

A cluster approach for the SnO₂ (110) face

T.S. Rantala^a, V. Lantto^a and T.T. Rantala^b

^aMicroelectronics Laboratory and ^bDepartment of Physics, University of Oulu, Linnanmaa, 90570 Oulu (Finland)

Abstract

Some results are given from a cluster approach for the electronic structure of the SnO₂ (110) face together with some oxygen vacancies and 'adsorbates'. Computations are based on *ab initio* methods, the local-density approximation and atomic orbitals as a basis set. Solutions were calculated self-consistently, but also using a composition of atomic potentials (for some smaller clusters). The atomic-orbital nature (origin) of the cluster levels was traced by projection onto the atomic basis set. The results here refer to a basic cluster [SnO₂]₁₃ with 17 surface atoms modelling the SnO₂ (110) face and the other 22 atoms in the next five surface layers. The effect of oxygen 'adsorbates' and oxygen vacancies in the few uppermost subsurface layers on the electronic structure was considered. In particular, the focus was on the levels related to oxygen vacancies and originating from Sn 5s orbitals, which are well-known donor levels in the deep bulk, making SnO₂ an n-type semiconductor. The results support some other theoretical and experimental predictions that oxygen vacancies behave as neutral defects at or near SnO₂ surfaces.

1. Introduction

Local energy levels, originating from oxygen vacancies at or near the SnO₂ surface, may have an important role in both the electrical transport and gas response properties of SnO₂ gas sensors [1]. Oxygen vacancies behave as double donors at elevated temperatures in the bulk SnO₂, making the material an n-type semiconductor. However, the theoretical prediction from band-structure calculations [2] that oxygen vacancies at the surface of SnO₂ do not act as donors is supported by UPS and some conductance measurements, and also by some conductance measurements after exposure to methane [1]. A cluster approach was used in the present study for a simulation of the surface effect on some energy levels of SnO₂ in relation to oxygen vacancies and 'adsorbates'.

Powerful computers together with good approximations to the Schrödinger equation have made use of the cluster models possible for the simulation of solid surfaces. Calculations with a cluster of up to fifty or more atoms simulate the characteristics of a large crystal surface, also reflecting the energy levels of the surface with band formation. The cluster can also include foreign atoms at the solid surface or surface defects like oxygen vacancies in oxidic semiconductors. 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 many other atoms, including foreign adsorbates and surface defects.

The rutile crystal structure of SnO₂ is 6:3 coordinated and has a relatively strong ionic character. The bulk electronic-structure calculations for SnO₂ [3] predict 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 a Sn–O axis. The optical band gap was found to be nearly free of surface states in a calculation for the surface electronic structure of the ideal (110), (001) and (100) surfaces of SnO₂ [4]. No surface-defect state in the gap was found at the (110) surface of SnO₂ with different oxygen-vacancy models in ref. 2.

2. Computational method

From a cluster model, the larger the cluster, the better it is to find the general features of the electronic structure of a solid material. This treatment for an infinite periodic solid, as a limiting case, even yields the band structure but it is not, however, the best method to describe such local phenomena as single adsorbates on a surface or point defects like vacancies at different sites. Semi-empirical methods allow larger clusters to be treated than *ab initio* methods, but would possibly bring in simultaneously some remnants from

the experiments or the environment in which the parameters were fitted. *Ab initio* cluster methods, being the most elaborate and therefore generally least attractive, are independent of such disadvantages.

We have chosen to use the linear combination of atomic orbitals (LCAO) method and the local-density approximation (LDA). LCAO allows us to project the electronic levels of the cluster onto the atomic basis functions, which is most convenient in explaining adsorption or vacancy formation in terms of atomic orbitals. LDA, on its behalf, makes the computational approach of relatively large clusters attractive and has been generally found to be the best *ab initio* scheme for the description of solid-state properties. Here we use the DMol code [5], which is now commercially available [6], and the von Barth–Hedin exchange-correlation functional [7], which is simple and straightforward to use.

Figure 1 shows the unit cell of the rutile structure of SnO_2 containing two Sn and four O atoms. Our computations refer to the SnO_2 (110) face which is the most stable, and thus the dominant crystallite face of SnO_2 . The (110) crystal plane is shown in Fig. 1 and Fig. 2 illustrates the cluster used for modelling the atomic structure on the (110) face. The top view of the cluster in the $\langle 110 \rangle$ direction is shown in Fig. 3. The cluster in Fig. 2 contains the basic cluster $[\text{SnO}_2]_{13}$ with 39 atoms together with two oxygen 'adsorbates' placed at the rutile structure sites (40 and 41). The basic cluster is stoichiometric and has 17 surface atoms modelling the (110) face and five subsurface atomic layers. Here the results refer only to different modifications of the basic cluster in Fig. 2, although smaller clusters were also used in computations, especially for adsorbate studies.

