Divacancy-Hydrogen Complexes in Zinc Oxide

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ABSTRACT

In the present work we study Zn+O divacancies filled up with varying amount of hydrogen atoms. Besides the structure and energy-related properties of such defects, we also investigate their capability to trap positrons taking into account positron induced forces. We show that the Zn+O divacancy may trap positrons when up to two hydrogen atoms are located inside the divacancy. The calculated properties are discussed in the context of other computational and experimental studies of ZnO.

INTRODUCTION

The nature of point defects in zinc oxide is not yet fully understood, but this subject attracts wide attention as it is of vital importance for various technological applications mainly in electronics. An important class of point defects in ZnO is represented by hydrogen-related defects that are also often considered in relation to the *n*-type conductivity of ZnO materials [1,2]. Recently, it has been found that nominally undoped commercially available ZnO single crystals contain an appreciable amount of hydrogen at a level of at least 0.3 at.% [3]. The forms in which such hydrogen atoms are incorporated into the ZnO lattice are not precisely known at present, and there are several possibilities, in principle. In particular, hydrogen may occupy interstitial positions and/or may be present in the form of H_2 molecules in 'channels' along the *c*-axis of the hexagonal ZnO lattice [1]. Hydrogen may also form complexes with other impurities though their concentrations are usually much smaller than that of H, as found in [3]. Furthermore, hydrogen atoms can enter open volume defects, like oxygen and zinc vacancies (see e.g. [4]) and related defects. Positron annihilation techniques are sensitive to such kind of defects and, as shown in [3], positron trapping in hydrothermally-grown ZnO materials occurs in Zn-vacancy-hydrogen related complexes. Namely, a suggestion has been given that positrons may get trapped in a Zn-vacancy occupied by one hydrogen atom. In the present work, we extend our study to Zn+O divacancies containing hydrogen atoms ($V_{Zn+O}+n$H complexes). We investigate their structure, energy-related properties, and also positron characteristics taking into account positron induced forces acting on the ions surrounding studied defects. Our previous positron studies as well as further motivations, explanations and references to other related literature can be found in refs. [3,5].

COMPUTATIONAL METHODS

Realistic configurations of studied defects were obtained by means of relaxing the total energy of corresponding supercells with respect to atomic positions. In particular, the Vienna ab initio simulation package (VASP) [6] was employed for this purpose. In the course of calculations, projector augmented-wave potentials within the local-density approximation (LDA) were used [7]. 96 atom-based supercells containing defects were utilized.

