

Computational studies for the interpretation of gas response of $\text{SnO}_2(110)$ surface

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Abstract

Tin dioxide is a widely used material in gas sensing applications. This is partly due to its stable surface structure and high sensitivity to many gases. The interaction of different gas components with an oxide surface may lead to changes in the lattice oxygen content at the surface in addition to changes in the amount of adsorbed species. The electronic and atomic structures of the surface change with the changes in the lattice oxygen content. This leads to surface relaxation and changes in the surface dipole layer of the ionic surface in addition to changes in the Schottky barrier which is a result of the charge accumulation onto the surface from the bulk of the semiconducting oxide. Changes in both the dipole layer and the Schottky barrier change the work function of the semiconductor and may reflect in its electrical conductivity. Here we have used first-principles calculations based on LDA-SCF to study changes in the electronic and atomic structures of the $\text{SnO}_2(110)$ surface as a result of oxygen exchange between the lattice and the ambient gas. The transducer function relating the changes at the surface to the changes in the conductivity of a ceramic microstructure is also described by an example. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The (110) surfaces are the most stable and most dominant surfaces of the cassiterite SnO_2 and they are experimentally very well characterised. SnO_2 does not cleave well, but fractures. The stoichiometry of $\text{SnO}_2(110)$ surfaces is sensitive to the processing conditions under which the surface is prepared. Perpendicular to the [110] direction the cassiterite structure is built up from neutral stacked layers of three alternating planes of (O), $(2\text{Sn} + 2\text{O})$, and (O) with the nominal ionic charges of $2-$, $4+$ and $2-$ in the surface primitive unit cell, respectively. The termination of the (110) plane with a neutral layer of three planes $[(\text{O})(2\text{Sn} + 2\text{O})(\text{O})]$ is possible, since it does not leave a repeating unit with a net dipole moment [1]. The surface terminates to 2-fold-coordinated bridging oxygen atoms. A schematic representation of this stoichiometric surface is shown in Fig. 1(a). Removal of the bridging oxygen ions to form a reduced (110) surface is possible in

the case where the 4-fold coordinated (from the removal of bridging oxygens) tin ions at the surface reduce to tin(II) form which removes the repeating dipole unit $[(4+)(2-)(2-)][(4+)(2-)(2-)]\dots$ from the structure [1] and creates a dipole layer $[(2+)(2-)]$ at the surface. Fig. 1(b) shows a schematic representation of the reduced $\text{SnO}_2(110)$ surface.

Experimentally, $\text{SnO}_2(110)$ surfaces can have partial occupation of the bridging oxygen sites and the surface can display $p(1 \times 1)$, $c(1 \times 1)$, $p(4 \times 2)$, $p(4 \times 1)$, or disordered structures [2]. Cox et al. [3] have described methods for producing nearly perfect stoichiometric $\text{SnO}_2(110)-1 \times 1$ surfaces.

2. Computational methods

Surfaces can be described with a slab model (layers of finite thickness) still retaining the benefits of full three-dimensional periodicity. To form a slab model of the (110) surface (in Fig. 2(a)) we used an orthorhombic supercell with 16 atoms (reduced, Sn_6O_{10}) or 18 atoms (stoichio-

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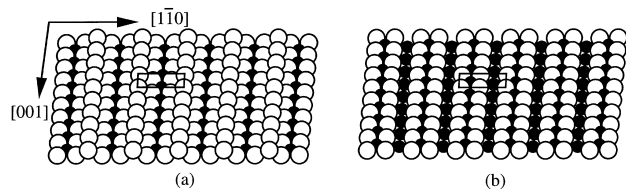


Fig. 1. Schematic representations of the $\text{SnO}_2(110)\text{-}1\times 1$ surfaces together with surface primitive unit cells (a) in the stoichiometric form with the outer plane of bridging oxygen ions and (b) in the reduced form with all bridging oxygens removed and rows of the 4-fold coordinated Sn cations now visible.

metric, $(\text{SnO}_2)_6$) oriented as shown in Fig. 2(b). In addition to the minimum slab thickness (6.7 Å without the bridging oxygens) we also used twice as thick one (13.4 Å). In both cases the thickness of the vacuum gap was chosen to be the same as that of the slab. All atoms except those in the centermost atomic plane were allowed to relax in the smaller slab and one more atomic plane in the double sized slab.