In order to make computations more attractive, C_{2v} symmetry was always retained and some limitations and

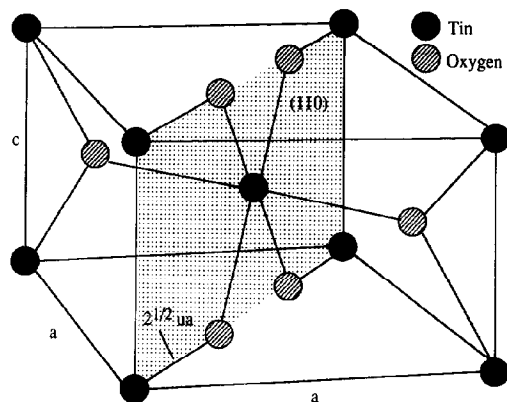


Fig. 1. The unit cell of the rutile structure of SnO_2 with tetragonal D_{2h}^{14} symmetry, parameter values $a = 4.737 \text{ \AA}$, $c = 3.186 \text{ \AA}$ and internal parameter $u = 0.306$ (each cation has two anions at a distance $\sqrt{2}ua$ in the surrounding distorted octahedron).

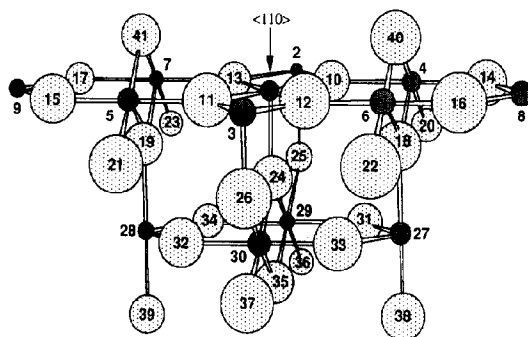


Fig. 2. Structure of the basic cluster $[\text{SnO}_2]_{13}$ together with two oxygen 'adsorbates' (40 and 41) for the simulation of the SnO_2 (110) face. The basic cluster contains 13 SnO_2 units with 13 tin atoms (dark balls) and 26 oxygen atoms (light balls) and has C_{2v} symmetry.

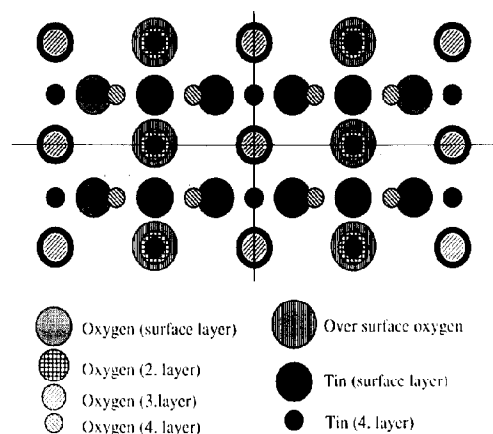


Fig. 3. Top view of the SnO_2 (110) face in the $\langle 110 \rangle$ direction illustrating the positions of tin and oxygen atoms in the four uppermost surface layers together with probable bridge sites of oxygen adsorbates on the surface.

approximations were adopted. A minimal basis set (tin orbitals up to 5p but without 4f and oxygen orbitals up to 2p) was used in computations together with the frozen-core approximation for tin orbitals in the K, L, M and N shells and for oxygen orbitals in the K shell. A unique projection of the cluster levels onto the atomic orbitals is an advantage from the use of the minimal basis set. The use of the frozen-core approximation is also justifiable (tin 4d and 5s orbitals are 27 and 10 eV, respectively, below the vacuum level, and oxygen 1s and 2s orbitals are, respectively, 510 and 24 eV below) and this was also tested and verified with a smaller cluster. Any relaxation of atoms or reconstruction of the rutile structure was not allowed.

Solutions were calculated self-consistently (SCF) for the basic cluster, but also using a composition of atomic potentials (atomic-potential approximation (APA)) for

some smaller clusters. Some vibration frequencies of oxygen adsorbates were also evaluated using an approximation based on finite differences with analytical gradients.

3. Results and discussion

The origin of the local energy levels related to the oxygen vacancies in SnO_2 is in the neighbouring tin atoms and, especially, in their 5s orbitals. In a tin atom the 5s level is about 10 eV below the vacuum level, but the bottom of the bulk conduction band of SnO_2 (90% Sn 5s-like state) is only about 4.5 eV below the vacuum level. Here we concentrate mainly on the energy and origin of the cluster levels around the 'band gap'. The atomic-orbital nature (origin) of the cluster levels was traced by the projection of levels onto the atomic basis set. The main interest is in the levels originating from the Sn 5s orbitals and, in particular, in the energy shifts of these levels due to changes in the coordination number of the different tin atoms.

