

Semi-Empirical and Ab Initio Studies of Low-Temperature Adsorption of Oxygen and CO at (110) Face of SnO₂

Vyacheslav V. Golovanov, Matti A. Mäki-Jaskari, and Tapio Tuomas Rantala

Abstract—Using a first principles electronic structure calculation method based on the density functional theory (DFT), and also using a semi-empirical (PM3) method, surfaces of the (110) face of SnO₂ with and without CO and oxygen adsorbates have been studied. For semi-empirical and DFT calculations, cluster models and the slab models were constructed, respectively. It was found that oxygen adatoms on a perfect stoichiometric (110) surface do not form without precursor for O₂ dissociation. The chemisorbed atomic oxygens are metastable, but may stabilize in the form of carbon-related complexes in CO environment, which is enhanced by the energy barrier for CO₂ formation. It is energetically favorable for CO to form structures like oxalate and bidentate carbonate. It is proposed that, in a low-temperature range, chemisorption processes may contribute to the sensitivity of SnO₂ film.

Index Terms—Chemistry, semiconductor films, sensors, surfaces.

I. INTRODUCTION

TIN dioxide, SnO₂, has found an important technical application in the field of chemical sensing due to its ability to transduce different gas-surface interactions to conductivity changes. However, despite that structure and electronic properties of SnO₂ based sensor surface have been experimentally studied in great details [1]–[3], highly specific and sensitive SnO₂ sensors are not yet available, and peculiarities of its operation are not fully understood. Thus, a strategic trend in gas sensor development is the transition from an empirical approach in gas sensor design and manufacturing to the basic-understanding approach, with the aim to obtain a complete description of the gas-sensing mechanism for SnO₂-based sensors.

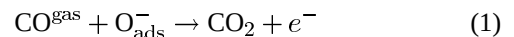
Appearance of modern computer codes and software [4], [5] allows one to perform accurate first-principles quantum mechanical calculations of ideal and reconstructed surfaces of metal oxides. Such approaches open possibilities to create an atomistic picture of sensing mechanisms and methods for prognosis of gas response properties of the semiconducting

materials. The main limitation for such calculations remains the size of cluster or unit cell in the case of slab calculations due to drastically increasing computer time with an increasing number of atoms in larger clusters. Therefore, *ab initio* geometric configurations of only a few tens of atoms could so far be calculated by minimizing the total energy of the cluster for fixed positions of the other atoms. On the other hand, self-consistent semi-empirical methods in quantum mechanical calculations, being more limited in description of the electronic structure, make it possible to determine the position of large number of atoms including defects, surfaces, and segregated grain boundaries in clusters within reasonable computer time.

It must be noted, also, that, despite the number of calculations, there is no consensus about the electronic structure and the related surface geometry of SnO₂, in particular, if the reduced and stoichiometric surfaces are compared. The main conclusion from the reviews on theoretical calculations is a substantial diversity of surface relaxation data of SnO₂ (110) face [6]–[8]. 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 the stoichiometric and reduced surfaces.

Recently, the (110) face of rutile structure SnO₂ (cassiterite) has been investigated with *ab initio*-DFT calculations with the local-density approximations (LDA) and the generalized-gradient approximation (GGA) [9]. In the present study, along with *ab initio* DFT-plane wave-pseudopotential approaches we also employ semi-empirical (PM3) cluster calculations, which are observed to lead to good enough geometric structures and total energies in comparison with *ab initio* methods.

The typical picture of SnO₂ interaction with reducing gases is based on the postulation that the ionosorbed oxygen is mainly responsible for the sensor signal during the catalytic oxidation of CO [10] through



where the released electron lowers the Schottky barrier between the SnO₂ grains leading to the conductance increase.

However, recent experimental results [11]–[13] testify that sensing mechanisms, especially in the presence of water, have more complex characters where different chemical reactions may predominate in different temperature ranges. Such complicated behaviors especially refer to the low-temperature range [14], [15]. The present study focuses on the theoretical investigation of CO interaction with SnO₂-based gas sensors.

Manuscript received October 1, 2001; revised July 3, 2002. This work was supported in part by EC in the frame of the INTAS program (Grant INTAS-01-0009) and by the Academy of Finland (MECA project). The associate editor coordinating the review of this paper and approving it for publication was Dr. Thaddeus A. Roppel.

V. V. Golovanov is with the Faculty of Physics, Odessa State University, Odessa, Ukraine.

M. A. Mäki-Jaskari and T. T. Rantala are with the Institute of Physics, Tampere University of Technology, Tampere, Finland (e-mail: alban@te.net.ua; matti.maki-jaskari@tut.fi; tapio.rantala@tut.fi).

