



## Hydrogen induced metallization of ZnO (1 $\bar{1}$ 00) surface: Ab initio study

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### ABSTRACT

Results of first principles hybrid calculations are presented for hydrogen atoms adsorbed upon non-polar ZnO (1 $\bar{1}$ 00) surface. The energy of surface atomic relaxation, H adsorption energy, electronic density redistribution and modification of the electronic structure are discussed. It is shown that hydrogen is adsorbed mainly on the surface oxygen ions and forms a strong bonding with them (2.7 eV). Adsorption of hydrogen on the surface zinc ions is energetically unfavorable (−4.4 eV). It also shown that surface hydrogen atoms are very shallow donors, thus, contributing to the electronic conductivity, and ZnO metallization.

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### 1. Introduction

Semiconductor ZnO with a band gap of 3.4 eV (at 2 K [1]) continues to attract great attention as a promising material for transparent conductive thin films used in optoelectronic devices, LED (light-emitting diode) based displays, solar cells, as well as for lasers and ultraviolet LEDs [2]. ZnO application in catalysis (for instance, methanol synthesis), gas detecting systems, hydrogenation and dehydrogenation stimulated a study of the atomic and electronic structure of its surface properties [2]. As is known, the optical, electronic and catalytic properties of ZnO are strongly affected by defects and impurities in the crystalline structure. These could be intrinsic defects, such as oxygen vacancies and interstitial zinc ions. However, recent first principles calculations [3,4] argue that the intrinsic defects hardly could play a significant role in the conductivity, since the energies of their creation are quite high and, thus, concentrations are low. On the other hand, hydrogen is unavoidably present during growth of ZnO samples, e.g., penetrating from plasma, which is believed to increase the ZnO conductivity [5,6]. Hydrogen atoms could occupy interstitial positions ( $H_i$ ) or substitute O ions ([5,7] and references therein).

Previous theoretical studies mainly focused on hydrogen in ZnO bulk, which serves as a shallow donor [4,8,9]. However, influence of hydrogen adatoms on the structural and electronic properties of different ZnO surfaces is not properly studied, only a few relevant papers were published on this topics so far [2,10–15], through this is important for improving production technologies of ZnO thin films. Specifically, the highest growth rate of ZnO thin films is achieved along the *c*-axis

and their external facets are usually (10 $\bar{1}$ 0) and (11 $\bar{2}$ 0). By controlling the growth kinetics, it is possible to change the ZnO growth behavior.

It was shown that hydrogen adsorption on ZnO surface plays an important role in both photochemistry and gas detecting [12]. Exposition of ZnO samples in hydrogen atmosphere results in a change of their electronic properties and, therefore, affects their conductance. A number of studies on adsorption of different species, including hydrogen, upon ZnO surfaces were performed using different experimental and theoretical methods. Thus, applying the method of photoelectron spectroscopy with angular resolution for the study of adsorption of atomic hydrogen, water and methanol upon the non-polar ZnO (10 $\bar{1}$ 0) surface, its metallization was observed [10]. A few experiments performed for the same ZnO surface (electron energy loss spectroscopy, He-atom scattering, and scanning tunneling microscopy) as well as the corresponding ab initio calculations clearly demonstrated that hydrogen adatom is presumably bonded to surface oxygen ions with release of a free electron [13]. This is confirmed by recent theoretical calculations of atomic hydrogen in ZnO bulk where H is characterized as a shallow donor [9]. According to theoretical predictions, bending of the band structure in the proximity of ZnO surface occupied by electrons released by hydrogen impurities leads to surface metallization. Analogous metallization effects were observed on SrTiO<sub>3</sub> (001) [16] and SnO<sub>2</sub> (110) [17] surfaces in the hydrogen presence.

Nevertheless, a series of recently performed ab initio calculations on hydrogenated ZnO surfaces gave quite contradictory results. For example, Wander et al. [14] did not observe metallization of ZnO (10 $\bar{1}$ 0) surface after hydrogen adsorption whereas calculations by Martins et al. [15] show that molecular hydrogen donates a fraction of the electronic charge to the surface. The density functional theory calculations on the adsorption of molecular hydrogen upon non-polar defect-containing ZnO (10 $\bar{1}$ 0) surface show also that hydrogen weakly interacts with

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**Table 1**

The LCAO calculated and experimental lattice parameters  $a$  and  $c$ , the atomic effective charges  $q(\text{Zn})$  and  $q(\text{O})$ , and the band gap  $E_g$  obtained using different exchange-correlation functionals.

