

A Cluster Approach for Modelling of Surface Characteristics of Stannic Oxide

Tuomo S. Rantala¹, Vilho Lantto¹ and Tapio T. Rantala²

¹ Microelectronics and Material Physics Laboratories, University of Oulu, Linnanmaa, FIN-90570 Oulu, Finland

² Department of Physics, University of Oulu, Linnanmaa, FIN-90570 Oulu, Finland

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Abstract

An ab initio cluster approach (LDA-SCF) is used to study the electronic structure of the SnO_2 (110)- 1×1 surface without any relaxation and reconstruction. Modelling is made for the ideal nonpolar surface and also for surfaces containing different kinds of oxygen vacancies, foreign impurities and adsorbates. Computations are based on the linear combination of atomic orbitals (LCAO), which allows the population analysis through projection of the molecular orbitals onto the atomic basis set. This is used to trace the atomic character of the cluster levels. A cluster with 103 atoms $\text{Sn}_{32}\text{O}_{71}$ is used to model the ideal SnO_2 (110) surface, the most stable and thus the dominant crystallite face of the polycrystalline SnO_2 , and the next few bulk layers. The results here refer to both the ideal nonpolar (110) surface and some oxygen-deficient polar (110) surfaces. Chromium and NO are taken as examples of impurity atoms and adsorbate molecules, respectively. Based on the results we are able to suggest an explanation for the observed strong decrease of conductivity of SnO_2 polycrystalline films and the enhanced adsorption and dissociation of NO on the SnO_2 surface due to adding of chromium impurities.

1. Introduction

Stannic oxide, SnO_2 , in its pure form is an n-type wide band-gap semiconductor. Its electrical conductivity results from point defects which are native (mainly oxygen vacancies) or foreign atoms that act as donors or acceptors. Some unique electrical and optical properties of SnO_2 make it useful for many applications, like gas reduction and detection. For instance, the majority of semiconductor gas sensors today use SnO_2 as the reactive element.

Local energy levels, originating from defects like oxygen vacancies at or near SnO_2 surfaces, may have an important role in both electrical transport and gas response properties of SnO_2 [1]. Oxygen vacancies behave as double donors in the bulk SnO_2 . However, the theoretical prediction from band-structure calculations [2] that oxygen vacancies at the surface of SnO_2 do not act as donors is supported by some UPS and conductance measurements [1]. Similar results were also obtained from our earlier cluster model [3], used for the simulation of the surface effects on some energy levels of SnO_2 in relation to oxygen vacancies.

Chromium impurities in SnO_2 have a strong effect on both its electrical conductivity and catalytic properties. Incorporation of small amounts (1% or less) of Cr into the surface layer of SnO_2 basically influences the surface properties of SnO_2 and results in a very effective catalyst for the low-temperature reduction of NO [4]. It seems likely that the high reactivity of Cr ions at the surface is responsible for the enhanced adsorption and dissociation of

NO. Only 0.1 wt% of Cr_2O_3 powder mixed with the SnO_2 powder has been shown to cause, after sintering, the conductance of some SnO_2 thick-film samples to drop by several orders of magnitude [5]. Due to the very high resistance values, the samples were not applicable for conductance measurements below 500 °C.

A cluster model of up to a hundred or more atoms will be shown to be able to simulate the characteristics of a large crystal surface, also reflecting the energy levels of the surface with band formation. The cluster model can also include foreign atoms at the solid surface or surface defects like oxygen vacancies in oxidic semiconductors. Furthermore, the model gives a detailed picture of the energy and shape of the individual orbitals of the surface atoms and their modification by the presence of impurities and adsorbates.

2. Computational method

In general, localised structures and phenomena of bulk solids or solid surfaces can be conveniently modelled with finite clusters. Point defects, foreign impurities and adsorbates on the surfaces are typical examples of such objects, as they induce local charge redistributions affecting on the atomic bonding network and electronic structure. Cluster models, on the other hand, do not reproduce the three dimensional band structure of the infinite and periodic solid, and therefore, special expertise may be needed in the model building and interpretation. Furthermore, the finite size effects should be under careful control and the following questions should be answered. What are the effects from the cluster boundaries, or conversely, what would be the effects of embedding the cluster onto the solid surface or bulk? What are the effects from the charge unbalance or lack of screening, if ionic species or strongly polarized clusters are considered? Should we always use stoichiometric clusters? The relevance of these questions vary within materials from metals to semiconductors and insulators and could, of course, be often simulated with some kind of embedding process [6].