Digital Object Identifier 10.1109/JSEN.2002.806307

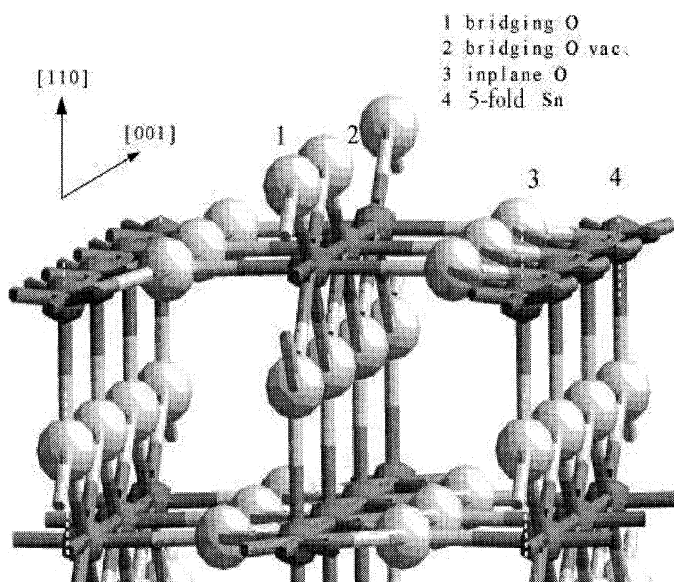


Fig. 1. Basic geometries of SnO_2 (110) surfaces in the case of slab calculations. The stoichiometric model corresponds to the case with all bridging oxygens included, in which case three surface unit cells are shown. The reduced model corresponds to the case without bridging oxygens.

II. MODELS AND METHODS

Our strategy was to save computational resources by first using a semi-empirical PM3 [16] method to discover possible initial geometries. The utilized DFT approach was based on the plane wave basis set and pseudopotential concept to describe electron-ion interaction. We use the CASTEP/CETEP code [17]. By using ultrasoft pseudopotentials (USP) [18], plane wave basis set could be considerably limited. In addition to the pseudopotential ion cores, oxygen and tin atoms were described by six and four explicit electrons, respectively. Plane wave kinetic cut-off energy was 400 eV, and to sample the Brillouin zone, one to six symmetrized Monkhorst-Pack k-points [19] were used, depending on size of the slab. The electronic interactions were taken into account within the generalized-gradient approximation (GGA) [20]. In the case of oxygen adsorbates, spin polarization was taken into account. The DFT approach predicts experimentally-known lattice parameters of SnO_2 crystal and bond lengths of O_2 , CO, and CO_2 molecules with an accuracy better than 2%.

Optimized geometries were studied by evaluating partial and total densities of states (DOS), Mulliken charges, and bond populations. A combination of the basic geometries of SnO SnO_2 (110) surfaces in the case of DFT-slab calculations are shown in Fig. 1. Stoichiometric $\text{Sn}_{60}\text{O}_{102}$ and reduced $\text{Sn}_{52}\text{O}_{78}$ clusters were used in PM3 semi-empirical calculations. Typically, the slab and cluster thickness consisted of three stannic atomic planes, but some experiments with thicker slabs were also made. Extensive calculations with other SnO_2 (110) surface geometries indicated that perfect stoichiometric (110) surface corresponds to an energy minimum. Therefore, the stoichiometric model is a preferred as a starting point in theoretical considerations.

III. ACTIVITY OF STOICHIOMETRIC AND REDUCED (110) SURFACES

We performed geometry optimization for stoichiometric and reduced surfaces by using DFT pseudopotential methods and PM3 method. The most prominent feature remains surface corrugation with the full coordinated in-plane oxygen relaxation outwards with respect to five fold tin atoms. It appeared to be about 0.3 Å at reduced surface, and only slightly less at stoichiometric surface. Strictly speaking, the in-plane oxygen relaxations are 0.3 ± 0.1 Å, since the two in-plane oxygens of the surface unit cell can also relax outwards nonsymmetrically, with the same total energy. Both of two independent methods, the DFT pseudopotential method and the semi-empirical PM3 method, predict similarly perpendicular surface relaxations. Our comparisons between different pseudopotential methods has shown that relaxations are similar, especially if a more accurate pseudopotential method is applied [21], instead of USP.

Due to the surface states, a decrease of indirect band gap between the conduction and the valence band in the reduced case was observed [21]. Appearance of these states was attributed to the rehybridization of 5 s and 5 p orbitals of subbridging Sn^{2+} atoms creating 5 s–5 p lone pair hybrids. The semi-empirical calculations of the surface relaxations suggest that the reason for the outward relaxation of in-plane oxygens is rehybridization of five-fold tin coupled with changes in the ionicity of the surface bonding. In the case of stoichiometric surface, the five-fold coordinated surface tin atoms are of particular interest in providing active sites for adsorbates. We will concentrate here on CO, O, and carbonate adsorbates on this site. The appearance of these adsorbates on top of the five-fold tins will cause the tin ions to relax outwards. On reduced surface the activity of five-fold tins is expected to be similar to stoichiometric since the geometry and charge density at five-fold Sn site do not differ strongly [22].

