Atomic and electronic structure of hydrogen on ZnO (1 $\overline{1}$00) surface: ab initio hybrid calculations


$^1$L.N. Gumilyov Eurasian National University, Astana, Kazakhstan
$^2$Institute of Solid State Physics, University of Latvia, Riga, Latvia
*E-mail: useinov_85@mail.ru

Abstract. Hydrogen atoms unavoidably incorporated into ZnO during growth of bulk samples and thin films considerably affect their electrical conductivity. The results of first principles hybrid LCAO calculations are discussed for hydrogen atoms in the bulk and on the non-polar ZnO (1 $\overline{1}$00) surface. The incorporation energy, the atomic relaxation, the electronic density redistribution and the electronic structure modifications are compared for the surface adsorption and bulk interstitial H positions. It is shown that hydrogen has a strong binding with the surface O ions (2.7 eV) whereas its incorporation into bulk is energetically unfavorable. Surface hydrogen atoms are very shallow donors, thus, contributing to the electronic conductivity.

1. Introduction

Understanding of the atomic and electronic structure of defective/doped ZnO is of great importance for improving performance of electrodes in optoelectronic devices based on transparent conducting oxides, e.g., LED displays, etc. A study of a role of hydrogen impurities penetrating into ZnO thin films from plasma is of particular interest. Hydrogen atoms could occupy interstitial positions (H$_i$) or substitute O ions ([1–4] and references therein).

Previous theoretical studies mainly focused on hydrogen in ZnO bulk, which is found to act as a shallow donor [3,4]. However, the effect of hydrogen on the structural and electronic properties of different ZnO surfaces remains unclear: only a few relevant studies have been published so far [5,6], although this is important for improving technologies of ZnO thin film production.

In the current study, we have performed ab initio calculations of the atomic hydrogen adsorption on the non-polar ZnO (1 $\overline{1}$00) surface characterized by quite low surface energy (as described below) and studied earlier experimentally by means of ellipsometry and electronic energy loss spectroscopy [7]. To draw conclusions on the hydrogen effect on the electronic conductivity, the total and projected densities of one-electron states (DOS, PDOS) have been calculated and accompanied by analysis of the electronic charge redistribution, lattice relaxation, hydrogen adsorption energy at surface and its incorporation into the bulk. The paper is organized as follows: details of calculations are discussed in Section 2, main results for H incorporated in ZnO bulk and upon ZnO (1 $\overline{1}$00) surface are analyzed in Section 3, and main conclusions are summarized in Section 4.

2. Computational details

Large-scale ab initio calculations have been performed using the method joining LCAO (linear combination of atomic orbitals) basis set and hybrid exchange-correlation Perdew-Burke-Ernzerhof (PBE0) functional [8] as implemented in CRYSTAL2009 computer code [9]. Such hybrid functionals allow us to perform very accurate calculations of the band gap, unlike standard LDA or GGA-type functionals. The atomic basis sets for Zn and O atoms have been taken from Ref. [10], and that for the hydrogen atom from Ref. [11]. Within the SCF procedure, the accuracies (tolerances) $10^{-7}$, $10^{-7}$, $10^{-7}$, $10^{-7}$, $10^{-14}$ have been chosen for calculations of Coulomb and exchange integrals. Effective charges on atoms have been estimated using Mulliken population analysis. The integration over Brillouin zone in the reciprocal space has been performed with a 6×6×4 Pack-Monkhorst grid. When modeling hydrogen absorbed in the bulk, the (2×2×2) supercell (periodic) model with 32 atoms has been chosen.
For (1T00) surface modeling, we have considered the slab model unit cell of finite thickness repeated along the chosen z axis. When simulating adsorption of isolated hydrogen atom on the (1T00) surface, the aforementioned slab extended in CRYSTAL calculations as 2x2 in the x and y directions correspond to the chosen periodic distribution of surface hydrogen atoms (Fig. 1). We have considered several hydrogen adsorption positions: above the surface atoms Zn (1), O (2) and in the “hollow” position (3) as shown in Figure 1 (b). In order to save computation time, we have performed partial geometry optimization, in which the relaxation has been provided for three upper layers.

The energy of hydrogen adsorption has been determined using the following expression:

\[
E_{\text{ads}} = E_{\text{tot}}^{\text{ZnO}} + E_{\text{tot}}^{\text{H}} - E_{\text{tot}}^{\text{ZnO/H}},
\]

where \(E_{\text{tot}}^{\text{ZnO}}\), \(E_{\text{tot}}^{\text{ZnO/H}}\) and \(E_{\text{tot}}^{\text{H}}\) are the total energies of slab with the adsorbed hydrogen atom, pure slab, and isolated hydrogen atom in the ground state, respectively. If the adsorption energy is positive, the process is energetically favorable.

![Unrelaxed 6-layer slab model of the ZnO (1T00) surface (a) and top views of three different positions of the hydrogen atom upon the surface (b).](image)

**Figure 1.** Unrelaxed 6-layer slab model of the ZnO (1T00) surface (a) and top views of three different positions of the hydrogen atom upon the surface (b).

