

EXPERIMENTAL AND THEORETICAL STUDIES ON THE RECEPTOR AND TRANSDUCER FUNCTIONS OF SnO_2 GAS SENSORS

V. LANTTO¹, T. S. RANTALA¹, T. T. RANTALA²

¹Microelectronics and Materials Physics Laboratories, University of Oulu, Linnanmaa, FIN-90570 Oulu, Finland

²Department of Physical Sciences, University of Oulu, Linnanmaa, FIN-90570 Oulu, Finland

Received January 19, 1999

ABSTRACT

Rutile-structure SnO_2 (cassiterite) is a wide-gap n -type semiconductor with oxygen vacancies as bulk donors. It has many technical applications, e.g., in the fields of oxidation catalysis and chemical sensing where its surface properties play a key role. Its ability to transduce different gas-surface interactions to conductivity changes makes it useful in gas-sensor applications. The gas-surface interactions, such as adsorption/desorption, removal of lattice oxygen and other chemical reactions with a solid surface product (e.g., a possible ion exchange in the case of volatile sulphides) form the basis for the receptor function. The removal of lattice oxygen from the $\text{SnO}_2(110)$ surface is considered here as an example of the defect mechanism for the receptor function. The electronic and atomic structures of the surface change with changes in the lattice oxygen content. This leads to a surface relaxation and changes in the dipole layer at the ionic surface in addition to changes in the Schottky barrier which is a result of the charge accumulation onto the surface from the bulk Bloch states of the n -type semiconductor. Changes in the dipole layer and the 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 the adsorption/desorption mechanism and the role of tin(II) ions at the reduced $\text{SnO}_2(110)$ surface is discussed in the case of the surface defect mechanism.

1. Introduction

In semiconductor gas sensors, the chemical signal is transduced through the electronic structure of the material to measurable electrical characteristics, such as a change in conductance. Tin dioxide, SnO_2 , is used in monitoring many minor constituents of air due to its stability up to high temperatures and environment dependent surface chemistry [1]. The “oxygen chemistry” at the grain surfaces of the usually porous SnO_2 material is strongly dependent on the surrounding gas atmosphere and temperature, and forms the basis for the receptor function of the sensor [2]. It is reflected in the easily measurable electrical conductance of the material which is the usual way to transduce the chemical information to an electrical signal. This transducing property depends also on the microstructure of the sensing material and can be very different, e.g., in sintered thick films and in sputtered thin films, respectively.

Oxide semiconductors form a group of compound semiconductors whose specific properties of interfaces

and surfaces are widely used in today's electronics. An exchange of lattice oxygen with the surrounding atmosphere, especially, at elevated temperatures, is a specific property of the oxide semiconductors. This is also a property which is of central importance for the use of semiconducting oxides as gas sensors. In many oxides, the oxygen exchange leads to a surface decomposition, already at relative low temperatures, which usually reflects in a serious stability problem in sensor applications [3]. An advantage of SnO_2 gas sensors is their good stability to irreversible surface changes. Tin is an element in Group IV of the Periodic Table and appears with two different valence states Sn^{4+} and Sn^{2+} in its compounds, such as SnO_2 and SnO , respectively. Owing to this variable valency, specific properties relate to the lattice-oxygen exchange at SnO_2 surfaces which are not possible at other oxide surfaces where the cation has only a single valence state, like in ZnO . For example, the exchange of the lattice oxygen at SnO_2 surfaces is possible without any contribution of conduction electrons from the bulk material.

