

Computational study of charge accumulation at $\text{SnO}_2(110)$ surface

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Abstract

Features of $\text{SnO}_2(110)$ surfaces with a surplus electron are considered computationally by applying density functional method. The additional charge is found to influence on surface energetics and surface relaxations considerably with respect to the corresponding surfaces without additional charge. This effect is pronounced in the cases of oxidized surfaces, where different oxygen adsorbates (O , O_2 and O_3) tend to capture the charge. On stoichiometric surface, these oxygen species are adsorbed on-top of the five-fold coordinated surface tin atoms and are attributed to adsorbed O^- , O_2^- and O_3^- species associated with spin polarization. Based on evaluated total energy differences formation of these species are compared. In cases of stoichiometric and slightly oxygen deficient surfaces without adsorbates, charge accumulation is qualitatively similar to the case of bulk SnO_2 with a considerable amount of the surplus charge enriched around Sn atoms. A pronounced charge accumulation is observed around under-coordinated surface tin atoms of stoichiometric and oxygen deficient (110) surfaces.

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1. Introduction

Buildup of electron density at metal oxide surfaces can occur because of many reasons, includ-

ing the presence of external potential, defects, electron excitations and occurrence of various reactions (protonation at surfaces, removal of adsorbed oxygen, alkali metal deposition, nucleophilic attacks etc.). Information concerning charged metal oxide systems is important in large number of cases. However, experimental measurements of such surfaces do not provide a high level of clarity. Therefore, an important approach for modeling

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of these charged surface systems is to use accurate density functional methods with periodic boundary conditions [1].

Tin dioxide is a wide band gap n-type semiconductor and its charge carrier density is increased by oxygen vacancies and other defects in the crystal structure including tin interstitial atoms [2–5]. Free charge concentration of transparent SnO_2 crystals and films can range between 10^{14} – 10^{21} cm^{-3} [6,7], showing features of conductor like surface plasma oscillations at free carrier densities of the order of 10^{18} cm^{-3} (0.16 C/cm^3) [7,8]. Associated surface charge and electrical conductivity phenomena are of importance for instance in the gas sensor and photochemical applications. In connection with SnO_2 gas sensors, a convenient way to enhance performance and sensitivity is to use very small grains or very thin films. The associated sizes are close to the size-scale that can be modeled by using density functional methods.

Oxygen atoms in different forms act usually as electron acceptors. In bulk and at surfaces of SnO_2 , like in related metal oxide materials, oxygen anions (nominally O^{2-}) are saturated and strongly stabilized by the surrounding Madelung fields. Oxygen molecules are known to trap additional charge (forming O_2^- type of ions) becoming ionosorbed at the surface at sufficiently low temperatures [9–11]. These species are reported to be observed on SnO_2 , as well as on other oxide surfaces, also at elevated temperatures [12,13]. Other adsorbed oxygen species include O^- dissociated onto SnO_2 surface as well as O_2^{2-} [10,14]. Adsorbed oxygen species are involved in different (electrophilic) catalytic oxidation reactions [9,14], like oxidation of CO, hydrocarbons, etc. In case of SnO_2 surfaces, mono-oxygen species (reacting as O^-) are interesting in providing highly active catalytic sites [9,12,15,16] and may be largely responsible for important sensing response of SnO_2 gas sensors [17]. Formation of these species on SnO_2 surfaces at temperature above 400 K is attributed to decrease of electrical conductivity [18]. Adsorbed oxygen has an important role in photocatalytic applications [19], for instance, recombination of electron–hole pairs near surface may be avoided by removal of electrons to unstable surface oxygen species.

For perfect and charge neutral bulk tin dioxide material, simple ionic model, with strongly localized charges, assumes that as oxygen atoms gain the closed shell charge ($-2e$) and are stabilized by Madelung energy, additional electrons are likely to occupy cation sites that have become empty [20–23]. Type and possible localization of calculated unoccupied energy levels can provide important information about appearance of small amounts of excess charge, especially in the case of isotropic bulk systems [22,24,28]. These approaches are related to evaluation of the Fukui functions ($\frac{\partial \rho(\mathbf{r})}{\partial N}$), which can be used to compare reactive sites of molecular systems [25–27]. On the other hand, charged surfaces are not straightforwardly modeled using bulk or charge neutral surfaces, since the additional charge can considerably alter surface relaxation and the distribution of excess charge is nonuniform. This behavior depends on the amount of the added charge and the presence of oxygen acceptors.

In the present paper we attempt to consider modeling and characters of different charged tin oxide surfaces with and without oxygen adsorbates whose geometries are calculated by using density functional method. It is important to find out where and how the charge is accumulated on different surfaces, what kind of oxygen species stabilize and how charge distribution and surface geometry responds to the presence of additional charge. To answer these questions, calculations have been done on average excess electron densities of the order of 10^{21} cm^{-3} at the most abundant (110) surface face using a slab model up to a effective film thickness of 2 nm. Deeply reduced (110) surfaces are not considered, which are expected to have characters related to SnO crystals [28]. From the point of view of oxygen adsorbates, (110) orientation is found to be special in providing adsorption sites for oxygen molecules. The distance between Sn atoms is minimal at this surface orientation (3.1 Å), being larger than the bond length of oxygen molecule (1.2 Å). Therefore, two surface Sn cations of the (110) surface can participate in binding of oxygen molecule.

