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REHYBRIDIZATION AT (110) FACES OF SnO₂

Rehybridization of surface atoms and relaxation of (110) face of SnO₂ is theoretically examined. Using molecular mechanics and *ab initio* data for surface relaxation we choose the best hybridization related force field for molecular dynamics (MD) simulations. The most prominent feature of relaxation, surface in-plane oxygen displacement of the reduced surface outwards of about 0.4 Å relative to the bulk position, is analyzed in details. This is done in terms of rehybridization of *s* and *p* orbitals of atoms at reduced surface of SnO₂.

1. Introduction

Tin dioxide (SnO₂) is a wide-gap semiconductor with applications as gas sensor material and catalyst. The structure and electronic properties of its surface have been experimentally studied in detail [1, 2]. Also theoretical investigations of oxide surfaces based on an accurate first-principles calculations have been carried out [3–6]. Such approaches allow to create the atomistic picture of sensing mechanisms and methods to prognosticate gas response properties of the semiconducting materials.

However, *ab initio* calculations of SnO₂ (110) face based on utilizing the different computational methods reveal diversity of bare surface relaxation data [3–6]. Therefore, calculations based on different methods are welcome to establish reliable structure of relaxed SnO₂ (110) atomic plane and to understand the related differences in rehybridization occurring at stoichiometric and reduced surfaces.

Recently, we have investigated the structure of (110) face of rutile structure SnO₂ (cassiterite) with *ab initio* — DFT calculations, the local-density approximation (LDA) and the generalized-gradient approximation (GGA) [5]. There are also semi-empirical approaches available for surface relaxation and electronic structure of (110) face of SnO₂ to compare with [10].

In the present study, by comparing with the *ab initio* data, we search for the best fitting Universal force field (UFF) of Rappe et al. [8], where hybridization is explicitly assigned to the atoms. Such comparison of the data from *ab initio* calculations and results of molecular mechanics (MM) minimization allows to judge between the various presupposed hybridizations.

A more detailed analysis of hybridizations based on our *ab initio* electronic structure results [5] has been included here, too. The Mulliken population analysis of LCAO electronic structure has been used to project molecular or crystal one-electron wave functions onto atomic orbitals, which were used as the basis set. Together with the energy eigenvalues,

this defines the hybridization of original atomic orbitals and also reveals the remaining lone pair electrons.

2. Slab Model and Computational Method

The rutile structure of SnO₂ is 6 : 3 coordinated and Sn⁴⁺ ions in the structure are centered in slightly distorted oxygen octahedron. (110) layers of the structure consist of neutral groups of three parallel planes O—Sn₂O₂—O and the cleavage cut between these groups of planes breaks the least number of cation—anion bonds. This results in (110) stoichiometric face, which is the most dominant surface of the SnO₂ material. Removal of the surfacemost bridging oxygen layer of stoichiometric surface results in the reduced (110) surface, see fig. 1, *a*.

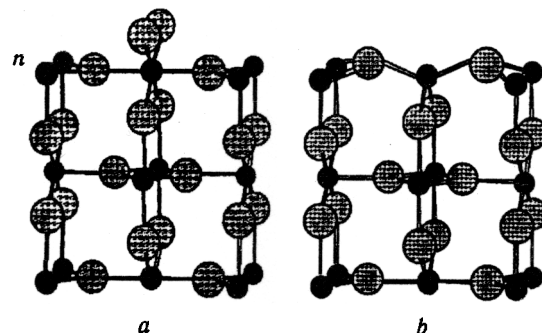


Fig. 1. Orthonormal supercell of the slab model of SnO₂ (110) surface:

a — for stoichiometric surface (upper) with bridging oxygens and reduced surface (lower), *b* — a schematic drawing of relaxations at the reduced surface

In the present study we examine the rehybridization of surface atoms. This is coupled with consideration of force field, as many details of potential functions are hybridization dependent. We employ the Universal force field (UFF) which is suitable for our purposes. It is a general purpose force field that has been parametrized from a set of rules based on element, hybridization and connectivity.

UFF has been carefully validated for many structure types. In UFF the hybridization is explicitly assigned to the atoms, defining the nearest neighbour coordination attributes, such as equilibrium bond lengths and angles. UFF has been developed in conjunction with the Charge Equilibration method. This approach predicting charge distribution in system makes it applicable for materials with high ionicity [9].