One of the important advantages of the cluster model is the easy calling of self-consistent (SCF) ab initio methods [7]. Also semiempirical methods could be employed allowing the treatment of larger clusters but possibly being more limited in the description of the electronic structure. We have chosen to use the linear combination of atomic orbitals (LCAO) method and local-density approximation [8]. This makes it possible to obtain a detailed picture of the bond formation and modifications, all based on the description

e-mail: Tuomo.Rantala@oulu.fi

using atomic orbitals. LCAO allows us to project the electronic levels of the cluster onto the atomic orbitals, which are used as basis functions. This is the most transparent way of explaining bond formation or breaking in adsorption or vacancy formation in terms of atomic orbitals. Therefore, the minimal basis set tin orbitals up to 5p but without 4f and oxygen orbitals up to 2p, was used. On the other hand, the core orbitals do not participate in the bonding. The tin 4d and 5s orbitals are 27 and 10 eV and oxygen 1s and 2s orbitals are 510 and 24 eV below the vacuum level, respectively. Hence, the frozen core approximation was adopted for tin orbitals in the K, L, M and N shells and for oxygen orbitals in the K shell. The justification of the frozen core approximation for these levels was verified using smaller clusters for comparative studies.

Ab initio methods (including electronic correlations) are computationally heavy. However, employment of the symmetry properties in the cluster arrangement reduces much of the labour, and the local-density approximation (LDA) of the density-functional theory makes the computational approach of relatively large clusters attractive. For very large systems or infinite solids the LDA is the only practical method which can be used to include the exchange and correlation effects. For computations we have used the DMol code [8] which is now also commercially available [9] and von Barth-Hedin exchange-correlation functional [10], which is simple and straightforward to use also in the spin-polarized form.

3. Cluster model

Figure 1 shows the unit cell of the rutile crystal structure of SnO_2 containing two Sn and four O atoms. The structure is 6:3 coordinated and has a relatively strong ionic character. The bulk electronic-structure calculations for SnO_2 [11] predicted a direct optical band gap of 3.6 eV in agreement with experimental results. The conduction-band minimum, which is about 4.5 eV below the vacuum level, is 90% Sn s-like state and surprisingly similar to that for the free-electron model. The valence-band maximum region of width 2 eV consists mainly of oxygen p lone-pair orbitals directed perpendicularly to the Sn-O bonds. In some calculations the optical band gap has been found to be nearly free of surface states [12] and surface defect states originating from different oxygen-vacancy models at the (110) surface [2]. However, the experimental results from UPS measurements [13] show that oxygen-deficient SnO_2 (110) surfaces display

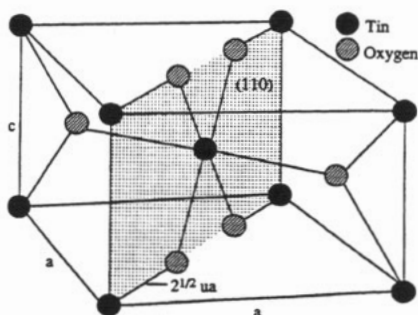


Fig. 1. Unit cell of the rutile structure of SnO_2 with the tetragonal D_{2h}^{14} symmetry and parameter values $a = 4.737 \text{ \AA}$, $c = 3.186 \text{ \AA}$ and the internal parameter $u = 0.306$ (each cation has two anions at the distance $\sqrt{2}ua$ in the surrounding distorted octahedron).

a significant density of surface states in the band gap up to the Fermi level, but oxidized (more ideal) surfaces show no significant density of band-gap states.

Our computations refer to the SnO_2 (110) face which is the most stable, and thus the dominant crystallite face of SnO_2 . The use of the (110) surface without any reconstructions in our computations is based on experimental findings of the thermally driven reconstructions of ion-bombarded SnO_2 (110) surfaces in Ref. [14]. The (110) crystal plane is shown in Fig. 1 and Fig. 2 illustrates the cluster $\text{Sn}_{32}\text{O}_{71}$ used for modelling the atomic structure of the ideal (110)- 1×1 surface. The cluster $\text{Sn}_{32}\text{O}_{71}$ in Fig. 2 with a C_{2v} symmetry has 103 atoms and in addition to that two atoms of a diatomic adsorbate over a surface tin (site 1). In the [110] direction, the crystal is seen to be composed of nonpolar "unit" layers, each containing three atomic planes, $[(\text{O}^{2-})(2\text{Sn}^{4+} + 2\text{O}^{2-})(\text{O}^{2-})]$ per (110) unit area. On ideal surfaces, containing also the "bridging" oxygens (98 and 100 in Fig. 2), there are equal numbers of fivefold- and sixfold-coordinated surface cations. The "bridging" oxygens appear as rows in the [001] direction at the outermost plane and occupy bridging positions between second-plane sixfold-coordinated tin atoms. Oxygen atoms in the second plane of the outermost nonpolar "unit layer" (20 and 24 in Fig. 2) are referred to as "in-plane" oxygens. The top view of the ideal (110) surface in the [110] direction is shown in Fig. 3.

