Periodic study on the structural and electronic properties of bulk, oxidized and reduced SnO$_2$(1 1 0) surfaces and the interaction with O$_2$

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Abstract

The structural and electronic properties of bulk and both oxidized and reduced SnO$_2$(1 1 0) surfaces as well as the adsorption process of O$_2$ on the reduced surface have been investigated by periodic DFT calculations at B3LYP level. The lattice parameters, charge distribution, density of states and band structure are reported for the bulk and surfaces. Surface relaxation effects have been explicitly taken into account by optimizing slab models of nine and seven atomic layers representing the oxidized and reduced surfaces, respectively. The conductivity behavior of the reduced SnO$_2$(1 1 0) surface is explained by a distribution of the electrons in the electronic states in the band gap induced by oxygen vacancies. Three types of adsorption approaches of O$_2$ on the four-fold tin at the reduced SnO$_2$(1 1 0) surface have been considered. The most exothermic channel corresponds to the adsorption of O$_2$ parallel to the surface and to the four-fold tin row, and it is believed to be associated with the formation of a peroxo O$_2$$^-$ species. The chemisorption of O$_2$ on reduced SnO$_2$(1 1 0) surface causes a significant depopulation of states along the band gap and it is shown to trap the electrons in the chemisorbed complex producing an electron-depleted space-charge layer in the inner surface region of the material in agreement with some experimental evidences. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

SnO$_2$ has been widely used as a component in microelectronic devices like gas sensor, varistor and catalyst [1–6], and its performance is believed to be governed by the interaction with molecular oxygen [2,6,7]. It has been suggested that the adsorption of
oxygen molecules on the SnO$_2$ surface produces an electron-depleted space–charge layer in the inner surface region of the particle and some anionic oxygen species on the surface [3,4,8–10]. As a result, a potential barrier between adjacent grains is created. The concentration and the nature of the anionic oxygen species are believed to control the main features, i.e. height and width of the potential barrier, which determine the electrical features of the material (conductivity and non-ohmic behavior). For instance, when exposed to an inflammable gas environment, the concentration of surface oxygen decreases due to the surface reaction, modifying the charge distribution at the interface of the particle and altering the shape of the potential barrier. Therefore, the conductivity is changed and the interacting molecule can be detected.

In addition to the physical/chemical properties of well-known materials, a wide variety of theoretical and computational techniques are available for the prediction of electronic structure of these materials even before experiments. The reliability and predictive capability for a great deal of computing methods have been revised elsewhere [11–14]. As far as SnO$_2$ surfaces are concerned, computational methods have been recently used to rationalize their electronic and chemical properties [15–20].

To the best of our knowledge, four theoretical studies have recently focused on the interplay between oxygen species and SnO$_2$(1 1 0) surface. Yamaguchi et al. [21,22] have investigated the stability of oxygen species O$^\cdot$ and O$_2$ and their role in the methane oxidation on the reduced SnO$_2$ surface by using a point–charge model together with DFT (B3LYP) and MP2 calculation. Their results reveal that O$^\cdot$ species on the surface is the main active center for the dissociation of a C–H bond of methane. Later, Yamaguchi et al. [23] have also investigated the adsorption of O$_2$ on reduced SnO$_2$(1 1 0) surface by means of the DFT calculation with the BLYP functional within the cluster models approach. It has been proposed that the side-on type adsorption is related to a peroxo O$_2^\cdot$ species, whereas the end-on one was assigned to a superoxo O$_2^ -$ species. However, such assignments conflict with previous photoemission study by some of these authors [10]. Catlow and coworkers [24] have compared three conceivable routes for dissociation of O$_2$ on reduced (1 1 0) SnO$_2$ surface. They have predicted an exothermic O$_2$ dissociation, where one bridging vacancy is occupied and one adatom is formed, by means of plane-waves LDA calculations.

Despite the results of these studies, the nature of the molecular mechanism by which the interplay between O$_2$ and SnO$_2$(1 1 0) surfaces occurs is still very poorly understood. In this work, we have carried out periodic DFT-B3LYP calculations in order to gain knowledge in the electronic and structural features related to the stoichiometric and reduced surfaces as well as the adsorption of O$_2$ on SnO$_2$(1 1 0) surface. The study of metal oxides, together with adsorption processes on their surfaces, constitutes a basic research area in our group, which has long maintained an interest in the theoretical and experimental study of these systems [25–27].