Analysis of charge distribution and dangling bond occupations does not support rehybridization of outwards shifted in-plane oxygen atoms that could lead to the dramatic increase in their catalytic activity due to unsaturated orbitals in their tetrahedral hybridization state. However, appearance of the of the four-fold coordinated Sn^{2+} ions with the orbitals directed to the vacuum is obviously the reason for increased catalytic activity of a reduced SnO_2 surface in comparison with an oxidized one [23]. Instead, even in case of the stoichiometric surface with bridging oxygen vacancies, the nonsaturated subbridging Sn ions may increase the catalytic activity of the surface, leading to the increase in the concentration of chemisorbed oxygen species. One possible mechanism for this is based on the decrease of dissociation barrier for O_2 on such surface. As a result, both bridging oxygen and O^- in the vicinity of the five-fold tin are formed.

Thus, in a case of adsorption of CO related species, nonsaturated surface cations are expected to show various effects on the sensing mechanism of SnO_2 films. On the one hand, the appearance of charged chemisorbed CO related complexes may have direct influence on the surface charge carrier density and conductivity due to the change of the surface potential and sur-

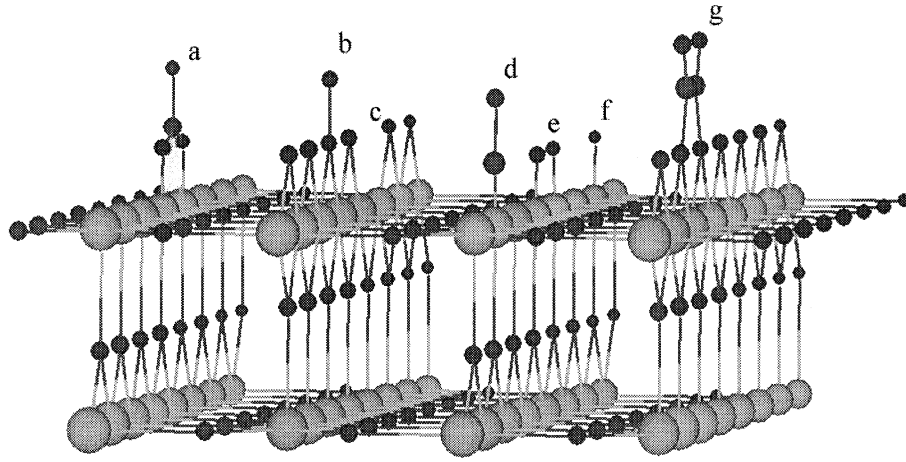


Fig. 2. Considered geometries with carbon and oxygen adsorbates: (a) bidentate carbonate, (b) columnar molecular oxygen, (c) bridging oxygen vacancy, (d) carbonyl, (e) bridging molecular oxygen, (f) atomic oxygen, and (g) oxalate. Smallest circles indicate oxygens and largest tins. Carbon atoms appearing in adsorbates are indicated by medium size circles.

face band gap. On the other hand, the appearance of complex adsorbates at catalytically active bare Sn ions may affect to the sensitivity by blocking of its catalytic activity. This effect especially refers to the low-temperature interval, where complex adsorbates are stable at the surface. We, thus, need to examine in more detail possible configurations and effects of CO- and oxygen-related species on surface.

IV. CARBON OXIDE AND OXYGEN ADSORBATES AT TIN OXIDE (110) SURFACE

It is generally accepted that adsorption/desorption processes of oxygen species define the gas sensing properties of metal oxide films [24], [25] and the sensitivity of the SnO₂ films is determined by CO reaction with ionosorbed oxygen, [reaction (1)]. However, analysis of response (τ_{res}) and recovery (τ_{rec}) times during exposure of SnO₂ to CO [26] reveals an important regularity. It was found that differing from high temperature ranges of (1/T) dependencies, where $\tau_{\text{rec}} \sim \tau_{\text{res}}$, for the low-temperature range strong relationship $\tau_{\text{rec}} > \tau_{\text{res}}$ has been observed. At $T_{\text{oper}} = 30\text{--}180\text{ }^{\circ}\text{C}$ this difference reaches amounts of three to four times. The TPD, FTIR, and EPR data for SnO₂ films in dry air suggest that molecular oxygen is the dominant adsorbate in the temperature range of 30 to 180 $^{\circ}\text{C}$. Exposure to CO leads to formation of different forms of carbonates detected up to $\sim 200\text{ }^{\circ}\text{C}$ and carboxylates detected up to 400 $^{\circ}\text{C}$ [27]. The correlation $\tau_{\text{res}} \sim \tau_{\text{rec}}$ observed at $T_{\text{oper}} > 180\text{ }^{\circ}\text{C}$ corresponds to the interaction of CO with intermediates due to dissociative adsorption of oxygen species. Formation of CO₂ as a reaction product between 240 and 400 $^{\circ}\text{C}$ was identified by FTIR [11]. Along with the sharp decrease in the concentration of molecular oxygen due to O₂ dissociation it has been detected also vanishing of carbonate species, which became unstable at these temperatures [28].

Based on these experimental results, we suppose that, differing from high temperature ranges, the adsorption/desorption processes may contribute to the sensitivity of SnO₂ to CO in the low-temperature range (30–180 $^{\circ}\text{C}$). It can be shown that, for gas detection, a reaction of second order relationship $\tau_{\text{res}} \sim \tau_{\text{rec}}$ takes place, while a reaction of first order obeys $\tau_{\text{rec}} > \tau_{\text{res}}$ [29].