Here the results refer only to different modifications of the basic cluster in Fig. 2, although smaller clusters were also considered, especially for adsorbate studies. Some molecular computations were carried out at the higher level, too. The

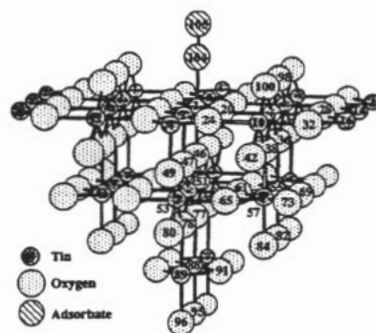


Fig. 2. Structure of the basic cluster $\text{Sn}_{32}\text{O}_{71}$ with C_{2v} symmetry and with a diatomic "adsorbate" (sites 104 and 105). This is the model for the ideal SnO_2 (110)- 1×1 surface.

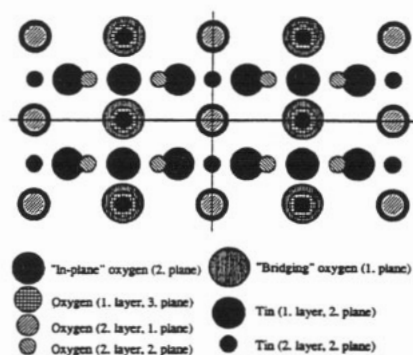


Fig. 3. Top view of the ideal SnO_2 (110)- 1×1 surface in the [110] direction illustrating the positions of tin and oxygen atoms in the five uppermost surface planes in two "unit" surface layers.

basis set was extended to include more functions to reveal any notable basis set effects. The spin-polarised treatment of molecular orbitals was allowed in search for the ground state of the molecule and to determine its contribution to the molecular energetics.

For the computational reasons the cluster size was limited to about one hundred atoms. A typical SCF run for such a cluster with 115 iteration cycles on Convex C3840 took about 500 minutes. Therefore, only molecular conformations and absorbate positions on the surfaces were optimized by minimizing the total energy, but any reconstruction of the cluster geometry was not allowed. Experimental results in Refs [13, 14] show that this is a very realistic assumption for the SnO_2 (110) surface. Any relaxation of the boundary layer atoms at the cluster surface could have enhanced the finite size effects only, instead of leading to the true local reconstructions.

4. Results and discussion

The 5s level of the free tin atom is about 10 eV below the vacuum level, but the oxygen octahedron around a tin atom in bulk SnO_2 pushes the bottom of the bulk conduction band of SnO_2 (90% Sn s-like state) up to about 4.5 eV below the vacuum level. Here we concentrate mainly on the energy and the origin of the cluster levels around the "band gap" region. Computed energy levels from the basic cluster in Fig. 2 (without any adsorbate) are shown in Fig. 4 at this energy region (zero energy in all Figs 4, 5 and 6 refers to the vacuum level). The symbols of the energy levels indicate the strongest atomic-orbital component from the projection together with the atom label from Fig. 2 as a subscript. For some mixed levels, also the second strongest component is given above the strongest. For example, the symbol $5s_{10}$ means that 5s orbital of the tin atom 10, but also the 5s orbitals of three other tin atoms because of the C_{2v} symmetry. The energy level with two full circles (spin degeneration) is the highest fully occupied level, while the level with two open circles is the lowest fully unoccupied level in the computation. The levels between these two have

