Surface Properties of Transparent Conducting Oxides from First Principles: In$_2$O$_3$, SnO$_2$, and ZnO

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We combine density functional theory and most modern quasiparticle calculations based on many-body perturbation theory to investigate the electronic surface properties of the transparent conducting oxides In$_2$O$_3$, SnO$_2$, and ZnO. We employ an alignment method based on the electrostatic potential to determine the ionization potentials and electron affinities for various surface orientations and terminations. We also calculate surface energies for different surface orientations and terminations of In$_2$O$_3$. We observe a large influence of the surface orientation and surface preparation technique on these fundamental quantities.

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I. INTRODUCTION

The transparent conducting oxides (TCOs) In$_2$O$_3$, SnO$_2$, and ZnO are routinely used as transparent electrodes in optoelectric and photovoltaic devices [1] and are promising candidates for future applications in transparent electronics based on doped oxides [2, 3]. They are transparent not only in the visible spectral region of about 400 to 700 nm but almost in the entire range of the solar spectrum and usually exhibit a high electron conductivity [4–6]. Such oxides are also used in silicon (Si) photonics and Si-based solar cells [7]. Electronic properties of their surfaces like ionization energy, electron affinity and the existence of surface states within the fundamental gap can be used to predict natural band discontinuities at the interfaces with other materials such as Si [8, 9]. Consequently, knowledge of these parameters is of great interest, but poor in practice.

Since density functional theory (DFT) is known to underestimate the fundamental band-gap of semiconductors, many body effects have to be taken into account correctly to describe the electronic properties of oxides [10–13]. Therefore, we use modern quasiparticle (QP) calculations based on many-body perturbation theory [12, 14] to predict the electronic bulk properties of the body-centered cubic (bcc) bixbyite as well as the rhombohedral (rh) geometry of In$_2$O$_3$, the most favored rutile (rt) geometry of SnO$_2$ and wurtzite (wz) structure ZnO. We combine the results with DFT ground-state calculations to obtain surface energies, ionization potentials and electron affinities for various surface orientations and terminations of the TCOs. The underlying theoretical and computational methods are described in Sec. II. In Sec. III our results are presented and their reliability discussed in the light of available measured values. Finally, in Sec. IV, we give a brief summary and conclusions.

II. COMPUTATIONAL METHODS

The ground-state properties of the oxides are determined in the framework of DFT [15], employing the local density approximation (LDA) [16] for exchange and correlation (XC). Explicitly, we use the XC functional of Ceperley and Alder [17]. The ground-state properties of ZnO have been computed in the generalized gradient approximation (GGA), using the PW91 functional to model XC [18]. All computations are done with the Vienna \textit{Ab initio} Simulation Package (VASP) [19]. The electronic wave functions are expanded using a plane-wave plane basis set up to cutoff energies of 550 (In$_2$O$_3$), 450 (SnO$_2$), and 500 eV (ZnO), respectively [10–14]. The projector-augmented wave (PAW) method [20] is used to describe the electron-ion interaction in the core region. Usually it allows for the accurate treatment of first-row elements such as oxygen and localized semiconductor states such as In $d$, Zn$3d$, and Sn$4d$ by modest plane-wave cutoffs. Brillouin-zone (BZ) integrations are emulated by summations over special points of the Monkhorst-Pack (MP) type [21]. Monkhorst-Pack meshes of $5 \times 5 \times 5$ (cubic) or $8 \times 8 \times 8$ (rhombohedral) $k$-points are found to be sufficient for In$_2$O$_3$ [10]. For hexagonal ZnO a $12 \times 7$ mesh is applied [12]. In the rt-SnO$_2$ case, we use a mesh of $8 \times 8 \times 14$ $k$-points [13].

Minimizing the total energy obtained within DFT-LDA or DFT-GGA we obtain the cubic ($a_0$) and non-cubic ($a$, $c$) lattice constants for bulk TCOs. For In$_2$O$_3$ we find values $a_0 = 10.09$ Å [10] (experiment: 10.12 Å [22]) and 5.48 Å [10] (experiment: 5.49 Å [22]) for the bcc and rh structure, respectively. In the case of rt-SnO$_2$ we get $a = 4.74$ Å and $c = 3.20$ Å [13] (experiment: $a = 4.74$ Å and $c = 3.19$ Å [23]), and, finally, for wz-ZnO we observe $a = 3.28$ Å and $c = 5.28$ Å (experiment: $a = 3.25$ and $c = 5.2$ Å [23]). With the exception of $c$ for wz-ZnO the lattice constants differ from the corresponding measured values by less than 1%.