The computations were carried out with two different self-consistent *ab initio* LDA (local-density approximation) methods. One of our computational tools, DSolid, is a commercially distributed software [4]. It allows self-consistent *ab initio* computation of periodic structures within the LCAO (linear combination of atomic orbitals), i.e., a localised basis set, and DFT (density-functional theory). Within DFT we restricted to the LDA and used two different parameterisations, which both gave similar results. The other computational tool, PlaneWave, is based on the pseudopotential (PP) description of valence-core interactions and the plane wave expansion of the valence (and conduction) electrons (PWPP) [4]. The pseudopotentials were chosen to be of extended-norm-and-hardness-conserving type [5] and linear core-valence exchange-correlation functionals were used. The size of the PW basis was determined by the simulation cell size and the cut-off energy of 40 Hartrees (80 Ry). The number of *k*-points was three, chosen according to the Monkhorst-Pack method [6] to optimally span the integration mesh over the Brillouin zone. Γ -point approximation was used with the LCAO calculations. Quality of this approximation was tested by doubling the size of the computational unit cell in two different coordinate directions.

3. Results and discussion

First, the methods were tested for the bulk relaxation. The total energy minimisation with PWPP led close to the experimental lattice constants (less than 0.5% expansion), whereas the values from the LCAO calculation were not as accurate when compared with the experimental values (about 3% isotropic expansion). To retain the comparabil-

ity with the further surface calculations we kept the experimental lattice parameters but allowed the relaxation of the atomic positions within the unit cell. The atomic positions relaxed negligibly with the PWPP and with the LCAO the oxygen atoms moved less than 0.05 Å. The surface relaxations of both stoichiometric and reduced $\text{SnO}_2(110)$ surfaces were carefully studied and the parameters shown in Fig. 3 were used to describe the relaxation of the (110) surfaces. Both surfaces relaxed without reconstructions preserving their truncated bulk symmetry properties. Calculated values of the relaxation parameters introduced in Fig. 3 are given in Table 1. There are no experimental values to compare with, but only calculated values, e.g., by Godin and LaFemina [2] from tight-binding (TB) calculations and by Manassidis et al. [7] from a PWPP calculation. The most prominent feature is that the oxygens in the $(2\text{Sn} + 2\text{O})$ plane of the reduced surface move outwards about 0.4 Å with respect to the tin atoms in the same plane. The stoichiometric surface is stabilised by the bridging oxygen ions and, therefore, relaxes to less extent. The relaxation of the surface layer tin atoms do not differ essentially at the two surfaces but the values reported in Ref. [7], and also in Ref. [2], are quite different from ours. Both of our methods predict a similar perpendicular relaxation for the reduced surface and there are only small differences in the predictions for the stoichiometric face. The general shapes of the density-of-states (DOS) distributions of the two surfaces and the bulk obtained from our PWPP calculations were in good agreement with the DOS distributions of Manassidis et al. [7]. In the case of the reduced surface, gap states appeared as a result of removing the bridging oxygens. With the analysis of the corresponding LCAO one-electron orbitals we were able to trace their localization to the surface tin atoms and oxygen atoms below the missing bridging oxygen sites. This supports the picture that the electrons left behind from the removed bridging oxygens occupy the gap states formed at the reduced surface tin (II) atoms. The gap states formed a band with relatively strong dispersion with *k* values.

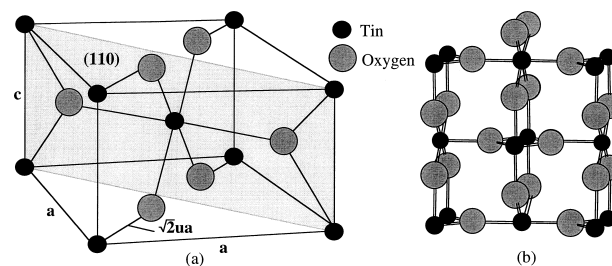


Fig. 2. (a) Primitive tetragonal unit cell of the bulk rutile SnO_2 with the basis $(\text{SnO}_2)_2$. The shaded region is a (110) cleavage plane. (b) The orthorhombic supercell of SnO_2 used in the thinnest slab model. The upper half of the supercell illustrates the stoichiometric and lower half the reduced $(110)\text{-}1\times 1$ surfaces. In the slab supercell $[6.70 \text{ Å} \times 3.19 \text{ Å} \times (6.70 + \text{vacuum}) \text{ Å}]$ there are 6 Sn and 10 O atoms (reduced) or 6 Sn and 12 O atoms (stoichiometric).