The computations were done for the basic $[\text{SnO}_2]_{13}$ cluster and for four modifications of it, each having C_{2v} symmetry. The results are shown in Fig. 4 in the

energy region from the upper part of the 'valence band' (about -7.5 eV) to the bottom of the 'conduction band' (about -2.5 eV). The scale is with reference to the vacuum level. The top of the 'valence band' may be related to the highest levels originating from the oxygen 2p orbitals while the bottom of the 'conduction band' may be similarly related to the 5s orbitals of those tin atoms with a coordination number of six (atoms 29 and 30 in Fig. 4(a), (b) and (c)). All the different energy levels in the 'gap' region are shown for each cluster modification in Fig. 4. The symbols of the energy levels in Fig. 4 indicate the name of the strongest atomic-orbital component from the projection together with the atom number from Fig. 2 as a subscript. For example, the symbol $5s_4$ means the 5s orbital of the tin atom 4, but also the 5s orbitals of tin atoms 5, 6 and 7 because of the C_{2v} symmetry requirements. 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 a partial population as an indication of the temperature effect. The total energies with reference to those of free atoms (binding energies, BE) were also computed and are shown in Fig. 4.

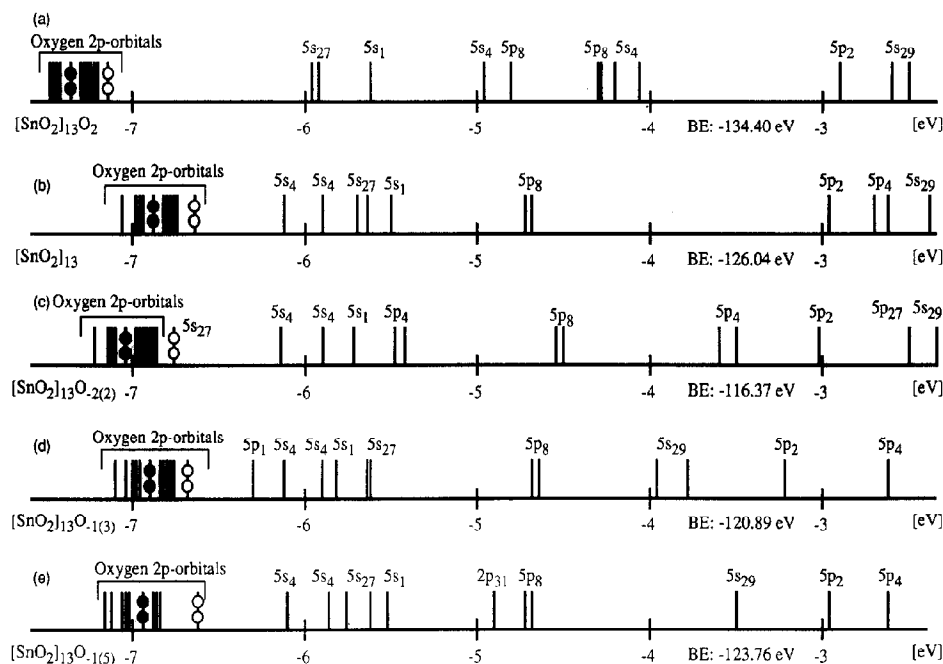


Fig. 4. Computed energy level diagrams around the 'band-gap' region for the basic cluster $[\text{SnO}_2]_{13}$ (b) together with its four modifications. The results in (a) refer to the cluster $[\text{SnO}_2]_{13}\text{O}_2$ in Fig. 2, while the other modifications contain the basic cluster with oxygen vacancies at sites 18 and 19 (c), at site 24 (d) and site 35 (e). The symbols for the levels refer to the main component of a cluster level from the projection onto the atomic basis set. The highest fully occupied and lowest fully unoccupied levels are marked with full and open circles, respectively. The energy values of the levels are with reference to the vacuum level. The cohesion energies of the cluster (binding energies, BE) are with reference to the free atoms.