The paper is organized as follows. The calculation method applied is described in Section 2. Then, in Section 3, the distribution of extra charge

in bulk SnO_2 crystal is considered. This provides a basis for consideration of charged stoichiometric and oxygen deficient $\text{SnO}_2(110)$ surfaces, which are discussed in Section 4. The presence of different oxygen adsorbates, which can capture charge, are examined in Section 5. In Section 6 conclusions are presented.

2. Method and SnO_2 surface slab model

The computational first-principles density functional (DFT) approach applied here is based on the plane wave basis set and pseudopotential concept to describe electron-ion interaction (CASTEP/CETEP code) [29]. Utilizing ultrasoft pseudopotentials (USP) [30] the plane wave basis set can be limited considerably [31]. The chosen plane wave cutoff is 400 eV. Oxygen atoms are described by 6 valence electrons and tin atoms by 4 plus the corresponding pseudopotential ion cores. The electronic interactions are taken into account with a generalized-gradient approximation allowing possible spin polarization (GGs) [32]. To sample Brillouin zone, the number of symmetrized Monkhorst–Pack k -points [33] was scaled so that it was 6 for the smallest 1×1 surface system. In separate test calculations the number of k -points were increased to check the convergence. For charged systems, the negative charge of the unit cell is balanced by using constant background charge density. Since such charged model systems can be expected to have the Fermi energy above the conduction band minimum (CBM), occupation numbers were broadened using Gaussian like smearing with a width of 0.1 eV.

Crystalline tin dioxide is composed of six-fold coordinated tin atoms (nominally Sn^{4+}) and three-fold coordinated oxygen atoms. Its (110) surface with different surface atom types is shown in Fig. 1. Stoichiometric (110) surface contains all surface bridging oxygens, and its composition corresponds to a bulk SnO_2 . This surface system is particularly representative among oxygen deficient tin oxide surfaces as the four-fold coordinated surface tin ions emerge in lower oxidation state of tin (Sn^{2+}) [34]. Clearly, many other oxygen deficient SnO_2 surfaces are possible [28] and some of them

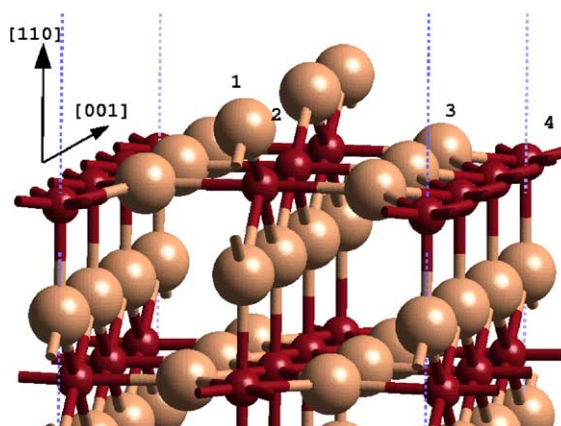


Fig. 1. Schematic representation of the $\text{SnO}_2(110)$ surface including a bridging oxygen vacancy. Bridging oxygen is indicated by label 1, bridging oxygen vacancy by 2, in-plane oxygen by three- and five-fold coordinated surface tin ($\text{Sn}5f$) by label 4. With all bridging oxygen atoms present (removed) the surface is called stoichiometric (reduced).

are taken into account here. Different tin oxide bulk and surfaces have been studied by using density functional methods with good reliability in predicting geometries, energetics and electronic structure [28,31]. However, one should be aware of limitations of DFT and related methods in description of localization and binding of electrons [35]. For instance, the evaluated ionization potentials of free Sn ions using GGS, show that valence Sn-s levels are too weakly bound, obviously due to incomplete description of electron self-interaction [35]. In this sense, due to the possibility of delocalization, the calculations provide a stringent test from the point of view of charge trapping.

The surface of SnO_2 is represented by different three-dimensional periodic slabs, consisting of 3–11 $\text{O}(\text{Sn}_2\text{O}_2)\text{O}$ layers, with a vacuum 'layer' in between. In all slabs the middle Sn_2O_2 layer is kept fixed in bulk geometry while all other atoms relax in geometry optimization. In most cases one or two extra electrons ($\delta n = 1\text{ e}$ or $\delta n = 2\text{ e}$) are added in charged cases to the unit cell which is neutralized by an equal amount of positive constant background charge density. Vacuum thickness (L_{vac}) exceeding 10 Å have been found to be optimal [28]. The presence of additional charges in the cell creates additional electrostatic interactions which change convergence of total energy with increasing

vacuum thickness [1]. Therefore, unit cells with same number of atoms and dimensions were compared, δn were kept low and relatively large unit cell sizes were chosen. Detailed investigations have indicated that these choices are essential to make the influence of associated spurious interactions insignificant [1,36–38]. To compare with, some results were obtained by providing the extra charge from oxygen vacancies (see below).

