The stability of polar oxide surfaces: The interaction of H$_2$O with ZnO(0001) and ZnO(0001$\bar{1}$)

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Recently, a new mechanism for the stabilization of the polar surfaces of ZnO has been proposed. This mechanism involves the transfer of electrons between the (0001) and (0001$\bar{1}$) surface. In the current study an alternative mechanism involving the adsorption of water onto the polar surfaces has been investigated using ab initio all electron, hybrid density-functional theory. On the basis of the current study, such a stabilization mechanism can be ruled out at low-temperatures and low-partial pressure of water. In addition, we present evidence that the ZnO(0001$\bar{1}$)–O surface may be a gas sensor for hydrogen. © 2001 American Institute of Physics. [DOI: 10.1063/1.1384030]

I. INTRODUCTION

Zincite (ZnO) is amongst the most widely studied of all metal oxide systems. Its surfaces display a number of interesting features including the observed stability of the clean, unreconstructed polar surfaces.1–3 Industrially, ZnO is an important material finding applications in a diverse range of activities including gas sensors and, in combination with copper, as a catalyst for methanol synthesis.

ZnO crystallizes in the Wurtzite structure which does not have a center of inversion. Consequently, when the crystal is cleaved normal to the c axis in a manner which breaks the fewest interatomic bonds, two different polar surface are formed on opposite sides of the crystal, each having only one type of ion in its outermost plane. The ideal polar surfaces may be modeled by a “slab” of material with the Zn cation outermost for the (0001)–Zn surface and the O anion outermost on the (0001)–O surface. If stoichiometry is to be conserved, and the slab to be charge neutral, any slab which has a (0001)–Zn surface on one side must have a (0001$\bar{1}$)–O surface on the other—as illustrated in Fig. 1. Within the ionic model it is clear that this slab generates an electrostatic field perpendicular to the surfaces and that its energy diverges with slab thickness.4 On the basis of the ionic model such surfaces are expected to be unstable.

In practice, a number of materials display polar surfaces. In general, these surfaces are stabilized by either reconstruction or by the presence of adsorbates on the surface which act to remove the macroscopic field.5,6 One much studied set of polar surfaces are the (111) surfaces of rocksalt materials displayed in Fig. 2. As shown in Fig. 2(a), a slab of material terminated by metal ions on one surface is terminated by a layer of oxygen ions on the other surface giving rise to a polar slab. The rocksalt surfaces can be stabilized by a (2 × 2) reconstruction, termed the octopolar reconstruction, which is shown in Fig. 2(b).7,8 In addition, such surfaces can also be stabilized by the dissociative adsorption of water. By adsorbing an OH group onto the metal terminated surface and an H atom onto the oxygen terminated surface, a fully symmetric slab with no net dipole moment can be constructed as shown in Fig. 2(c) which, on the basis of total energy calculations, has been shown to be more stable than the clean (100) surface.9,10

However, in the case of zincite such mechanisms do not have to operate, and clean, unreconstructed surfaces that show no significant defect concentration11,12 are remarkably stable, although partial occupation of surface sites13 has been deduced from grazing incidence x-ray diffraction data. Recently it was proposed that these polar surfaces can be stabilized by an electronic rearrangement in which charge is transfered from the (0001$\bar{1}$)–O surface to the (0001)–Zn surface11,14 as had been previously suggested by cluster calculations.15 Similar charge rearrangements have been proposed for rocksalt materials, but invariably lead to very high cleavage energies, which are typically greater than 10 J m$^{-2}$ (Refs. 9,16,17) and thus these surfaces are likely to adopt alternative stabilization mechanisms. For ZnO, the cleavage energy resulting from the charge rearrangement was shown to be only 4 J m$^{-2}$ which is comparable to the cleavage energy for the nonpolar surfaces.