For MM calculations we have adopted the same periodic slab that was used for the *ab initio* calculations [5]. We adopt the slab model of (110) surface with orthorhombic supercell with 16 atoms (reduced, Sn_6O_{10}) or 18 atoms (stoichiometric, $(\text{SnO}_2)_6$) oriented as shown in fig. 1, *a*. Vacuum between the surfaces was chosen to occupy half of slab supercell. The upper and the lower surfaces were treated identically.

3. Results and Discussion

Total energy minimization of the bulk SnO_2 using *ab initio* calculations and starting from the experimental lattice constants with LCAO method leads to about 2% expansion, whereas the expansion with PWPP is somewhat less [5]. We were able to find a force field for molecular mechanics calculations that exhibited negligible shrinking of lattice constants (0.001%), table 1. These bulk relaxed structures were used as reference to surface relaxation.

Table 1

Bulk relaxation of cassiterite, SnO_2

	Experimental	LCAO	PWPP	PWPP [3]	MM
<i>a</i>	4,737	4,832	4,730	4,637	4,721
<i>c</i>	3,186	3,266	3,212	3,060	3,185
<i>u</i>	0,307	0,307	0,306	0,307	0,307

The bonding between atoms in SnO_2 has a relatively strong ionic character. At stoichiometric surface, tin atoms appear also to be fivefold coordinated with less ionic character. Removal of the bridging oxygen changes the coordination of tin atoms from sixfold to fourfold, which in turn, change ionic character of bonding. Reduction of the surface leads to rehybridization of surface tin atoms and oxygen atoms that couples to surface reconstruction or relaxation. Establishing the correct electronic structure of reduced and stoichiometric SnO_2 surfaces is important for the further investigations of adsorption/desorption and catalytic properties connected with construction of adsorbate-surface site conformations and understanding of the different reaction paths at tin oxide surfaces.

The most prominent feature of surface relaxation confirmed by two different *ab initio* methods is outward displacement of in-plane oxygen of 0.4 *E* relative to perfect-lattice (or truncated bulk) positions. On one hand, such surface deformation at reduced surface may be connected with rehybridization of

in-plane oxygen environment. On the other hand, strong outward displacement of in-plane oxygen not connected directly with rehybridization of Sn and/or O surface ions may be attributed to the changes in electrostatic interactions between atoms, coupled with changes in the ionicity of surface bonding.

Possible rehybridizations at the (110) surface of SnO_2 , leading to the outward displacement of in-plane oxygen ions, may be assigned to subbridging tin atoms, in-plane oxygen itself, or both of those at the same time.

Most of surface Sn^{4+} ions usually have the octahedral valence state of hybrid sp^3d^2 orbitals. At fully oxidized surface Sn^{4+} ions carry two oxygen monodentately coordinated on it. If these oxygens are eliminated then the cations becomes four-coordinated. This arrangement is energetically less favorable owing to the relatively high degree of coordinate unsaturation of the cation and could lead to the surface reconstruction. The possible mechanism of the reconstruction is the change in rehybridization of cation into some inactive form, for example, into distorted sp^3 . Usually [10, 11], the surface reconstruction resulted in such rehybridization displaces the superficial cations down and causes oxygen raise above the surface plane (fig. 1, *b*).

Another possible reason for the relaxation leading to the outward displacement of in-plane oxygen atoms at reduced surface is rehybridization of in-plane oxygen from bulk configuration, which is sp^2 plus non-bonding, lone-electron pair. At reduced surface, oxygen atoms are in effort to lower their electronic energies, attempt to move out from surface into more tetrahedral sp^3 configuration.

It would be noted, that change in coordination of subbridging tin from sixfold to fourfold at reduced surface, generates unsaturated dangling bonds, making rehybridization highly probable. In-plane oxygen at reduced surface remains three-fold coordinated and its rehybridization can take place only if it is energetically more favorable.

The surface geometry of SnO_2 (110) face from *ab initio* calculations and molecular mechanics (MM) minimization with various hybridizations is shown in table 2. For reduced surface both octahedrally and tetrahedrally hybridized tin and oxygen are considered. For stoichiometric surface octahedrally hybridized tin leads to a better description of relaxation. According to previous predictions [10, 11] tetrahedral hybridization of subbridging tin atoms at reduced surface is accompanied by outward displacement of in-plane oxygens. At the same time, subbridging tin atoms move down significantly, that displays main difference between the MM calculations and *ab initio* results, where an outward displacement is found, instead. Such strong difference between MM and *ab initio* results makes this choice of FF rather unreliable.

