Hydrogen complexes in Zn deficient ZnO

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This work presents a study of H complexes in Zn deficient ZnO by density functional calculations. It is found that the location of two H atoms at the Zn vacancy $\left(V_{Zn}\right)$ is energetically more preferable than the distant H and V_{Zn}. Each of the two H atoms saturates one dangling O bond by forming a $O-H$ bond. The resulting defect can be considered as $2\left(O-H\right)-V_{Zn}$ complex. Since there are four O dangling bonds at the V_{Zn}, the site can host four H atoms. It is shown that V_{Zn} with four H atoms is energetically more preferable than distant H and V_{Zn}. Depending on the number of H atoms at the V_{Zn}, the influence of the H-V_{Zn} system on the electronic structure of Zn deficient ZnO can be qualitatively different. V_{Zn} without a H is a double acceptor, and V_{Zn} containing one H, i.e., $1\left(O-H\right)-V_{Zn}$ complex, is a single acceptor. ZnO with $2\left(O-H\right)-V_{Zn}$ complexes is insulator with Fermi level located at the top of the valence band. A donor level is formed by the $3\left(O-H\right)-V_{Zn}$ and $4\left(O-H\right)-V_{Zn}$ complexes. Two H involved into $2\left(O-H\right)-V_{Zn}$, $3\left(O-H\right)-V_{Zn}$, and $4\left(O-H\right)-V_{Zn}$ complexes do not contribute to free carrier concentration and will cause discrepancy in the free electron and H concentrations. The influence of the complexes on the electrical and optical properties of ZnO is discussed.

1. Introduction

ZnO has attracted much attention because of its many useful technological applications for optoelectronic, transparent, and spintronic devices. H plays an exceptionally important role in the applications.[1-8] The role of H as a shallow donor at the interstitial H_i and O vacancy sites has been supported by theoretical[1-3] and experimental[9, 10] studies. Recently, it was reported that H in ZnO can exist in hidden[11-13] or diatomic complex H_2^* form[8] also, which do not contribute to free electron concentration at room temperature. In the regions of ZnO, which do not contain structural point defects or impurities other than the H, the complex H_2^* is found to be energetically more preferable than distant H atoms providing shallow donor levels. The "hidden" H and H_2^* can cause decrease of the free electron concentration with time according to the bimolecular law,[11, 13] discrepancy in the concentration of H determined by SIMS from that of free electrons measured by Hall method,[14] can form deep traps responsible for green luminescence,[8] etc. These findings indicate that "hidden" H and the H_2^* complex can be detrimental for device applications of ZnO. The "hidden" H can be annealed at temperatures near 400 °C.[13] However, dissociation energy of the H_2^* complex is large ~0.92 eV, which means that it can be annealed out at much higher temperatures than 400 °C. These findings create the necessity for the search of the alternative ways, when the shallow donor H is energetically more preferable than the H_2^* complex or "hidden" H. One of such ways is creation of structural defects or incorporation of impurities into ZnO. Analysis of literature shows that similar way has been used before. For example, upon doping with N, the H_2^* complex becomes more stable than H_2 molecule in GaP,[15] and in

GaAsN.[16] Earlier it was reported that that formation energy of O vacancy and Zn interstitial in ZnO are large.[17] However, it can be reduced by doping with N, which leads to formation of the Zn_i-N_O complex.[18] In the present paper we follow this experience and study the problem as to whether the H_2^* in ZnO remains to be the energetically most favourable complex around Zn vacancy V_{Zn}.

2. Computational details

The Vienna *ab initio* simulation package (VASP)[19, 20] has been used for the computations within the generalized-gradient approximation (GGA) following the Perdew-Burke-Ernzerhof scheme (PBE)[21] for the exchange-correlation functional and with the multiorbital mean-field Hubbard potential GGA+*U*. The latter approximation requires explicit values of the parameters *U* and *J* to account for orbital dependence of the Coulomb and exchange interactions, which is absent in the GGA. Analysis of literature (see, e.g. Refs.[22-24]) shows that the calculated band parameters can be more accurate if the values *U*=6 *eV* and *J*=1 *eV* are chosen, and these values are, therefore, used herein.