TABLE I
CALCULATED DFT TOTAL ENERGY DIFFERENCES (eV) OF CO/SnO₂ (110) ADSORBATE STRUCTURES PER ONE CO MOLECULE IN O₂ ATMOSPHERE. THE COVERAGE PER SURFACE UNIT CELL IS 1.0 IN THE CASE OF CO AND 1 IN THE CASE OF O ON TOP ON TOP OF THE FIVE FOLD COORDINATED SURFACE TIN

Adsorbate/ surface site	Adsorption energy, eV
CO (g) + stoich.surf.	0 (reference)
CO/bridging oxygen	Not stable
CO ₂ (g) + bridging oxygen vacancy	−0.4
Oxalate/stoich.surf.	
(C ₂ O ₂)/bridging oxygen	−0.6
CO/5-fold Sn	−0.4
Carbonate/5-fold Sn	−3.2
CO ₂ (g) + stoich.surf.	−3.4
2O/5-fold Sn (top)	+3 (per O ₂)

First order corresponds to the reaction of gas detection, limited by adsorption/desorption processes, and the second order corresponds to reactions limited by dissociative adsorption with formation of oxygen intermediate species (e.g., O). In other words, adsorption/desorption processes may play essential roles in the sensing mechanism of SnO₂ films.

It is assumed that carbon monoxide adsorbs mainly on oxygen species at SnO₂ [30], [31]. Some evidences of carbonyl stretches have been also found by in situ DRIFT-spectroscopy [13]. It is reported that carboxylates do not reveal a strong influence on the surface conductivity of SnO₂ [12]. Taking into account presence of the molecular oxygen as a main adsorbate at SnO₂ surface in the temperature range 30–180 $^{\circ}\text{C}$ in dry air and detection of carbonates, presence in the low-temperature range during exposure to CO, we have comparatively analyzed the bounding character of molecular and atomic oxygen, carbonyl stretches, and carbonate related species coordinated at SnO₂ (110) surface. Fig. 2 illustrates the considered geometries with carbon and oxygen adsorbates. The adsorption energies corresponding to these configurations are presented in Table I.

First, we will focus on a few cases with oxygen adsorbates on perfect stoichiometric surface that are expected to be involved in the surface conformations and reactions at low temperatures.

Adsorbed oxygen, if present in dissociated (atomic) form, may occupy positions on the top or between the five-fold Sn sites with binding energies of 1.5 eV and 1.3 eV per oxygen atom, respectively. Bridging oxygens are found to be more stable at the surface than these oxygen adatoms. With respect to O_2 gas, 3 eV per each O_2 were needed for chemisorption of two atomic oxygens above five-fold Sn atoms. Also, other conformations for metastable oxygen adsorbates has recently been introduced [32]. The stability of the oxygen adsorbates is slightly improved in conformations that are associated with; more fully coordinated oxygen adsorbate, decreased repulsion between oxygen ions, and surface layer deformations. However, in experimental studies with oxygen annealed (110) surfaces, high oxygen coverages are associated with clustering [33]. The calculations indicated significantly higher metastabilities for oxygen to be accommodated above and between bridging oxygens than near five-fold Sn sites. This implies that there is a significant diffusion barrier for oxygen adatoms to overcome bridging oxygens. The low stability of atomic oxygens chemisorbed on perfect stoichiometric (110) surface of SnO_2 indicates that such adsorbates probably result from O_2 transformation at nonsaturated tin sites, diffusion of oxygen below the surface [34] and/or from surface defects rather than from O_2 adsorbed at five-fold tin ions. To indicate the possibility for O_2 transformations, an alternative, but less stable, geometry of columnar O_2 adsorbate (see Fig. 2) was examined. This geometry is most simply realized as O_2 adsorbed at bridging oxygen vacancy site with binding energy 1.2 eV. The geometry may also be attributed as a precursor for O_2 dissociation that is in agreement with the prediction made above on catalytic activity of bridging oxygen vacancy sites.

In a case of carbon monoxide interaction with (110) SnO_2 surface, the occurrence of reaction (1) was first checked by comparing the total energies of two separate systems. One consist free CO plus perfect stoichiometric slab, and the other free CO_2 plus stoichiometric slab including bridging oxygen vacancy. The comparison indicates that CO actively burns bridging oxygen with release of an exothermic energy of 0.4 eV per each CO_2 formation. Even higher reactivity CO exhibits toward the oxygen chemisorbed at five-fold Sn site, releasing 5 eV per CO molecule. On the other hand, we have an evidence to suggest that these reactions have a significant energy barrier. In an idealized case of CO aligned and approaching bridging oxygen along [110] direction, the approaching molecule is pushed back to vacuum by an energy barrier exceeding 2 eV. Similarly, in the case of CO interaction with loosely bound oxygen on the top of five-fold tin, CO_2 formation is associated with an energy barrier, which can exceed 0.4 eV. Thus, for CO_2 formation at bridging oxygen site, elevated temperature is required.