As it follows from MM calculations (table 2), assignment of tetrahedral hybridization to in-plane oxygen ions is not enough to provide an outward displacement of 0.4 *E*.

Table 2

Vertical displacements of the surface atoms from their original «bulk cut» lattice sites (in E) from the *ab initio* calculations (LCAO and PWPP) and molecular mechanics (zero temperature molecular dynamics). Tin is considered in octahedral and tetrahedral, and oxygen in trigonal and tetrahedral hybridizations

	LCAO (GGA) [5]	PWPP (GGA) [5]	Sn-oct O-tri	Sn-oct O-tet	Sn-tet O-tri	Sn-tet O-tet
Stoichiometric						
Bridging tin (6 fold)	+0,13	+0,21	+0,043	+0,033		
Bridging oxygen	+0,05	+0,13	-0,038	-0,050		
In-plane oxygen	+0,18	+0,22	+0,100	+0,124		
Reduced						
Bridging tin (4 fold)	+0,14	+0,20	-0,125	-0,147	-0,26	-0,33
In-plane oxygen	+0,39	+0,49	+0,034	+0,073	+0,38	+0,50

Moreover, minimization of flexible outermost surface layer of (110) SnO_2 face, consisted of local environment of superficial Sn and O ions, reveals antisymmetrical (110) surface for oxygen in tetrahedral state (fig. 2, *b*), and makes this setting less

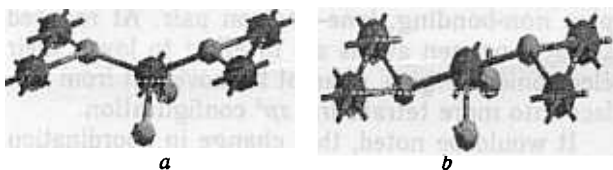


Fig. 2. Model of the outermost surface layer of (110) SnO_2 face for the hybridization states:

a — Sn-tet + O-tri, *b* — Sn-oct + O-tet

probable. The surface symmetry was restored, however, for more rigid slab model (fig. 1, *b*). Nevertheless, applying the tetrahedral hybridization for tin and oxygen surface atoms leads to increase of slab total energy (table 3), which demonstrates that such

Table 3

Comparison of the total energies of stoichiometric and reduced slabs with different hybridizations

	Sn-oct O-tri	Sn-oct O-tet	Sn-tet O-tri	Sn-tet O-tet
Reduced	-151,12	-153,11	-165,15	-166,38

choice is energetically less favorable. Such results are also in good agreement with [10], where it was concluded that oxygen atoms cannot fully rehybridize, because of the large local strain field (i. e., the large energy cost associated with significant accompanying changes in bond lengths).

Mulliken population analysis of LCAO electronic structure gives information on rehybridization at

tin oxide surface directly. Computed energy levels from the stoichiometric and reduced surfaces of reduced, Sn_6O_{10} or stoichiometric, $(\text{SnO}_2)_6$ slabs are presented in fig. 3.

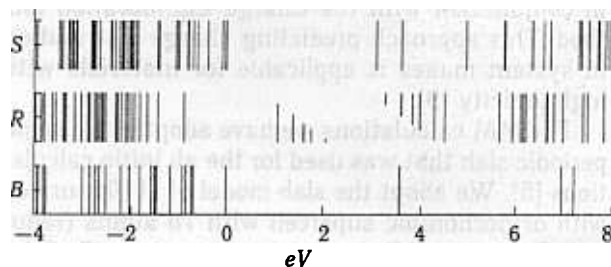


Fig. 3. Computed LCAO one-electron levels for:

S — stoichiometric $(\text{SnO}_2)_6$ surfaces, *R* — reduced, Sn_6O_{10} surfaces, *B* — for the bulk. A scissor operator of 2,2 eV has been applied to make band gap close to its bulk value. The fractional occupation numbers in the case of reduced surface are illustrated by the barlength. For bulk and stoichiometric cases, VBM is adjusted to 0 eV and for reduced case it is adjusted to fit the bands in ref. 5b

Mulliken population analysis performed for stoichiometric and reduced surfaces of SnO_2 displays presence of lone-electron pair at in-plane oxygen atoms in both surface states (fig. 3) indicating that these ions remain in trigonal hybridization state — sp^2 plus a non-bonding, lone-electron pair. Such conclusion is in agreement with results of our MM calculations.

