



Electronic structure of SnO₂ (110) surface

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Abstract

The electronic structure of the stoichiometric and reduced SnO₂ (110) surfaces is studied with first-principles calculations. Calculations are carried out with two complementary self-consistent *ab initio*–DFT–GGA methods. Surface relaxation is considered, where the most prominent feature turns out to be the surface layer in-plane oxygen displacement of the reduced surface outwards, about 0.4 Å with respect to the surface layer tin atoms. The electronic structure of the relaxed surfaces is considered in terms of atomic orbitals and rehybridization, and the surface band structure. The bands are flat at the stoichiometric surface, but strong dispersion occurs at the reduced surface. The dispersion results in electronic levels into the band gap, which have also been experimentally observed. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Electronic structure of the material is responsible for most of its observable properties. This is true for surfaces, too. The atomic surface geometries, driven by the energy minimization of the electronic configuration, present a variety of structures in different materials. This is due to lower symmetry at the surfaces as compared with the bulk. These surface phenomena include relaxation, reconstruction and even larger rearrangements like surface diffusion or reactions with the gas atmosphere. In the case of ionic compound materials these phenomena may appear to be exceptionally strong and have to be included in a proper calculation of the electronic structure.

Tin dioxide SnO₂ is an ionic compound, which is generally used in gas sensing applications due to its environment dependent surface chemistry. The ‘oxygen chemistry’ at the grain surfaces of the porous SnO₂ material is strongly dependent on the surrounding gas atmosphere and it is reflected in the easily measurable electric conductance [1,15]. Recently, we investigated the detailed structure of the (110) face of the rutile structure SnO₂ (cassiterite) with *ab initio*–DFT calculations with the local-density approximation (LDA) [2]. Now, we update our results with new ones from calculations with the generalized-gradient approximation (GGA) and make a closer look at the surface electronic structure.

Experimentally, the surface electronic structure has been investigated with various spectroscopies [3], the surface topology with LEED and latest with STM, see Ref. [4] and further references therein. Depending on the experimental conditions at least (1 × 1), (1 × 2) and (4 × 1) reconstructions are observed. It seems obvious,

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however, that the ideal reduced and stoichiometric surfaces appear in the (1×1) reconstruction, which is an underlying assumption in our study, too.

There are several theoretical investigations of the bulk SnO_2 and the (110) surface, too. Bulk band structure calculations of Palummo et al. [5] proved the importance of relaxation within the DFT calculation scheme. Munnix and Schmeits calculated the electronic structures of several ideal (unrelaxed) SnO_2 surface faces using a tight-binding (TB) method [6,16]. Godin and LaFemina [7] carried out TB calculations for the surface relaxation of the SnO_2 $(110)-1 \times 1$. The most complete account was made by Manassidis et al. [8,17] with the first-principles LDA slab calculations of the SnO_2 (110) surfaces with varying oxygen contents, Goniakowski et al. investigated bulk and surface properties of SnO_2 (and TiO_2) with gradient corrected LDA [9,18]. Finally, we can mention our finite-cluster LDA approaches to the SnO_2 surfaces [10,19].

Despite the number of calculations there is no consensus about the electronic structure and the related surface geometry, in particular, if the reduced and stoichiometric surfaces are compared. In addition to the surface relaxation, another major open question relates to the origin of the electronic surface levels in the band gap at the reduced surface, which were experimentally observed by Cox et al. [3].

In the next two sections we describe our models for the surfaces and the two computational approaches. These are followed by two sections about the relaxed surface geometries and electronic structures, respectively. In the last section the conclusions are given.