	PBE0, this paper	B3LYP [9]	Expt [28]
$a$ , Å	3.274 (3.257) <sup>a</sup>	3.278	3.242
$c$ , Å	5.267 (5.223)	5.287	5.187
$u$	0.382	–	0.382
$q(\text{Zn}, \text{O}), e$	$\pm 1.0$	–	–
$E_g$ , eV	3.57 (3.18)	3.38	3.44 [1]

<sup>a</sup> Results in brackets were obtained using the plane-wave basis set [8]

the point defects [12] and its influence on the electronic structure of ZnO substrate is almost neglecting which correlates with the results obtained earlier in Ref. [14].

Aforementioned disagreements between results of various experimental and theoretical studies stimulated us to perform large-scale ab initio calculations of the atomic hydrogen adsorption upon the non-polar ZnO ( $\bar{1}\bar{1}00$ ) surface, which morphology is identical to that of non-polar ( $10\bar{1}0$ ) surface. Both are characterized by quite low surface energy (see below) and were studied earlier experimentally by means of ellipsometry and electronic energy loss spectroscopy [18]. To draw conclusions on the hydrogen influence on the electronic conductivity, we have calculated the total and projected densities of the electronic states (DOS, PDOS) which have been accompanied by analysis of the electronic charge redistribution, lattice relaxation and adsorption energy of H atom upon the ZnO ( $\bar{1}\bar{1}00$ ) surface. The paper is organized as follows: details of calculations are discussed in Section 2, main results for perfect and H-covered ( $\bar{1}\bar{1}00$ ) surfaces are analyzed in Section 3, while main conclusions are summarized in Section 4.

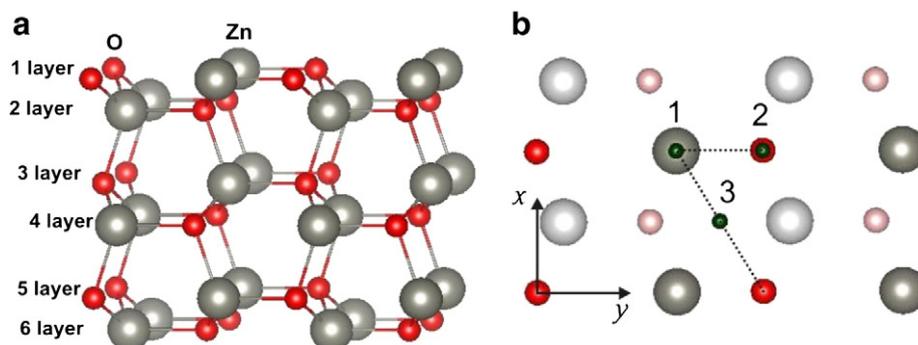
## 2. Model and method of calculations

Large-scale ab initio calculations have been performed combining the basis set of linear combination of atomic orbitals (LCAO) method with the hybrid exchange-correlation Perdew–Burke–Ernzerhof (PBE0) functional [19], which contains Perdew–Burke–Ernzerhof exchange and correlation functionals as implemented in the CRYSTAL2009 computer code [20]. The percentage of exact exchange in the PBE0 functional is 25%. Such hybrid functionals allow us to perform very accurate calculations of the band gap, unlike standard local density approximation (LDA) or generalized gradient approximation (GGA)-type functionals (Table 1). The all-electron atomic basis sets for Zn and O atoms have been taken from Ref. [21] while that for the hydrogen atom from Ref. [22]. For SCF procedure, the tolerances  $10^{-7}$ ,  $10^{-7}$ ,  $10^{-7}$ ,  $10^{-7}$  and  $10^{-14}$  have been chosen for calculations of the Coulomb overlap, Coulomb penetration, exchange overlap, first exchange pseudo-overlap

