

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 changes in the lattice oxygen content. This leads to surface relaxation and changes in the dipole surface layer of an 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 a 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 computational methods 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 ambient gas. The transducer-function relating the changes at the surface to changes in the conductivity of a ceramic microstructure is also discussed.

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. In the perpendicular [110] direction the cassiterite structure is built up from stacked neutral layers of three alternating planes of (O), (2Sn + 2O) 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 the neutral layer of three planes [(O)(2Sn + 2O)(O)] is possible, since it does not leave a repeating unit with a net dipole moment [1]. The surface terminates to twofold-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 4-fold coordinated (from the removal of bridging oxygens) tin ions at the surface reduce to tin(II) which removes the repeating dipole unit [(4+)(2-)(2-)][(4+)(2-)(2-)]... from the structure [2]. 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 amorphous structures [3]. Cox et al. [4] have developed 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 ("stoichiometric", $(\text{SnO}_2)_6$) oriented as shown in Fig.2(b). In addition to the minimum slab thickness (6.7Å without bridging oxygens) we also used the double size of that (13.4Å). In both cases the vacuum thickness was chosen to be the

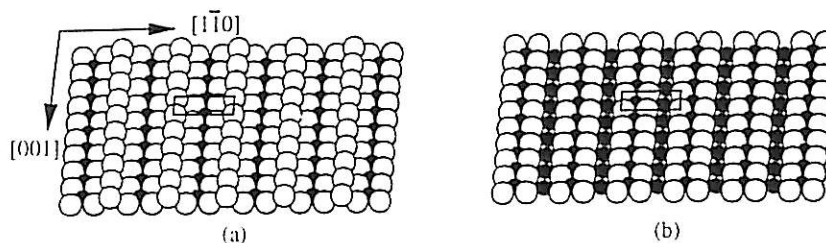


Figure 1: Schematic representations of the $\text{SnO}_2(110)-1 \times 1$ surfaces together with surface primitive unit cells (a) in the "stoichiometric" form with outer plane of bridging oxygen ions and (b) in the "reduced" form with all bridging oxygens removed and rows of the 4-fold coordinated Sn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

same as that of the slab. All atoms except for those in the centermost atomic plane were allowed to relax in the smaller slab and one more atomic plane in the double sized slab.

Calculations are carried out with two different self-consistent *ab initio* LDA (local-density approximation) methods. One of our computational tools, DSolid, is commercially distributed software [5]. 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 parametrisations, which both gave similar results. The other computational tool, Plane-Wave, is based on the pseudopotential (PP) description of ion cores and a plane wave expansion of the valence (and conduction) electrons (PWPP) [5]. The pseudopotentials were of generalised norm-conserving type 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 40 Hartrees.

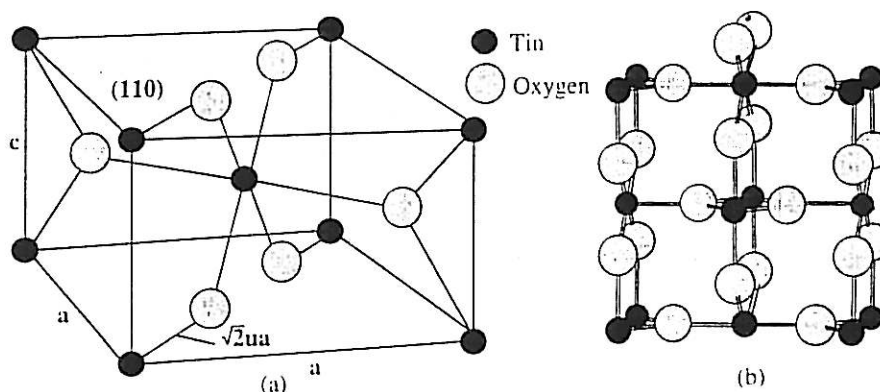


Figure 2: (a) Primitive tetragonal unit cell of the bulk rutile SnO_2 . The shaded region is a (110) cleavage plane. (b) The orthorhombic supercell of SnO_2 used in the thinnest slab model. The upper half of the supercell illustrates the "stoichiometric" and lower half the "reduced" $(110)-1 \times 1$ surfaces.