Although the proposed charge transfer mechanism can stabilize the clean surfaces of ZnO, other mechanisms may also operate. In particular, for zincite crystals grown within an aqueous environment the crystal surfaces could be stabilized by the presence of adsorbates on the surface planes in a manner analogous to the rocksalt surfaces shown in Fig. 2(c). The (0001)–O surface will show a natural affinity for H atoms while the (0001)–Zn surface should be reactive towards OH radicals. Hence, we can envisage a near symmetric crystalline slab in which both the (0001) and the (0001$\bar{1}$) surfaces are terminated by OH groups as shown in Fig. 3. However, since the crystal does not contain a center of inversion, the slab does not have the mirror plane parallel to its surfaces achieved for the rocksalt structure. Nevertheless the presence of OH groups terminating both surfaces may con-

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tribute significantly to the stability of the surface by helping to quench the field that would otherwise be present. In the current study we have employed all electron first principles calculations based on hybrid exchange-correlation potentials to examine this possibility.

II. METHODOLOGY

All calculations were performed with the CRYSTAL code\(^{18}\) which is based on the use of periodic \textit{ab initio} LCAO (linear combination of atomic orbitals). The radial factors of the atomic orbitals were expressed as a linear combination of Gaussian type functions, and high quality basis sets at the all electron level were used throughout. Triple valence basis sets with polarization functions were used, which had been optimized in our early studies of ZnO.\(^{19}\) The relative charges on the atoms were calculated using a Mulliken partition of the total charge density. This is a somewhat arbitrary choice, since there is no unique method of performing the partition of the charge density. However, the choice of a given scheme is still extremely useful in comparing the results of calculations performed using similar basis sets.\(^{20}\) Hence, we can consistently compare the results of bulk and surface calculations.

In CRYSTAL the convergence of the real space summation of the Coulomb and exchange contributions to the Hamiltonian matrix are controlled by five overlap criteria. The control of these approximations is described in detail elsewhere.\(^{18}\) The values used in this study were \(10^{-6}, 10^{-6}, 10^{-6}, 10^{-6}, \text{and } 10^{-12}\) which result in a numerical error in the binding energy of order 1 mHartree and/or 0.01 mHartree in relative energies of different structures.
Optimization of the surface structures was performed by energy minimization using an unconstrained Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm as implemented in the DOMIN software\textsuperscript{21} with gradients of the energy being calculated by numerical differentiation with a finite difference step of 0.002 Å. Extensive tests have shown that the energy surface is smooth on this scale and that the choice of a step of 0.002 Å leads to accurate gradient determinations. A hybrid exchange and correlation functional, B3LYP, was employed.\textsuperscript{22,23} The B3LYP functional is known to model the energetic, geometric, and electronic properties\textsuperscript{24} of materials with significantly greater accuracy than gradient corrected functionals and has previously been shown to provide an excellent description of bulk ZnO, and its (10\bar{1}0)\textsuperscript{25} (11\bar{2}0)\textsuperscript{26} and the clean, unreconstructed (0001)/(00\bar{1}1)\textsuperscript{11} surfaces.

For the surface calculations a periodic two-dimensional slab of material was used. This is in contrast with many studies in which a three-dimensional supercell geometry is employed. In such studies, the slab of material is repeated in three dimensions, with equivalent slabs being separated by a vacuum gap and care must be taken to converge results with respect to the size of the gap. Within the current two-dimensional periodic calculations the boundary condition perpendicular to the slab is that the wave function decays to zero at infinity. One consequence of this choice of boundary condition is that the slab can support an electric field perpendicular to its surface if it is energetically favorable to do so. Hence, the convergence of the surface energy with respect to slab thickness can only be achieved if the electronic structure generates a field which converges to a finite value. This boundary condition is an essentially prerequisite if an unbiased examination of potential stabilization mechanisms is to be achieved. It also allows various chemical, structural, and electronic mechanisms to be studied on the same footing. In many previous studies boundary conditions that explicitly remove the field, such as the use of artificially symmetric slabs which are often non-Stoichiometric, or by the imposition of specific reconstructions have been utilized. The use of such schemes to study the stability of polar surfaces precludes the critical issue of how the macroscopic field has been quenched.