This paper is organized as follows: Section 2 summarizes the model systems and computing method; results and discussion are presented in Section 3, while a final section of conclusions closes the work.

2. Model systems and computing method

2.1. Bulk and surfaces models

The 6-atom tetragonal rutile unit cell of SnO$_2$ is characterized by two lattice parameters $a$ and $c$ and the internal parameter $u$ [28,29]. In this study, a full geometrical relaxation is carried out to determine the bulk equilibrium structure. SnO$_2$(1 1 0) surface is the most stable of the low-index faces [3,19,30] and hence, the dominant crystallite arrangement of SnO$_2$. However, due to the variable valence of Sn, the material readily loses surface oxygen, which allows the SnO$_2$(1 1 0) surface to be obtained in different oxidation degrees depending on the experimental conditions employed: oxidized (stoichiometric), partly reduced, reduced and defective. In the present study we have concentrated our attention on oxidized and reduced surfaces. Detailed description of these surfaces can be found elsewhere [3,31,32].
The structures of SnO$_2$(1 1 0) surfaces will be briefly commented, as they constitute a background for understanding the following discussion. The oxidized SnO$_2$(1 1 0) surface is shown in Fig. 1a. The outermost atomic layer is composed of two-coordinate oxygen anions O$_{2c}$, which occupy bridging positions between tin fully coordinated cations Sn$_{6c}$ located in the second layer. The second atomic layer also exposes unsaturated five-coordinate tin atoms Sn$_{5c}$ as well as fully three-coordinated oxygen atoms O$_{3c}$. The third atomic layer is constituted of sub-bridging oxygen atoms. The removal of the bridging oxygen layer from the oxidized surface results in what is called the reduced (1 1 0) surface, shown in Fig. 1b.

Our calculations on the oxidized and reduced surfaces have been done by using slab models of nine and seven thick atomic layers, infinite and periodic in directions transverse to the surface plane, as shown in Fig. 1a and b. The thickness of the models was determined by convergence tests on surface energy values and charges distribution with respect to the number of atomic layers as previously reported [25].

2.2. Computing method

The calculations were made in the framework of the density functional theory with the hybrid functional B3LYP [33,34], which has been
demonstrated by Muscat et al. [35] to be suitable for calculating structural parameters and band structures of a wide variety of solids. Sn and O centers have been described in the scheme [DB]-31G and [DB]-21G, respectively, where [DB] stands for the Durand–Barthelat’s non-relativistic large effective core potential [36]. The definition of core and valence electrons is as follows: Sn = [Kr]5s²5p² and O = [He]2s²2p⁴. The corresponding exponents and coefficients for the valence double-zeta basis set representing the Sn and O centers as well as the pertinent optimization process has already been reported in our previous study [25].

All the calculations have been carried out with the crystalline orbital program CRYSTAL98 [37]. Optimizations have been made with the Powell algorithm [38] until a convergence in energy of 10⁻⁶ hartree is found. Mulliken population analysis was used in this work. This choice was based on the simplicity, frequent application of the method in theoretical calculations of similar systems and convenient interpretation of the results in the light of the chemical intuition. The XCrysDen program was used to design the density of states (DOS, total number of electronic states per unit energy) diagrams [39].

We have assumed singlet electronic state for the calculations on the adsorption process of oxygen molecule on SnO₂ surface because it is believed that distribution of spin density of O₂ molecule (fundamental triplet state) is not retained when it is absorbed. This assumption has also been invoked by Markovits and Minot [40] in ab initio periodic calculations of O₂ dissociation in perfect Si(1 0 0) surface, based on the fact that the more stable systems when the adsorption is completed correspond to a singlet electronic state. For the triplet oxygen adsorption on the SnO₂ surface no minimum in the potential energy surface was found for the different orientation approaches.