Different methods are used to analyze properties of charged systems, giving qualitatively consistent and complementary results. These methods include; partial density states (PDOS), Mulliken population analysis and distribution of the Kohn–Sham orbitals. Mulliken population analysis gives charges of atoms and bond populations of atom pairs as calculated in terms of density matrix and overlap matrix [39]. These are obtained from projections of the one-electron eigenfunctions to the atomic orbitals. The spilling parameter, representing completeness of the Mulliken analysis, is always less than 0.5%. Accumulation of the additional charge around some particular site is also checked by subtracting total charge of the neutral system from the total charge of the corresponding charged system at that site. Such charge difference investigations are made in the case of the 3 and 5 layer slabs.

3. Extra charge at bulk SnO_2

Calculations for charged ($\delta n = 1 \text{ e}$) bulk tin dioxide were performed with $2 \times 10^{21} \text{ cm}^{-3}$ free charge density, which is close to the upper limit of predicted realistic free charge densities. Different unit cells up to the maximum size of $\text{Sn}_{16}\text{O}_{32}$ were tested. The charge density maps and the band structure of neutral and charged systems are essentially similar as expected due to relatively small increase of charge per atom (0.02 e/atom). From the band structure plot it can be noticed that the conduction band minimum (CBM) that becomes occupied is essentially of s-type. In the case of the charged system, the spherical charge density around Sn sites increases, which is seen in the total charge difference plot evaluated by subtracting the charge density of uncharged system (see Fig. 2

left). Mulliken population analysis indicates that charge is indeed accumulated more around Sn sites (0.1 e/Sn) than around O atoms (0.01 e/O increase of charge). The results are in agreement with other calculations [24,40], and experimental UPS measurements of doped SnO_2 [6,41], having revealed that CBM is mostly of Sn-5s character.

Intrinsically, oxygen anions have a substantial part of the valence charge around them (about 7 e according to Mulliken population analysis) compared to tin cations (about 2 e respectively). Their positions and charge distribution respond to the increased charge. Oxygen atoms contribute also to CBM, that will be occupied by the extra charge, which is seen in evaluated PDOS and its orbital charge density [28]. Part of the response of oxygen atoms is attributed to a small displacement of its charge distribution as the system tends to expand to compensate increased charge density. As a consequence, the evaluated charge difference distribution around O atoms were noticed (Fig. 2 (left)) to be more complicated and it depends on details of calculation procedures. Due to these reasons, we also estimate how charge distribution is disturbed in excitation of charge from the valence band to conduction band (in uncharged system). This is simulated by broadening the occupation numbers leading to small transfer of occupation from valence band maximum to CBM.

Fig. 2 (right) illustrates that in this case the charge enrichment is similar and again more considerable around Sn atoms. The charge distribution around O atoms changes slightly. The associated charge decrease plot (not shown) indicates that the charge increase of Sn atoms originates from O-p orbitals.

4. Extra charge at $\text{SnO}_2(110)$

In cases of stoichiometric and oxygen deficient (110) surfaces, which will be considered next, the charge enrichment is qualitatively similar to the case of bulk tin dioxide. Tin atoms, especially at the surface, have an ability to accept extra electron charge.

Stoichiometric surfaces were modeled by using different slab sizes. The largest of them was

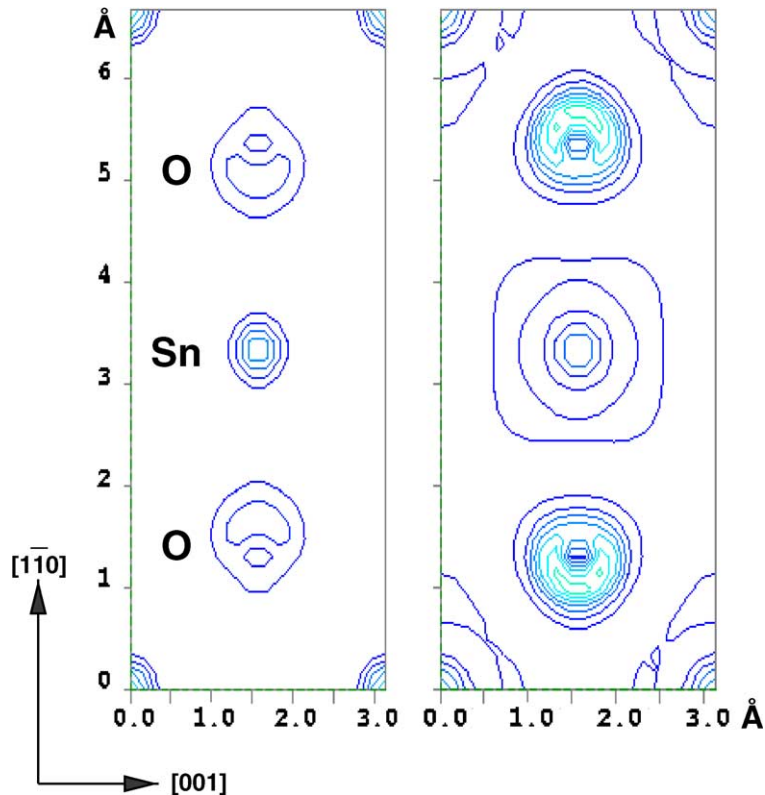


Fig. 2. Charge difference contour plots showing accumulation of different types of extra charge in SnO_2 crystal. The (110) plane of $\text{Sn}_{16}\text{O}_{32}$ is viewed with symmetrically equivalent O atoms. (left) A charge distribution without additional charge is subtracted from the distribution of the charge of the system charged with 1 e. The charge density increases stepwise, with steps of value $0.005 \text{ e}/\text{\AA}^3$, starting from a density of $0.005 \text{ e}/\text{\AA}^3$. (right) A charge distribution with a modest band broadening is subtracted from a charge distribution of the system associated with an elevated band broadening (1 eV width). The density steps are $0.00025 \text{ e}/\text{\AA}^3$ and start from a density of $0.00025 \text{ e}/\text{\AA}^3$.