The basic repeat unit perpendicular to the polar surfaces of zincite is a two layer slab of material consisting of a Zn–O bilayer. Calculations were performed for slabs with increasing numbers of bilayers, and the optimum geometry of the slab for each thickness was found by energy minimization with respect to the atomic positions. A slab with a single repeat unit is denoted by S1, two repeat units by S2 etc., and consequently the slab shown in Fig. 3 is referred to as an S7 slab. The surface termination of the (0001)–Zn surface is taken to be a single Zn–O bilayer, and hence the assumed cleavage is via a long bond of the Würzite lattice. This choice breaks the fewest number of inter-atomic bonds and hence is expected to be the most stable termination for the polar surface.\textsuperscript{11} The relaxation of the surface geometric and electronic structure converges rapidly with slab thickness and the results are fully converged for an S7 slab.

### III. RESULTS AND DISCUSSION

#### A. Surface structure and stability

As expected, the near symmetric slab has no electrostatic field across it and hence does represent a possible stabilization mechanism for the polar surfaces. The full geometric relaxations of the system are shown in Table I. The H ions on both surfaces have similar charges of $-0.22|e|$ for the H on the (00\bar{1}1)–O surface and $-0.30|e|$ for that on the (0001)–Zn surface. This should be compared to a value of $-0.06|e|$ for an isolated water molecule and $-0.47|e|$ for the H in an isolated OH\textsuperscript{-} group calculated using identical computational conditions. The OH\textsuperscript{-} group terminating the (0001)–Zn has a bond length of 0.918 Å compared to 0.973 Å for the water molecule and 0.969 Å for the OH\textsuperscript{-} group.

### TABLE I. Bond lengths of the ZnO (0001)Zn–OH and (00\bar{1}1)–O–H surfaces. All values are given in Å, and the subscripts refer to bilayers numbered from the surface plane (e.g., Zn\textsubscript{1} and O\textsubscript{1} are the Zn and O ions in the surface bilayer). Unlabeled atoms refer to the adsorbed object.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0001)–Zn–OH</td>
<td></td>
</tr>
<tr>
<td>H–O</td>
<td>0.918</td>
</tr>
<tr>
<td>O–Zn\textsubscript{1}</td>
<td>1.879</td>
</tr>
<tr>
<td>Zn\textsubscript{1}–O\textsubscript{1} (in bilayer)</td>
<td>1.973</td>
</tr>
<tr>
<td>O\textsubscript{1}–Zn\textsubscript{2} (along c axis)</td>
<td>1.992</td>
</tr>
<tr>
<td>(00\bar{1}1)–O–H</td>
<td></td>
</tr>
<tr>
<td>H–O</td>
<td>0.993</td>
</tr>
<tr>
<td>O\textsubscript{1}–Zn\textsubscript{1} (in bilayer)</td>
<td>1.974</td>
</tr>
<tr>
<td>Zn\textsubscript{1}–O\textsubscript{1} (along c axis)</td>
<td>1.991</td>
</tr>
<tr>
<td>O\textsubscript{1}–Zn\textsubscript{1} (in bilayer)</td>
<td>1.973</td>
</tr>
<tr>
<td>Zn–O (in bilayer)</td>
<td></td>
</tr>
<tr>
<td>Zn–O (along c axis)</td>
<td>1.99</td>
</tr>
</tbody>
</table>
On the (0001) – O surface the O–H bond length is 0.993 Å. Consequently, the nature of the OH groups on both surfaces is intermediate between that of an isolated OH− and the OH group within a water molecule.

Interestingly, the slab pictured in Fig. 3 is unstable with respect to the clean surface and an isolated H2O molecule by about 0.1 eV per molecule in the athermal limit (i.e., at zero temperature and pressure). The calculation used here models the simultaneous formation of both ZnO(0001)–OH and ZnO(0001)–H. This is a necessary consequence of the unbiased modeling of the polar system. Within this model it is not possible to discuss the bond energies or stabilities of adsorption on the individual surfaces. Instead, we define the stability of the slab relative to the cleavage energy of the (0001)/(0001) system and a water molecule. The instability of the slab means that the simple mechanism for the stabilization of polar surfaces involving the dissociative adsorption of water, which have been proposed for systems such as MgO9,10 do not operate for zincite. This is in line with experimental observations of the interaction of water with the polar surfaces of ZnO in which adsorption is only observed at temperatures below 130 K and appears to be molecular in nature.28,29

Although the water terminated slab will become stable as the temperature and pressure are raised, the fundamental quantity of interest when discussing the stability of the polar oxide surfaces is the zero temperature and pressure limit. The electronic mechanism11 is thus outcompeting the chemical stabilization mechanism, which is an indication of effectiveness of the charge transfer mechanism in stabilizing the polar surfaces of zincite.