Instead of the CO_2 formation, at least several other end results of reactions with CO can be thought of to be effective at the lower temperature range. First, CO was noted to prefer to adsorb on five-fold coordinated tin sites associated with a bond between C and Sn atoms (shown in Figs. 2 and 3). It is predicted that 0.4 eV per each CO is released in such an event, based on calculation made by using a slab consisting of seven stannic atomic planes. At this site, CO carbonylic stretch has a nature of a donor rather than acceptor, which is seen by Mulliken charges and polarization of Sn-C bond charge [35]. It is

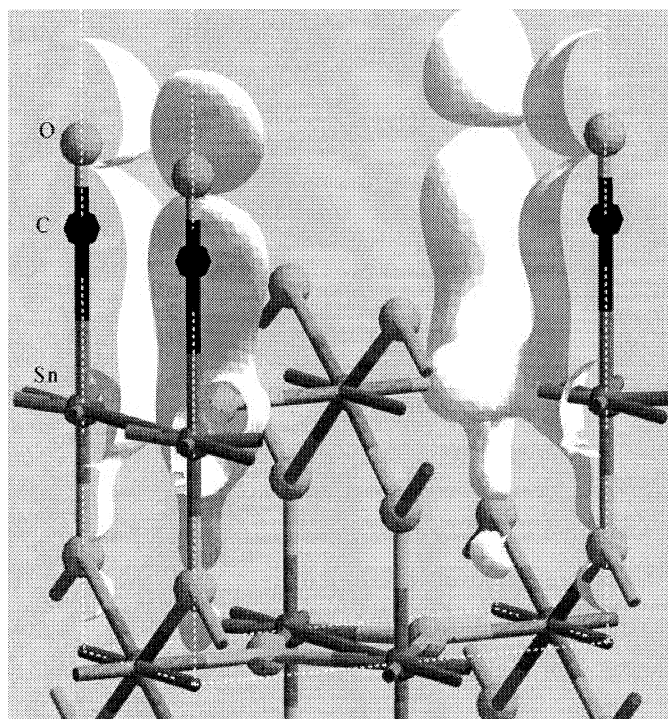


Fig. 3. Lowest occupied orbital of the upper valance band of CO carbonyl adsorbate on SnO_2 (110) surface calculated by using slab-DFT model. Notice significant overlap between adsorbate and surface.

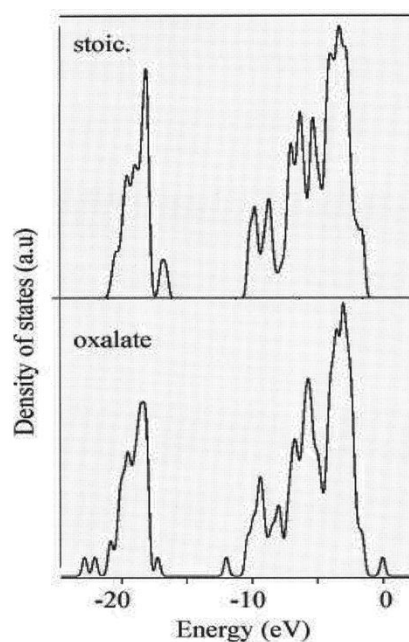


Fig. 4. Valence band total density of states of stoichiometric slab and oxalate adsorbed above bridging oxygens. The density peaks existing in the oxalate case, but not in the stoichiometric case, are associated to oxalate.

possible that carbon monoxide on top of five-fold tin may act as a precursor for reaction (1).

As a second possibility, instead of CO_2 formation, a structure like oxalate, shown in Fig. 2, may be formed. This structure is predicted to be associated with 0.6 eV energy release per CO, based on calculation made by using a slab consisting of seven stannic atomic planes. It is interesting to notice that this

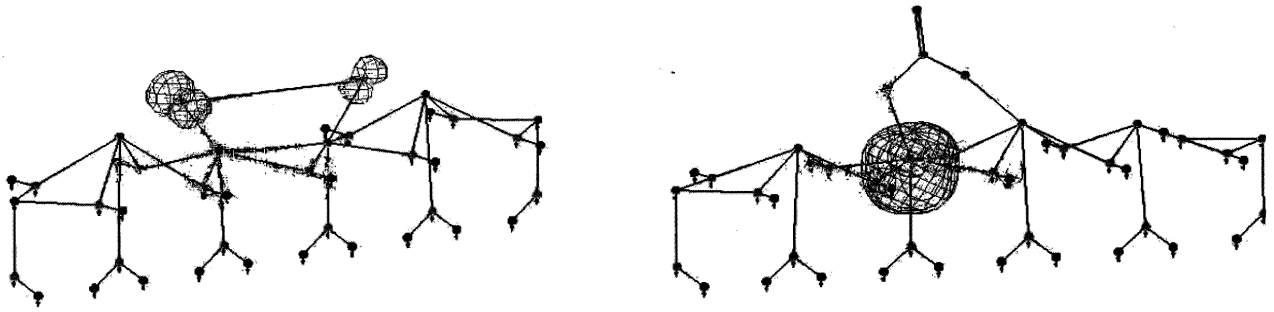


Fig. 5. Models of the Sn_6O_{16} clusters for PM3 calculations with molecular oxygen (left) and bidentate carbonate coordinated at five-fold coordinated Sn atoms (right). Mesh contours depict the spin density isosurfaces, which display distribution of an electron localized at the chemisorption complex.

