Stability of diatomic hydrogen in oxygen deficient ZnO

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In recent studies it is reported that "hidden" H and diatomic H complex H_2^* do not contribute to free electron concentration and are more stable than distant interstitial H providing shallow donor level in the band gap of ZnO. Dissociation energy of these complexes is large and they can be annealed out upon heating at elevated temperatures. Here we report comparative analysis of stability of different configurations of diatomic H and oxygen vacancy V_O in O deficient ZnO. It is found that in O deficient environment two spatially separated H, one occupying the interstitial site H_i and the other one substituting the O atom H_O, which form shallow donor levels, can be energetically more favourable than the H_2^* complex and other possible locations of H and V_O.

1. Introduction

ZnO has attracted much interest because of its applications in optoelectronic devices and it is established that oxygen vacancy (V_O) and H play important role in its electrical and optical properties.[1-10] The V_O is reported to have a low formation energy leading to O deficiency.[1] Furthermore, V_O has a metastable shallow state, explaining the paradoxical co existence of coloration and conductivity.[1] Using the corrected formation energy by thermodynamic simulations defect and carrier concentrations have been studied as a function of growth temperature.[1] The origin of the green luminescence of ZnO has been attributed, in particular, to V_O.[11-13] In theoretical studies by the density functional theory (DFT) there existed uncertainty in transition energy between 2+/0 charge states of V_O,[14-15] which was found to be in lower half (Ref. [16]) or upper half (Ref. [17]) of the band gap of ZnO. This uncertainty has been removed by all electron calculations within the local spin density approximation,[15] which showed that the transition is in lower half of the band gap.

Shallow donor role of H located at the interstitial or O sites have been reported by theoretical[2-5, 14] and experimental[10, 18] studies. Recently it is reported that H in ZnO can exist in "hidden"[8, 19] and diatomic complex H_2^* form[9] also, which do not contribute to free carrier concentration at room temperature.[9, 19-21] The origin of the "hidden" H in ZnO seems to be identified[22-23] in recent studies of the local vibrational modes of H. The complexes are energetically more preferable than the shallow donor H. They can result in decrease of the free electron concentration according to bimolecular law,[19-20] as well as discrepancy in concentration of H determined by SIMS from that of free electrons measured by Hall method.[24] "Hidden" H can be annealed out at ~400 °C.[19] However,

dissociation energy of H_2^* is ~0.92 eV,[9] which is large and it can be annealed out at ~400 ^{o}C. In earlier studies of GaP,[25] GaAs,[26] and ZnO[27] it was shown that stability of such complexes can be modulated by doping. Such features can be favourable in ZnO due to small migration energy H.[7, 28] Here we report that although the H_2^* is the most stable complex in pure stoichiometric ZnO, in close vicinity of V_O it is less stable than two distant H, substituting the O site (H_O) and occupying the interstitial (H_i) position. In this configuration both distant H atoms can be shallow donor.

2. Computational methods

Vienna *ab initio* simulation package (VASP)[29-30] has been used for the computations within the generalized-gradient approximation (GGA) following the Perdew-Bueke-Ernzerhof scheme (PBE)[31] for the exchange-correlation functional and with the multiorbital mean-field Hubbard potential GGA+U. For the lattice optimizations 4×4×4 **k**-mesh has been used. The approximation allowed to solve partially the deficiencies of the DFT calculations within GGA such as wrong estimation of location of the Zn 3d bands, the spin-splitting and crystal-field energies,[32-34] artificial hybridization of the bands with the O 2p band, falsification of the band dispersion, strong reduction of the band gap of ZnO, etc.[35-36] This way requires explicit values of the parameters U and J as input. Analysis of literature (see, e.g. Refs.[32-34]) shows that the calculated band parameters can be more accurate if U=6 eV and J=1 eV.

Non-norm-conserving pseudopotentials generated in accordance to the projector-augmented-wave (PAW) method[35-36] have been used. It allowed us to construct orthonormalized all-electron-like wave functions for the Zn-3d, -4s, O -2s and -2p, H-1s

valence electrons. The self-consistent calculations were performed using a 4×4×4 mesh of special **k**-points. All configurations were fully relaxed using the conjugate gradient method. The lattice was fully relaxed using the conjugate gradient method. Plane-wave cut-off of 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 $Å^{-1}$ and the energy difference between two iterations was $<10^{-7}$ eV. The experimentally determined lattice parameters of wurtzite phase of ZnO $a = b \approx 3.250$ Å, $c/a \approx 1.602$ Å, and $u \approx 0.382$ (Ref. [2]) were used as input in the computations for the lattice relaxations, which has lead to the following optimized lattice parameters $a = b \approx 3.244$ Å, $c/a \approx 1.550$ Å, and $u \approx 0.389$ in satisfactory agreement with the measured data.