The resulting structural parameters are used for the...
The calculation of the QP band structures \([14, 24]\). The QP equation with a self-energy in Hedin’s GW approximation is solved perturbatively on top of the self-consistent solution of a generalized Kohn-Sham (gKS) equation. In the zeroth approximation we describe the GW self-energy by the spatially non-local XC potential \(V_{XC}(x,x')\) using the hybrid functional HSE06 of Heyd, Scuseria, and Ernzerhof \([25–28]\). The QP shifts for the gKS eigenvalues are computed within the \(G_0W_0\) approach \([29]\). It has been demonstrated that for the compounds investigated this treatment leads to energy gaps in excellent agreement with measured values \([10, 12–14, 30]\).

The surface calculations are carried out using the repeated slab supercell method. The number of layers in the slab is 9 (bcc-In\(_2\)O\(_3\)(001)), 8 (bcc-In\(_2\)O\(_3\)(110)), 11 (rh-In\(_2\)O\(_3\)(001)), 8 (rt-Sn\(_2\)O\(_3\)(001)), 19 (rt-Sn\(_2\)O\(_3\)(100)), 6 (wz-ZnO(1010)), and 20 (wz-ZnO(0001)), with 12 \(\AA\) of vacuum each. Usually orthorhombic slabs are applied resulting typically in \(N\times N\times 1\) MP meshes, with \(N = 3, 8, 8,\) and 12 for bcc-In\(_2\)O\(_3\), rh-In\(_2\)O\(_3\), Sn\(_2\)O\(_3\)(001), and ZnO, respectively. For the Sn\(_2\)O\(_3\)(100) slab we use an MP mesh of \(8 \times 14 \times 1\). For polar directions, i.e. bcc-In\(_2\)O\(_3\)(001), Sn\(_2\)O\(_3\)(001), and ZnO(0001), we come up against the fundamental problem of a net dipole moment within the slab, and the additional difficulty that a slab with two non-equivalent surfaces does not allow the computation of surface energies. To get around these obstacles we employ symmetric slabs by breaking the stoichiometry within the supercell and adding an additional layer of oxygen or, alternatively, metal atoms. Since the ZnO(0001) direction cannot be symmetrized this way due to different bond lengths in the [0001] and the [001] direction, respectively, we mirrored this slab along a central Zn-layer, thereby creating an unphysical strain in the center of the slab. Since the lateral cell-size of the (0001)-1 \(\times\) 1 slab is small, we make the slab thick enough to obtain a converged electrostatic potential exhibiting bulklike oscillations, but due to the unphysical and unknown strain we cannot calculate surface energies for this surface orientation.

To obtain the electronic energy levels in the slabs one needs to determine the electrostatic potential \(V(z)\) acting on the electrons. It can be derived from the effective single-particle potential occurring in the Kohn-Sham equation \([16]\) or the generalized Kohn-Sham equation \([14]\) and is defined as the local part of the electron-ion interaction represented by the pseudopotentials and the Hartree potential of the electrons. This holds independently of the local (LDA), semi-local (GGA) or non-local (HSE06) description of the exchange-correlation part of the effective single-particle potential.

The ionization energy

\[
I = E_{vac} - E_v
\]

and the electron affinity

\[
A = E_{vac} - E_c
\]

are defined as the energy difference between the vacuum level \(E_{vac}\), i.e. the electrostatic potential seen by an electron in the vacuum, and the valence band maximum (VBM) \(E_v\) and the conduction band minimum (CBM) \(E_c\), respectively. To obtain QP values for \(I\) and \(A\), one has therefore to align the QP bulk band structure with the electrostatic potential as obtained through the DFT-LDA slab calculations. As an example, the alignment for the ZnO(1010) surface is shown in Fig. 1. The plane averaged electrostatic potential \(V(z)\) exhibits the characteristic atomic oscillations in the area of the slab and reaches a plateau in the vacuum region. By aligning the atomic oscillations in the slab with those obtained via the bulk calculation one can calculate \(I\) and \(A\).

In computing \(I\) and \(A\) using this method we come up against a theoretical problem in the QP description. The GW approximation sets the vertex function \(\Gamma\) for the calculation of the XC self-energy \(\Sigma = GW\) to \(\Gamma = 1\). It has been shown that the inclusion of vertex corrections changes the position of the SiO\(_2\) VBM by 0.6 eV while the gap is closed by 0.5 eV, so that \(I\) and \(A\) are reduced by 0.6 eV and 0.3 eV, respectively \([31]\). Therefore, a variation of the band edges of about 5—10 % due to further many-body effects cannot be excluded.