energy release is slightly larger than the energy release of CO_2 formation from bridging oxygen and the energy release of CO adsorption on five-fold tin site. The stability can also be recognized from the DOS as a formation of new low energy surface DOS features, as shown in Fig. 4. The ionic nature of the atoms participating is decreased with respect to other bulk and surface ions, which was noticed from decreased Mulliken charges and increased bond populations. Mulliken charges indicate also that oxalate may act as a donor, since the total negative charge of the C_2O_4 unit is less than the charge of the two bridging oxygens. The structure will not decompose if one of the two one-fold coordinated surface oxygens is removed. Consequently, the oxygens of oxalate may be associated to the O^- type of oxygen adsorbate. The formation of oxalate-like structures maybe the reason of carbon signal increase during exposure to CO, what was detected by XPS [36].

In the case of chemisorbed oxygen present at the surface, formation of carbonates was found to be possible. In a basis of energetics, the geometry corresponding to a bridging bidentate carbonate (shown in Fig. 2) can be formed in an environment of CO and O_2 . The energy difference between this geometry, and combined 2 CO, 2 O_2 species with stoichiometric surface slab, was calculated to correspond release of 3.2 eV when the carbonate is formed. However, in CO_2 and O_2 environment, the structure may not stabilize because 0.2 eV per each CO is needed. Consequently, at elevated temperatures, carbonates are obviously decomposing from the surface with formation of CO_2 .

Concerning adsorption structures on (110) SnO_2 surface in CO environment, we end up to a surface coexisting of bridging lattice oxygens, bridging oxygen vacancies, carbonyls, oxalates in different forms, bidentate carbonates, and oxygen adsorbates. Supporting this picture, we found no conformation for CO alone to stabilize in the vicinity of bridging oxygen vacancy site more strongly than on top of five-fold Sn site.

Models of the SnO_2 charged clusters with adsorbed molecular oxygen and bidentate carbonate used for PM3 semi empirical calculations are shown in Fig. 5. Regarding molecular oxygen chemisorbed at five-fold tins, the O_2 coordination in parallel to the surface was considered rather than columnar O_2 molecule oriented normal to the surface. Indeed, results of EPR study of ion-radical (O_2^-) on SnO_2 and TiO_2 testify that both oxygen atoms in O_2^- molecule chemisorbed at the surface are equal by their properties [37]. In the case of columnar configuration, two oxygen atoms must have different charge and orbital occupation. At that, bonding must have much more covalent character [38].

Mulliken population analysis indicates that in the case of molecular oxygen an extra electron density is distributed between π^* -orbitals of O_2 revealing acceptor character of O_2 coordination. On the other hand, in the case of carbonate bounding, analysis of charge distribution demonstrates much more covalent nature of its chemisorption. These facts indicate that appearance of carbonyls, oxalates, and carbonates instead of oxygen as adsorbates results in decrease of the electron density at the chemisorbed complex. This leads to the decrease in the surface potential and, hence, the increase in the surface conductivity.

V. CONCLUSION

Calculations based on *ab initio* (DFT) and semi-empirical (PM3) methods imply that perfect SnO_2 (110) surfaces are associated with about 0.3-Å corrugation with in-plane oxygens relaxing outwards. It was found that oxygen adsorbates on perfect stoichiometric (110) surface are metastable, but may stabilize in the form of carbon related complexes in CO environment. This is obviously the case at low-temperature conditions in which CO_2 formation is inhibited because of the energy barrier that was found to exist for CO_2 formation. It is energetically favorable for CO to form an adsorbate structure like oxalate, which is associated with a bond between carbon atoms and contains oxygen with decreased ionic nature. Also, a structure of bidentate carbonate may form above five-fold surface tin sites. Bridging oxygen vacancy sites can be occupied by oxygen molecules, leading to a formation of weakly bound oxygen surface adatom.

Analysis of experimental and theoretical results supports conclusion that in temperature range 30–180 °C chemisorption processes may contribute to the sensitivity of SnO_2 film. This may relate to the appearance of carbonyl and/or partial conversion of adsorbed oxygen molecules into carbon related complexes that result in decreasing of the negative charge at the chemisorbed complex. Formation of CO related chemisorbed complexes may either directly cause changes in the surface potential and accordingly in the surface conductivity or lead to the blocking of dissociative activity of nonsaturated tin cations, leading to the decrease in the concentration of O^- chemisorbed ions.

ACKNOWLEDGMENT

The authors would like to thank the Center for Scientific Computing (CSC, Project TTKK-4585), Finland, for their computational resources.