$\text{Sn}_{44}\text{O}_{88}$ with two surface unit cells, a slab thickness of 40 Å and with $\delta n = 4 \text{ e}$, which corresponds to a uniform charge density of the order of 10^{21} cm^{-3} and 0.03 e/atom. The surface layer was noticed to have an ability to accumulate additional charge. All surface Sn atoms gain (Mulliken) charge more than Sn atoms inside the slab. In more detail, Mulliken population analysis shows most of the additional charge to be in the vicinity of coordinatively unsaturated five-fold coordinated surface Sn atoms (Sn5f), and to a slightly less extent around fully coordinated Sn atoms bound to the surface bridging oxygen. In case of the largest slab, both of these two types of Sn atoms gain charge more than 0.1 e of the total of 4 e. Part of the extra charge accumulation around

Sn5f is observed at the surface side of the Sn5f atoms. This is clearly seen by subtracting the charge distribution of the charge neutral ($\delta n = 0 \text{ e}$) surface slab from the charge distribution of the charged surface slab (shown in Fig. 3). The additional charge causes the Sn5f atoms to relax outwards about 2% (0.04 Å) with respect to nearest oxygen, and therefore positions of Sn5f sites of uncharged slab were made to coincide when charge difference is evaluated (after geometry optimization). Charge accumulation below the surface remains qualitatively similar to the case of bulk SnO_2 . Calculations made with thinner slabs give similar results, but indicate also that charge accumulation is more pronounced and is dependent on slab thinness. Among oxygen atoms, largest

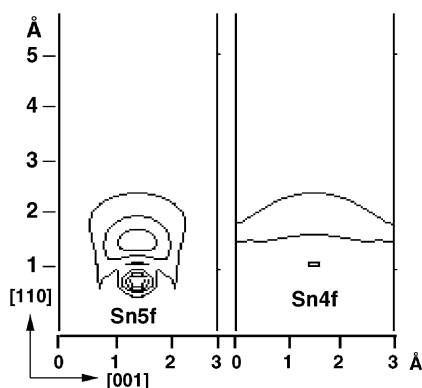


Fig. 3. A contour plot of charge accumulation around surface Sn atoms. (left) Charge difference between charged and neutral stoichiometric surface slabs at the position of five-fold coordinated surface tin atom; (right) charge difference between charged and neutral reduced surface slabs at the position of four-fold coordinated surface tin atom. Charge density increases stepwise, with steps of value $0.02 \text{ e}/\text{\AA}^3$, starting from a density of $0.01 \text{ e}/\text{\AA}^3$.

but very small increase of the Mulliken charge is observed at bridging oxygen atoms (0.05 e).

At the reduced surface (see Fig. 1) the surface charge accumulation is more considerable due to enrichment of the additional charge around the surface four-fold coordinated surface tin atom (labeled as Sn^{2+} and Sn4f). This is illustrated in the charge difference plot shown in Fig. 3. In the case of the largest slab $\text{Sn}_{44}\text{O}_{84}$ of thickness of $40 \text{ \AA}$ with two surface unit cells and with $\delta n = 4 \text{ e}$, Mulliken analysis indicates a considerable increase of charge around the Sn^{2+} ion (0.4 e). The charge accumulation around the associated surface Sn5f atom is weaker and depends on the slab thickness. The accumulation of charge at reduced surface becomes evident by calculations with a geometry where both surfaces coexist so that the other side of the slab surface is stoichiometric and the other is reduced. Such calculations were made in the case of $\text{Sn}_{10}\text{O}_{19}$ slab of thickness $14 \text{ \AA}$ ($\delta n = 1 \text{ e}$ were compared to $\delta n = 0 \text{ e}$). The results indicate that the charge accumulation phenomena remains essentially similar as described above. The charge is enriched around surface tin atoms, and the Sn5f atoms of the reduced surface were noticed to be capable of increasing its accumulation by 0.2 e . The net accumulation of the added charge

at reduced surface becomes larger because of the larger number of Sn atoms that can capture the charge.

Simple heat treatments are expected to produce different surfaces with bridging oxygen vacancies (see Fig. 1). Once a single bridging oxygen from the row of bridging oxygens along $[001]$ is removed, yet another type of local surface environment with five-fold coordinated surface tin atoms is formed. To model this kind of surface, a slab was tripled in the $[001]$ direction (a composition $\text{Sn}_{30}\text{O}_{60}$) and one of the three bridging oxygens of the both surfaces of the slab were removed. In the charge density map of Fig. 4 it is illustrated that charge density of the excess charge $\delta n = 2 \text{ e}$ becomes localized at the site of removed oxygen and around the associated under-coordinated surface Sn atom. Each of these Sn atoms gain charge most considerably (0.23 e) and relax outwards with respect to nearest oxygens.