B. Surface electronic structure

Within the water terminated zincite slab, all charges on the ions are close to their bulk values except for the bilayer terminating the (0001) – O surface. This includes the bilayer terminating the (0001)–Zn surface which is metallic in nature for the clean surface.11 Upon OH adsorption the metallic Zn-4s band, which is occupied at the clean surface, rises above the Fermi energy and the Zn-ions in the surface layer revert to essentially the bulk ZnO charge state. Thus, adsorption of OH makes the (0001)–Zn surface nonmetallic. After H adsorption at the (0001)–O surface the Zn-ions in the surface bilayer have an addition charge of $-0.144|e|$ relative to those in the bulk. The excess electrons occupy Zn-4s states which are apparent in the slab band structure displayed in Fig. 4. The strongly dispersing Zn 4s band is confined to the outermost bilayer of the surface. This band is partially occupied and hence we predict that the (0001)–O surface will display metallic conductivity upon exposure to hydrogen.

The induction of metallic conductivity upon exposure of the (0001)–O surface to H is strongly indicative of gas sensing action. Zincite is a well-known gas sensing material which displays electronic rather than ionic conductivity.30 The well-known tendency of density-functional theory to underestimate band gaps, and thus to favor the metallic state, does not significantly affect these conclusions as the hybrid B3LYP functional used here has recently been demonstrated to accurately model the band gap in a wide range of ionic, semi-ionic and covalent systems.24

To the best of our knowledge, gas sensing activity has not previously been demonstrated within an ab initio calculation. Our previous studies of H adsorption onto the (1010) surface of zincite showed no evidence of either band gap states or band gap closing,27 and hence, that surface would appear to be inactive as an H gas sensor. Instead, the metallization of the polar surface upon exposure to hydrogen is an intrinsic property of the (0001)–O surface and is intimately linked to the charge-transfer mechanism which stabilizes the polar surfaces of zincite.

Although the current calculations are strongly indicative of gas sensing action within slabs of zincite terminated by polar surfaces, they do not demonstrate that the (0001)–O surface will act as a hydrogen gas sensor. Within our calculations, we have adsorbed H onto the (0001)–O surface and an OH group onto the (0001) surface. The stabilization mechanism of idealized slab used to model the polar surfaces involves a strong coupling between the two faces of the material via charge transfer, and hence the observed surface properties of one face of a polar crystal of zincite are strongly dependent on the state of the other face of the crystal. It is likely that in practice bulk and surface defects will destroy this coupling and may affect the metallization of the surface layer. Further simulation and detailed measurements are required to elucidate the sensitivity of the surface electronic structure to defects. In addition the data presented here has direct implications for experimental studies of high quality, thin film metal oxides that display polar surfaces since it implies that both faces of the crystal must be prepared and cleaned simultaneously.

IV. CONCLUSIONS

The polar surfaces of zincite are not stabilized by the dissociative adsorption of water. This implies that the recently proposed electronic mechanism13 involving charge transfer between the (0001) and (0001) surfaces is extremely efficient at stabilizing these surfaces. In addition, we have
shown that the interaction of hydrogen with the \((000\overline{1})\)–O surface of zincite gives rise to surface metallization which is strongly indicative of gas sensing activity. This surface metallization is associated with partial occupancy of a Zn-4s band localized in the surface bilayer of \((000\overline{1})\)–O surface. The metallization occurs for unreconstructed, defect free surfaces and does not depend upon the presence of pre-adsorbed oxygen on the surface. No evidence of similar effects has been observed in studies of the ZnO(10\overline{1}0) surface and hence it appears that the ability of zincite to act as a gas sensor may be an intrinsic property of the unique electronic rearrangement needed to stabilize its polar surfaces.