

Atomistic understanding of tin-dioxide gas sensor

V. Lantto¹, T.S. Rantala¹ and T.T. Rantala²

¹Microelectronics and Materials Physics Laboratories and ²Department of Physical Sciences,
University of Oulu, Linnanmaa, FIN-90570 Oulu, Finland
E-mail: vila@ee.oulu.fi

SUMMARY

Our fundamental understanding of the operation principles of semiconductor gas sensors is still insufficient. The abundance of phenomena on open oxide-semiconductor surfaces at elevated operation temperatures of the sensors is the main reason for the situation. An atomistic approach for the understanding of tin-dioxide gas sensor is given here. Especially, we consider the oxygen chemistry at the SnO₂(110) surface together with its connection to dipole layers and band-gap surface states at the surface. A transistor model is also given to describe the transducing properties of semiconductor gas sensors.

INTRODUCTION

There is considerable interest in understanding the electronic and structural properties of the low-index surfaces of the rutile SnO₂. This is due to the gas-sensing applications of this widely used material. Atomistic understanding of surfaces is the basis for the understanding of the chemical phenomena in gas-surface interactions and the mechanisms which transduce these phenomena to a conductivity change of the material. Oxygen chemistry at oxide semiconductor surfaces has the key role for the operation of ceramic gas sensors. The most stable surface of SnO₂ is (110) which is the surface which we mainly consider here.

A lot of experimental research has been done on SnO₂ surfaces [1,2]. Modern computer codes permit theoretical investigations of SnO₂(110) surface based on accurate first-principles calculations [3-5]. Development of such approaches allows one to create an atomistic picture of sensing mechanisms and methods for prognosis of gas response properties of the material. On the other hand, the applicability of *ab initio* methods is restricted to zero temperature, whereas lattice expansion with temperature and thermally driven surface reconstruction may significantly alter atomic and electronic structure of the surface. Since, absolute majority of oxide-based sensors operate at elevated temperatures (around 500°C), the changes introduced by temperature stimulated surface reconstruction may strongly influence chemisorption and catalytic processes at the surface. The use of molecular dynamics (MD) methods for the calculation of the

(110) surface of SnO₂ allows one to perform simulations at elevated temperatures, and therefore, to complement *ab initio* calculations with temperature effects. E.g., the Universal force field (UFF) of Rappe et al. [6] is a possibility for these calculations.

Here we consider gas-surface interactions which are based on adsorption/desorption phenomena and lattice oxygen exchange with the ambient atmosphere at SnO₂(110) surface. The atomic and electronic structures of the surface change with a change in the lattice oxygen content. This leads to a surface relaxation and change in the dipole layer at the ionic surface, in addition to a change in the Schottky barrier which is the result of the charge accumulation onto the surface from the bulk of the n-type semiconductor. Changes in the dipole layer and Schottky barrier change the work function of the semiconductor oxide and may reflect in its electrical conductivity. Grain contacts together with electrode-ceramic interfaces play the key role for the transducer function in the structure of a porous ceramic gas sensor. A transistor model is described for the transducer function in the case of a porous ceramic sensor and the role of tin(II) ions at the reduced SnO₂(110) surface is discussed.

SLAB MODEL OF SnO₂(110)-1x1 FACE

The rutile structure of SnO₂ is 6:3 coordinated and the bonding between atoms has a relatively strong ionic character. The tetragonal unit cell contains two tin and four oxygen atoms, see Fig.1(a). Perpendicular to the surface in the [110] direction the rutile structure is built up from neutral stacked

layers of three alternating planes (O), (2Sn+2O), and (O) with the nominal ionic charges of 2-, 4+ and 2-, respectively, in the surface unit cell. The termination of the $\text{SnO}_2(110)$ face with these three planes is possible, since it does not leave a net dipole moment in the structure. This is called the stoichiometric surface (see Fig.1(b), top face). Removal of the topmost bridging-oxygen atoms results in the reduced (110) surface (Fig.1(b), bottom face) where tin atoms below the missing bridging oxygens are in the form of Sn^{2+} ions and remove the polarization from the structure. However, this kind of termination creates a dipole layer at the surface and leads to a relaxation of the surface.