The (110) crystal face of SnO_2 has the lowest surface energy and, therefore, it is the most stable and dominant face of the rutile-structure SnO_2 . The stoichiometry of the $\text{SnO}_2(110)$ surface is sensitive to the processing conditions under which the surface is prepared. Viewed perpendicular to the [110] direction, the rutile structure is built up from neutral stacked layers of three alternating planes of (O), $(2\text{Sn} + 2\text{O})$, and (O) with the nominal ionic charges of 2^- , 4^+ and 2^- in the surface primitive cell, respectively. The termination of the (110) face with a neutral layer of three planes $[(\text{O})(2\text{Sn} + 2\text{O})(\text{O})]$ in FIG. 1a is possible, since it does not leave a repeating unit with a net dipole moment [4]. The surface terminates to 2-fold-coordinated bridging oxygen atoms. A removal of the bridging oxygen atoms to form the reduced (110) surface in FIG. 1b is possible in the case where the 4-fold-coordinated (from the removal of bridging oxygens) tin ions in the surface plane reduce to tin(II) ions which removes the repeating dipole unit $[(4^+)(2^-)(2^-)][(4^+)(2^-)(2^-)] \dots$ from the structure and creates a nominal dipole layer $[(2^+)(2^-)]$ at the surface. Experimentally, the (110) face can have different partial occupations 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 disordered structures [5]. COX ET AL. [6] have described methods for producing nearly perfect stoichiometric $\text{SnO}_2(110)-1 \times 1$ surfaces.

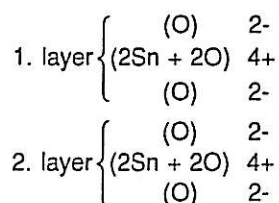
The applications of stannic oxide in gas sensing and as an oxidation catalyst have stimulated intensive study of its surfaces both experimentally and theoretically. The surface electronic structure has been investigated with various spectroscopies and surface states in the band gap were found in the case

of reduced surfaces [6]. It was concluded that they arise from the bridging oxygen vacancies, because the states were absent at the stoichiometric surface. The atomic structure at the (110) face has been investigated with LEED and also with STM, see [4] and further references therein. Computational methods are now also at a level to give realistic results for both atomic and electronic structures of surfaces. Cluster models have been used to study the unrelaxed $\text{SnO}_2(110)$ surface computationally with the density-functional theory and local-density approximation (DFT-LDA) [7]. The unrelaxed (110) surface was investigated with different oxygen contents [8] and other adsorbates [9, 10]. It was found in agreement with the experimental observations in [6] that surface states arise in the band gap from the bridging oxygen vacancies. However, the relaxation of the surface is essential in explaining the surface electronic structure and the finite-size cluster effects have to be eliminated in order to obtain reliable quantitative results. This is possible using a three-dimensional periodic slab model [11–13].

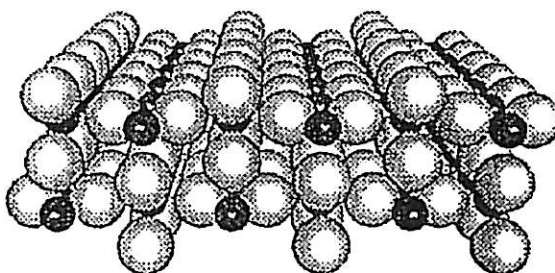
2. Two mechanisms for the receptor function

Two different mechanisms have been used for the semiconductor gas sensors to describe gas-surface interactions. In the adsorption/desorption mechanism [14], the interactions restrict only to adsorbed species and their mutual reactions while the surface defect mechanism is based on different surface defects origi-

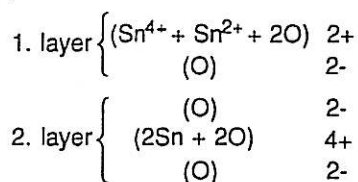
a) Stoichiometric surface



Non-polar: $[(2^-)(4^+)(2^-)][(2^-)(4^+)(2^-)] \dots$



b) Reduced surface



Polar surface: $[(2^+)(2^-)][(2^-)(4^+)(2^-)][(2^-)(4^+)(2^-)] \dots$
dipole layer

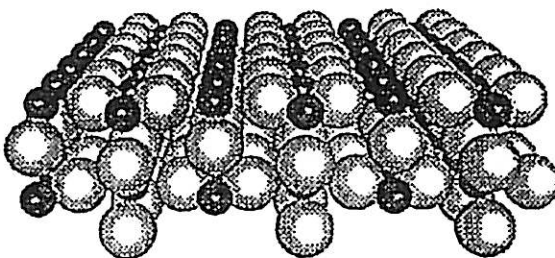


FIG. 1. Perspective view of stoichiometric (a) and reduced (b) $\text{SnO}_2(110)-1 \times 1$ surfaces (after [12]). Nominal ionic charges in the primitive surface cell are also shown for different atomic planes in the two uppermost layers.

nating in the gas-surface interactions [15]. The two phenomena may appear also simultaneously and, then, there is a need to combine the two mechanisms. A schematic illustration of the two mechanisms in a band picture is shown in FIG. 2.