As discussed above, the charge accumulation at surface Sn and its outward relaxation occur together. A simple explanation for this conjunction is provided by the ionic approximation. The decrease of binding energy associated to electrostatic attraction is lowest in the case of lowest number of nearest anion neighbors. Consequently, under-

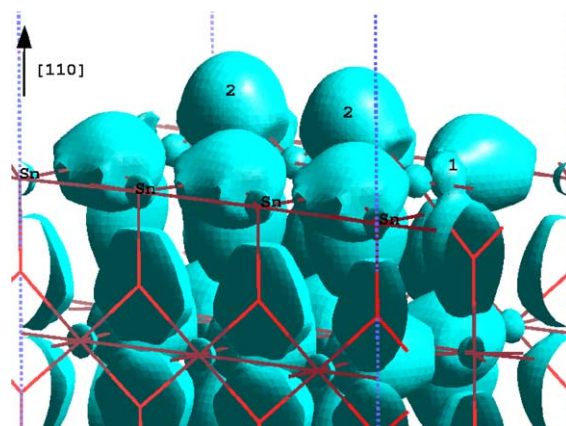


Fig. 4. 3D-total charge distribution isosurface ($0.25 \text{ e}/\text{\AA}^3$) of the stoichiometric surface without one bridging oxygen. Charge distributions around bridging oxygens are indicated by label 2. Localized charge distribution associated to the removed bridging oxygen is seen (label 1). This charge distribution is absent in the corresponding charge neutral surface.

coordinated cations become occupied and the attraction between nearest anions decreases causing the outward relaxation.

It is worth noting that spin polarization was not observed in any of the above mentioned cases. This feature is in contrast with $\text{SnO}_2(110)$ surfaces with oxygen adsorbates, which will be considered next.

5. Oxygen adsorbates on charged $\text{SnO}_2(110)$ surface

Different possibilities for appearance of oxygen species on tin oxide and related metal oxide surfaces are possible as shown in several computational investigations [42–48]. It has been found that O atoms are meta-stable at stoichiometric $\text{SnO}_2(110)$ surface compared to free O_2 [47,49]. Surface oxygen vacancies provide active sites where oxygen gas molecules can stabilize and rearrange with decrease of total energy. These results are in agreement with related experimental studies which concern mostly TiO_2 surfaces [51–53]. Oxygen adsorbates are likely to be ionosorbed at metal oxide surfaces by charge injection from supporting surface as they transform to negatively charged counterparts (O^- and O_2^-). Such species may be relatively stable [9] and bind to surface by electrostatic interaction and covalent bonding. Different charged oxygen species can be produced by activating the surface using ionizing radiation or thermal treatments [9,12], and as a product of chemical reactions [46,54]. Their identification is possible by electron paramagnetic resonance measurements [9].

Fig. 5a illustrates schematically O atom adsorbed on top of Sn5f atom. This geometry has been considered also in cases of related TiO_2 and RuO_2 metal oxide surfaces [42,43,49]. As shown in Fig. 5b, adsorbed oxygen may alternatively bind with bridging oxygen atoms. The geometry is predicted to be energetically preferred in the case without extra electrons, and it can be attributed to O_2^{2-} molecule which is adsorbed at the bridging oxygen vacancy site [45,47,50]. Importantly, this energetically preferred adsorption geometry changes when the additional charge is introduced.

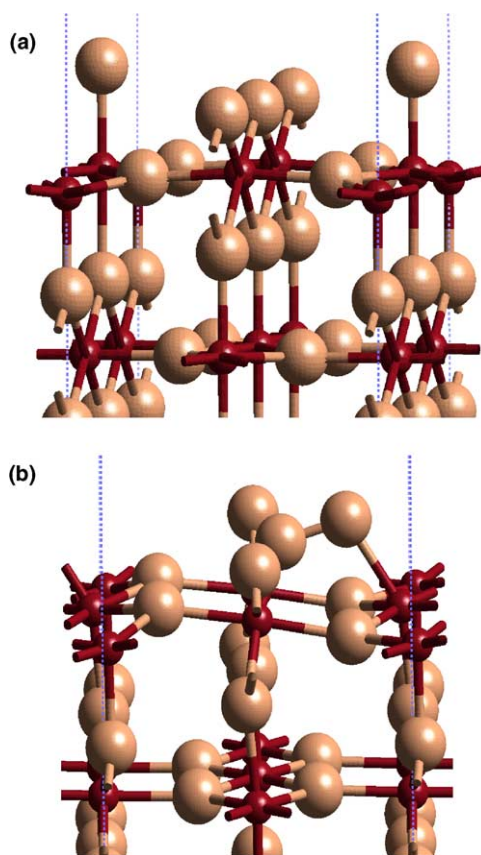


Fig. 5. Geometries of oxygen adsorbed on stoichiometric surface, in the case of (a) charged and (b) neutral surface.

This geometry corresponds to the geometry shown in Fig. 5a, where oxygen is adsorbed (O_{ads}) on top of Sn5f . In the case of $\text{Sn}_{20}\text{O}_{42}$ with $\delta n = 2$ e, the geometry of Fig. 5a is 2 eV more stable than the geometry of Fig. 5b.