Non-norm-conserving pseudopotentials generated in accordance to the projector-augmented-wave (PAW) method[25, 26] have been used. It allowed us to construct orthonormalized all-electron-like 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 cut-off 500 eV is employed to ensure the convergence which is sufficient to reproduce ground state and high pressure structural properties. The convergence was achieved when the forces acting on the atoms were smaller than 10 meV $\mathring{A}^{-1}$. Bulk ZnO

in the wurtzite phase was used in the computations with the following optimized lattice parameters $a=b\approx3.244$ Å, $c/a\approx1.550$ Å, and $u\approx0.389$ in satisfactory agreement with experimentally determined parameters $a=b\approx3.250$ Å, $c/a\approx1.602$ Å, and $u\approx0.382$.[2]

The computations have been performed for 3×3×2 and 4×3×2 supercells of ZnO, containing two H atoms, which correspond to H concentrations of $\sim2.2\times10^{21}$ and $\sim1.7\times10^{21}$ cm^{-3}, respectively. Different locations of H and V_{Zn} have been analysed. In the first of them, hereafter denoted as V_{Zn}, H_i, H_i the two H atoms have been located at two different interstitial sites H_i on Zn-O bonds aligned with the c-axis far away each from other and from V_{Zn}. Throughout the paper such defects shall be called as distant defects. The second configuration, denoted as V_{Zn}, H_2^*, contains a distant H_2^* (Fig. 2 (a)) and V_{Zn}. In the third configuration, one H atom is located at V_{Zn} and forms one $(O-H)$ complex (Fig. 1 (b)), whereas the other H is located at the interstitial site H_i. The complex is denoted as $1(O-H)-V_{Zn}$, H_i. In the fourth configuration denoted as $2(O-H)-V_{Zn}$, both H atoms have been located at the V_{Zn} site. Each of them forms an $(O-H)$ bond (Fig. 1 (c)).

3. Results

Dependence of the total energy E_{tot} of the system on volume V has been studied for the optimized structures. The magnitude of E_{tot} and V corresponding to minimum of the dependence $E_{tot}(V)$ is considered as the ground state total energy E_{tot}^{eq} and the equilibrium volume V_{eq}. Figure 2 (a) displays the results for the 3×3×2 supercells of ZnO

with two H and V_{Zn}. Analysis of Fig. 2 (a) shows that V_{eq} is almost the same for all the

defect configurations, whereas E_{tot}^{eq} vary in the following sequence in decreasing order:

$$E_{tot}^{eq}\left[V_{Zn}, H_2^*\right] > E_{tot}^{eq}\left[V_{Zn}, H_i, H_i\right] > E_{tot}^{eq}\left[1(O-H)-V_{Zn}, H_i\right] > E_{tot}^{eq}\left[2(O-H)-V_{Zn}\right].$$

Consequently, the latter configuration possesses the smallest E_{tot}^{eq} and it can be

considered as the energetically most favourable one. It is even more stable than the H_2^*

complex, which is the most stable configuration in the regions of ZnO without any

defects and impurities other than H.

It should be noted that before optimization of the lattice with $2(O-H)-V_{Zn}$, the

H atoms have been in the close vicinity to the center of V_{Zn}. After relaxations of the

lattice, each of the H atoms have been shifted towards their nearest O neighbours and

saturate their dangling bonds leading to formation of two $O-H$ complexes. The

corresponding $O-H$ bond length ~0.99 Å is in good agreement with 0.998 Å

calculated[27] by DFT. Since at the V_{Zn} site there are four O dangling bonds, one can

expect that V_{Zn} can host up to four H atoms. To check whether such a system can be

stable, we have studied 3×3×2 ZnO supercells containing a V_{Zn} and four H atoms. In the

first configuration $4(O-H)-V_{Zn}$ all four H atoms are located at the V_{Zn} site and form

four $(O-H)$ complexes. The other configuration denoted as $3(O-H)-V_{Zn}$, H_i consists

of distant $3(O-H)-V_{Zn}$ (Fig. 1 (d)) and H_i. The third one denoted as $2(O-H)-V_{Zn}$,