in direct space and second exchange pseudo-overlap in a reciprocal space, respectively. The force gradients with respect to atomic coordinates and lattice parameters are evaluated analytically. The equilibrium structure is determined using a quasi-Newton algorithm with a Broyden–Fletcher–Goldfarb–Shanno Hessian updating scheme [20]. Convergence in the geometry optimization process is tested on the root-mean-square (rms) and the absolute value of the largest component of both the gradients and nuclear displacements. For all atoms, the thresholds for the maximum and the rms forces have been set to 0.000450 and 0.000300 a.u., and those for the maximum and the rms atomic displacements to 0.001800 and 0.001200 a.u., respectively. Effective charges on atoms have been estimated using the Mulliken population analysis. The integration over the Brillouin zone in the reciprocal space has been performed within a  $6 \times 6 \times 4$  Pack–Monkhorst grid.

Initially, we have calculated the bulk properties of a pure ZnO using 32-atoms periodic supercell, which gave reliable results close to the experimental data (Table 1). The optimized lattice parameters  $a$  and  $c$  slightly overestimate those obtained in experiments ( $\approx 1\%$ ). The calculated effective charges indicate considerable covalency of Zn–O chemical bonds whose population is  $0.137e$ . The error in estimate of band gap width ( $\approx 3.6\%$ ) obtained using the two types of hybrid calculations are much smaller than error in standard GGA calculations (resulted in a huge underestimate of the band gap: 0.74 eV [8]). It is a well known shortcoming of LDA and GGA that both methods predict the Zn( $3d$ ) bands to be about 3 eV higher in energy as compared to experiment [23,24]. As a consequence, the Zn( $3d$ ) states hybridize stronger with the O( $2p$ ) valence bands, shifting these states unphysically close to the bottom of the conduction band. The underestimate for the band gap is therefore even more severe in ZnO than in other semiconductors. The band gap and the position of the Zn( $3d$ ) bands can be improved significantly, if a self-interaction correction (SIC) is used [25]. Usually SIC calculations are very time-consuming, however, if the SIC effects are incorporated into the pseudopotential [26], the additional computational cost is modest. Unfortunately, the SIC pseudopotential scheme does not improve the structural properties of ZnO [26] and also causes some problems when accurate atomic forces are needed [27]. If the calculated atomic geometry of the selected surface does not require the correlation of the electronic structure, it is possible to use the LDA and GGA approaches without SIC.

For simulation of hydrogen adsorption on the ( $\bar{1}\bar{1}00$ ) surface, the slab model of finite thickness along the  $z$  axis and extended by  $(2 \times 2)$  in the  $x$  and  $y$  directions corresponding to the periodic distribution of surface hydrogen atoms has been chosen (Fig. 1a). We have considered several hydrogen adsorption positions (Fig. 1b): above the surface atoms Zn (1), O (2) and in the “hollow” site (3). In order to save computation time, we have performed partial geometry optimization, in which the relaxation has been performed only for three upper layers in the surface slab model. Fig. 3a shows the calculated density of states of the



**Fig. 1.** Six-layer slab model of the ( $\bar{1}\bar{1}00$ ) surface (a) and top view of the three possible positions of the adsorbed hydrogen atom. Light gray and red balls denoted subsurface Zn and O ions whereas a dark gray and red ball is the surface Zn and O ions, respectively.

**Table 2**

The surface energy  $E_s$  ( $\text{J}/\text{m}^2$ ) for  $(1\bar{1}00)$  and  $(11\bar{2}0)$  surfaces and the effective charges  $q(e)$  of Zn and O ions on the  $(1\bar{1}00)$  surfaces of ZnO, with different thicknesses.

Number of layers	$E_s$		$q(\text{Zn})$	$q(\text{O})$
	$(1\bar{1}00)$	$(11\bar{2}0)$ [30]		
6	1.604		0.95	−0.92
8	1.606	1.4	0.98	−1.00
10	1.606	1.4	0.98	−1.00
12	1.605	1.4	0.98	−1.00
14	1.605	1.4	0.98	−1.00

**Table 3**

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.

