO with H-related complex and two spatially well-separated H atoms. (b) Formation energies of H_2^*-complex and single H in ZnO as a function of Fermi level. (c) Dependence of dissociation energy of the H_2^* complex on H-H bond distance.

other. This result explains the reason of the experimentally established findings of Refs. 39 and 40 as to why concentration of electrons in the near-surface regions of the H plasma treated *n*-ZnO crystals and thin films is considerably larger than that in the bulk. Furthermore, concentration of electrons in the surface region of H-plasma treated, good quality ZnO is found[40] to be in one-to-one correspondence with the H concentration determined from SIMS. However, in the bulk ZnO, H concentration found from SIMS is much larger than free-electron concentration found from Hall measurements.

Figure 4(b) displays formation energy calculated by Eq. (2) for H_2^* complex and single H. It is seen that at high doping levels by H, corresponding to location of Fermi level considerable close to CB minimum, H_2^* becomes more stable than positively charged single H. This result is in agreement with that of Refs. 3, 20, and 21.

Figure 4(c) demonstrates dissociation energy ΔE_d calculated as the difference of total energies for the unit cell with the H-related complex and separated from each other, H as a function of the H-H $L_{\text{H-H}}$ distance. It is seen that absolute value of ΔE_d decreases with increasing $L_{\text{H-H}}$. However, at small H-H distances ~ 1.2 Å, $\Delta E_d \approx 0.92$ eV. This result is in agreement with that of Refs. 43 and 44, which reported about ~ 1.0 eV diffusion activation energy of H derived from effusion data. Furthermore, an increase in electrical conductivity of ZnO has been observed[45,46] at temperatures >200 °C due to indiffusion of H with activation energy of 0.91 (Ref. 46) and 1.12 eV.[45] The large value of the binding energy indicates that annealing of ZnO even at ~ 600 °C can be insufficient to remove H completely. Hence, the H_2^* complex can be one of the candidates, which is responsible for reduction in the intensity of near-gap photoluminescence after 700 °C anneals. Such complex has been previously ascribed to the H-implantation-induced recombination centers.[40] The I_4 line of the bound-exciton luminescence, which has been reduced at >600 °C,[47] can be attributed to stable H complex which can be the H_2^*.

Since single H atoms are mobile at moderate temperatures, they can easily form the quite stable H_2^* complexes with large dissociation energy. As a result, surface blistering in ZnO can require larger fluencies of H than those in Si. This suggestion is consistent with recent experimental finding of the H-implantation-induced exfoliation of ZnO at $\geq 2.8 \times 10^{17}$ cm^{-2}.[48]

The above results related to inhibition of shallow donor feature of the interstitial H by another interstitial H in ZnO are similar to those well known as passivation of donors by H in Si,[49–52] dilute nitrides,[53] etc.

IV. CONCLUSION

In conclusion, we have found that the shallow donor feature of interstitial H can be inhibited by another interstitial nearby H. It is shown that although there is a chemical bonding between two H atoms, they cannot necessarily be considered as a H_2 molecule because the Zn-H and O-H bonds are stronger than the H-H bond. The defect molecule can be called as H_2^* complex, which can form a deep trap level in the band gap and can be responsible for modulation of electrical and optical properties of ZnO. At Fermi levels closer to CB minimum, formation of the H_2^* complex is energetically more preferable than two distant H atoms. We show that in strained part of ZnO, e.g., around voids and grain boundaries, the distant H atoms are energetically more preferable than the H_2^* complex. Formation of the complex can be one of the reasons for the doping limit in ZnO (saturated by atomic H) and for high H fluencies to cause H-implantation-induced exfoliation.

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