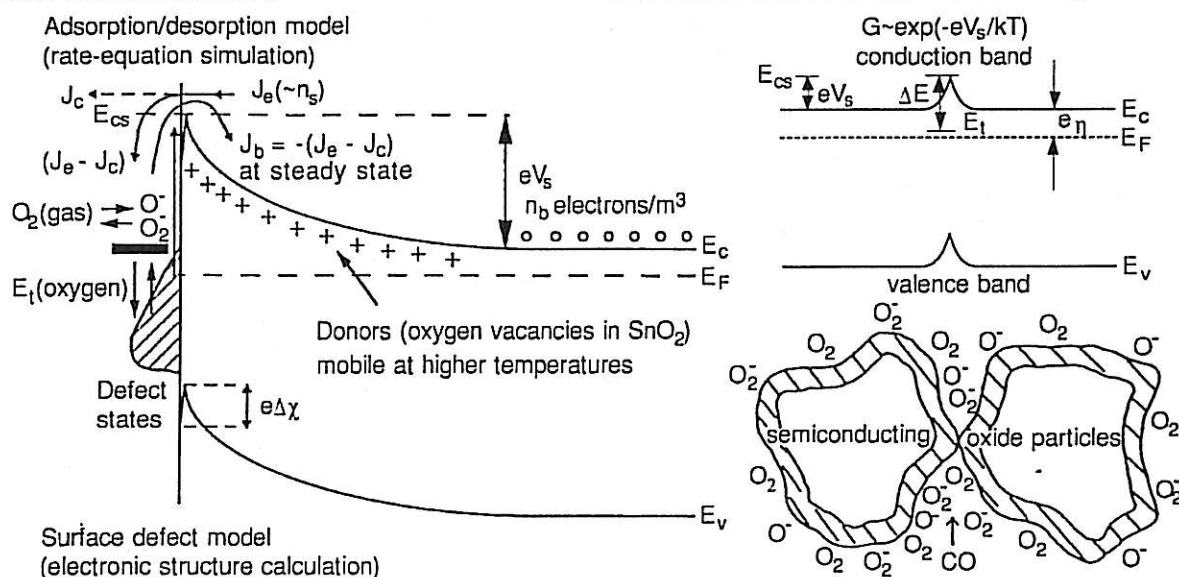


FIG. 2. Schematic band drawing (left) describing some possible surface and bulk phenomena in an *n*-type oxide semiconductor (see text), and a schematic picture of a grain contact (right) where oxygen ions generate a depletion layer and a Schottky surface barrier as is sketched in the band picture above the grains.

The adsorption/desorption mechanism is based on adsorbed oxygen ions (O_2^- , O^-) on the semiconductor surface. According to the general electronic theory of chemisorption, this is due to discrete energy levels introduced by oxygen within the band gap at the semiconductor surface (E_i in FIG. 2). A band bending, together with a surface Schottky barrier (eV_s in FIG. 2), follow the oxygen ionosorption on the surface. The height of this Schottky barrier is usually related to the activation energy of conductance G in a porous ceramic (FIG. 2) and it controls the current through the material. A simple Schottky relation connects the barrier height eV_s to the trapped electron density N_t at the surface in the case of a constant donor concentration N_d :

$$eV_s = \frac{e^2 N_t^2}{2\epsilon_s N_d} \quad (1)$$

where ϵ_s ($= \epsilon_r \epsilon_0$) is the permittivity of the semiconductor. In the case of mobile donors, the relation has the form [16]:

$$eV_s = -kT \ln \left[1 - \left(\frac{e^2 N_t^2}{2\epsilon_s N_d kT} \right)^{1/2} \right] \quad (2)$$

where N_{ds} is the donor concentration at the surface. Ionosorption of oxygen and other oxidizing gases and catalytic surface reactions between the oxygen ions and reducing gases form the receptor function for the adsorption/desorption mechanism.