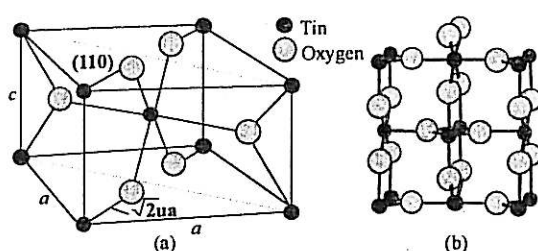


Fig.1: (a) The primitive tetragonal unit cell of the bulk SnO_2 . The lattice parameters are $a = 4.737 \text{ \AA}$, $c = 3.186 \text{ \AA}$ and $u = 0.306$. (b) An example of a small unsymmetrical orthorhombic supercell of the SnO_2 used in the slab model. The top face models stoichiometric and the bottom face reduced (110) face, respectively.

A TRANSISTOR MODEL FOR THE GAS RESPONSE

In a porous ceramic microstructure of SnO_2 gas sensor, necks between grains with different size and shape together with an electron depletion in the grains transduce the chemical surface phenomena to conductivity changes. A transistor model is introduced to describe the transducing properties of semiconductor gas sensors [7]. The model bears a resemblance to the model of the bipolar transistor. The injection current of trapped electrons from the surface (e.g., in oxygen ions) into the bulk forms the base current in the transistor model (J_b in the schematic band drawing in Fig.2(a)) which is amplified by a current-gain factor to the signal current of the sensor (the collector current J_c in the drawing in Fig.2(a)). The electron injection rate from the surface traps to the bulk conduction band controls the sensor current of a porous ceramic oxide in this transistor model, similarly, as the base current controls the collector

current in the bipolar transistor, and the injection-rate and current-gain factors are the two important factors in the model. The model is ideal for small ideal contacts between the grains (neck in Fig.2(b)) and also for small grains without band bending (flat-band situation).

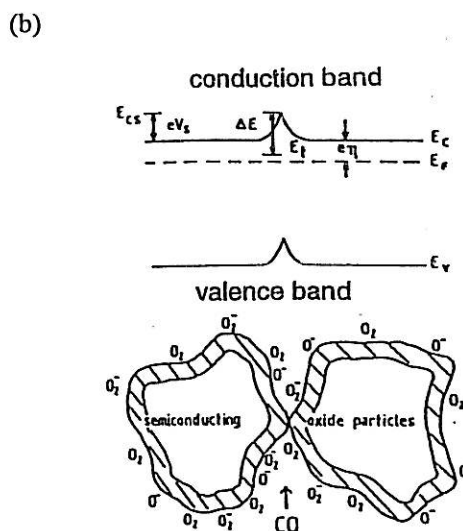
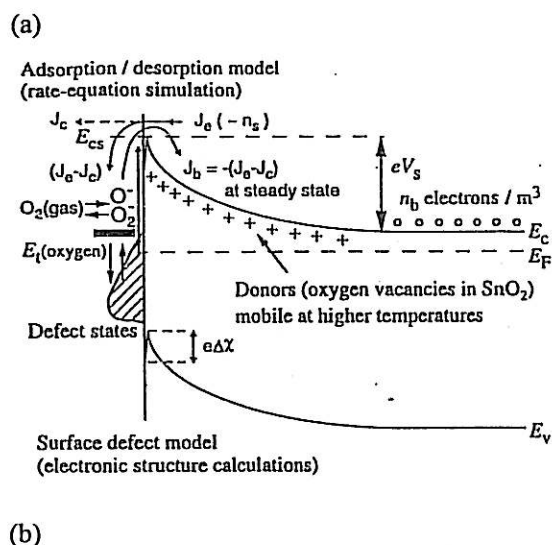


Fig.2:(a) Schematic band drawing describing some possible phenomena at the surface and in the bulk of an n-type oxide semiconductor like SnO_2 , and (b) a schematic picture of a grain contact where oxygen ions generate a depletion layer and a Schottky surface barrier eV_s as is sketched in the band picture above the grains. The current densities J_b , J_a and J_c at the top in the band drawing (a) relate to the transistor model and the affinity change $e\Delta\chi$ originates in surface dipoles.

The Schottky barrier at the surface, eV_s in Fig.2(a), is very sensitive to the surface density of trapped electrons N_t . This means that N_t is practically constant during the adsorption/desorption phenomena and temperature which is the well-known Weisz limitation [9]. Therefore, the sensor current in the transistor model is insensitive to the conduction electron concentration in the bulk (donor concentration) and the temperature dependence of the current follows the temperature dependence of the rate constant for the electron injection from the surface traps.