3. Results and discussion

3.1. Bulk structural and electronic features of SnO₂

The optimized parameters for SnO₂ bulk are shown in Table 1. The resulting relaxed parameters of \( a = 4.718 \) Å, \( c = 3.187 \) Å and \( u = 0.307 \) Å, are in good agreement with both experimental and previous theoretical data.

The calculated bulk SnO₂ band structure along the symmetry lines of the simple tetragonal Bravais lattice is illustrated in Fig. 2. The most important feature of the calculated bulk band structure of SnO₂ reported here is the band gap value of 3.3 eV, very close to the experimental value of 3.6 eV. It should be pointed out that we have calculated all photoelectron features taking no account of electronic relaxation associated with the electronic transition. The band gap is located at the \( \Gamma \)-point of the Brillouin Zone (BZ) and corresponds to a direct transition, in agreement with experimental results. Except for changes in scale, the band structure of SnO₂ reported here is topologically similar to those previously calculated by other authors [41–43] and some of us (DFT at GGA-PW level) [25]. The theoretical valence band (VB) width of \( \approx 9.0 \) eV is found to be in excellent agreement with experimental results, 9.0 eV [44].

Total DOS for the bulk SnO₂ and the most relevant projected DOS for Sn and O atoms are depicted in Fig. 3. The traced line is the calculated Fermi level with respect to the vacuum level and corresponds to a value of \(-4.0 \) eV (different from the band structure shown in Fig. 2, where the Fermi level is fixed to 0.0 eV). A value of \(-4.35 \) eV was recently determined by photoemission yield spectroscopy (PYS) [45]. Projections onto the 5s and 5p orbitals of the tin atoms are depicted in Fig. 3a and b, respectively. It is observed that these states are predominantly located in the conduction band (CB) of the bulk SnO₂, although a smaller
contribution is also found in the VB. 2p states of the oxygen atoms concentrate in the VB, as shown in Fig. 3d; on the other hand, 2s states are observed in the most internal region, 8.5 eV far from the lower extreme of the VB, as shown in Fig. 3c. As a result, the VB is mostly located in the oxygen atoms, whereas the CB concentrates on the tin atoms. The upper extreme of the VB is constituted of 2p states of the oxygen atoms, whereas the lower extreme of the CB is formed by 5s states of the tin atoms.

The overlapping between neighboring atoms orbitals using the density matrix is a measure of the covalent character of the bond. The difference in energy between the valence states of the oxygen atoms, 2p, and those of the tin atoms, 5s and 5p, reveals that the ionic character exhibited by the oxide predominates in the Sn–O bonds.

3.2. Oxidized and reduced SnO$_2$(110) surfaces

Once examined the bulk SnO$_2$ relaxation, we first have built up the slab models for representing the oxidized and reduced SnO$_2$(110) surfaces employing the crystallographic parameters derived from the theoretical equilibrium structure of the SnO$_2$ bulk. We have also calculated the surface energy for the unrelaxed-oxidized surface, usually defined as the total energy per repeating cell of the slab minus the total energy of the same number of atoms of the perfect crystal, divided by the surface area per repeating cell of the two sides of the slab. The calculated surface energy for the slab model representing the non-relaxed-oxidized surface is 2.4 J/m$^2$. However, there is no reason for the surface atoms to keep the geometry imposed by the bulk. The atoms contained in the first and second outermost layers of both faces of the oxidized (110) surface were allowed to relax perpendicularly to this plane, whereas for the reduced surface only the atoms at the outermost layer of both faces were relaxed.

When allowed to relax, both the oxidized and reduced surfaces are somewhat distorted from their bulk positions. The corresponding displacements away from the bulk equilibrium position are given in Table 2 and are compared with values obtained by other theoretical results reported in the literature. The general pattern of the dislocations is the same reported in the literature, although the corresponding magnitudes are different. For the oxidized surface the five-fold tin atoms Sn$_{5c}$ experience an inward displacement of 0.07 Å, whereas in-plane oxygen O$_{3c}$ and bridging tin atoms Sn$_{6c}$ exhibit an opposite movement of 0.11 and 0.12 Å, respectively. Relaxation of the
oxidized surface promotes a decrease in the surface energy of 0.3 J/m². Manassidis et al. [15] reported an additional stability of 0.46 J/m² associated with the relaxation of the oxidized surface. The relaxation of the reduced surface is not very different from that exhibited by the oxidized surface. It means that the formation of oxygen vacancies does not cause appreciable distortions in the structure of the surface. In particular, Oviedo and Gillan [20] have very recently investigated the dependence of oxygen vacancies concentration on the structure of the SnO₂(110) surface and for all coverage.