ZnO exhibits the wurtzite crystal structure and it can be considered as a network of ZnO_4 tetrahedra interconnected at their corners (see e.g. figure 1 in ref. [3]). A $V_{Zn+O}+n$H complex can be considered as a part of such a tetrahedron with H atoms inside, missing Zn central atom and one O corner atom and, thereby, $V_{Zn}(V_O O_3)+n$H 'formula' describes the situation, which will be useful for defect structure explanations (see figure 1). We studied defects based on one of possible two configurations of the V_{Zn+O} divacancy in which the removed/missing nearest neighbor Zn+O pair has a non-zero projection to the basal plane of the ZnO hexagonal wurtzite lattice.[1] For this configuration we placed $n = 0$, 1, and 2 hydrogen atoms into various possible positions in V_{Zn}, as described in [3], and also in the center of V_O [4]. In particular, for $n = 1$ we have three non-equivalent configurations denoted further by $V_{Zn+O}+1$H OV, $V_{Zn+O}+1$H Oab, and $V_{Zn+O}+1$H Oc. Here the suffix OV marks the configuration with a H atom in the center of V_O, and suffixes Oab and Oc mark, respectively, configurations with a H atom close to an O atom around V_{Zn} with the O-H pair having a non zero projection to the hexagonal basal plane and lying along the c-axis direction (see figure 1a). In the case of $n = 2$, there are totally four configurations $V_{Zn+O}+2$H Oab$V$ (figure 1b), $V_{Zn+O}+2$H OcV, $V_{Zn+O}+2$H Oab, and $V_{Zn+O}+2$H Oabc. The meaning of these abbreviations can be derived from that given above for $V_{Zn+O}+1$H complexes, considering that there are always two H atoms that cannot occupy the same position inside V_{Zn+O}.
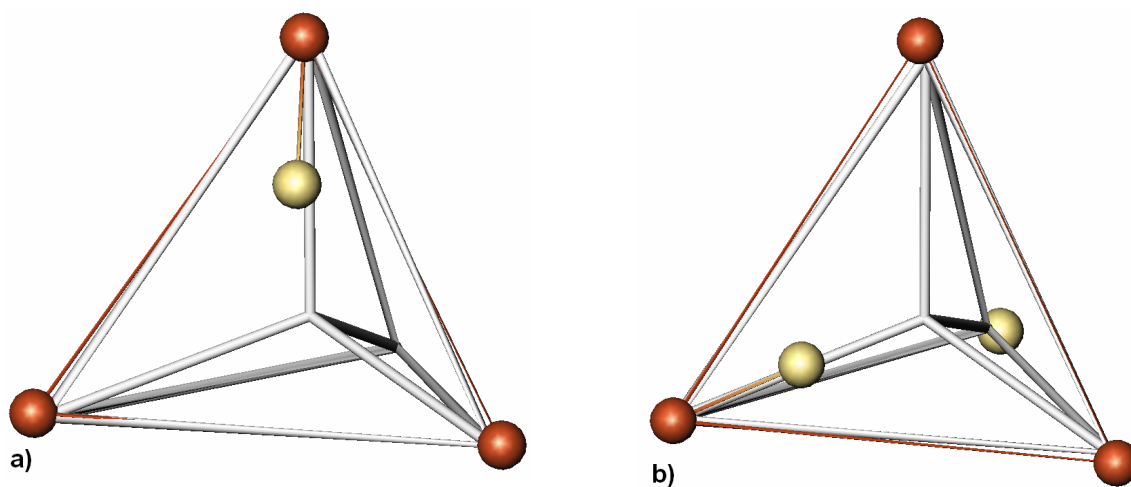
Figure 1: Relaxed configurations of a) $V_{Zn+O}+1$H Oc and b) $V_{Zn+O}+2$H Oab$V$ complexes. Dark (light) spheres represent O (H) atoms. The original (nonrelaxed) ZnO_4 tetrahedra are plotted by thick solid lines. Thinner (darker) lines join relaxed positions.

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[1] The second configuration with the Zn-O pair oriented along the c-axis direction will be the subject of another study.

Formation energies (E_f(D; q, E_F)) for various defects (D) with and without hydrogen in dependence on the Fermi level position (E_F) and defect charge state (q) have been estimated. For this purpose, the formula from ref. [8], where we added also terms related to hydrogen (following ref. [1]), was employed

$$E_f(D; q, E_F) = E(D; q, n_{Zn}, n_O, n_H) - (n_{Zn} - n_O)\mu_{Zn} + n_O E_{ZnO} - n_H \mu_H + q E_F . \qquad (1)$$

Here E(D; q, n_{Zn}, n_O, n_H) and E_{ZnO} are, respectively, the energy of the corresponding supercell containing the defect D considered (in charge state q) and the energy per one ZnO pair in bulk ZnO material. n_{Zn}, n_O, and n_H specify the number of Zn, O, and H atoms in the supercell, respectively. μ_{Zn} and μ_H are the chemical potentials of Zn and H. We will not repeat the whole discussion [8] here and mention only that in binary systems/compounds chemical potentials of constituent atoms (i.e. Zn and O in our case) are not fixed, but depend on the conditions to which the material is exposed. For this reason one can specify a lower and an upper limit for both chemical potentials (μ_{Zn} and μ_O) and one can thus principally distinguish between Zn-rich (O-poor) and Zn-poor (O-rich) conditions. Hydrogen is treated as an impurity [1] and its chemical potential is taken to be one half of the free H_2 molecule energy. Formation energies were evaluated on the basis of energies obtained within the LDA framework so, in principle, they suffer from the well know LDA band gap underestimation issue (cf. ref. [9]), which we intend to address in a future work.