Charge density increase, around the O atom adsorbed on top of Sn5f , was considered by subtracting the charge density of free oxygen atom from the total density. Fig. 6 illustrates that the charge of the adsorbed O atom is substantially increased. It can also be seen from Fig. 6, that the associated charge increase is almost similar with the other O atoms. Quantitatively, the bond population and bond length of the $\text{O}_{\text{ads}}\text{-Sn}$ bond are within the limits of the other O–Sn bonds. The Mulliken charge of O_{ads} increases from 6 e (neutral O atom), to 6.5 e in the case of $\delta n = 1$ e/ O_{ads} . The valence

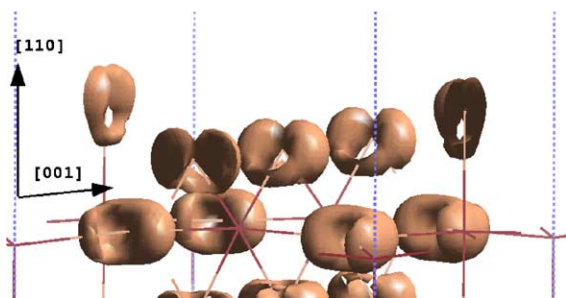


Fig. 6. Charge increase at stoichiometric $\text{SnO}_2(110)$ surface including O_{ads}^- . The superposition of atomic charge densities is subtracted from total charge density. Charge distribution isosurface with a density of $0.16 \text{ e}/\text{\AA}^3$ is shown. Notice similarity of the charge accumulation around O_{ads}^- with other O atoms.

charge of the oxygen atoms inside the slab is about 7.0 e and consequently increase charge 1 e with respect to neutral O atom. That is, the O atom adsorbed on top of $\text{Sn}5\text{f}$ gains valence charge only half of the valence charge increase of the bulk O ions. Since the latter O atoms are commonly designated as O^{2-} ions, the adsorbed O atom can be attributed to O^- ion and it will be here labeled as O_{ads}^- . The O_{ads}^- adsorbate can be expected to include unpaired electron density.

Accordingly, it is associated with a magnetic moment $1 \mu\text{B}$, which becomes also evident from the evaluated electron spin density difference between spin-up and spin-down electrons. The PDOS and corresponding PDOS difference between spin-up and to spin-down charge density of O_{ads}^- are illustrated in Fig. 7. A considerable splitting of spin-up and spin-down levels is observed at all energies. The adsorbed oxygen contributes to DOS slightly below the top of the valence band, which can be attributed to a stabilization of the adsorbed oxygen including its trapped charge. However, if the DOS is compared with the DOS of free oxygen atom, or oxygen ions of the SnO_2 surface (not shown), the O-p density of states is concentrated more strongly around both sides of the Fermi level. The peak in PDOS around -3 eV originates considerably from p-type orbitals of O_{ads}^- oriented along $[1\bar{1}0]$, which was observed from evaluated orbital charge distribution. According to the DOS curves, around -15 eV the oxygen s-type levels can significantly overlap with Sn type of levels (not shown).

The DFT calculations predict that the geometries of Fig. 5 can be produced by dissociative adsorption of O_2 at bridging oxygen vacancy site. In this case, one of the O atoms of O_2 occupy a bridging oxygen vacancy site, and the other is adsorbed as in Fig. 5. It is expected that this reaction can occur exothermally also in the case of charged system. To study this hypothesis, total energy of a surface system containing an oxygen vacancy together with O_2 molecule in vacuum, were compared with a total energy of corresponding O_{ads}^- on stoichiometric surface (with $\delta n = 1 \text{ e}$). In the initial geometry, O_2 and a five layer slab with a bridging oxygen vacancy, are in the same unit cell separated by a vacuum region of thickness $10 \text{ \AA}$ (the surface to surface distance is $20 \text{ \AA}$). As a result, it is found that there is a considerable energy release between the initial and final geometries, which exceed $2 \text{ eV}/\text{O}_{\text{ads}}^-$. The corresponding energy release in the case of $\delta n = 0 \text{ e}$ is less than 2 eV [47]. Thus, it is predicted that the extra charge can make the dissociative adsorption even more likely.

Returning to the case of surface with oxygen vacancies, we may now explore how surface oxygen vacancies alone can provide the extra charge and enhance binding of O_{ads}^- . Such surface oxygen arrangements are also of interest methodologically, and if certain surface reactions are considered (though the O_{ads}^- is likely to occupy the O vacancy site, as discussed above). These experiments were made with $\text{Sn}_{24}\text{O}_{48}$ slab and 1×3 surface unit cell (see Fig. 1) with none, one or two bridging O atoms removed from one surface which includes O_{ads}^- . In the case of two bridging O vacancies, the Sn^{2+} type of surface ion is present. It is found that with O vacancies, the increase of the Mulliken charge of the O_{ads}^- is larger than in the case of extra charge ($\delta n = 1 \text{ e}/\text{O}_{\text{ads}}^-$). The binding of O_{ads}^- is assumed to be stronger, than in the case of $\delta n = 1 \text{ e}$. This is observed from the decrease of O–Sn bond length, from $2.03 \text{ \AA}$ to $1.92 \text{ \AA}$ as well as from the evaluated binding energies of O_{ads}^- . In the case of the unit cell with the extra electron the corresponding O_{ads}^- –Sn bond length were $2.00 \text{ \AA}$. To form the O_{ads}^- , together with the bridging O vacancy, 0.1 eV is needed, when evaluated with respect to half of the energy of free spin