Fig. 3. Total and projected DOS diagram for the relaxed SnO₂ bulk: (a) 5s-projected DOS for Sn; (b) 5p-projected DOS for Sn atom; (c) 2s-projected DOS for O atom; (d) 2p-projected DOS for O atom; and (e) total DOS.
ratios no distortion larger than 0.1 Å was found for ions situated around the corresponding vacancies. The vacancy formation energy ($E_{\text{vac}}$) has also been calculated following the equation used by Oviedo and Gillan [20]:

$$E_{\text{vac}} = (E_{\text{red}} + 1/2E_{\text{O}_2} - E_{\text{oxi}})/n$$

where $E_{\text{red}}$ and $E_{\text{oxi}}$ are the energies of the relaxed-reduced and oxidized surfaces, respectively, and $E_{\text{O}_2}$ the energy of the oxygen molecule. The equation assumes the vacancy formation as the removal of $n$ oxygen atoms from oxidized surface, which combine in the gaseous phase forming $1/2n$ molecules of $\text{O}_2$ in their ground state, which is a triplet state. The calculated vacancy formation energy is 4.0 eV. This value is larger than that calculated by Oviedo and Gillan (2.29 eV) [20], but it practically reproduces the value of 3.9 eV reported in our previous study based on cluster models [27].

It is important to notice that the formation of the reduced surface occurs along with the reduction of the tin atoms near to the vacancy. The charge, within the Mulliken’s scheme, over the atoms $\text{Sn}_{6c}$ at the reduced surface is $\approx 50\%$ larger than that of the corresponding $\text{Sn}_{6c}$ atom at the oxidized surface. This fact agrees with the classical model in which the formation of oxygen vacancies reduces the nearby tin atoms oxidation state from $(+4)$ to $(+2)$ [3].

The bridging oxygen’s valence basis set were not left in place for the possibility of the formation of color center. Both bridging oxygen atoms ($\text{O}_{2c}$) and its basis functions were removed simultaneously from the oxidized surface model so as to gives rise to the reduced one. In addition, it has been showed that on the ideal (stoichiometric or oxidized) surface all cations are (formal) $\text{Sn}^{4+}$, but when bridging oxygen atoms are removed, the two electrons left behind occupy orbitals on surface Sn ions, converting half of them ($\text{Sn}_{6c}$) to $\text{Sn}^{2+}$ [46,47]. However, it is worth noting that the formation of a color center is supposed to occur as a result of the formation of in-plane oxygen ($\text{O}_{3c}$) vacancies, not due to formation of bridging oxygen ($\text{O}_{2c}$) vacancies [48].

DOS diagrams for the relaxed-oxidized and reduced surfaces (1 1 0) were built for the analysis of the corresponding electronic structures. The rigorous study of the topology of DOS diagrams of both surfaces is important since the differences between such diagrams provide information so that spectroscopic techniques can be employed in the distinction between $\text{SnO}_2$ and $\text{SnO}$ [49,50]. Fig. 4 presents the total and the main projected DOS diagram for the oxidized surface. It is observed that the length of the VB is 10.4 eV, in agreement with the experimental XPS value for the oxidized surface of $\text{SnO}_2$ [50]. According to the projected DOS diagrams, the region between $-7.8$ and $-9.3$ eV in the upper extreme of the VB of the oxidized surface is mainly constituted of $2p$ orbitals of the $\text{O}_{2c}$ atoms. In particular, the first peak corresponds to $2p_z$ orbitals, while the other is associated to the $2p_x$ orbital. The peak around $-9.5$ eV is dominated by $2p_z$ orbital contributions from the sub-bridging oxygen atoms, while the region between $-10.0$ and $-12$ eV is mainly composed of $2p$ orbital from in-plane $\text{O}_{3c}$ atoms and a quite minor contribution from $2p_x$ and $2p_y$ orbitals. Along the