3. Model considered

The computations have been performed for 3×3×2 and 4×3×2 supercells of ZnO containing V_O and two H atoms, which correspond to H concentrations of 2.2×10^{21} and 1.7×10^{21} cm^{-3}, respectively. Analysis of literature shows that the above H concentrations considered in the theoretical studies are not far from reality. For example, the H concentrations of 2.5×10^{22} cm^{-3} have been observed in electrochemically doped single crystals of ZnO,[37] $\sim 10^{22}$ cm^{-3} is reported in high dose implanted single crystalline ZnO,[38] and $\sim 10^{21}$ cm^{-3} H concentration has been found[39] in rf magnetron sputtered ZnO. As noted in Ref.[40] high concentrations of intrinsic defects and interactions between them might enhance significant reduction in their formation energies.

Five configurations of these defects have been considered. In one of them denoted as $(H_2)_O$ both H atoms have been located at the O vacancy (V_O) (Fig. 1 (a)). The other configuration consists of two distant H atoms located at two different interstitial sites (H_i) on Zn-O bonds aligned with the *c*-axis far away each from other and from the O vacancy V_O. Third and fourth configurations contain a diatomic H complex (H_2^*, Fig. 1 (b)) or a water molecule H_2O (Fig. 1 (c)), respectively, located far away from V_O. Here the angle between two O-H bonds in H_2O is ~103°, which is smaller than 109.5^o of the water molecule. In the fifth configuration (Fig. 1 (d)) one of the H atoms is located at the vacancy site (H_O) and the other one is located at the interstitial site H_i on a Zn-O bond to be denoted as H_O, H_i. In the above configurations neutral state of V_O and H_2^* has been considered.

4. Results and discussion

For analysis of stability of the defect configurations the total energy E_{tot}^{eq} and the equilibrium volume V_{eq} corresponding to the ground state have been studied for the 3×3×2 supercells of ZnO. For these purposes structural optimization has been performed for all the defect configurations considered in the present work by the following procedure: first atomic positions, volume, and shape of the crystal have been relaxed altogether. Magnitude of E_{tot}^{eq} for the above configurations varies in the following order:

$$E_{tot}^{eq}[H_2O] > E_{tot}^{eq}[(H_2)_0] > E_{tot}^{eq}[V_O, H_2^*] > E_{tot}^{eq}[V_O, H_i, H_i] > E_{tot}^{eq}[H_O, H_i] \qquad (1)$$

Total energy differences are listed below:

$$E_{tot}^{eq}[V_O, H_i, H_i] - E_{tot}^{eq}[H_O, H_i] = 0.416 \text{ eV}, \quad E_{tot}^{eq}[V_O, H_2^*] - E_{tot}^{eq}[V_O, H_i, H_i] = 0.115 \text{ eV}.$$

$$E_{tot}^{eq}\left[(H_2)_0\right]-E_{tot}^{eq}\left[V_O,H_2^*\right]\approx 0.006 \text{ eV}, \ E_{tot}^{eq}\left[H_2O\right]>E_{tot}^{eq}\left[(H_2)_0\right]=0.812 \text{ eV}.$$

Analysis shows that the differences are quite large for the configurations except $E_{tot}^{eq}\left[(H_2)_0\right]-E_{tot}^{eq}\left[V_O,H_2^*\right]$. Contribution of the latter two configurations to total energy of the system is almost the same. It follows from these results that the configurations with water molecule H_2O and $(H_2)_O$ possess the largest total energy, so they are the least stable ones. Furthermore, H_2^* in close vicinity of V_O is expected to decompose into distant H. These findings are consistent with diffusivity of H in ZnO due to its small migration energy H.[7, 28]

As it is well-known from literature both H_O and H_i are shallow donors. H_i forms O-H complex and H_i should be positively charged. However, because of underestimation of the band gap at Fermi levels closer to conduction band (CB) minimum formation energy of H_i^- is smaller than that of H_i^+.[2] As a result H_i can be in negatively charged state (H_i^-). H_O is anion, which accepts the electrons donated by the nearest four Zn atoms. Consequently, it is negatively charged.

Sometimes for the studies of defects in solids by DFT the lattice constants are fixed to those of the perfect crystal. However, doping of the solid with a particular defect can cause lattice expansion or shrinkage as in the case of, e.g., H_i in ZnO.[2] The feature is used to clarify by XRD measurements whether V_O or H_i is controlling the concentration of free electrons or not.[24] Consequently, the defect studies which optimizes not only atomic positions, but also volume and shape of the lattice can be more close to reality.