DIPOLE LAYERS AT $\text{SnO}_2(110)$ SURFACES

The ionosorption of oxygen (electron trapping) on oxide surfaces is important for the gain factor in the transistor model. On the other hand, the injection-rate factor in the model depends on temperature, catalytic surface reactions, especially with oxygen ions, and on the condition of a specific surface face. The surface condition depends, e.g., on the electron affinity of the surface which can change due to the lattice-oxygen exchange between the surface and ambient atmosphere (Fig.2). The affinity changes originate in surface dipoles which arise from the removal of lattice oxygen at an ionic surface. Similar dipoles also result, e.g., from the adsorption and dissociation of water on the surface.

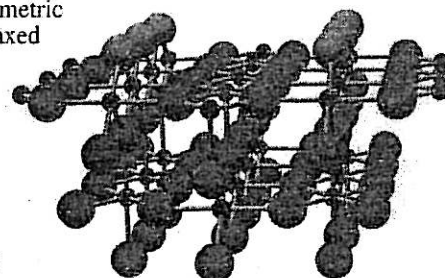
The removal of the bridging oxygens to form the reduced $\text{SnO}_2(110)$ surface (Fig. 1(b), bottom face) creates a nominal dipole layer $[(2+) (2-)]$ at the surface, since half of tin ions in the surface plane are Sn^{2+} ions [7]. A potential difference of about 2 V follows from the release of the bridging oxygens at the $\text{SnO}_2(110)-1 \times 1$ surface without ionic and electronic polarizations (see Fig.3) [8]. The ionic polarizations through the surface relaxation, respectively, of the stoichiometric and reduced $\text{SnO}_2(110)$ surfaces were calculated in Ref. 4. The most prominent feature in the relaxation at the reduced surface is that the oxygens in the surface plane move outwards about 0.4 Å with respect to the surface tin atoms, as illustrated in Fig.3(b) [4]. This relaxation decreases the potential difference of the dipole layer at the reduced surface by about 0.6 V [8]. In the case of mixed-valence cations, such as tin, the electronic polarization can be high at oxygen-deficient surfaces. This is the case at the reduced $\text{SnO}_2(110)$ surface where half of the tin ions appear with the valence +2. The two electrons

from a bridging-oxygen vacancy form band-gap states and reduce a surface-plane tin below the bridging-oxygen vacancy to Sn^{2+} ion where a high electronic polarization follows from the stereochemical position occupied by the $\text{Sn}5s-5p$ hybrid lone-pair electrons pointing outwards of the surface, as shown in the sketch in Fig. 3(b).

$\text{SnO}_2(110)-1 \times 1$ SURFACES

Stoichiometric
Non-relaxed

(a)



● Tin
● Oxygen
● Bridge Oxygen
! Lone electron pair

Reduced
Relaxed

(b)

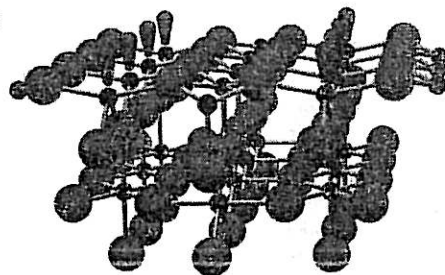


Fig.3: Perspective view (a) of stoichiometric $\text{SnO}_2(110)-1 \times 1$ surface without relaxation and (b) of the same surface in the reduced and relaxed form where $\text{Sn}5s-5p$ hybrid lone-pair electrons of tin(II) ions occupy stereochemical positions upwards of the surface.

SURFACE STATES AT THE REDUCED $\text{SnO}_2(110)$ SURFACE

A schematic drawing of a line of tin(II) ions together with their lone-pair electrons at the reduced $\text{SnO}_2(110)$ surface is shown in Fig. 4(a). The line corresponds to a "1-dimensional crystal" with the lattice constant c (of SnO_2). There is an essential overlap between the wave functions of the lone-pair electrons in the line and, therefore, their energies form a 1-dimensional band with a relative high dispersion in the k space (in fact, the wave functions overlap in both directions at the surface and there is a two-dimensional band

structure of surface states). According to the first-principles calculations [3,4], surface-state energies $E(k)$ occupy the energy gap of SnO_2 from the top of the valence band up to near the Fermi level in the n-type SnO_2 . A sketch of the situation is shown in Fig. 4(b) where the band width of 3.0 eV continues from the valence band edge E_v of SnO_2 up and reaches the maximum at the Brillouin-zone boundary ($k = \pm b/2$) where $E(k)$ is about 0.6 eV below the conduction band edge E_c (the band gap $E_g = 3.6$ eV in SnO_2). The conduction band (second band) of the "1-dimensional crystal" in Fig. 4(b) is above E_c and, therefore, a possible injection of the lone-pair electrons from the tin(II) ions with increasing temperature may happen to the conduction band of SnO_2 . Therefore, the surface-state band may be important for the operation of SnO_2 gas sensors and it is a great interest for its exact position and structure in the band gap.