The surface energy \(E_{SF}\) is defined as the energy cost for creating the surface. For stoichiometric cells with symmetric slabs with surface area \(A\) containing \(N\) bulk unit cells it can be easily calculated by

\[
E_{SF} = \frac{E_{slab} - NE_{bulk}}{2A}.
\]

where \(E_{slab}\) and \(E_{bulk}\) are the calculated total energies for the slab and the bulk unit cell respectively. For non-stoichiometric slabs we have to generalize the formalism to include the chemical potential \(\mu_{cat}\) and \(\mu_{ox}\) of the cation (i.e. In, Sn, or Zn) and oxygen atom, respectively \([32]\). For a slab with \(N_{cat}\) cations and \(N_{ox}\) oxygen atoms equation (3) then turns into

\[
E_{SF} = \frac{1}{2A} \left[ E_{slab}(N_{cat}, N_{ox}) - N_{cat}\mu_{cat} - N_{ox}\mu_{ox} \right].
\]

The chemical potentials of the atoms are related by

\[
N_{cat}\mu_{cat} + N_{ox}\mu_{ox} = \mu_{bulk},
\]

where \(N_{cat}\) and \(N_{ox}\) denote the number of cations and oxygen atoms per formula unit, respectively.
The vacuum level is used as energy zero.

\[ E_{\text{bulk}}/n_{\text{unit}} \]

is the chemical potential per formula unit, and \( n_{\text{unit}} \) the number of formula units per bulk unit cell. Substituting Eq. (5) into Eq. (4), we obtain

\[ E_{\text{SF}} = \frac{1}{2A} \left[ E_{\text{slab}} - \frac{N_{\text{cat}}}{n_{\text{cat}}} \mu_{\text{bulk}} + \left( \frac{n_{\text{cat}}}{n_{\text{cat}}/N_{\text{cat}} - N_{\text{O}}} \right) \mu_{\text{O}} \right] \text{.} \tag{6} \]

This enables us to determine surface stabilities in dependence on the chemical potential of the oxygen atom, usually given in relation to \( \mu_{\text{O}} \), the chemical potential of the free \( \text{O}_2 \) molecule as obtained via a LDA total energy calculation of a free oxygen molecule.

### III. RESULTS AND DISCUSSION

We determine the ionization energies and electron affinities of the TCOs for different surface orientations and terminations. The results are listed in Table I and displayed in Fig. 2.

There are only few measurements of the surface properties of \( \text{In}_2\text{O}_3 \) and Sn-doped-\( \text{In}_2\text{O}_3 \) (Indium-Tin Oxide, ITO). The electron affinity seems to vary in the range of \( A = 4.1...5.0 \) eV in dependence on the doping concentration (see Ref. 33 and references therein). Together with the measured gap of 3.6 eV, ionization energies of \( I = 7.7...8.6 \) eV may be derived. Klein [34] suggested values of \( A = 3.5 \pm 0.2 \) eV and \( I = 7.1 \pm 0.15 \) eV for evaporated \( \text{In}_2\text{O}_3 \) films. In a more recent paper [35] the same author gave values of \( A = 4.45 \) eV and \( I = 8.05 \) eV for ITO samples. Our theoretical values show a strong influence of the surface orientation and termination. The oxygen-terminated (001)-surface differs from the indium-terminated surface by more than 3 eV. This is due to the strong influence of the direction of the surface dipole in highly polar materials like the TCOs. Dangling bonds located at the oxygen atoms will most likely increase polarity and, hence, the surface dipole of the slab. On the other hand, the In-termination will decrease the dipole, lowering the surface barrier for electrons. To illustrate this, we have plotted the plane average \( V(z) \) of the electrostatic potential for different terminations of the \( \text{bcc}-\text{In}_2\text{O}_3 \) (001) surface in Fig. 3 (a). The atomic structure of the different surfaces is shown in Fig. 3 (b) along with isosurface plots of the electrostatic potential \( V(x) \) that illustrate the higher surface barrier for the oxygen termination of this surface. All in all, our predictions seem to overestimate the experimental findings. The discrepancies to the largest experimental values are of the order of 0.5 eV. Apart from uncertainties in the theoretical description, like the neglect of vertex corrections in the GW approximation, several problems of the real-structure surfaces such as doping influence, surface coverage (and, hence, surface dipole), and sample quality may occur. Also the gap value of 3.6 eV taken from optical measurements deviates by 0.5 eV from the recently predicted one [36], mostly due to the fact that the lowest interband transitions are dipole-forbidden in the bixbyte structure [37].