H_i, H_i consists of distant $2(O-H)-V_{Zn}$ (Fig. 1 (c)) and two H_i. Figure 2 (b) presents

the dependence $E_{tot}(V)$ for these defect configurations. Analysis of Fig. 2(b) shows that

V_{eq} is almost the same for the three cases considered. E_{tot}^{eq} decreases in the following

sequence: $E_{tot}^{eq}[2(O-H)-V_{Zn}]<E_{tot}^{eq}[3(O-H)-V_{Zn}]<E_{tot}^{eq}[4(O-H)-V_{Zn}]$. Hence, $4(O-H)-V_{Zn}$ is the most stable configuration. It is energetically more preferable for the V_{Zn} to host four H atoms than formation of the distant V_{Zn} and $4H_i$. The dissociation energy required to release a H atom is equal to 1.1 eV for $3(O-H)-V_{Zn}$ and 0.8 eV for $4(O-H)-V_{Zn}$.

Analysis of literature shows that V_{Zn} in ZnO is a double acceptor. However, the influence of V_{Zn} populated by H, i.e. the complex $m(O-H)-V_{Zn}$, on the electronic structure of ZnO depends on number of H atoms (m=1, …, 4) at the V_{Zn} site. Figure 3 presents the total density of states (DOS) for ZnO containing $m(O-H)-V_{Zn}$ (m=1, …, 4). It is seen that $1(O-H)-V_{Zn}$ is a single acceptor. However, $2(O-H)-V_{Zn}$ does not have any level in the band gap of ZnO. Furthermore, it is consistent with previous theoretical[28] and experimental[27] findings. This result is supported by cathodoluminescence studies of ZnO,[29] which reported about suppression of green luminescence centered around 2.2 eV after H plasma treatment at 400 $^{\circ}$C. According to DFT calculations,[17] the origin of the luminescence is, probably, related to V_{Zn}. Reduction of the green luminescence and appearance of $2(O-H)-V_{Zn}$ related local vibrational modes has been observed after H treatment[27] as well. The dissociation energy of the above-mentioned H-V_{Zn} complexes has been estimated and found to be equal to 0.8 eV for $1(O-H)-V_{Zn}$ and 1.1 eV for $2(O-H)-V_{Zn}$ per H atom. Similar to "hidden" H and diatomic H_2^* complex, $2(O-H)-V_{Zn}$ does not contribute to free electron concentration.

The complexes $3(O-H)-V_{Zn}$ and $4(O-H)-V_{Zn}$ form donor levels. Analysis of band occupancy and band decomposition shows that in the latter three configurations, the two H atoms do not form any levels in the band gap and do not contribute to free electron concentration. This is one of the distinguishing features of the $2(O-H)-V_{Zn}$ complex from the diatomic H_2^* complex, which forms a deep trap band.

One of the interesting points to be discussed is the influence of the above mentioned H complexes on the electrical conductivity σ in the dark. Below, such an analysis shall be performed for ZnO with $m(O-H)-V_{Zn}$ (m=1, …, 4) and V_{Zn} with concentrations N_m m=1, …, 4 and $N_V = \sum_{m=0}^{4} N_m$, respectively. Here N_0 is the concentration of V_{Zn} without a H atom. The net H concentration is N_H. Kinetics of population of V_{Zn} with different number of H atoms can de described by the following system of equations

$$\frac{dN_m}{dt} = -\left(\sum_{m \neq n} a_{mn}\right)N_m + \left(\sum_{n \neq m} a_{nm}\right)N_n . \tag{1}$$

Here the first term describes capture/dissociation of one H atom to/from $m(O-H)-V_{Zn}$ (m=0, …, 4) whereas the second term corresponds to reverse process characterized by the coefficients a_{mn} and a_{nm}, respectively. The processes described in the Eq. (1) are schematically shown in Fig. 4.