2. Reduced and stoichiometric (1×1) surfaces of SnO_2 (110) face

The rutile crystal structure of SnO_2 is 6:3 co-ordinated and the tetragonal unit cell contains two tin and four oxygen atoms, see Fig. 1a. The (110) direction of

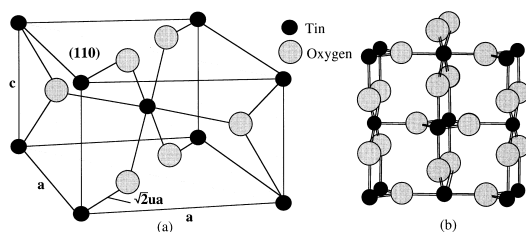


Fig. 1. (a) Primitive tetragonal unit cell of the bulk SnO_2 . The experimental lattice parameters are $a = 4.737 \text{ \AA}$, $c = 3.186 \text{ \AA}$ and $u = 0.306$. (b) Orthorhombic supercell of the slab model. The top face of the supercell illustrates the stoichiometric and bottom face the reduced (110) surface [2].

the structure consists of neutral groups of three parallel planes $\text{O}-\text{Sn}_2\text{O}_2-\text{O}$ and the cleavage cut between these groups of planes breaks the least number of cation–anion bonds. This results in what is called the stoichiometric surface. Therefore, the (110) face is the most stable and most dominant surface of the crystallites of the usually porous SnO_2 material. Removal of the surfacemost ‘bridging’ oxygen layer of the stoichiometric surface results in what is called the reduced (110) surface, see Fig. 1b.

We adopt the slab model of the (110) surface with an orthorhombic supercell with 16 atoms (reduced, Sn_6O_{10}) or 18 atoms (stoichiometric, $(\text{SnO}_2)_6$) oriented as shown in Fig. 1b. With LCAO, however, we found it necessary to double the unit cell in the smallest dimension ($3.186 \text{ \AA} \rightarrow 6.372 \text{ \AA}$) resulting in 32 and 36 atom supercells. Vacuum between the surfaces was chosen to occupy half or 2/3 of the slab supercell. All atoms except for those in the innermost atomic plane were allowed to relax. The upper and lower sides were treated identically.

3. LCAO and PWPP approaches

For the computations we employ commercial software from MSI [11] and carry out both linear-combination-of-atomic-orbitals (LCAO) and plane-wave-pseudopotential (PWPP) calculations at the DFT–GGA level. The LCAO basis functions are one-electron orbitals of free atoms and free ions. For oxygen and tin we used the basis sets: $1s^2, 2s^2, 2p^4, 2s^{0*}, 2p^{0*}, 3d^{0*}, 3d^{0*}$, and $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 5s^2, 5p^2, 4d^{10*}, 5s^{0*}, 5p^{0*}, 5d^{0*}$, respectively. The orbitals denoted by asterisk were generated in ions rather than in neutral atoms.

The other computational tool, CASTEP, is based on the pseudopotential description of ion cores and a plane wave expansion for the valence and conduction electrons. The pseudopotentials were chosen to be of extended-norm-and-hardness-conserving type [12] after careful testing. The chosen hard pseudopotentials made it necessary to use an unusually large plane wave basis, up to the cut-off of 1000 eV (40 Hartrees). The number of $\mathbf{k}$ -points is eight, chosen according to the

Table 1
Bulk relaxation of cassiterite, SnO_2^a

	Experimental	LCAO	PWPP	PWPP [8]
a	4.737	4.832	4.730	4.637
c	3.186	3.266	3.212	3.060
u	0.307	0.307	0.306	0.307

^a The parameters a , c (in $\text{\AA}$) and u are defined in Fig. 1a.

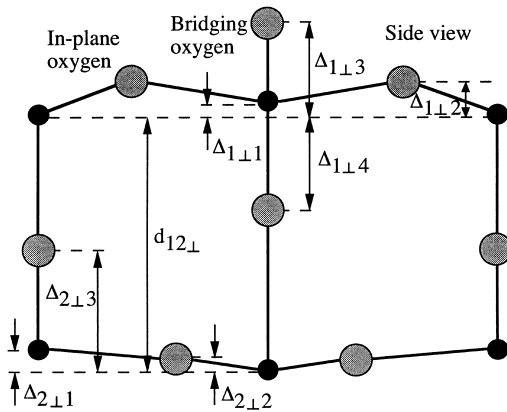


Fig. 2. Relaxation parameters of SnO_2 (110) surface [2].