REFERENCES

- [1] V. E. Henrich and P. A. Cox, Eds., *The Surface Science of Metal Oxides*. Cambridge, U.K.: Cambridge Univ. Press, 1994, p. 464.
- [2] W. Goepel, J. Hense, and H. Baltes, Eds., *Sensors Update*. New York: VCH, 1996, vol. 1, p. 350.
- [3] W. Goepel and K. D. Schierbaum, "SnO₂ sensors: Current status and future prospects," *Sens. Actuators B*, vol. 26, pp. 1–12, 1995.
- [4] *User Guides of Dsolid and Plane Wave*, MSI, San Diego, CA, 1996.
- [5] L. J. Clarke, I. Stich, and M. C. Payne, "Large-scale ab initio total energy calculations on parallel computers," *Comp. Phys. Comm.*, vol. 72, pp. 14–19, 1992.
- [6] T. T. Rantala, T. S. Rantala, and V. Lantto, "Surface relaxation of the (110) face of rutile SnO₂," *Surf. Sci.*, vol. 420, pp. 103–109, 1999.
- [7] I. Manassidis, J. Goniakowski, L. N. Kantorovich, and M. J. Gillan, "The structure of the stoichiometric and reduced SnO₂ (110) surface," *Surf. Sci.*, vol. 339, pp. 258–271, 1995.
- [8] T. J. Godin and J. P. LaFemina, "Surface atomic and electronic structure of cassiterite SnO₂ (110)," *Phys. Rev. B*, vol. 47, pp. 6518–6523, 1993.
- [9] T. T. Rantala, T. S. Rantala, and V. Lantto, "Electronic structure of SnO₂ (110) surface," *Mater. Sci. Semicond. Processing*, vol. 3, pp. 103–107, 2000.
- [10] K. D. Schierbaum, U. Weimar, W. Gopel, and R. Kowalkowski, "Conductance, work function and catalytic activity of SnO₂-based gas sensors," *Sens. Actuators B*, vol. 3, pp. 205–214, 1991.
- [11] N. Barsan, M. Schweizer, and W. Gopel, "Fundamental and practical aspects in the design of nanoscaled SnO₂ gas sensors: A status report," *Fresenius J. Anal. Chem.*, vol. 365, pp. 287–305, 1999.
- [12] D. Kohl, "Oxidic semiconductor gas sensors," in *Gas Sensors*, G. Sberveglieri, Ed. Dordrecht, The Netherlands: Kluwer, 1992, pp. 43–88.
- [13] S. Emiroglu, N. Barsan, U. Weimar, and V. Hoffmann, "In Situ Diffuse Reflectance Infrared Spectroscopy Study of CO Adsorption at SnO₂," *Thin Solid Films*, vol. 391, pp. 176–185.
- [14] V. Golovanov, "Comparative study of differently coordinated surface sites: Cd_xS- and Sn_xWO_y-based gas sensors," *Sens. Actuators B*, vol. 36, pp. 398–403, 1996.
- [15] H. Torvela, C. Pijolat, and R. Lalauze, "Dual response of tin dioxide gas sensors characteristic of gaseous carbon tetrachloride," *Sens. Actuators B*, vol. 4, pp. 445–450, 1991.
- [16] J. J. P. Stewart, "Optimization of parameters for semiempirical methods. I. method," *J. Comput. Chem.*, vol. 10, pp. 209–20, 1989.
- [17] V. Milman, B. Winkler, J. A. White, C. J. Pickard, M. C. Payne, E. V. Akhmatkaya, and R. H. Nobes, "Electronic structure, properties, and phase stability of inorganic crystals: Pseudopotential plane-wave study," *Int. J. Quant. Chem.*, vol. 77, pp. 895–910, 2000.
- [18] D. Vanderbilt, "Soft self-consistent pseudopotentials in a generalized eigenvalue formalism," *Phys. Rev. B*, vol. 41, pp. 7892–7895, 1990.
- [19] H. J. Monkhorst and J. D. Pack, "Special points for Brillouin-zone integrations," *Phys. Rev. B*, vol. 13, pp. 5188–5192, 1976.
- [20] J. P. Pedrew and Y. Wang, "Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation," *Phys. Rev. B*, vol. 46, pp. 6671–6687, 1992.
- [21] M. A. Mäki-Jaskari and T. T. Rantala, "Band structure and optical parameters of the SnO₂ (110) surface," *Phys. Rev. B*, vol. 64, pp. 075407–075414, 2001.
- [22] T. S. Rantala, T. T. Rantala, and V. Lantto, "Computational studies for the interpretation of gas response of SnO₂ (110) surface," *Sens. Actuators B*, vol. 65, pp. 375–378, 2000.
- [23] Yamaguchi, Y. Nagasawa, S. Shimomura, K. Tabata, and E. Suzuki, "A density functional theory study of the interaction of oxygen with a reduced SnO₂ (110) surface," *Chem. Phys. Lett.*, vol. 316, pp. 477–482, 2000.
- [24] D. Kohl, "Surface processes in the detection of reducing gases with SnO₂-based devices," *Sens. Actuators*, vol. 18, pp. 71–113, 1989.
- [25] N. Barsan, A. Heilig, J. Kappler, U. Weimar, and W. Gopel, *CD Proc. Eurosens. XIII*, Hague, The Netherlands, Sept. 12–15, 1999, pp. 367–369.
- [26] G. Korotchenkov, V. Brinzari, V. Golovanov, and M. Moroseac, "CO water interaction with SnO₂ gas sensors: Role of orientation effects," *Proc. Int. Conf. Eurosensors XVI*, Sept. 15–18 2002.
- [27] J. F. McAleer, P. T. Moseley, J. O. W. Norris, and D. E. Williams, "Tin dioxide gas sensors. Part 1. Aspects of the surface chemistry revealed by electrical conductance variations," *J. Chem. Soc., Faraday Trans.*, vol. 1, pp. 1323–46, 1987.
- [28] S. R. Morrison, *The Chemical Physics of Surfaces*. New York, Plenum, 1977.
- [29] I. Lundström, "Approaches and mechanisms to solid state based sensing," *Sens. Actuators B*, vol. 35, pp. 11–19, 1996.
- [30] M. J. Willet, P. T. Moseley, J. O. W. Norris, and D. E. Williams, Eds., *Techniques and Mechanisms in Gas Sensing*. Bristol, U.K.: IOP, 1991, ch. 3, pp. 61–107.
- [31] J. Tamaki, M. Nagaishi, Y. Teraoka, N. Miura, N. Yamazoe, K. Moriya, and Y. Nakamura, "Adsorption behavior of carbon monoxide and interfering gases on tin dioxide," *Surf. Sci.*, vol. 221, pp. 183–96, 1989.
- [32] J. Oviedo and M. J. Gillan, "First-principles study of the interaction of oxygen with the SnO₂ (110) surface," *Surf. Sci.*, vol. 490, pp. 221–236, 2001.
- [33] M. Li, W. Hebenstreit, L. Gross, U. Diebold, M. A. Henderson, D. R. Jennison, P. A. Schultz, and M. P. Sears, "Oxygen-induced restructuring of the TiO₂ (110) surface: A comprehensive study," *Surf. Sci.*, vol. 437, pp. 173–190, 1999.
- [34] B. Kamp, R. Merkle, and J. Maier, "Chemical diffusion of oxygen in tin dioxide," *Sens. Actuators B*, vol. 77, pp. 534–542, 2001.
- [35] M. Melle-Franco and G. Pacchioni, "Co adsorption on SnO₂ (110): Cluster and periodic ab initio calculations," *Surf. Sci.*, vol. 461, pp. 54–66, 2000.
- [36] K. Veltruska, N. Tsud, V. Brinzari, G. Korotchenkov, and V. Matolin, "CO adsorption on Pd clusters deposited on pyrolytically prepared SnO₂ studied by xps," *Vacuum*, vol. 61, pp. 129–134, 2001.
- [37] C. Naccache, P. Meriaudeau, and A. J. Tench, "Identification of oxygen species adsorbed on reduced titanium dioxide," *Trans. Faraday Soc.*, vol. 67, pp. 506–12, 1971.
- [38] P. F. Cornaz, J. H. C. van Hoof, F. J. Pluym, and G. C. A. Schuit, "Surface coordination of oxygen on oxygen-deficient TiO₂ and MoO₃ as revealed by electron spin resonance measurements," *Disc. Faraday Soc.*, vol. 41, pp. 290–304, 1966.