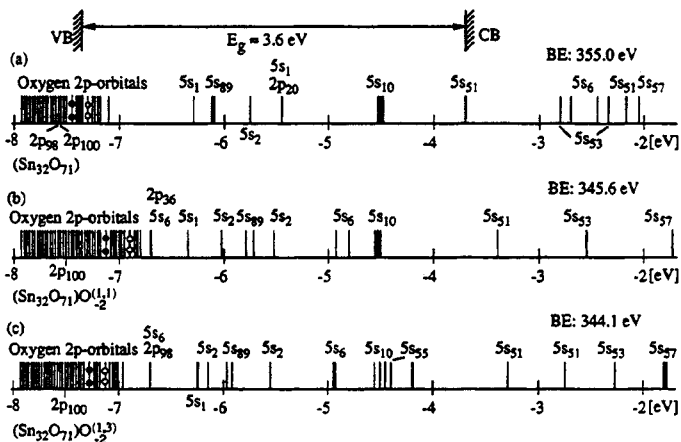


Fig. 4. Computed energy level diagrams around the "band-gap" region ($E_g \approx 3.6$ eV) (a) of the basic cluster $\text{Sn}_{32}\text{O}_{71}$ in Fig. 2 and of its two modifications. The modifications contain the basic cluster with two oxygen vacancies at sites 98 and its C_{2v} symmetry site (b) and at sites 36 and its C_{2v} symmetry site (c). The energy values of the levels are given with reference to the vacuum level. The cohesion energies of the clusters (binding energies, BE) are given with reference to the free atoms.

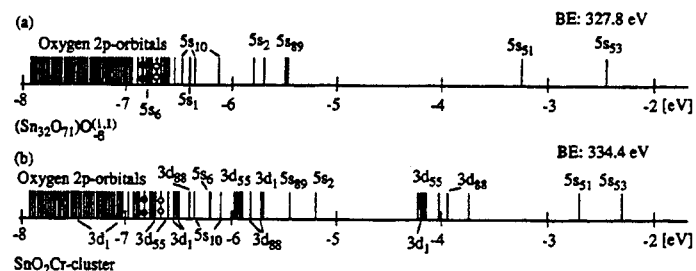


Fig. 5. Computed energy level diagrams around the "band-gap" region of (a) a cluster $(\text{Sn}_{32}\text{O}_{71})\text{O}^{(1,1)}$ where all six "bridging" oxygens (sites 98, 100 ...) in the basic cluster are removed, and of (b) its modifications SnO_2Cr where four tin atoms at sites 1, 55 and its C_{2v} symmetry site and 88 are replaced by chromium impurities. The vacuum level and the free atoms are the references for the energy levels and binding energies (BE), respectively.

a partial population as an indication of the thermal distribution of occupations. The total cohesion energies with reference to those of free atoms (binding energies, BE) are also given in the figures. The conduction-band minimum is connected to the $5s_{51}$ (5s orbital of tin atom 51) level (-3.7 eV), since Sn at the site 51 may be the best representative for the bulk tin in the cluster. The valence-band maximum in Fig. 4 is fixed to the top region of oxygen 2p orbitals corresponding quite well to the true band-gap value of 3.6 eV. Some surface states, originating from Sn and O atoms at the sites 10 and 20 at the (110) surface, are also shown in the "band gap".

The origin of the local energy levels, related to oxygen vacancies in SnO_2 , is in the neighbouring tin atoms and, especially, in their 5s orbitals. Electronic structures of two clusters, both with two oxygen vacancies in the surface layer, are also shown in Fig. 4. The cluster $(\text{Sn}_{32}\text{O}_{71})\text{O}^{(1,1)}$ has two oxygen vacancies in the 1. plane of the 1. layer (the "bridging" oxygens 98 and its C_{2v} symmetry partner in Fig. 2 are missing). In the cluster $(\text{Sn}_{32}\text{O}_{71})\text{O}^{(1,3)}$ the two oxygen vacancies are in the 3. plane of the 1. layer, when the two oxygen atoms 36 and its C_{2v} symmetry partner in Fig. 2 have jumped to the "bridging" vacancies in the cluster $(\text{Sn}_{32}\text{O}_{71})\text{O}^{(1,1)}$. Sn at the site 6 is the neighbouring tin atom to the oxygen vacancy in both clusters. New energy levels in the "band gap", originating from 5s orbitals, are

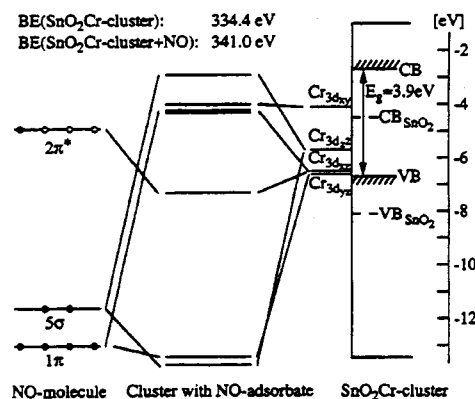


Fig. 6. Computed energy level diagrams of the NO molecule, the cluster SnO_2Cr with four Cr impurities [Fig. 5(b)] and of the interaction of NO molecule with the Cr impurity on the SnO_2 (110) surface (site 1 in the cluster). The vacuum level and the free atoms are the references for the energy levels and binding energies (BE), respectively. Band edges CB and VB for both the cluster and bulk SnO_2 (---) are also shown in the figure. The subscripts of Cr 3d orbitals describe different symmetries of these orbitals.