Monkhorst–Pack method [13]. The GGA of Perdew and Wang [14] was used with both of the methods for the non-local exchange and correlation approximation.

4. Minimum energy structures

Total energy minimization starting from the experimental lattice constants with the LCAO method led to about 2% expansion, whereas the expansion with PWPP is less, see Table 1. These bulk relaxed structures were used as a reference to the surface relaxation. This is perhaps the most significant difference to our previous LDA calculation [2], where the experimental geometry was used as the reference.

Both surfaces relaxed without reconstructions preserving their truncated bulk symmetry. The parameters used to describe the relaxation are introduced in Fig. 2 and their calculated values are given in Table 2. In the

present ‘GGA update’ cf. Ref. [2], the changes in the parameters are negligible, less than 0.05 Å for all coordinates considered. To what extent these changes relate to the differences between LDA and GGA, and on the other hand, to the change in the reference geometry (experimental–relaxed bulk), is not resolved.

As the most prominent feature remains the in-plane oxygen relaxation outwards with respect to 5-fold tin atoms ($\Delta_{1\perp 2}$). It appears to be strong about 0.4 Å at the reduced surface but much weaker at the stoichiometric surface. The differences that we find in comparison with the results from other DFT calculations, mainly those of Manassidis et al., most probably arise from the effect of Sn 4d-electrons, which are explicitly included in our treatment.

The case of bridging oxygens on top of SnO_2 (110) surface is interesting. The net relaxation is clearly out from the surface, see $\Delta_{1\perp 3}$ in Table 2. This is quite different from the relaxation of stoichiometric TiO_2 (110) surface (with the same rutile structure), where the bridging oxygens have been experimentally observed to relax strongly inwards. Unfortunately, there are no experimental relaxation data for SnO_2 (110) surface available, yet.

In Table 2, we see that both of our two independent methods, LCAO and PWPP, predict similar perpendicular surface relaxation. The remaining differences can be considered as confidence intervals of the evaluated parameters. For the electronic structure, however, these two methods give complementary information, as described in the next section.

5. Electronic levels and bands

The band gap is known to become poorly described with DFT–LDA. Palummo et al. [5], e.g., obtained about 50% underestimate, if compared with the experimental 3.6 eV. This is close to our result, which is about 1.4 eV. Thus, our value is smaller, although we apply GGA. Therefore, we have used the ‘scissor operation’, a shift of the conduction bands upwards by 2.2 eV in Fig 3, where both the LCAO levels at Γ -point and the bands from PWPP are shown. We present the bands for $\Gamma \rightarrow X'$, which corresponds the c -direction in Fig. 1a. Note that as both sides of the slab are allowed to relax there are no one-electron eigenstates from the ‘truncated bulk’ surface in our description.

The calculated bulk valence band width is less than 8 eV and compares well with the experimental 7.5 eV. For surfaces it is somewhat larger, about 8–9 eV. The valence bands of the stoichiometric surface are flat and originate mainly from the oxygen 2p with mixing of tin 5s and 5p, see Fig. 3a. These levels are responsible for the cohesion. The topmost levels at the valence

Table 2
Relaxation parameters of the SnO_2 (110) surface as defined in Fig. 2^a

Parameter	Unrelaxed	LCAO	PWPP	PWPP [9]
Stoichiometric				
$\Delta_{1\perp 1}$	0	+0.20	+0.26	+0.30
$\Delta_{1\perp 2}$	0	+0.25	+0.27	+0.22
$\Delta_{1\perp 3}$	1.29	1.41	1.47	1.46
$\Delta_{1\perp 4}$	1.29	1.26	1.21	
$d_{12\perp}$	3.35	3.27	3.29	
Reduced				
$\Delta_{1\perp 1}$	0	+0.14	−0.13	+0.41
$\Delta_{1\perp 2}$	0	+0.40	+0.43	+0.26
$\Delta_{1\perp 4}$	1.29	1.27	1.33	
$d_{12\perp}$	3.35	3.41	3.41	

^a All values are given in Å.