Kinetics of electrical conductivity σ is strongly affected by that of N_m, which is connected to free electron and hole concentrations n and p through the electroneutrality condition

$$n + N_1 + N_t \frac{n}{n + n_1} + N_0 \frac{n}{n + n_V} = p + N_3 + 2N_4 + N_i. \qquad (2)$$

Here N_i is the concentration of interstitial H, N_t is the concentration of the diatomic H_2^* complex. n_1 and n_V are the concentration of electrons, when Fermi level coincides with energy level of H_2^* and V_{Zn}, respectively. Analysis of Eqs. (1) and (2) shows that variation of σ with increasing N_H can be complicated. Similar to H_2^*, the $m(O-H)-V_{Zn}$ (m=2, 3, 4) complex in Zn deficient ZnO can result in a discrepancy between the H and free electron concentrations. For $N_V < 4 N_H$, the V_{Zn} sites can be filled with four H atoms. The remaining H located at interstitial sites can form H_2^* or "hidden" H complexes. Then, σ can decrease with further increasing N_H up to the level determined by $N_V = 4 N_H$. For $N_V > 4 N_H$, V_{Zn} and the $m(O-H)-V_{Zn}$ (m=2, 3, 4) can co-exist. In un-annealed samples distant V_{Zn}, H_i, and $m(O-H)-V_{Zn}$ (m=1, ..., 4) can co-exist as well. Since the distant V_{Zn} and H_i are not the energetically preferable states, upon time they can be converted into more stable ones. For example, H can move to V_{Zn} site thus reducing the V_{Zn} induced green luminescence and enhancing p-type electrical conductivity, which is also unstable. The complex can be transferred to more stable $3(O-H)-V_{Zn}$, and then $4(O-H)-V_{Zn}$, thus providing n-type electrical conductivity. So, upon increasing the time conversion of electrical conductivity type from n-type to p-type takes place.

4. Conclusion

Thus by DFT calculations it is shown that location of the diatomic H at the zinc vacancy V_{Zn} site is energetically more favourable than the other possible locations. At V_{Zn}, each of the H saturate dangling O bonds by forming $O-H$ bonds. The configuration is the most stable one than the other configurations, e.g., distant V_{Zn} and diatomic H_2^*, which is the most stable one in stoichiometric ZnO. Since there are dangling bonds at all four O atoms at the V_{Zn} site, four H atoms are found to be hosted by the site, which is energetically more preferable than the other modifications of the V_{Zn}-H_i system. It is shown that influence of V_{Zn} sites with different numbers of H atoms on the electronic structure of ZnO can qualitatively differ each from other. ZnO possesses an acceptor level if only one H is at V_{Zn}. Two H at the V_{Zn} can produce no level in the band gap and thus providing insulating behaviour. The V_{Zn} with three or four H atoms contribute to free electron concentration. However, two the H atoms do not participate in the contribution. V_{Zn} and H_2^* related deep trap and related luminescence can always be available, which reduces transparency of the samples in visible region of the solar spectra. Concentration of free electrons and H can differ each from other.

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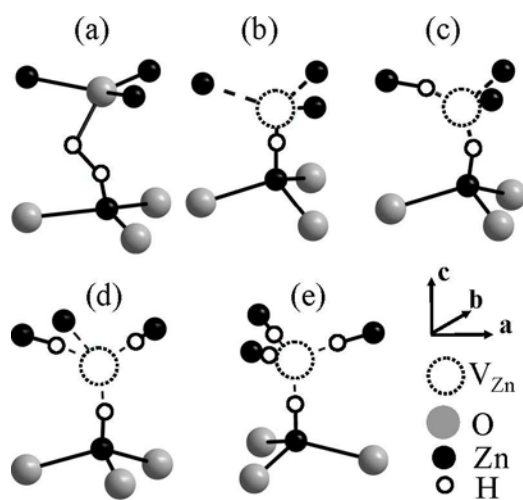[29] T. Sekiguchi, N. Ohashi, and Y. Terada, Jpn. J. Appl. Phys. P.2 - Lett. **36**, L289 (1997).