<table>
<thead>
<tr>
<th>Computing methods</th>
<th>Oxidized surface</th>
<th>Reduced surface</th>
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<tr>
<td></td>
<td>$\text{Sn}_{6c}$</td>
<td>$\text{Sn}_{5c}$</td>
</tr>
<tr>
<td>DFT (B3LYP)$^a$</td>
<td>0.12</td>
<td>$-0.07$</td>
</tr>
<tr>
<td>DFT (B3LYP) [18]</td>
<td>0.26</td>
<td>$-0.12$</td>
</tr>
<tr>
<td>Tight-binding [41]</td>
<td>0.10</td>
<td>Frozen</td>
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<tr>
<td>DFT (LDA-CA) [15]</td>
<td>0.15</td>
<td>$-0.15$</td>
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<tr>
<td>DFT (GGA-PW) [20]</td>
<td>0.22</td>
<td>$-0.11$</td>
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Positive and negative values imply an outward and inward displacement, respectively. Values from previous theoretical results are also included.

$^a$ This study.
VB from $-9.5$ eV to approximately $-16$ eV, a small interaction between the 5p orbitals from tin atoms and 2p orbitals from oxygen atoms is observed. The region ranging from $-15$ to $-18$ eV exhibits small interaction between tin 5s orbitals and oxygen 2p orbitals. This weak overlapping between orbitals is responsible for the modest covalent character of the material. Concerning the CB, it is mainly constituted of tin orbitals; in particular, the lower extreme of the CB is constituted of tin 5s orbitals.

As above-mentioned, the completely reduced surface is obtained by removing all bridging oxygen atoms from the oxidized surface. In Fig. 5 the
total and the main projected DOS diagrams for the reduced surface are presented. A decrease in the value of the band gap is observed, together with a shift of the Fermi level towards higher energies. The electronic states near to Fermi level overlap the inferior region of the CB, which is composed of a mixture of 5s and 5p orbitals of tin atoms (Sn4c) adjacent to the oxygen vacancies. In other words, the formation of oxygen vacancies introduces some extra electrons into the CB. A high density of occupied states in the band gap is found, in qualitative agreement to the experiment [48]. The distance, in energy, between the bottom of the VB and the Fermi level in the DOS diagram of the reduced surface is \( \approx 12.7 \text{ eV} \), larger than the corresponding oxidized surface, and in accord with the XPS value of 12 eV [50]. Cavicchi et al. [51] have shown that sputter-annealed surface, which is expected to be comparable to the reduced surface, exhibits a well-defined Fermi edge that is separated from the valence band maximum by \( 3.6 \pm 0.2 \text{ eV} \), in agreement with our calculated value of 3.7 eV.
The upper region of the VB between $-6.8$ and $-7.6$ eV is predominantly constituted by $p_y$ orbitals from sub-bridging oxygen atoms, whereas the region ranging from $-7.6$ to $-9.0$ eV consists mainly of $p_z$ orbital from $O_{3c}$ atoms at the surface. Tin orbitals again exhibit low overlapping with oxygen $2p$ orbitals.

It is worth noting that on going from the oxidized to the reduced surface the Fermi level is moved towards highest energy values in accord with work function measurements, whose values give the position of the Fermi level with respect to the vacuum level, once it has been reported that the work function generally decreases as surface oxygen atoms are removed [45,48,51]. The conductivity behavior of reduced SnO$_2$(110) surface can be explained by a distribution of the electrons in the electronic states along the band gap induced by oxygen vacancies. Therefore, the reduced surface is less resistive than the oxidized one as it has been experimentally verified [3]. However Cox et al. [48] have suggested that the removal of bridging oxygen atoms has only a relatively small effect on the surface conductivity. The observed conductivity changes would be then dominated by other type of surface defect like in-plane oxygen vacancies, although there was no conclusive evidence for the formation of this kind of defect. Our results support that differences between the VB topology for oxidized and reduced surfaces can be used in order to distinguish the oxidation state of the SnO$_2$(110) surfaces.