shown in Fig. 4. The levels are at the bottom of the "band gap" and also above the middle point of the "band gap" in agreement with experimental findings in Ref. [13]. There are also some differences in the "electron affinity" between the three clusters in Fig. 4. After removal of a "bridging" oxygen, for instance, its extra electrons may reside at the tin atom below it (Sn^{2+} instead of Sn^{4+}) making some polarity to the "unit" surface layer.

All six "bridging" oxygens in the cluster in Fig. 2 are removed in the cluster $(\text{Sn}_{32}\text{O}_{71})\text{O}_{-6}^{(1,1)}$. The energy levels of this cluster are shown in Fig. 5 together with levels for its modification where four tin atoms (sites 1, 55 and its C_{2v} symmetry partner, and 88 in Fig. 2) are replaced by chromium impurity atoms. The energy levels originating from 5s orbitals of the tin atoms below the removed "bridging" oxygens in the cluster $(\text{Sn}_{32}\text{O}_{71})\text{O}_{-6}^{(1,1)}$ are near the "valence-band" edge, which means that these tin atoms at the oxygen-deficient (110) surface are in the divalent form Sn^{2+} . The band-gap levels, observed to continue up to the Fermi level in the case of oxygen-deficient (110) surfaces [13], may arise from "in-plane" oxygen surface vacancies. The "band-gap" levels, originating from 3d orbitals of Cr impurities in Fig. 5, are in two groups. One is near the bottom of the "gap" and the other above the middle point of the "gap". The levels originating from the surface chromium ($3d_1$) are in the lower group. Deep trap levels in the band gap, originating from Cr bulk impurities, decrease the concentration of conduction electrons in n-type SnO_2 . The levels from the Cr surface impurities, near the bottom of the band gap, trap electrons and increase the surface energy barrier of this n-type semiconductor. Thus, both bulk and surface impurities may have a very strong effect on conductivity of polycrystalline films.

Figure 6 shows energy level diagrams describing the interaction of the NO molecule with the Cr impurity on SnO_2 (110) surface, computed from the cluster SnO_2Cr with four Cr impurities in Fig. 5(b) together with the NO molecule above the surface chromium (site 1 in Fig. 2). Three most important energy levels 1π , 5σ and $2\pi^*$, computed without spin polarization for NO, are also shown in Fig. 6. A smaller cluster was used to model the SnO_2 (110) surface with a Cr impurity when the position of the NO molecule above the surface impurity was optimized. This position was used in the computation of the electronic structure in Fig. 6 with the large cluster. The energy difference between the bonding 1π and antibonding $2\pi^*$ orbitals has decreased from the value 8.1 eV in the free NO molecule to 6.1 eV as a result of NO adsorption. The transient formation and dissociation of NO^- species has been assumed to be important in

the catalytic reduction of NO [4]. The transfer of an extra electron from surface Cr to the antibonding $2\pi^*$ orbital of NO leads to the significant weakening of the N-O bond. The results in Fig. 6 are in good agreement with the above reasoning. It may be possible to relate the deep surface traps (mixed $2\pi^*$ states in Fig. 6) with the high reactivity of Cr surface impurities to explain the enhanced adsorption and dissociation of NO.

5. Conclusions

Band-gap levels were found to arise from "bridging"-oxygen vacancies at the SnO_2 (110) surface in agreement with experimental findings in Ref. [13]. The levels were near the valence-band edge when "bridging" oxygens were removed from the (110) surface (Fig. 5). Chromium bulk impurities were found to create deep trap levels in the band gap which may decrease concentration of conduction electrons in n-type SnO_2 . The levels from chromium surface impurities were near the bottom of the band gap. These levels can trap electrons and increase the surface band bending of SnO_2 . Thus, both types of Cr impurities are likely to decrease conductivity of SnO_2 polycrystalline films. An electron transfer from chromium surface impurity to adsorbed NO molecule may weaken the N-O bond and explain the enhanced adsorption and dissociation of NO on SnO_2 surfaces having chromium impurities.

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