### 3. Results and analysis

#### 3.1 Hydrogen in the ZnO bulk

The analysis of the calculated density of states (DOS) in Fig. 2 shows the two effects: (i) narrowing of the band gap (\(E_g = 2.72\) eV) as well as (ii) H contribution in a wide energy spectrum below and within the conduction band. Appearance of such a broad H band can be explained by a relatively high defect concentration used in our calculations (1/16 ≈ 6%) and a proximity of H atom energy level to the bottom of the conduction band. This is in qualitative agreement with previous conclusion about H as a shallow donor [1]. (The hybrid B3LYP calculations for 400-atom supercell have predicted H energy position only 0.1 eV below the bottom of conduction band [4] whereas O–H bond length is 0.98 Å, very close to our result – 0.982 Å). The strong interaction between H and O is also observed in the differential electron density map (Fig. 3a), accompanied by a polarization of surrounding atoms.

The calculated energy of H incorporation is found to be 1.8 eV, in qualitative agreement with the value of 1.0 eV obtained in the GGA calculations when using the energy of H atom in a free H₂ molecule [2] as the reference state. For a comparison, our energy has to be reduced by half the binding energy in a molecule (2.26 eV) which gives 0.67 eV. Similar calculations for the larger (3x3x2) supercell have gave a slightly larger value of 1.88 eV, which means that the interaction of periodically distributed H atoms is small, while in the 2x2x2 supercell it is large enough.
3.2. Hydrogen upon the surface

Similar calculations have been performed for hydrogen adsorbed on the nonpolar \((1\bar{1}00)\) surface (Fig. 1). The \((1\bar{1}00)\) surface energy varies only slightly with increase of the number of layers. Therefore, 6-layer slab model has been selected for calculations of the relaxation of surface geometry and the electronic properties of a pure surface. The analysis of calculations on the absolute and relative displacements of surface ions shows that after slab relaxation the surface Zn ions are displaced inwards, to the slab center, whereas O ions are shifted outwards, which is typical for oxide surfaces. This leads to a relatively small surface rumpling.

The adsorption energies of H atom have been obtained for three possible surface sites (Fig. 1 and Table 1): energetically the most favorable is the one atop the surface oxygen ions \((E_{\text{ads}} = 2.71 \text{ eV})\). (It is also energetically favorable for adsorption of H atoms in the hollow positions.) As mentioned above, if hydrogen atoms before adsorption are produced by dissociation of \(H_2\) molecules, the adsorption energy with such the reference state will by smaller by half of its binding energy. This means that only adsorption atop surface O atoms would be energetically favorable, with the energy of 1.58 eV, whereas H adsorption in other configurations mentioned in Table 1 turn out to be unfavorable.

The calculated DOS (Fig. 2b) shows that hydrogen atoms adsorbed on ZnO surface act as very shallow donors, while H contribution in the energy range close to the bottom of conduction band is much higher by amplitude than in the bulk. The electronic density redistribution also confirms

**Figure 2.** DOS projected onto all orbitals on Zn (black), O (red), H (blue), and the total density of states (cyan): a) hydrogen in \((2\times2\times2)\) supercell ZnO; c) hydrogen adsorbed on the \((1\bar{1}00)\) surface of ZnO. For the hydrogen atom, PDOS is increased by a factor of 50. \(E_F\) denotes the Fermi level.

**Figure 3.** The differential electron density plots are drawn for the hydrogen atom positioned a) in \((2\times2\times2)\) ZnO bulk supercell; b) upon the ZnO \((1\bar{1}00)\) surface. The solid (red) and dotted (blue) isolines correspond to positive (excess) and negative (deficiency) electron density, respectively. Increment for isolines is 0.001 e within the range from \(-0.1\) e to \(0.1\) e.
formation of a strong O–H bonding (Fig. 3b). Thus, adsorbed H atoms are expected to contribute strongly to the electronic conductivity.

Table 1. Adsorption energy $E_{\text{ads}}$ (eV) of the hydrogen atom in different positions (Fig. 1b), the effective charge of surface ions $q_{\text{eff}}$ (e), their vertical displacements $\Delta z$ (Å) from defect-free lattice sites, as well as the distance $d$ (Å) between the adsorbed H atom and a surface ion.

<table>
<thead>
<tr>
<th>Site</th>
<th>$E_{\text{ads}}$</th>
<th>$q_{\text{eff}}$</th>
<th>$\Delta z$</th>
<th>$d_{\text{Zn(O)-H}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>2.71</td>
<td>-0.79</td>
<td>0.071</td>
<td>0.96</td>
</tr>
<tr>
<td>Zn</td>
<td>-4.42</td>
<td>0.85</td>
<td>-0.31</td>
<td>1.61</td>
</tr>
<tr>
<td>Hollow</td>
<td>0.41</td>
<td>-0.18</td>
<td>1.074</td>
<td>1.91</td>
</tr>
</tbody>
</table>

$^a$ Effective charge of H atom (e); $^b$ Hydrogen distance from the surface (Å); $^c$ Distance between the hydrogen atom and surface Zn ion.

4. Conclusions
As a result of first principles hybrid LCAO calculations, we have obtained the atomic and electronic properties of ZnO:H in the bulk and on the non-polar (100) surface. The interstitial anti-bonding hydrogens act as shallow donors, and this is the more so on the (1100) surface. Incorporation energy of hydrogen atoms from plasma into interstitial positions is quite large (1.8–1.9 eV), whereas their adsorption atop surface O ions is energetically strongly favorable (2.7 eV). Thus, one could expect a high concentration of plasma-induced hydrogen on ZnO surfaces with a considerable contribution to the electronic conductivity.

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