Positron calculations have been performed using a real space method as implemented in the atomic superposition (ATSUP) method [10]. Positron-induced forces acting on atoms around the defect were implemented according to the scheme developed by Makkonen et al. [11]. In such calculations, the so-called conventional scheme [11,12] for positron calculations is considered, which means that the electronic structure is not primarily influenced by the presence of the positron trapped in a defect. On the other hand, the positions of ions (Zn, O, and H) are influenced by the presence of the positron through the positron-induced forces (PFs). In the following, we shall distinguish between two schemes for positron calculations. In both of them, we use self-consistent (SC) and relaxed (RE) electron charge densities and Coulomb potentials. The first scheme neglects PFs (hence SC RE), whereas the second one takes them into account (SC RE PF). In positron calculations, the approach of Boroński and Nieminen [13] to the electron-positron correlations and enhancement factor – with the correction [14] for incomplete positron screening with the high frequency dielectric constant $\varepsilon_\infty = 4$ – has been used. We further refer readers to refs. [11,12] concerning theoretical background of positron calculations and to refs. [3,5] regarding our previous calculations for ZnO.

RESULTS AND DISCUSSION

We shall now present and discuss the results for the studied $V_{Zn+O} + n$H defects from the viewpoint of structural, energy-related, and positron properties.

<u>**Structure of defects**</u>

Examples of relaxed defect configurations are shown in figure 1. Hydrogen atoms that were initially placed in the center of the V_O-part of the divacancy remain roughly at their positions

after relaxation, i.e. they are surrounded by three Zn atoms like in the oxygen vacancy – just one Zn atom is missing due to V_{Zn} (figure 1b). Also O-H pairs preserve their character in relaxed configurations keeping the O-H distance at approximately 1 Å (figure 1a).

Table I gives energies of charge neutral configurations of $V_{Zn+O}+1H$ and $V_{Zn+O}+2H$ complexes. These energies are calculated with respect to the lowest energy in either group of complexes. One can see that complexes with H atoms located in the V_O-part of the V_{Zn+O} divacancy have apparently larger energies than those containing O-H pairs only. This stems from the fact that V_O is positively charged relative to the lattice (even though the whole supercell is neutral), as is also the H atom because it is losing a 'part' of its electron. Thus, V_O and H atom are mutually repulsive. This indicates that lower energy configurations (i.e. without any O...V part) in either group of studied complexes should preferably be found in reality.

Table I. Calculated energy-related and positron characteristics for studied $V_{Zn+O}+nH$ complexes. E_r is the energy of a given configuration with respect to the lowest energy configuration (see the text). τ and E_b denote, respectively, the positron lifetime and positron binding energy to defects.

Defect	E_r (eV)	τ (ps)	E_b (eV)	τ (ps)	E_b (eV)
V_{Zn+O}	—	265	1.1	224	1.0
$V_{Zn+O}+1H$ OV	1.78	246	1.0	218	0.9
$V_{Zn+O}+1H$ Oab	0.00	223	0.4	208	0.3
$V_{Zn+O}+1H$ Oc	0.08	217	0.4	207	0.3
$V_{Zn+O}+2H$ Oab$V$	0.20	199	0.3	185	0.2
$V_{Zn+O}+2H$ OcV	0.24	199	0.3	183	0.2
$V_{Zn+O}+2H$ Oab	0.00	154	~0	154	~0
$V_{Zn+O}+2H$ Oabc	0.05	154	~0	154	~0
		SC RE		SC RE PF	

Formation energies

Figure 2 shows resulting formation energies for studied complexes and other selected defects calculated using equation 1 for Zn-rich, 'intermediate', and Zn-poor conditions. By intermediate conditions we understand the case when the chemical potential μ_{Zn} is just in the middle between its upper and lower limit. When H-related defects are not considered for the moment, formation energy diagrams follow those shown in refs. [8,9].

As for $V_{Zn}+nH$ defects, the corresponding energies to calculate formation energies were taken from [3]. One can see that these defects have lowest formation energies from all the defects considered for n-type materials under O-rich (Zn-poor) and intermediate conditions. This suggests that $V_{Zn}+nH$ complexes exist in ZnO under broad growth conditions.