There are several measurements regarding the surface barrier of \( \text{wz-}\text{ZnO} \), which vary over a wide range. Jacoby et al. [38] found electron affinities of \( A = 3.7, 4.5 \), and 4.6 eV depending on surface orientation and termination. Other electric measurements yield an electron affinity of \( A = 4.64 \) eV [39]. A value of \( A = 4.05 \) eV is derived from studies of the semiconductor-electrolyte interface [40] which yields \( I = 7.45 \) eV taking into account the known gap [41]. Another measurement gave \( I = 7.82 \) eV [42]. Again, it seems that we overestimate the measured values.

The surface properties of \( \text{SnO}_2 \) are hardly known. Measurements gave \( A = 4.44 \) eV [40] which, in combination with the gap of 3.6 eV measured for \( rt-\text{SnO}_2 \) [41], yields an ionization energy of \( I = 8.04 \) eV. For tetragonal \( \text{SnO}_2 \), a variation in the interval \( I = 7.9 - 8.9 \) eV, depending...
TABLE I: Characteristic energies: fundamental gap $E_g$, electron affinity $A$ and ionization energies $I$ of transparent conducting oxides derived from QP calculations. All values in eV. The surface orientation used for the calculation of $I$ and $A$ is indicated by the Miller indices ($hkl$) or (hkl). Experimental values are given in parentheses.

| Crystal     | Orientation | $E_g$  | $A$  | $I$  |
|-------------|-------------|--------|------|------|
| $\tau$-In$_2$O$_3$ | (0001)      | 3.79   | 6.11 | 9.41 |
|             | (0001)      | 3.02   |      |      |
| bcc-In$_2$O$_3$ | (001)       | 3.15   | 6.10 | 9.25 |
|             | (001)       |        | 9.22 | 12.37|
|             | (110)       |        | 5.30 | 8.45 |
| rt-SnO$_2$  | (100)       | 3.64   | 4.10 | 7.73 |
|             | (001)       | 3.58   | 3.50 | 7.08 |
|             |             | (3.5−5.0) |      |      |
| wz-ZnO      | (0001)      | 3.21   | 5.07 | 8.24 |
|             | (1010)      | 3.65   | 4.41 | 6.84 |
|             |             | (3.38) | (7.1−8.6) |      |

The results were compared with the few experimental data available. Even though the experimental values are at variance, we found nevertheless a slight but systematic overestimation of ionization energy and electron affinity in our predictions. This is most likely due to the omission of vertex corrections in the quasiparticle calculations. The only exception to this rule was SnO$_2$, possibly due to the influence of states within the fundamental gap.

IV. SUMMARY AND CONCLUSIONS

We have investigated the electronic properties of the transparent conducting oxides In$_2$O$_3$, SnO$_2$ and ZnO by means of quasiparticle calculations based on many-body perturbation theory. The resulting band structures with rather accurate fundamental band gaps were combined with density functional theory calculations of material slabs to investigate electronic surface properties for different surface orientations and terminations. For this purpose the bulk and surface electronic structures have been energetically aligned using the electrostatic potential as reference.

The surface energy $E_{SF}$ per unit area of the In-terminated (black) and O-terminated (red) (001) surface as well as the non-polar (110) surface (blue) of bcc-In$_2$O$_3$ surfaces in dependence of the chemical potential $\mu_O$ of the oxygen atom. The energy zero is set to half the chemical potential of a free O$_2$ molecule.

FIG. 4: Surface energy $E_{SF}$ per unit area of the In-terminated (black) and O-terminated (red) (001) surface as well as the non-polar (110) surface (blue) of bcc-In$_2$O$_3$ surfaces in dependence of the chemical potential $\mu_O$ of the oxygen atom. The energy zero is set to half the chemical potential of a free O$_2$ molecule.

80 meV, this changes drastically in oxygen-poor environments, and the In-terminated surface becomes equally stable or even energetically favored over the oxidized surface. The non-polar (110) surface with a surface energy $E_{SF} = 0.11$ eV/Å$^2$ is energetically favored to both (001) phases in practically all settings. We therefore conclude, that the ionization energy and electron affinity of bcc-In$_2$O$_3$ strongly depends on the preparation conditions of the sample.
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