A theoretical analysis on electronic structure of the (110) surface of TiO$_2$–SnO$_2$ mixed oxide

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Abstract

Mixed oxide compounds, such as TiO$_2$–SnO$_2$ system are widely used as gas sensors and should also provide varistor properties modifying the TiO$_2$ surface. Therefore, a theoretical investigation has been carried out characterizing the effect of SnO$_2$ on TiO$_2$ addition on the electronic structure by means of ab initio SCF-LCAO calculations using all electrons. In order to take into account the finite size of the cluster, we have used the point charge model for the (TiO$_2$)$_{15}$ cluster to study the effect on electronic structure of doping the TiO$_2$ (110) surface. The contracted basis set for titanium (4322/42/3), oxygen (33/3) and tin (4333/4333/43) atoms were used. The charge distributions, dipole moments, and density of states of doping TiO$_2$ and vacancy formation are reported and analysed.

Keywords: Mixed oxide; Titanium oxide; Surface defects; Clusters; ab initio

1. Introduction

Interest in new materials such as TiO$_2$ and SnO$_2$ has grown in the last years due to their important technological applications [1–7]. On the other hand, mixed oxide systems have recently attracted considerable attention [8–21]. The good stability of sensing properties of SnO$_2$ for reducing gases, combined with the good chemical stability of TiO$_2$ at high temperatures, stimulate the study on the applications of TiO$_2$–SnO$_2$ [13,16]. In particular, TiO$_2$–SnO$_2$ system combines the positive features of both materials being used in gas detection. Otherwise, previous studies performed in our group, show evidence that this binary system should also provide varistor properties [22].

Both TiO$_2$ and SnO$_2$ are considered as gas sensors due to the changes in electrical conductivity over gas adsorption. They have useful varistor properties also being used as semiconductor devices [4,22–25], which present high non-linearity between the current
density and electric field. Most of the chemistry of metal oxides is due to the presence of highly reactive defective sites such as cation or anion vacancies and/or a doping process by substitution of metal cations [13,26–28]. The experimentally studied metal oxide surfaces contain defects resulting from preparation conditions or from ionic or electronic bombardment. The yielded material has a high reactivity due to the change of their electronic nature.

Theoretical-computational studies, based on ab initio calculations can yield important information regarding the electronic and structural properties of solid materials [29–32]. This technique provides a framework for the interpretation of experimental data and can be used in order to determine the influence of defects and impurities that commonly control important aspects of solid-state chemistry. We have recently used ab initio calculations in order to study oxygen vacancies and doping processes of Nb/Cr/V and Co/Cu/Zn species on TiO₂ and SnO₂ (110), respectively [33–35]. In particular, our group has developed SnO₂ varistors doped with CoO, Nb₂O₅, La₂O₃ and Cr₂O₃ with high non-linearity coefficients [36–41]. The metal/TiO₂ system has been also investigated due to its application by means of experimental techniques [42–45]. Rekas and coworkers [13] reported an experimental study on the effect of Nb, Cr and Sn additions on the electronic structure of TiO₂.

Considerable works have been performed on the electronic structure of rutile [46–49]. However, to the best of our knowledge there are only a few experimental and theoretical analyses on the electronic structure of mixed oxides. Cao et al. investigated the photocatalytic activities by plasma-enhanced chemical vapor deposition (PECVD) for the binary TiO₂–SnO₂ film [18]. Eisenstein and coworkers presents a comparative analysis of TiO₂–SnO₂, emphasizing decomposition features in the solid solution that govern the temperature stability of the structure of the chemical sensor [20]. Liu et al. carried out the experimental results which showed that photocatalytic efficiency of TiO₂ catalyst was greatly enhanced by adding SnO₂ into TiO₂ [7,50]. Lin and coworkers show that Sn substitution for Ti in rutile TiO₂ lattice has been found to increase the photoactivity of the rutile by up to 15 times for the oxidation of acetone and can effectively slow down the recombination rate [50]. The substitution of Sn⁺⁴ for Ti⁺⁴ in the structure should form solid solution reducing the effect of non-densities mechanisms and thus allowing the densification. Thus, the Sn⁺⁴ substitution should also modify the nature of the chemical bond and properties. Therefore these materials are extremely interesting and these justify each more study about the binary systems.

In this work, we have performed calculations based on Hartree–Fock ab initio method in order to investigate the electronic structures on TiO₂–SnO₂ (110) surface. The aim of the present paper was to improve the electronic structure information of this mixed oxide at the molecular level.