Electronic structure of ZnO depends on the defect configuration. Below this point is discussed for ZnO containing V_O, the defect configurations $(H_2)_O$, distant V_O and H_2^*, as well as distant V_O and water molecule H_2O (Fig. 2). As expected, the fundamental band gap is underestimated because of the well known deficiency of DFT. Band gap corrections has not been applied. So, in Fig. 2 the gap between the V_O-derived band and topmost valence band is too small (~9 meV). This result fairly agrees with recent DFT calculations,[41] which reported that the V_O derived band is located at 0.15 eV above the topmost valence band. Correct location for the band of V_O at 2.5-2.6 eV below the bottommost conduction band (CB) and band gap of ZnO has been obtained in recent computations[14] by hybrid Hartree-Fock density functional studies. As noted above, our results correspond to neutral V_O, so that the Zn atoms located in close vicinity of V_O has been shifted toward the vacancy compared to their position in ideal lattice. When two H atoms reside at V_O, the atoms form a molecule, which, as we demonstrate later, do not form chemical bonding with the four nearest neighbour Zn atoms. Similar to positively charged V_O^{++} the Zn atoms shall be repelled out of V_O compared to their position in ideal lattice. Consequently, those Zn atoms, which donated electrons either to O atom in ideal lattice or to neutral V_O, might contribute their excess charge to CB thus shifting the Fermi level to the CB and enhancing free electron concentration (Fig. 2). The ZnO supercell with distant V_O and H_2^* contain the band of V_O and well localized trap of H_2^*. The result is consistent with recent findings of Ref.[9, 17] regarding deep traps formed by H_2^* in ZnO without Zn or O vacancies. Similar to $(H_2)_O$ water molecule H_2O also enhances free electron concentration. The reason, probably, is that the Zn cations located

around the H_2O molecule donate their electrons to the CB thus ascribing electronic conductivity to ZnO.

It is interesting to know interaction of the defect configurations with environment of ZnO. Here we concentrate attention on charge density and electron localization function (ELF) around $(H_2)_O$ and H_2O (Fig. 3 (a)-(d)). Analysis shows that $(H_2)_O$ and H_2O can be called as H_2 and water molecule, respectively, because chemical bonding in the molecule is stronger than that between the molecule and ZnO. In the ELF for H_2O charge is seen between H and O atoms. It indicates to presence of covalent character of chemical bonding. However, electron affinity of O is stronger than that of H atoms, so unequal sharing of the bonding electrons will take place between O and H atoms. Consequently, the O-H bonds in H_2O can be said as polar covalent. In H_2 molecule both H atoms have equal attraction and none of them has been bonded into Zn or O atoms. Consequently, the bonding electrons are equally shared between the two H atoms. So, the H-H bond in $(H_2)_O$ can be said as non polar covalent bond.

Below we discuss influence of the system of defects consisting of diatomic H and V_O in concentrations N_H and N_V, respectively, on electrical properties of ZnO. At $N_H < N_V$, all H can be at V_O site thus becoming shallow donor and one should not expect decrease of free electron concentration n according to bimolecular law. Furthermore, H concentration determined from SIMS can be equal to that of electron concentration measured from Hall set up. However, H_O can co exist with V_O. So, the H induced enhancement of electrical conductivity will co-exist with V_O induced reduction of transparency to visible light. For $N_H > N_V$, the relation $n \geq N_H$ can be valid. Then, part

of H can be incorporated to H_2^* or "hidden H". Consequently, one can expect the electrical and optical properties similar to that of stoichiometric ZnO, i.e. decrease of electron concentration with time according to bimolecular law and discrepancy between free electron and H concentrations.

One of the questions to be discussed is related to stability of H_2^* to variations of its charge state. The study of this point shows that upon removal of one or two electrons from H_2^*, it becomes unstable. As a result, upon optimization of the lattice the diatomic can H decompose. One of the H atoms of the complex, which is located closer to the Zn will be shifted toward one of the nearest O atoms to form O-H complex.

5. Conclusion

In conclusion, by DFT calculations it is found that at ambient pressures the configuration of diatomic H atoms located separately each other at the O and interstitial sites is energetically more favourable than the diatomic H_2^* complex and other locations of the two H considered in this work. The stable configuration provides shallow donor levels in the band gap of ZnO. Upon compression other configurations of the diatomic H such as the diatomic complex H_2^* and H molecule at the O site $(H_2)_O$ can become energetically more preferable. Influence of the diatomic H on lectronic structure and electrical properties of ZnO is discussed. It is found that at concentrations of H atoms exceeding that of the O vacancy formation of the diatomic complex can become energetically more preferable.

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Table I. Bond distance (in Å) for H-H (d_{H-H}) and H-V_O (d_{H,V_O}) of a unit cell and the smallest (d_{min}) H-H and H-V_O distances between two nearest neighbour unit cells of the relaxed lattices of ZnO containing two H atoms and one V_O.