Vyacheslav V. Golovanov received the M.Sc. degree in material science in 1983, the Ph.D. degree in 1988, and the Dr.Sc degree in 1998, for studies in the fields of surface physics, solid-gas interfaces, and physics of semiconductors, from Odessa State University, Odessa, Ukraine.

Currently, he is a Professor at the Faculty of Physics, South Ukrainian University, where he is also Head of the Sensors Electronics and Technology Laboratory, aimed at activities in manufacturing of semiconductor gas instruments. His current research

interests focus on *ab initio* study of chemisorption and catalytic effects on the surface of semiconductors and sensor systems for environmental monitoring.



Matti A. Mäki-Jaskari received M.Sc. degree in applied physics from the Department of Engineering, Physics and Mathematics, Helsinki University of Technology, Helsinki, Finland. He is currently pursuing the Ph.D. degree at the Semiconductor Physics Laboratory, Tampere University of Technology, Tampere, Finland.

His work is focused on atomistic modeling of materials.



Tapio Tuomas Raranta received the M.Sc. degree in physics in 1978, the M.Sc. degree in technical physics (materials science) in 1984, and the Ph.D. degree in physics for DFT studies on metals and metal surfaces in 1987, all from the University of Oulu, Finland.

Currently, he is a Professor of physics and the Head of the Semiconductor Physics Laboratory, Institute of Physics, Tampere University of Technology, Tampere, Finland. His current research interests include theoretical and computational studies of compound semiconductors and their surfaces and interfaces, in particular.