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

2. Models and method

Both TiO₂ and SnO₂ crystallize in tetragonal rutile structure with similarities in the electronic structure where the (110) surface is the most stable of the rutile low-index faces [3,51]. The (110) surface can be obtained in different oxidation degrees, depending on the experimental conditions employed: the stoichiometric and reduced surface (Fig. 1) [33–35, 52–54]. On the (110) surface, the rows of bridging oxygen ions are tightly bound, and the removal of these bridging oxygen ions gives a drastic change in the surface electronic structure. Therefore, our study is mainly applied to model the oxygen vacancy defects.

The structure of the TiO₂ (110) surface was fixed at its bulk geometry without relaxation. In particular, several theoretical studies of relaxation on (110) surface have been reported [29,30], and the optimization of the geometry would greatly enhance the computational work [55,56]. In addition, the relaxed geometry was also used with reliable results [57–59]. Otherwise, these clusters are not large enough in order to describe the non-negligible geometrical relaxation of the surfaces. Therefore, our model is a compromise between accuracy and molecule size that can be treated in a reasonable computational effort. The cluster approach was
chosen because it is particularly suitable to study local phenomena [60].

The neutral cluster models are embedded in a point charge potential (PC) at the lattice points of the TiO₂ rutile crystal in order to represent the Madelung field of the extended crystal (Fig. 2). The charge values (Ti = 1.6 a.u. and O = −0.8 a.u.) used for the PC were optimized in order to avoid spurious behavior [34]. Large cluster models were selected to simulate the embedded stoichiometric (Ti₁₅O₃₀) and reduced (Ti₁₅O₂₈) surfaces (Fig. 1). The reduced surface was obtained by removing the bridging oxygen atoms from position 10 (O₁₀) from the stoichiometric surface (Fig. 1).

The calculations were carried out with the Gaussian98 package [61]. The ab initio Hartree–Fock (HF) level of the theory was employed with the contracted basis set for titanium (4322/42/3), oxygen (33/3) and tin (43333/4333/43) atoms developed by Huzinaga et al. [62]. The orbital exponent and contraction coefficients of the atomic wave function were determined by optimizing the total energy [63]. Although these basis sets are of the minimal type, they give the valence shell orbital energies that are close to double zeta quality [64]. Atomic charge values on atoms are calculated using the Mulliken population analysis. The HOMO–LUMO difference was used as the theoretical quantity to be qualitatively compared.
with the experimental band gap value throughout the text, despite the severe restrictions in this methodology, e.g. the calculated value of LUMO energy. The words band and density of states (DOS) were used throughout the text in order to designate the corresponding distribution of SCF molecular energy levels.

3. Results and discussion

Fig. 3 depicts the DOS for the Ti15O30 and Ti15O28 embedded cluster models. Our theoretical results show that the valence band maximum of the Ti15O30 has a dominant O 2p orbital character and the conduction bands are composed mainly of atomic Ti 3d and 4s orbital levels. These results are in accordance with other theoretical works [48,65–69]. In the Ti15O28 (reduced surface) the valence and conduction bands are essentially the same as for the stoichiometric Ti15O30 valence and conduction bands. Although, for the reduced surface there are states that appear in the band gap (Fig. 3) which are mainly Ti 3d orbitals, because the surface reduction should induce the filling of the empty Ti d levels of the stoichiometric surface. The cluster calculation yields to discontinuous levels, which are interpolated and the top of the lowest state of the band gap nearly reaches the bottom of empty state of the band gap. Fig. 4 shows the DOS features for Ti13O30Sn2 and Ti13O28Sn2 models. Experimental results suggest that the SnO2 additions to the TiO2 matrix influence the electronic structure of TiO2. The valence band maximum in Ti13O30Sn2 are composed of Ti 3d and O 2p orbitals and the upper conduction bands are composed by admixture of atomic Ti 3d, Sn 5s and 5p states and small contributions of O 2p and O 2s orbital. Otherwise, the DOS analyses on Ti13O28Sn2 show that the valence band is predominantly composed of O 2p, Ti 3d and Sn 5s orbitals and the conduction band has a dominant Sn 5s, 5p and Ti 3d orbitals.

For the sake of comparison we constructed the model Ti12O28Sn3 in order to study the increase of Sn

Fig. 2. Structure of the Ti15O30 cluster model embedded in a point charge potential.
doping atoms in position Ti$_4$ (Fig. 1). Fig. 5 shows the DOS features for this surface. The valence band maximum has a dominant admixture of atomic Sn 5s, 5p states and O 2p. The conduction band are composed of Ti 3d, 4s, Sn 2p, 5s and O 2p orbitals. The conduction band shows an increase of 5s character which suggests a modification of the electronic structure from the TiO$_2$ d-type to the SnO$_2$ s-type character of the conduction band. These results agree with the conjecture of Zakrzewska et al. [13].