At stoichiometric surface *d*-orbitals are involved in the bonding of subbridging tin ions, supporting conclusion made from MM calculations about the octahedral valence state of the hybrid sp^3d^2 orbitals. It is extremely significant that *d*-orbitals are still involved in the bonding of subbridging tin atoms at the reduced surface. Such results exclude capability for tetrahedral sp^3 state of the superficial tin orbitals and also go along with data of MM calculations. Participation of *d*-orbitals in the bonding of subbridging tin atoms allows to assume, for instance, the distorted trigonal bipyramidal sp^3d hybridization state for such cations, where $5s$ — $5p$ hybrid lone pair occupying stereochemical position on the vacuum side of ions.

P. A. Cox et al [12] has suggested that, after removal of bridging oxygen atoms at (110) face, two electrons remains at subbridging tin making it Sn^{2+} . The defect states near valence-band maximum (VBM) are due to rehybridization of Sn $5s$ — $5p$ states at reduced Sn^{2+} sites adjacent to oxygen vacancies or in local SnO -like environments at surface. An alternative suggestion explaining appearance of Sn^{2+} -like ions is that the inert pair of $5s$ electrons occupies the apex of tetragonal pyramid, as it takes place in tetragonal SnO structure.

Mulliken population analysis performed on SnO_2 structure allowed to attribute an occupied electron energy levels related to subbridging tin ions with $5s$ — $5p$ hybrid lone pair located near the VBM ($-4,33$ eV), fig. 3. Removal of bridging oxygen atoms

results in strong dispersion at VBM, which has four-fold tin $5s$ and $5p$ character. These levels do not relate to the bonds to the neighbouring in-plane oxygen atoms, however. Thus, these are loosely bound electrons from bridging oxygen vacancies, the levels which are experimentally seen in band gap [12].

Mulliken population analysis allows one to understand the ionic character of the bonding in crystal. Localized orbitals may be constructed from hybrids on both Sn and O and these overlap, forming occupied bonding and unoccupied antibonding orbitals. Because of the very different electronegativities of Sn and O, the bonding orbitals are concentrated on O atoms and antibonding — on Sn. The ionic crystal can be, therefore, regarded as the case where bonding and antibonding orbitals become completely localized on oxygen and metal, respectively. It was found, that at the reduced surface the bonding orbitals related to subbridging tin atoms were localized on the metal ions rather than on oxygens, displaying covalent character of the bonding for such tin atoms. This is in agreement with well-known covalent character of the bonding in SnO crystal.

The results of the *ab initio* and MM calculations indicate that two electrons left behind after removal of bridging oxygen ions occupy orbitals (a mixture of $5s$ and $5p$) on surface Sn ions, converting them to Sn^{2+} [12, 13] and abnormal stereochemistry with inert electron pair at reduced surface of SnO_2 is due to this $s-p$ hybridizations. Therefore observed strong outward displacement of in-plane oxygen ions cannot be connected directly with tetrahedral rehybridization neither superficial tin or oxygen atoms and may be attributed to the changes in electrostatic interactions between atoms, coupled with changes in the ionicity of surface bonding.

As it has been mentioned SnO_2 must be regarded as essentially ionic crystal. On the other hand, appearance of Sn^{2+} atoms at reduced surface of SnO_2 changes the character of the bonding to the essentially covalent. Therefore, bond between subbridging tin and in-plane oxygen became weaker at reduced SnO_2 surface. Atomic configuration of the surface is determined by superposition of stretching surface bondings and repulsion electrostatic interaction with neighbouring oxygen atoms. Weakening of the superficial $\text{Sn}-\text{O}$ bonding, due to the reduction of tin ions from Sn^{4+} to Sn^{2+} leads to the domination of electrostatic repulsion interaction and results in the observed outward displacement of in-plane oxygen atoms.

4. Conclusion

Relaxation of (110) surface of SnO_2 occurs essentially in the perpendicular direction, only. In-plane relaxation is negligible. Symmetry breaking reconstruction was found only in case where the in-plane oxygen has been allowed to rehybridize. The most prominent feature is the surface layer anion relaxation outwards with respect to their bulk positions at the reduced surface. This appears to be strong at the reduced surface, about $0.4 E$. The mechanism responsible for such relaxation is supposed to be rehybridization of the subbridging tin cation from octahedral to tetrahedral state. Some arguments were found to assume that in-plane oxygen remains in trigonal hybridization state.

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