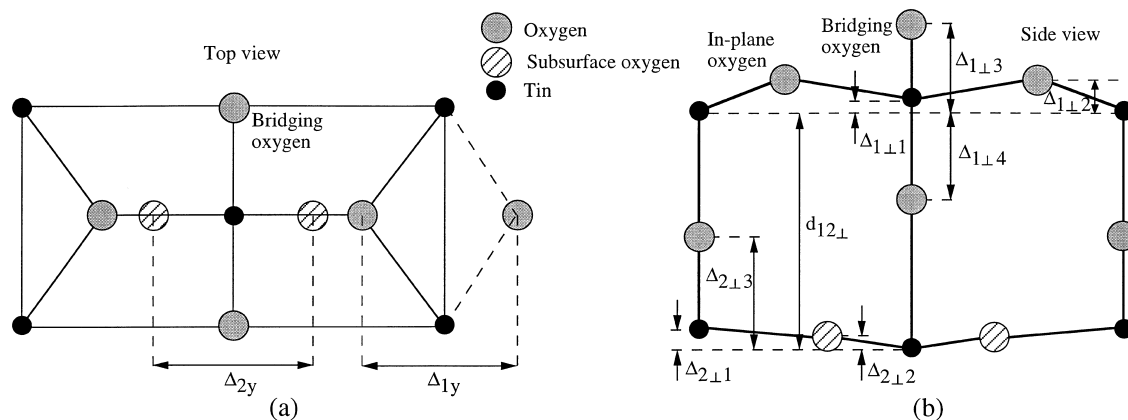


Fig. 3. The relaxation parameters used to describe the relaxation of the $\text{SnO}_2(110)\text{-}1 \times 1$ surface; (a) top view and (b) side view. The hatched symbols represent oxygen atoms in subsurface layers.

The ideal stoichiometric (110) surface is non-polar, but a surface dipole layer originates in the removal of bridging oxygens. When the two electrons of each bridging oxygen are trapped by tin(II) ions in the $(2\text{Sn} + 2\text{O})$ plane we can give for the potential difference V over the dipole layer $[(2+) (2-)]$ at the reduced (110) surface an equation: $V = 2qN\langle d \rangle / \epsilon_s$, where N is the surface density of tin(II) ions ($= 4.7 \times 10^{18} \text{ m}^{-2}$), $\langle d \rangle$ is the average distance between opposite charges in the dipole and ϵ_s and q are the permittivity at the surface and elementary charge, respectively. If we use the value of the atomic distance between tin(II) and O^{2-} ions in the case of non-relaxed reduced (110) surface, 1.29 Å (Table 1), for $\langle d \rangle$ and the

bulk permittivity ($\sim 12\epsilon_0$) for ϵ_s (thus neglecting the decrease of ϵ_s from the bulk value in the interface between air and SnO_2), we get a value of 1.8 V for the potential difference V . The stereochemical positions occupied by the $\text{Sn}5s\text{-}5p$ lone-pair hybrids of tin(II) ions in the structure (electronic polarization of tin(II) ions) may, of course, decrease this value, to a large extent. The obtained relaxation (ionic polarization) for the reduced (110) surface decreased, from calculations as above, the potential difference over the dipole layer by about 0.6 V. The preliminary value for the potential difference over the dipole layer at the relaxed $\text{SnO}_2(110)$ surface from our ab initio calculations was about 0.2 V and, therefore, smaller than the values obtained in our earlier cluster calculations with non-relaxed surfaces [8]. The affinity (and work function) of the reduced $\text{SnO}_2(110)$ surface decreased by the amount of the potential difference over the dipole layer. An affinity decrease of about 0.2 eV was found also by Cox et al. [3] from their ultraviolet photo-electron spectroscopy (UPS) measurements upon heating an oxidized (stoichiometric) $\text{SnO}_2(110)$ surface in vacuum up to 700 K. From their ion-scattering spectroscopy (IIS) and UPS measurements they further conclude that the bridging oxygens disappear from the oxidized surface during heating up to about 700 K in vacuum.

The results in Ref. [3] show also that the $\text{SnO}_2(110)$ surface can remain reduced in air at low temperatures, but oxidizes to the stoichiometric form during heating up to 700 K in air. Now, the bridging oxygens may give an explanation for the conductance behaviour in Fig. 4 which shows conductance of a pure SnO_2 thick-film sample and of samples doped with Sb (100 ppm) and with Al (1000 ppm and 1%) measured in dry synthetic air as a function of inverse temperature [9]. In the temperature range 420–500 K, the Arrhenius plots are nearly linear. From the extrapolation of these straight lines to higher temperatures, it is possible to calculate, using the equation for the conductance: $G = G_0 \exp(-eV_s/kT)$ with constant G_0 , an increase of about 0.2 eV for the activation energy eV_s of each sample between 500 and 700 K. The disappearance of

Table 1

The relaxation parameters of the stoichiometric and reduced $\text{SnO}_2(110)\text{-}1 \times 1$ surfaces as described in Fig. 3 from LCAO (large supercell) and PWPP (small supercell) calculations. All values are in Å