Table 1 presents the results for the band gap (SCF HOMO–LUMO), which shows the influence of oxygen vacancies and the presence of Sn atoms on
the TiO$_2$ lattice. The gap value decreases significantly (Table 1) from 6.6 to 1.55 eV, from the stoichiometric to the reduced surface, respectively. When the Sn added atoms are present in the reduced TiO$_2$ surface, the band gap value and the $|\text{HOMO}|$ energy decrease from 6.87 to 3.95 eV and 10.08–6.76 eV, from stoichiometric to reduced surface, respectively. The oxygen vacancy reduces the surface and the two electrons left by the missing neutral oxygen atom fill some empty levels of the stoichiometric surface. It is well known that Hartree–Fock method yields large band gap in relation to experimental value [70]. Otherwise experimental studies of TiO$_2$ reduced surface [71] indicate a band gap value lower than the value of stoichiometric surface. The dipole moment is almost the same for all systems (Table 1) and the embedded PC does not affect its direction.

Table 2 shows the Mulliken population analysis for all models. These analyses are not free from limitations and must be considered with care. The nominal charge for Ti$_4$ has decreased by 33%, after oxygen vacancies, whereas there are no significantly changes in the charge for Ti$_5$ and Ti$_6$ sites. These results suggest that an intermediate ion between Ti$_4^{+4}$ and Ti$^{2+}$, the Ti$^{3+}$ ion, can be formed during vacancy formation. On the other hand, the results point out that the oxygen surface is reduced and the surface charge is redistributed when oxygen vacancies are formed. This assumption is in agreement with several experimental and theoretical works [34,35,72,73]. After the substitution of two titanium atoms by two Sn atoms in position Ti$_3$ in the stoichiometric model, the Ti$_4$ neighbor increases the positive charge. For the model Ti$_{13}$O$_{28}$Sn$_2$, Ti$_4$ atom decreases the positive charge about 20%, whereas the positive charge of Sn decreases 59%, from Ti$_{13}$O$_{30}$Sn$_2$ to Ti$_{13}$O$_{28}$Sn$_2$ models. All titanium atom charge values in bottom layer (Ti$_1$, Ti$_2$ and Ti$_3$) are affected by the presence of oxygen vacancy, whereas Ti charges are weakly modified in the presence of Sn atoms in the lattice.

![Graph](image-url)  
*Fig. 5. Density of states for the Ti$_{12}$O$_{28}$Sn$_3$.*

<table>
<thead>
<tr>
<th>Stoichiometry</th>
<th>Gap (eV)</th>
<th>HOMO (eV)</th>
<th>Dipole moment (a.u.)</th>
</tr>
</thead>
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<tr>
<td>Ti$<em>{15}$O$</em>{30}$</td>
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<td>−6.76</td>
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Table 2
Mulliken charge (a.u.) for the Ti$_{15}$O$_{30}$, Ti$_{15}$O$_{28}$, Ti$_{13}$O$_{30}$Sn$_2$ and Ti$_{13}$O$_{28}$Sn$_2$ clusters model. Fig. 1 shows the numbered atoms

<table>
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<tr>
<th></th>
<th>Ti$<em>{15}$O$</em>{30}$</th>
<th>Ti$<em>{15}$O$</em>{28}$</th>
<th>Ti$<em>{13}$O$</em>{30}$Sn$_2$</th>
<th>Ti$<em>{13}$O$</em>{28}$Sn$_2$</th>
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<td>1.84</td>
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4. Conclusions

We have performed HF/Huzinaga calculations on Ti$_{15}$O$_{30}$, Ti$_{15}$O$_{28}$, Ti$_{13}$O$_{30}$Sn$_2$ and Ti$_{13}$O$_{28}$Sn$_2$ PC embedded cluster models in order to investigate the electronic structures of TiO$_2$–SnO$_2$ (110) systems. This analysis is important for the understanding the behavior of mixed oxides and related materials. The conclusions can be summarized as follows: (i) the simulation shows that the formation of oxygen vacancies leads to a decrease in HOMO value; (ii) the band gap value decreases from stoichiometric to the reduced surface in accordance to the experimental results; (iii) the band gap values are strongly affected by the presence of Sn atoms in the TiO$_2$ lattice; (iv) two different valence states of titanium atoms may coexist in the surface, Ti$^{4+}$ and Ti$^{3+}$; (v) the stoichiometric and the reduced cluster models have a dominant O 2p orbital character at the valence band and the conduction band is composed of atomic Ti 3d and 4s orbitals; (vi) for the Ti$_{13}$O$_{28}$Sn$_2$ model the valence band is composed of Ti 3d and conduction band has a dominant Sn 5s and 5p, Ti 3d and O 2p orbitals; (vii) the conduction band shows an increase of 5s character which suggests a modification of the electronic structure from the TiO$_2$ d-type to the SnO$_2$ s-type character of the conduction band.

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