3.3. O$_2$ adsorption on the reduced SnO$_2$(110) surface

The adsorption of O$_2$ was investigated on the previously relaxed-reduced surface (110), although there are some indications that O$_2$ can be weakly adsorbed on the oxidized surface [3]. This surface exhibits two different sites subjected to the adsorption of O$_2$: $Sn_{5c}$ and $Sn_{4c}$. Although there are experimental evidences of a very weak interaction of O$_2$ with the $Sn_{5c}$ sites [9], in the present study only the adsorption on the $Sn_{4c}$ centers was taken into account, due to the fact that these centers concentrate residual charge (formally Sn$^{2+}$) resulting from the formation of oxygen vacancies.

Three adsorption types of O$_2$ on the four-fold tin at the reduced SnO$_2$(110) surface have been considered: an end-on type, involving O$_2$ perpendicular to the surface, and two side-on types involving O$_2$ parallel to the surface, namely, side-on-$x$ ($O_2$ parallel to the surface and to the column of Sn$_{4c}$) and side-on-$y$ ($O_2$ parallel to the surface and perpendicular to the column of Sn$_{4c}$). The adsorption is simultaneously modeled in both faces of the slab model and only full-coverage was considered.

To the best of our knowledge no experimental data about O$_2$ coverage extension on SnO$_2$ surface is available. Our assumption for using only a full-coverage model is based on the mass 32 TPD spectra data of SnO$_2$(110) surface exposed to a wide range of O$_2$ pressures, namely, 0.25, 1.25, 5, 40 and 100 L (1 Langmuir = 1.32 mbar s). The main features of such a spectra are shown to be independent of coverage, characteristic of first-order desorption and hence the presence of an O$_2$ adsorbate [9]. For each channel, the internuclear distance between the oxygen atoms in O$_2$, as well as the distance between the Sn$_{4c}$ site and the midpoint of the O$_2$ molecule were simultaneously optimized, while the surface remains unchanged at the previous relaxed geometry. Stationary points were characterized by systematic construction of the potential energy surface for each approach way. BSSE (basis set superposition error) corrections were also estimated by means of the counterpoise method [52].

We are unable to calculate the energy difference between the reduced surface with absorbed O$_2$ and the oxidized surface inasmuch as our supercell models for representing the oxidized surface and that for the reactant complex (absorbed O$_2$ molecule on SnO$_2$ surface) contain distinct number of atoms. However, it is worth noting that the reconstruction of the oxidized surface by O$_2$ exposure is a thermally activated process requiring a temperature of about 700 K. The corresponding activation barrier is probably associated, at least in part, with the dissociation of adsorbed oxygen from a molecular to an atomic form [8,48].

The equilibrium geometry for the end-on type involves a Sn$_{4c}$–O$_2$ distance of 1.95 Å, and an internuclear O–O distance of 1.37 Å. Adsorption energy is $-28.3$ kcal/mol. The side-on-$x$ channel
renders a surface–O$_2$ distance of 1.90 Å and exhibits an internuclear distance of 1.45 Å. Adsorption energy in this case is $-38.9$ kcal/mol. The side-on-$\gamma$ approach is the most favorable interaction, in which the oxygen molecule lies at 1.95 Å from the Sn$_{4c}$ site and presents an internuclear distance of 1.55 Å. Adsorption energy for this system is $-42.3$ kcal/mol. In the three cases, the process occurs with charge transfer from the surface to the adsorbed species, being the electronic

Fig. 6. Total and projected DOS for the most favorable channel related to the chemisorption of O$_2$ on Sn$_{4c}$ at the relaxed-reduced SnO$_2$(1 1 0) surface: (a) 2p-projected DOS for O$_2$ molecule; (b) 2p-projected DOS for O$_{3c}$ atoms at the surface; (c) 2p-projected DOS for sub-bridging oxygen atoms (O$_{sb}$); (d) 2p-projected DOS for all oxygen atoms; (e) 5s-projected DOS for all tin atoms; (f) 5p-projected DOS for all tin atoms; and (g) total DOS.
transfer related to the side-on type interactions (0.72 e\textsuperscript{−} per molecule) bigger than that end-on one (0.55 e\textsuperscript{−} per molecule). Such a result qualitatively supports the operation model of SnO\textsubscript{2}-based electronic devices, which asserts that the electronic behavior of the material is governed by the presence of oxygen anionic species formed on the surface of the oxide [2,6,7]. An analysis of both the internuclear O–O distance exhibited by these adsorbed species and the charge transfer suggests that the most favorable interactions could be associated to the formation of a peroxo unit O\textsubscript{2}\textsuperscript{−} [53].