Parameter	Unrelaxed	LCAO	PWPP
Stoichiometric			
$\Delta_{1\perp 1}$	0	$\text{Sn}_{10}\text{O}_{20}$ +0.08	Sn_6O_{12} +0.21
$\Delta_{1\perp 2}$	0	+0.04	+0.22
$\Delta_{1\perp 3}$	1.29	1.36	1.41
$\Delta_{1\perp 4}$	1.29	1.36	1.22
Δ_{1y}	2.59	2.63	2.50
Δ_{2y}	2.59	2.71	
$d_{12\perp}$	3.35	3.33	3.26
$\Delta_{2\perp 1}$	0	−0.01	
$\Delta_{2\perp 2}$	0	+0.01	
$\Delta_{2\perp 3}$	1.29	1.35	1.28
Reduced			
$\Delta_{1\perp 1}$	0	$\text{Sn}_{10}\text{O}_{18}$ +0.05	Sn_6O_{10} +0.11
$\Delta_{1\perp 2}$	0	+0.45	+0.40
$\Delta_{1\perp 4}$	1.29	1.39	1.33
Δ_{1y}	2.59	2.70	2.45
Δ_{2y}	2.59	2.71	
$d_{12\perp}$	3.35	3.45	3.41
$\Delta_{2\perp 1}$	0	+0.01	
$\Delta_{2\perp 2}$	0	0.00	
$\Delta_{2\perp 3}$	1.29	1.41	1.36

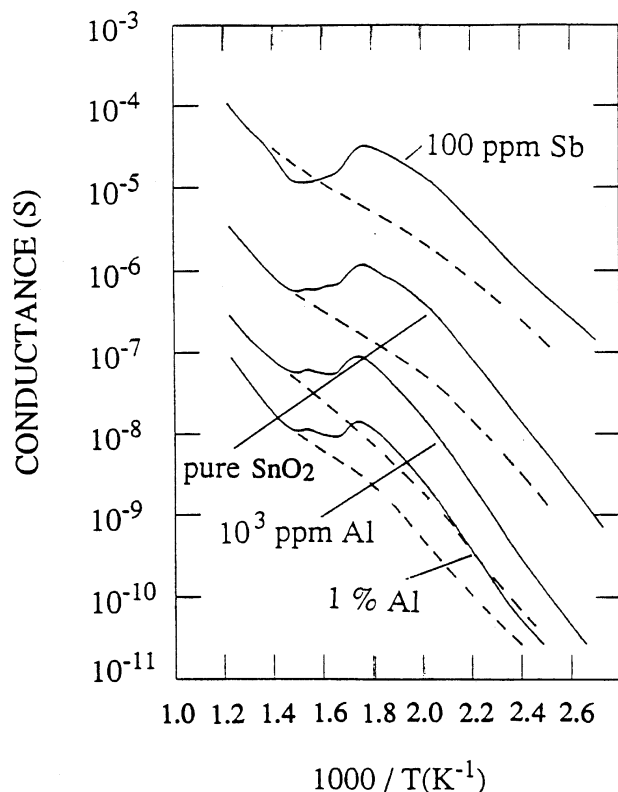


Fig. 4. Conductance of pure, Sb- and Al-doped SnO_2 thick-film samples with Au electrodes in dry synthetic air as a function of inverse temperature, measured at a cooling (---) and heating (—) rate of 2.4 Kmin^{-1} [9].

the bridging oxygens during a long stay in dry synthetic air at a low temperature and reappearance during heating may be the reason for the conductance hysteresis during the heating-cooling cycle in Fig. 4 [9].

4. Conclusions

Surface relaxation together with a high polarization of tin(II) ions increase the surface permittivity and decrease effectively the strength of the dipole layer at the reduced $\text{SnO}_2(110)$ surface. The most prominent feature in the relaxation is the translation of oxygen outwards with respect to surface layer cations. This appears to be strong,

about $0.4 \text{ \AA}$, for the reduced surface, but much smaller for the oxidized surface. The electrons from the bridging oxygen vacancies form a band of gap states and reduce the surface layer tin atoms below the bridging oxygen vacancies to tin(II) ions which have a high polarization from the $\text{Sn}5s\text{--}5p$ hybrid lone-pair electrons pointing outwards of the surface. The bridging oxygens at the stoichiometric surface and the lone-pair electrons at the reduced surface together with the change in the surface dipole layer with changing coverage of bridging oxygens seem to have important effects to both the receptor and transducer functions of the SnO_2 -based gas sensors.

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