The results for the basic $[\text{SnO}_2]_{13}$ cluster are shown in Fig. 4(b), while the results in Fig. 4(a) relate to the cluster in Fig. 2 having two oxygen adsorbates (40 and 41). The results for a cluster $[\text{SnO}_2]_{13}\text{O}_{-2(2)}$ in Fig. 4(c) relate to the basic cluster with two oxygen vacancies in the second (first subsurface) layer (atomic sites 18 and 19 in Fig. 2). The atomic cluster $[\text{SnO}_2]_{13}\text{O}_{-1(3)}$ in Fig. 4(d) means the basic cluster with an oxygen vacancy in the third layer (atom site 24), while in the cluster $[\text{SnO}_2]_{13}\text{O}_{-1(5)}$ in Fig. 4(e) there is an oxygen vacancy in the fifth layer (atom site 35). Tin atoms 8 and 9 in Fig. 2 have a coordination of two and tin atoms 2 and 3 have a coordination of three in all cluster modifications in Fig. 4. Energy levels originating from the 5s orbitals of these tin atoms are deep (below the top of the 'valence band'), while the energy levels originating from the 5p orbitals of these atoms are shown in the 'gap' region in Fig. 4. Tin atoms 27 and 28 in the cluster $[\text{SnO}_2]_{13}\text{O}_{-2(2)}$ also have a coordination of three and the level $5s_{27}$ is at the edge of the 'valence band' and level $5p_{27}$ at the edge of the 'conduction band' in Fig. 4(c). In other cluster modifications in Fig. 4 tin atoms 27 and 28 have coordinations of four, as do tin atoms 4, 5, 6 and 7 in the cluster modifications in Fig. 4(d) and (e). The levels originating from the 5s orbitals of these tin atoms with the coordination of four are about 1 eV above the 'valence-band' maximum in Fig. 4. In the cluster in Fig. 4(a) tin atoms 4, 5, 6 and 7 have coordinations of five and, correspondingly, the level $5s_4$ in Fig. 4(a) is about 1.5 eV higher than $5s_4$ in Fig. 4(d) and (e). The level $5s_1$ in all modifications in Fig. 4 originates from tin atom 1 with the coordination of five. Tin atoms 29 and 30 have the full coordination of six in the clusters in Fig. 4(a), (b) and (c) and therefore the 'conduction-band' edge is shown at about 2.5 eV below the vacuum level. In the case of an oxygen vacancy in the third layer in Fig. 4(d), the energy level $5s_{29}$ (related to the vacancy) is about 1.5 eV below the 'conduction-band' edge. When the oxygen vacancy is in the fifth layer, as in Fig. 4(e), the energy level $5s_{29}$ is only about 1 eV below the 'conduction-band' edge.

Energy levels related to the surface tin atoms with a proper coordination (1, 4, 5, 6 and 7) in Fig. 4(b) are at the bottom of the 'band gap' (at about 1 eV above the 'valence-band' edge). Oxygen 'adsorbates' in the atom sites 40 and 41 move the surface states $5s_4$ about 1.5 eV upwards, but shift other levels together

with the 'valence band' downwards in Fig. 4(a). A value of 4.2 eV is obtained for the binding energy of an oxygen 'adsorbate' from the difference between the binding energies of the two clusters in Fig. 4(a) and (b). A computation with a larger cluster decreased the value still further to 3.8 eV.

This can be compared with our computed singlet-state binding energy of the free O_2 , 1.8 eV/atom, or with the experimental value of 2.6 eV/atom (triplet state). The band gap of the bulk SnO_2 can also be estimated from the O_2 2p-originated levels and the levels originating from the 5s orbitals of the bulkmost Sn atoms. The difference of these levels in the $[\text{SnO}_2]_{13}$ cluster results in a value larger than 4 eV, but a larger cluster $[\text{SnO}_2]_{32}$ leads to a value of 3.8 eV, which is close to the experimental band gap of 3.6 eV.

4. Conclusions

The present results show a strong shift of the energy levels originating from tin 5s orbitals due to the change of coordination number of the corresponding tin atom. These results also support other theoretical and experimental predictions that oxygen vacancies on or near the SnO_2 surfaces behave as neutral defects and are not electrically active until they are at a certain distance below the surface. The sites 40 and 41 above the (110) face may be important for the catalytic properties of tin(IV) oxide.

References

- 1 D. Kohl, Oxidic semiconductor gas sensors, in G. Sberveglieri (ed.), *Gas Sensors*, Kluwer, Dordrecht, 1992.
- 2 S. Munnix and M. Schmeits, Electronic structure of oxygen vacancies on TiO_2 (110) and SnO_2 (110) surfaces, *J. Vac. Sci. Technol. A*, 5 (1987) 910-913.
- 3 J. Robertson, Electronic structure of SnO_2 , GeO_2 , PbO_2 , TeO_2 , and MgF_2 , *J. Phys. C*, 12 (1979) 4767-4776.
- 4 S. Munnix and M. Schmeits, Electronic structure of tin dioxide surfaces, *Phys. Rev. B*, 27 (1983) 7624-7635.
- 5 T.T. Rantala, B. Wästberg and A. Rosén, Potential energy curves for diatomic molecules calculated with numerical basis functions, *Chem. Phys.*, 109 (1986) 261-268.
- 6 *DMol User Guide, Version 2.2*, Biosym Technologies, San Diego, CA, 1992.
- 7 U. von Barth and L. Hedin, A local exchange-correlation potential for the spin-polarized case: 1, *J. Phys. C*, 5 (1972) 1629-1642.