Total and projected DOS diagrams for the most favorable side-on interaction are depicted in Fig. 6. It is important to notice that differences between this diagram and the corresponding to the oxidized surface arise; thus, reconstruction is not expected to occur from the reduced surface exposure to molecular oxygen. The 2p orbitals of the adsorbed fragment are distributed along both the VB and CB. They interact on the one hand with 2p orbitals of in-plane and sub-bridging oxygens in the upper part of the VB, and on the other hand with the 5s and 5p tin orbitals in the region next to the Fermi level. It is observed that the O\textsubscript{2} adsorption causes a significant depopulation of states along the band gap. This finding is consistent with UPS measurements [48]. The decrease in the amount of defect states as a result of the chemisorption of O\textsubscript{2} is also supported by the conductivity measurements on oxygen-rich SnO\textsubscript{2}(1 1 0) surface prepared via oxygen plasma treatment [51]. The upper region of the VB (−11.2 to −12.3 eV) as well as the bottom of the CB (−7.2 to −8.8 eV) are mainly dominated by electronic states associated to 2p orbital from the absorbed O\textsubscript{2}. In addition, the Fermi level is located about 1.5 eV above the inferior extreme of the CB. As a result, the chemisorption of O\textsubscript{2} on reduced SnO\textsubscript{2}(1 1 0) surface is shown to trap electrons in the chemisorption complex (O\textsubscript{2}\textsuperscript{2−}) producing a electron-depleted space–charge layer in the inner surface region of the material. This layer is responsible for the formation of a potential barrier at the interface between grains in the oxide, whose features control the electronic behavior of SnO\textsubscript{2}-based electronic devices in agreement with some experimental evidences.

4. Conclusions

The electronic and structural characteristics of the bulk and of the oxidized and reduced SnO\textsubscript{2}(1 1 0) surfaces as well as the adsorption process of O\textsubscript{2} on the reduced SnO\textsubscript{2}(1 1 0) surface were theoretically investigated by periodic DFT calculations at B3LYP level. The main results are summarized below.

(i) Bulk SnO\textsubscript{2} electronic structure shows a direct band gap of 3.3 eV, in very good agreement with experimental results. The difference in energy for the tin and oxygen valence atomic orbitals indicates a predominant ionic character for this material.

(ii) Relaxation of the oxidized (1 1 0) surface involves an ascendant movement of the in-plane Sn\textsubscript{6c} and O\textsubscript{3c} atoms, whereas the Sn\textsubscript{5c} atoms experience an opposite displacement. Reduced surface is found to relax in an analogous way, providing an additional stability of 0.3 J/m\textsuperscript{2}.

(iii) Electronic structure for both oxidized and reduced surfaces shows significant differences. The conductivity behavior of the reduced SnO\textsubscript{2}(1 1 0) surface is explained by a distribution of the electrons between the electronic states introduced in the band gap by oxygen vacancies.

(iv) The three types of chemisorption of O\textsubscript{2} on Sn\textsubscript{4c} site at the reduced SnO\textsubscript{2}(1 1 0) surface correspond to exothermic processes. The most thermodynamically favorable process is associated to the O\textsubscript{2} adsorption along the [\textsuperscript{1\textsubscript{1\textsubscript{1\textsubscript{0}}}]} di-
rection, i.e. perpendicular to the Sn\textsubscript{4c} atomic row. This adsorption mode causes a significant depopulation of states along the band gap. In this process, the chemisorption complex O\textsubscript{2}\textsuperscript{2−} is shown to trap electrons producing an electron-depleted space–charge layer in the inner surface region of the material. Such a charge separation is responsible for the formation of a potential barrier at the interface between grains in the oxide, whose features control the electronic behavior of this material. The O\textsubscript{2} adsorption on the reduced surface does not finally reconstruct the oxidized surface.
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