Concentration	25% coverage		100% coverage	
	Zn	O	Zn	O
$E_{\text{ads}}$	−4.4	2.7	− <sup>a</sup>	4.0
$q_{\text{eff}}$	0.85	−0.98	− <sup>a</sup>	−0.73
$\Delta z$	−0.31	0.07	− <sup>a</sup>	−0.05
$d_{\text{Zn(O)}-\text{H}}$	1.61	0.96	− <sup>a</sup>	0.97

<sup>a</sup> No convergence.

defect-free surface slab. The energy of hydrogen adsorption has been determined using the following expression:

$$E_{\text{ads}} = E_{\text{tot}}^{\text{ZnO}} + E_{\text{tot}}^{\text{H}} - E_{\text{tot}}^{\text{H/ZnO}}, \quad (1)$$

where  $E_{\text{tot}}^{\text{H/ZnO}}$  is the total energy of  $(1\bar{1}00)$  surface slab with the adsorbed hydrogen atom,  $E_{\text{tot}}^{\text{ZnO}}$  the total energy of defect-free slab, and  $E_{\text{tot}}^{\text{H}}$  the energy of an isolated hydrogen atom in the ground state. It follows from Eq. (1) that if adsorption energy is positive, the process is energetically favorable.

### 3. Results and analysis

First, the surface energy of perfect  $(1\bar{1}00)$  surface has been calculated as a function of a slab thickness and has been compared with that for other  $(10\bar{1}0)$  and  $(11\bar{2}0)$  non-polar surfaces. Table 2 shows that the  $(1\bar{1}00)$  surface energy varies only slightly with increase of the number of layers. Therefore, six-layer slab model has been selected for calculations on both: (i) the relaxation of surface geometry and (ii) the

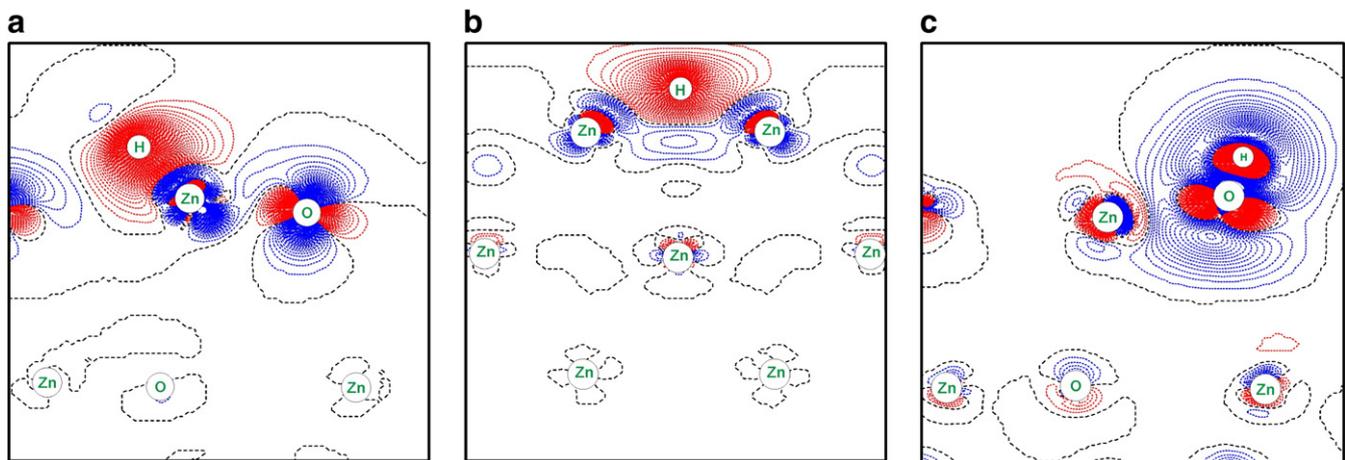
electronic properties of a pure surface. The analysis of the absolute and relative displacements of surface ions shows that after slab relaxation the surface Zn ions are displaced inwards, to the slab center, whereas O ions are shifted outwards, which is specific for non-polar surfaces of ZnO. This leads to a relatively small *surface rumpling*.