3. RESULTS AND DISCUSSION

First, the methods were tested to the bulk relaxation. The total energy minimisation with PWPP led close to the experimental lattice constants, whereas the values from the LCAO calculation were not as accurate with the experimental values. Surface relaxation of both "stoichiometric" and "reduced" $\text{SnO}_2(110)-1 \times 1$ surfaces was carefully studied and the parameters shown in Fig.3 were used to describe the relaxation of the (110) surface. The most prominent feature is that oxygens in the $(2\text{Sn} + 2\text{O})$ plane of the "reduced" surface move outwards about $0.4\text{\AA}$ 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 ideal "stoichiometric" (110) surface is non-polar, but surface dipole layers origin in the removal of bridging oxygens. If the two electrons of the bridging oxygen are trapped by a tin(II) ion in

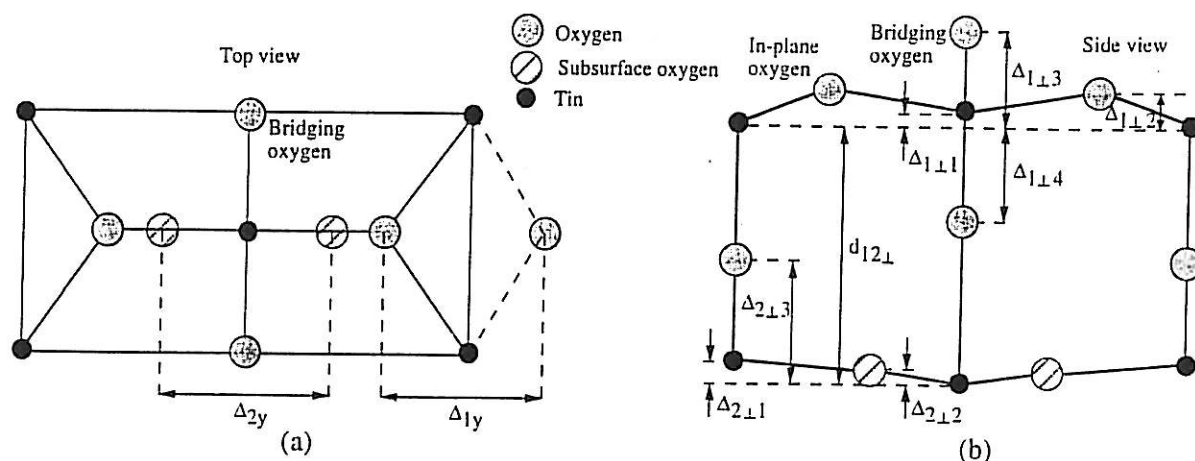


Figure 3: Independent structure parameters used to describe the relaxation of the $\text{SnO}_2(110)-1 \times 1$ surface: (a) top view and (b) side view. The hatched symbols represent oxygen atoms in subsurface layers.

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: $V = 2qN\langle d \rangle / \epsilon$, 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 of charges in the dipole and ϵ and q are the permittivity and elementary charge, respectively. If we use the value of the atomic distance between tin(II) and O^{2-} in the case of non-relaxed "reduced" (110) surface, $1.3 \text{ \AA}$, for $\langle d \rangle$, we get a value of 1.84 V for the potential difference V . The stereochemical positions occupied by Sn $5s-5p$ lone-pair hybrids of tin(II) ions in the structure may, of course, decrease this value, to some extent. The obtained relaxation for the "reduced" (110) surface decreased, from calculations as above, the potential over the dipole layer by about 0.6 V . The results for the dipole potential at relaxed surfaces from our *ab initio* calculations were, therefore, smaller than the values obtained in our earlier cluster calculations with non-relaxed surfaces [6].

4. CONCLUSIONS

The simple estimations above demonstrate that strong surface dipole layer may origin in the variation in the oxygen content at an ionic surface. Surface dipole layer also changes in the relaxation of an ionic surface. Surface dipole changes may also affect the conductivity of an oxide semiconductor which is of central importance in the case of chemical sensing with these oxides.

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