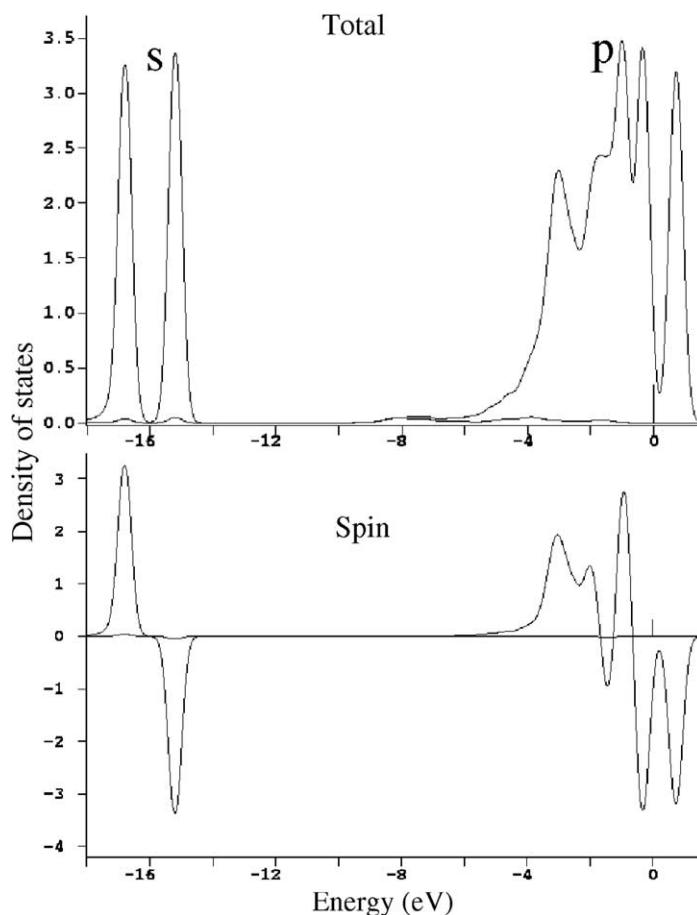
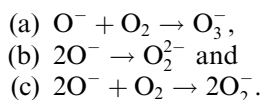


Fig. 7. Partial-density-of-states of the O^-_{ads} ion. (upper) PDOS resolved to O-s and O-p contributions; (below) corresponding difference between spin-up and spin-down density-of-states. Zero refers to the Fermi energy.

polarized O_2 molecule plus stoichiometric slab. In the case of the two vacancies, a slight energy release was evaluated. Without the vacancy, the corresponding energy cost is considerable (1.5 eV). Thus, the presence of oxygen vacancies considerably enhances O^-_{ads} formation, providing the additional charge. Quantitatively, this effect is noticed to be different with different oxygen vacancy arrangements (which will not be considered here for the sake of brevity). Taking this into account, we emphasize that the concept of extra charge applied provides a more independent basis for studies of charged metal oxide surfaces.

Instead of the formation of individual mono-oxygen species, it is expected to be energetically

preferred to combine oxygen species as larger number of bonds are associated. In gaseous state, species like ozonide, peroxide or hyperoxide ions can be formed from O^- [14]. This can occur by reactions



In order to study whether related reactions can occur, with O^- adsorbed on stoichiometric surface, surface geometries for adsorbed O_2 and O_3 were determined (shown in Fig. 8). These oxygen species capture charge similarly to O^- . In more

detail, if an electron is added into the cell with one O_2 or O_3 adsorbed, both capture a charge of order $0.5 e$ and become spin polarized with total magnetic moment of order $1 \mu_B$. Thus, these species can be attributed to adsorbed O_2^- and O_3^- species. The charge of the former remains essentially unchanged even if two electrons (instead of one) are added into the cell. Thus, contrary to the reaction (b), O_2^{2-} is not formed. The left side of reactions (a) and (c) were modeled by including O_2 molecule in the same unit cell at $10 \text{ \AA}$ above the surface layer. In the case of the reaction (c), the surface unit cell were doubled along $[1\bar{1}0]$ direc-

tion including two O_{ads}^- species. The first reaction scheme, producing charged O_3 , is expected to be simple and such molecules are reported to be created in the case of MgO surface [55]. It is evaluated to be associated with an energy release of $0.5 \text{ eV}/O_{ads}^-$ on the surface. The energy releases of reactions (b) and (c) on the surface are evaluated to be slightly larger ($0.9 \text{ eV}/O_{ads}^-$). It can be concluded that these results partly explain the experimental observation of O_2^- adsorbed on SnO_2 surface, instead of the O^- , O_2^{2-} or O_3^- species. Obviously, there has to be a sufficient density of O_{ads}^- ions to be combined in the reactions. On the other hand, we would like to emphasize that there may be also other adsorption geometries which are relevant depending on the type of the surface, temperature, pressure and other conditions.