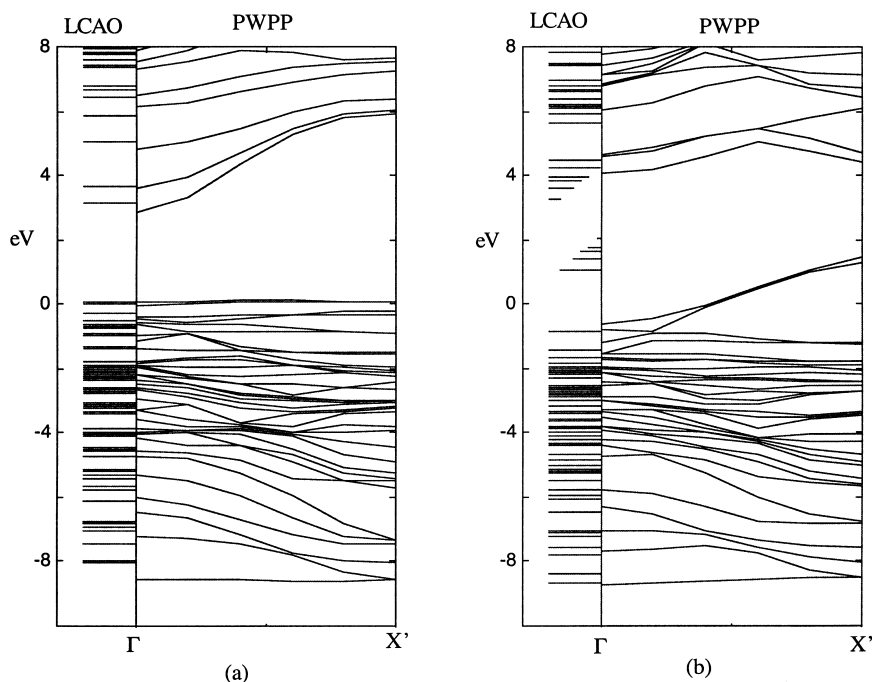


Fig. 3. One-electron levels (LCAO) and the bands $\Gamma \rightarrow X'$ (PWPP) of the (a) stoichiometric and (b) reduced surfaces. The $\Gamma \rightarrow X'$ direction is the larger of the two unit vectors defining the two dimensional surface Brillouin zone.

band maximum (VBM) are localized at the bridging oxygens and the next levels below relate to the lone-pair electrons of other oxygen atoms. In the tin 5s related conduction band minimum (CBM), the dispersion is strongest. These bands have considerable five-fold tin 5s character. All this is in a good agreement with the overview in Refs. [6,16].

Removing the bridging oxygen atoms results in strong dispersion at the VBM, which now has four-fold tin 5s and 5p character. These levels do not relate to bonding to the neighbouring in-plane oxygen atoms, however. Thus, these are loosely bound electrons from the 'bridging oxygen vacancies', the levels that are experimentally seen in the band gap [3].

When underestimating the band gap our LCAO calculation leads to overlapping VBM and CBM resulting in fractional occupations as denoted in Fig. 3b. This also leads to the description of the VBM and CBM in terms of same tin 5s and 5p character.

6. Conclusions

Relaxation of the (110) surface of SnO_2 occurs essentially in the perpendicular direction, only. Lateral relaxation is negligible and symmetry breaking recon-

struction was not found. The most prominent feature is the surface layer anion relaxation outwards with respect to surface layer cations at the reduced surface. This appears to be strong at the reduced surface, about 0.4 Å, but much weaker at the oxidized surface.

The valence band maximum is flat at the stoichiometric surface but strong dispersion is found at the conduction band minimum. At the reduced surface strong dispersion occurs at both sides of the band gap. These bending bands can be interpreted as surface gap states: the electrons released from the bridging oxygen vacancies, which reduce the surface layer tin atoms from Sn^{4+} to Sn^{2+} .

The extent of relaxation and the consequent effects on the electronic structure can be expected to be essential for the surface chemistry of SnO_2 .

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