Regarding $V_{Zn+O}+nH$ complexes, we considered only neutral defects at this stage of research. Corresponding formation energies are positioned quite high (figure 2) and, therefore, should not be populated to a large extent when compared to other defects considered, depending also on the Fermi level position and conditions (Zn-rich, Zn-poor). However, charge states need to be investigated too in order to obtain the full picture. Though the creation of $V_{Zn+O}+nH$ complexes could be hindered due to energy reasons, we note that V_{Zn+O} divacancies can be introduced into ZnO materials e.g. by irradiation.
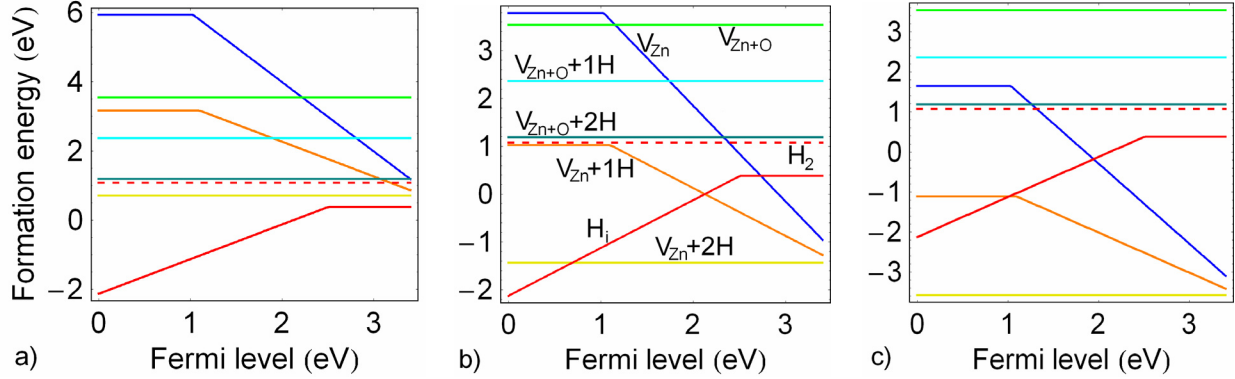
Figure 2: Formation energies of various defects in ZnO for a) Zn-rich, b) intermediate, and c) O-rich conditions in dependence on the Fermi level position. The zero Fermi level corresponds to the valence-band maximum and the maximum Fermi level (3.4 eV) corresponds to the conduction band maximum. The slope of some segments indicates a charge state (see refs. [1,8] for details).

Positron characteristics

Positron lifetimes and binding energies to defects for studied complexes are listed in table I, both for SC RE and SC RE PF computational schemes. The SC RE PF scheme yields systematically lower lifetimes and binding energies due to the attractive interaction between the positron and surrounding oxygen ions, which results in lowering the free volume available to the positron compared to the case when positron induced forces are not considered. This indicates that positron induced forces are inevitable in order to obtain realistic positron characteristics.

The calculated bulk positron lifetime is 154 ps [3] and agrees well with the experimental value (151 ± 2) ps given in ref. [5]. We refer to [3] for a detailed summary of the ZnO bulk lifetime measurements and calculations. The positron lifetime and binding energy for the V_{Zn+O} divacancy show that this defect is a deep positron trap as is also the V_{Zn+O}+1H OV complex. But other V_{Zn+O}+1H complexes are shallower traps due to the fact that the V_O part of the divacancy repulses positrons and the free volume of the V_{Zn}-part is reduced due to the presence of the H atom. Analogous considerations can be applied to V_{Zn+O}+2H complexes for which the positron lifetime is further lowered (table I). V_{Zn+O}+2H Oab and V_{Zn+O}+2H Oabc complexes even do not trap positrons as the remaining free volume is not enough to trap positrons and their positron lifetimes approach that for delocalized positrons.

CONCLUSIONS

We have studied selected V_{Zn+O}-hydrogen complexes in ZnO and determined their structure, energy-related characteristics and positron properties. In such complexes, H atoms can occupy either the V_O-part of the divacancy, which is not energetically favorable, or more likely they are bound to an O atom in the vicinity of the V_{Zn}-part of the divacancy. V_{Zn+O}+nH complexes seem to exhibit quite a high formation energy though charged states were not studied yet. In contrast, V_{Zn}+nH complexes have lower formation energies and should exist in large concentrations under O-rich (Zn-poor) conditions for n-type ZnO materials, which seems to be supported by recent

positron annihilation experiments. The positron lifetime and binding energy for $V_{Zn+O}+n$H defects show a decreasing trend with increasing number of H atoms, which is similar to that for $V_{Zn}+n$H complexes investigated recently. Further calculations are in progress in order to obtain a more complete and accurate description of $V_{Zn+O}+n$H complexes, which will assist in advanced defect identification and defect resolution in ZnO materials.

ACKNOWLEDGMENTS

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