Considering binding properties of the O_2^- adsorbate, it is expected that the associated covalent bonds between the oxygen and tin atom of the surface are weaker, than in the case of O_{ads}^- . The length of the O–Sn bond of the adsorbed O_2^- is $2.26 \text{ \AA}$ and the associated bond population is 0.2. Respective values for the O_{ads}^- are $2.0 \text{ \AA}$ and 0.5, which are in accordance with the stronger covalent bonding. The bonding between the oxygen atoms of the O_2^- adsorbate is expected to be weaker than in the case of a free oxygen molecule. The comparison of these two cases can be readily made by evaluating elastic constant along the associated double bond. This offers also a possibility to estimate the difference of the associated vibration frequencies. These calculations were made with a slab of composition $Sn_{32}O_{66}$, when the O–O bond is elongated and contracted by $0.06 \text{ \AA}$ from the equilibrium case. Corresponding calculations were made also in the case of O_2 molecule. It was found that the spring constant becomes decreased by a factor of 0.5 in the case of the O_2^- . This amounts to a down scaling of the vibration frequency by a factor of 0.71. Assuming that the vibration frequency of the free O_2 molecule is 1580 cm^{-1} , the vibration frequency is estimated to become of order 1120 cm^{-1} in the case of adsorbed O_2^- . This is in a good agreement with experimentally measured vibration frequencies of O_2^- adsorbed on SnO_2 surface (1045 cm^{-1} and 1190 cm^{-1}) [56].

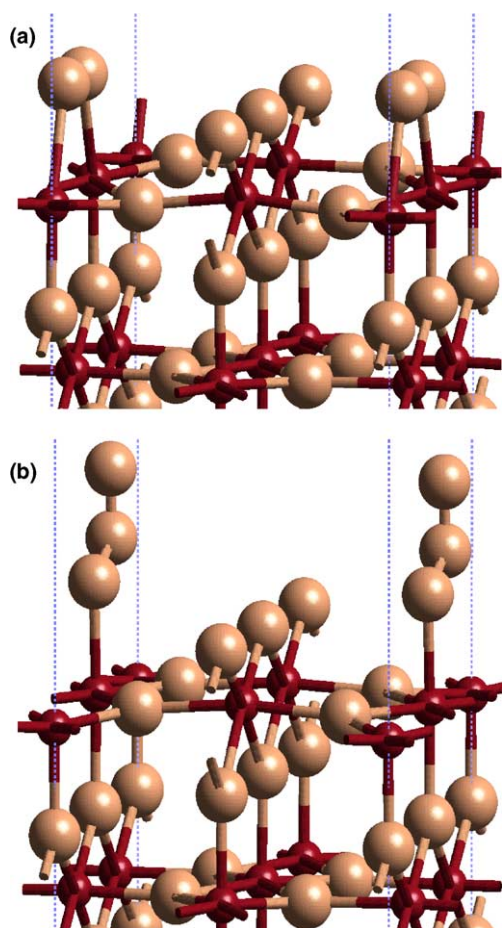


Fig. 8. Geometries of O_2 (upper) and O_3 (below) molecules adsorbed on stoichiometric (110) surface when there is an additional electron in the unit cell.

6. Conclusions

Different charged tin dioxide (1 1 0) surfaces and charged SnO₂ crystal were investigated computationally using first principles density functional method. The additional electron density was of the order of 10²¹–10²² cm^{−3}. This system corresponds to a model system for doped n-type SnO₂ film predicting a connection between the presence of excess charge and surface chemistry, having an influence to important adsorption and catalytic reactions at surface.

In the case of SnO₂ crystal, increased spherical distribution of the charge density around tin cations is observed, while the charge distribution of O anions responds by a small reshuffling. In the cases of stoichiometric and oxygen deficient surfaces considered, charge enrichment due to the excess charge is observed around under-coordinated surface tin atoms associated with outward relaxation. Spin polarization was not found to be present in these cases. Different charge accumulations are observed around, and at the surface site of; five-fold coordinated surface Sn, four-fold coordinated surface Sn atom and around a single bridging oxygen vacancy. The four-fold coordinated surface Sn atom has stronger charge trapping character than five-fold coordinated Sn atom. The charge trapping at the latter decrease when slab thickness is enlarged.

Importantly, tin dioxide can share the excess charge with adsorbed oxygen species. In the case of mono-oxygen adsorbates, the preferred adsorption geometry changes when the additional surface charge density is introduced. In this geometry, oxygen is adsorbed on top of Sn5f surface atom. The electronic structure of this atom is studied and it is indicated to have characteristics of O[−] adsorbate. The associated charge considerably enhance formation of O_{ads}[−] on stoichiometric surface, with respect to free O₂ molecule. Based on the evaluated total energy differences, it is predicted that formation of the O_{ads}[−] is exothermal if formed by dissociative adsorption substituting bridging oxygen vacancy site. With respect to formation of O_{ads}[−], it is evaluated to be energetically preferred to form O₂[−] and O₃[−] adsorbates at low temperature conditions. The adsorbed O[−], O₂[−] and O₃[−] species considered are associated with spin polarization.

The binding properties of adsorbed O[−] and O₂[−] were considered. It is also indicated that the extra charge can be provided by bridging oxygen vacancies, differently, depending on the vacancy arrangement.

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