Fig. 1. Schematic presentation of H-V_{Zn} defect complexes in relaxed lattices of ZnO 3×3×2 supercells: (a) H_2^*, (b) $1(O-H)-V_{Zn}$, (c) $2(O-H)-V_{Zn}$, (d) $3(O-H)-V_{Zn}$, and (e) $4(O-H)-V_{Zn}$.
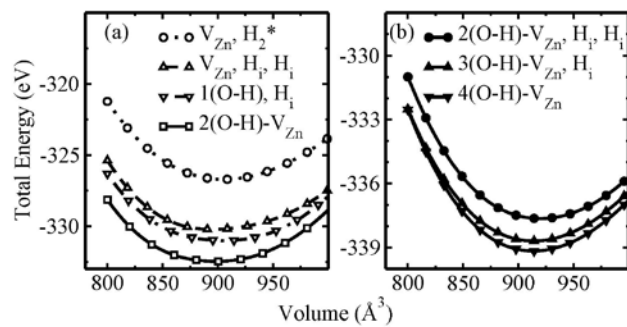
Fig. 2. Dependence of total energy on volume for 3×3×2 supercells of ZnO for different configurations of V_{Zn} and (a) two H, and (b) four H.
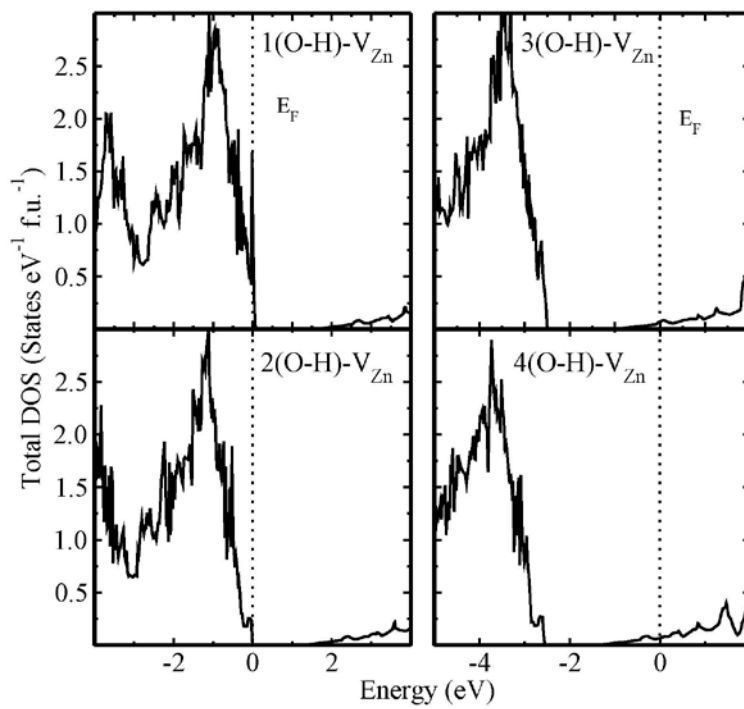
Fig. 3. Total DOS for ZnO with different number of H atoms at the V_{Zn}. Fermi level E_F is set to zero.
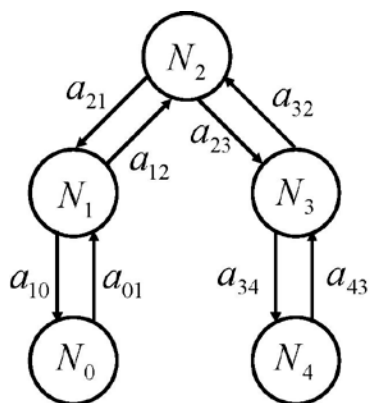
Fig. 4. Schematic presentation of transferring of V_{Zn} with m=0, …, 4 H atoms into another state characterized by increased or reduced to one H atom.