The calculated surface energy for ZnO  $(1\bar{1}00)$  is close to that for other low-index non-polar  $(11\bar{2}0)$  surface [18,29,30]. The effective charges on  $(1\bar{1}00)$  surface are smaller than in the bulk, which indicates the increased covalency of surface Zn–O bonds. The calculated displacements of atoms on the defect-free  $(1\bar{1}00)$  surface are:  $-0.212$  Å (O) and  $-0.426$  Å (Zn), in accordance with aforementioned tendency.

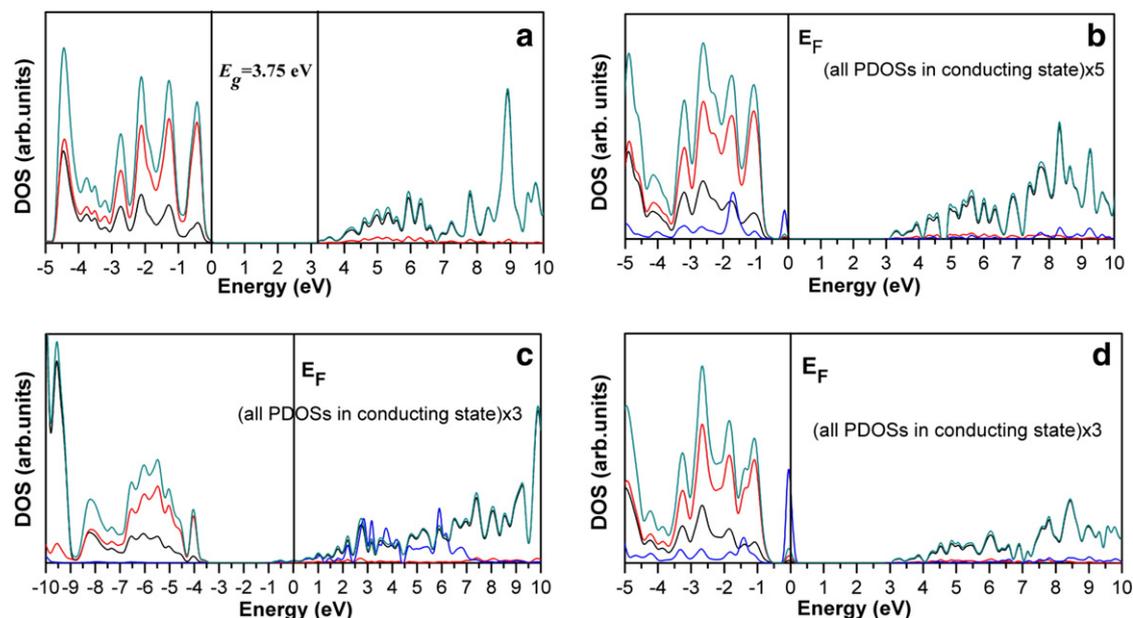
The hydrogen atom adsorption energies have been obtained for three possible positions on the surface (Table 3): at 1/4 monolayer (ML) coverage the most favorable energetically is H atom location atop the surface oxygen ions ( $E_{\text{ads}} = 2.7$  eV). An increase of H coverage above 1/4 ML, up to 1 ML leads to an increase of the binding energy of H atop the surface O ions from 2.7 to 4 eV, whereas its adsorption atop Zn remains unfavorable. Adsorption of single H atom in the *hollow* position is also energetically possible ( $E_{\text{ads}} = 0.41$  eV). If hydrogen atoms before adsorption were produced by dissociation of  $\text{H}_2$  molecules, the adsorption energy with such the reference state will be smaller by half of its binding energy. This means that only adsorption atop surface O atoms would be energetically favorable with the binding energy of 1.58 eV, whereas other configurations turn out to be unfavorable. The high resolution electron energy loss spectroscopy shows that hydrogen is adsorbed on the position atop the surface oxygen ion, whereas the hydrogen adsorption in position above the surface Zn ion is not observed at all [31,32]. This experimental observation is in a full agreement with our results.