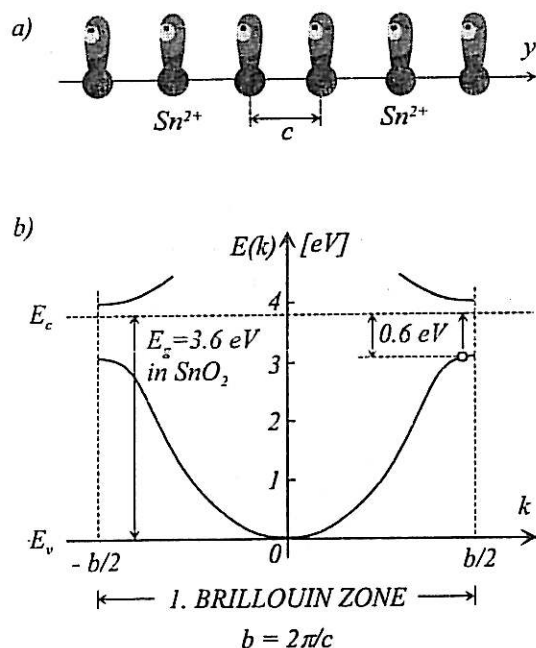


Fig. 4: (a) Schematic description of a line of tin(II) ions with the spacing c and with their lone-pair electrons at the reduced $\text{SnO}_2(110)$ surface and (b) a sketch of the band structure of this "1-dimensional crystal" in the band gap of SnO_2 .

CONCLUSIONS

An atomistic model with an analogy to the bipolar transistor is used to describe the transducing properties of semiconductor gas sensors. For the atomistic understanding of tin-dioxide gas sensor,

atomic and electronic structures of $\text{SnO}_2(110)$ face are considered in the case of lattice-oxygen exchange between the surface and ambient atmosphere. Surface dipoles together with band-gap surface states follow from the removal of bridging oxygen at the (110) face.

ACKNOWLEDGEMENTS

The authors acknowledge the Academy of Finland for funding within the projects nr. 37778 and 37781 (MECA). The Center for Scientific Computing (CSC) in Finland is acknowledged for providing us the computational resources within the project nr. oy1199.

REFERENCES

- [1] V. A. Henrich and P. A. Cox, *The Surface Science of Metal Oxides*, University Press, Cambridge, 1994.
- [2] R.G. Egdell, in *The Science of Ceramics Interfaces II*, ed. J. Nowotny, Elsevier, N.Y., 1994.
- [3] I. Manassidis, J. Goniakowski, L.N. Kantorovich and M.J. Gillan, *The structure of the stoichiometric and reduced SnO_2 surface*, *Surf.Sci.* 339, 1995, pp. 381-394.
- [4] Tapio Rantala, Tuomo Rantala and Vilho Lantto, *Surface relaxation of the (110) face of rutile SnO_2* , *Surf. Sci.*, 420, 1999, pp. 103-109.
- [5] J. Goniakowski and M.J. Gillan, *The adsorption of H_2O on TiO_2 and SnO_2 (110) studied by first-principles calculations*, *Surf. Sci.*, 350, 1996, pp. 145-158.
- [6] A.K. Rappe, C.J. Casewit, K.S. Colwell, W.A. Goddard III and W.M. Skiff, UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulation, *J. Am. Chem. Soc.*, 114, 1992, pp. 10024-10035.
- [7] Vilho Lantto, Tuomo S. Rantala and Tapio T. Rantala, *Experimental and theoretical studies on the receptor and transducer functions of SnO_2 gas sensors*, *Electron Technology*, in press.
- [8] Tuomo S. Rantala, Tapio T. Rantala and Vilho Lantto, *Computational Studies for the interpretation of gas response of $\text{SnO}_2(110)$ surface*, *Sensors and Actuators B*, in press.
- [9] P.B. Weisz, *Effect of electronic charge transfer between adsorbate and solid on chemisorption and catalysis*, *J. Chem. Phys.* 21, 1953, pp. 1531-1538.