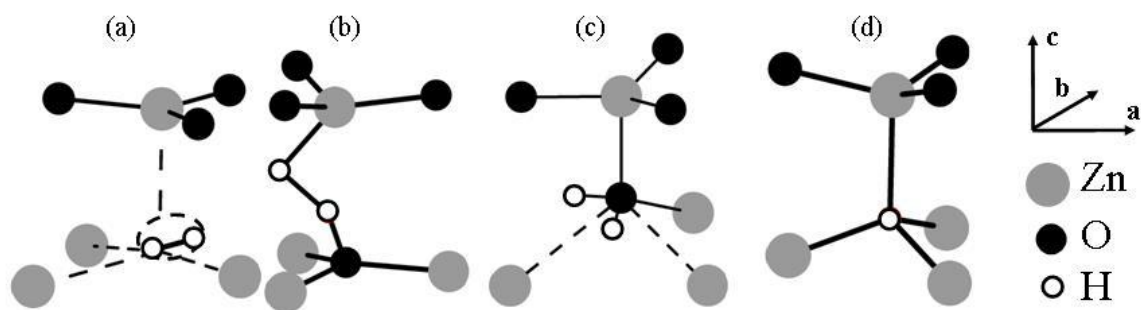| Distance	$[(H_2)_O]$	$[V_O, H_2^*]$	$[V_O,H_2O]$	$[H_i, H_O]$	$[H_i, H_i, V_O]$
d_{H-H}	0.77(0.74)	1.25	1.60	5.7	8.93
d_{H,V_O}	0	7.50	6.78 105.23 ($\angle$HOH)		5.87
d_{min}	9.3 (H,H)	6.00(V_O,H), 9.10(H,H)	8.09 (V_O,H), 9.87(V_O,V_O)	9.9 (H-H)	7.17(V_O,H) , 9.87(V_O,V_O)

Fig. 1 Schematic presentation of (a) $(H_2)_O$, (b) diatomic H complex H_2^*, (c) water molecule H_2O, and H substituting O site H_O for relaxed lattices of ZnO 3×3×2 supercells. Continuous lines indicate to existing bonds between atoms whereas broken lines correspond to weak or non-existing bonds.
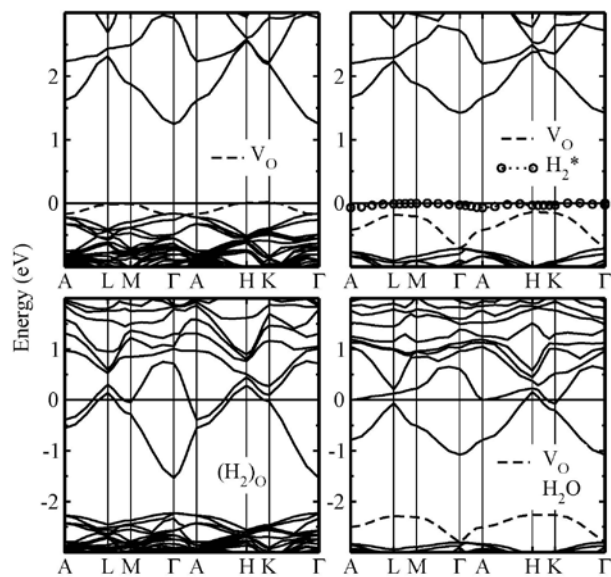
Fig. 2. Band structure for optimized ZnO unit cells containing $\left(H_2\right)_O$, an V_O, distant V_O and H_2^*, as well as distant V_O and water molecule H_2O for the 3×3×2 supercells of ZnO.
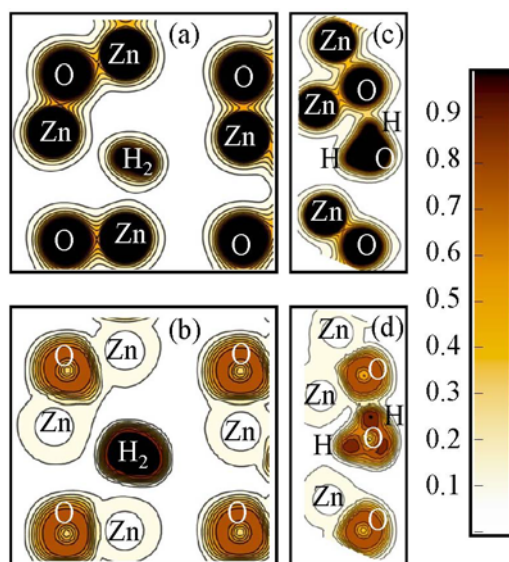
Fig. 3. (Colour online) (a), (c) Charge density and (b), (d) ELF in close vicinity of (a), (b) $(H_2)_O$ and (c), (d) water molecule H_2O.