The length of the chemical bond between the hydrogen and a surface oxygen ion is  $d_{\text{O-H}} = 0.96$  Å, considerably shorter than that in the bulk (0.982 Å), whereas its bond population is 0.215e, which is much larger than that in the bulk (0.137e). The same strong interaction between hydrogen atom and surface oxygen ion (as in the case of ZnO bulk) is also observed in the differential electron density map (Fig. 2b). Hydrogen atom also strongly polarizes nearest Zn and O ions (Fig. 2a, c). Table 3 shows also displacements of the surface Zn and O ions along the  $z$  axis, due to a presence of hydrogen on the surface (25% coverage). A comparison with ionic displacements on a perfect surface shows that both surface O and Zn ions are displaced outwards and preserve the same ordering: O ions lie higher than Zn ions. The low energy electron diffraction data for  $(10\bar{1}0)$  surface [33] give a similar pattern:  $-0.05$  Å (O) and  $-0.45$  Å (Zn).

The calculated relaxation energy for hydrogenated surface is found to be  $\sim 0.35$   $\text{J}/\text{m}^2$ , whereas for a perfect surface we have obtained



**Fig. 2.** Differential electron density plots are drawn for the hydrogen atom upon the surface positioned a) atop surface Zn ion; b) atop surface O ion; and c) atop the *hollow* position. The solid (red) and dotted (blue) isolines correspond to positive (excess) and negative (deficiency) electron density, respectively. Increment for isolines is 0.001e within the range from  $-0.1$  to 0.1e.



**Fig. 3.** DOSs projected onto all orbitals on Zn (black), O (red), H (blue) atoms, and the total density of states (cyan) for a) perfect ZnO surface, b) adsorbed hydrogen positioned atop the surface Zn ion, c) hydrogen atop the surface O ion, and d) atop the *hollow* position. Hydrogen concentration 25%. The  $E_F$  is the Fermi level. For the hydrogen atom, PDOSs are increased by a factor of 20.

$\sim 0.73 \text{ J/m}^2$ . This is in a line with the theoretical prediction [34] that the adsorbed hydrogen reduces the surface energy. The density of states (DOS) for hydrogen atom in three different positions is plotted in Fig. 3. H atop surface Zn ions reveals no energy levels in the gap, whereas hydrogen atop surface O ions could be characterized as a shallow donor. Already at 25% coverage the adsorbed hydrogen shows the density of states in the energy range overlapping the bottom of conduction band, thus transforming ZnO thin films into a conducting state (*metallization*). An increase of hydrogen coverage up to 1 ML leads to a disappearance of the band gap (not shown here).

In previous GGA calculations of atomic H adsorption on the  $(10\bar{1}0)$  surface of ZnO [13], it was claimed that if during adsorption the odd number of electrons is transferred from hydrogen atoms to the surface (1 ML coverage), this leads to partially filled electronic states (mostly consistent from 4s state of the surface Zn atoms), and should result in surface metallization. However, if all surface dangling bonds (even Zn) were saturated by hydrogen atoms, the system should change for insulating state. As indicated above, plane wave-GGA calculations strongly underestimate the band gap of ZnO (0.78 eV) which requires self-interaction corrections [29], and affects the position of the highest occupied atomic orbital in the band structure. However, in the case of 1 ML H coverage atop the surface O ions, the results of both methods reveal that hydrogen atoms can be adsorbed atop the surface oxygen atoms only, being characterized as a shallow donor, in agreement with experimental observations.

#### 4. Conclusions

As a result of the first principles hybrid LCAO calculations, we have obtained the atomic and electronic properties of ZnO with atomic hydrogen adsorbed upon the non-polar  $(1\bar{1}00)$  surface. Analysis of the electronic structure of ZnO  $(1\bar{1}00)$  surface confirms that an adsorbed hydrogen is a shallow donor at surface coverage 25% hydrogen density of state which overlaps with the conduction band bottom. Increase of H coverage beginning with  $\frac{1}{4}$  ML up to 1 ML leads to increase of the binding energy of H atop the surface O ions from 2.7 to 4 eV, whereas its adsorption atop Zn remains unfavorable. Incorporation energy of hydrogen atoms from plasma upon sample growth into interstitial positions is predicted to be energetically costly (1.8–1.9 eV) whereas

H adsorption atop surface O ions is energetically strongly favorable (2.7 eV). Thus, we expect high concentration of hydrogen on ZnO surfaces with a considerable contribution to the electronic conductivity (surface metallization).

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