The $\text{SnO}_2(110)$ face is used here for the discussion of the surface defect mechanism. An exchange of the bridging oxygens at the surface (FIG. 1) with the surrounding atmosphere is now possible without an electron transfer between the bulk and surface, since tin(II)

ions at the surface can store the electrons from the bridging oxygen vacancies. Therefore, the exchange of the bridging oxygens with the ambient atmosphere does not reflect in the band bending (Schottky barrier) at the surface. On the other hand, a dipole layer $[(2+)(2-)]$ is formed at the reduced (110) surface (FIG. 1), but the surface relaxation together with a high polarization of the tin(II) ions compensate, to a large extent, the dipole layer strength at the surface [17]. The bridging oxygen vacancies originating, e.g., in catalytic reactions with reducing gases form now the basis for the receptor function on the $\text{SnO}_2(110)$ surface. These vacancies may also have an important effect on the adsorption/desorption phenomena which means that the two mechanisms are closely connected.

3. A transistor model for the transducer function in the case of the adsorption/desorption mechanism

The Schottky barrier, eV_s , in Eqs. (1) and (2) is very sensitive to the surface density of trapped electrons N_t . This means that N_t stays practically constant during the adsorption/desorption phenomena and temperature which is the well-known Weisz limitation [18]. The current density $J_b = -eKN_t$ in FIG. 2 (arrows show the direction of electrons in FIG. 2) depends now on the injection rate K of electrons from the surface traps (oxygen ions) to the conduction band. By continuing with an analogy to the bipolar transistor (J_b is the

base current density), the current density from the surface to the bulk (the emitter current density from the average flux of electrons impinging against the surface from the bulk in FIG. 2) $J_e = 1/4 ev_{th} n_s$ (similarly with the thermionic emission current density in Schottky diodes), where n_s is the conduction electron concentration at the surface and v_{th} is the average thermal velocity of the electrons $(8 kT/\pi m^*)^{1/2}$ (m^* is the effective mass of electrons) for the Maxwell-Boltzmann distribution of electrons. The capture cross-section together with the unoccupied trap density at the surface can now be used to describe the fraction, γ , of the impinging electrons which is captured by the surface traps (adsorbed oxygen). At a steady state, the current density from this capture fraction, γJ_e , is equal to $-J_b$. The rest of the electrons impinging against the surface (the current density J_e) are assumed to continue to a neighbouring grain at a grain contact (FIG. 2) and now the current density at the grain contact (the collector current density) $J_c = (1 - \gamma)J_e$ and the current gain:

$$\beta = \left| \frac{J_c}{J_b} \right| = \frac{(1 - \gamma)J_e}{\gamma J_e} = \frac{1 - \gamma}{\gamma}. \quad (3)$$

Here, we assume, in fact, that the oxygen traps are present also inside the contact (pressed ceramic). In the case of no electron traps inside the grain contact, the gain factor $\beta = 1/\gamma$. The electron injection rate from the surface traps to the bulk conduction band controls the current in a porous sample in this transistor model for the adsorption/desorption mechanism, similarly, as the base current controls the collector current in a bipolar transistor. In the model, the sensor current is independent of the conduction electron concentration in the bulk (dependence only on n_s) and the temperature dependence of the current follows the temperature dependence of the rate constant, K , for the electron injection from the surface traps (according to the Weisz limitation N_t is insensitive to temperature). It is possible to derive expressions for γ and K , e.g., from a rate-equation simulation model for the Schottky barrier, eV_s , in [19] and [20]. It is also possible to apply the transistor model in the case of both frozen and mobile donors [21, 22], respectively.

4. Transducing with defects at SnO₂(110) surfaces

Two different terminations, stoichiometric and reduced, of the SnO₂(110) face is shown in FIG. 1. All bridging oxygens are absent from the reduced surface, but the surface can also have a partial occupation of bridging oxygens between the two extreme situations in FIG. 1. A nominal dipole layer $[(2+)(2-)]$ in FIG. 1)

increases at the surface with the decreasing bridging oxygen content, since the two electrons from each bridging oxygen vacancy are trapped in a tin(II) ion. The strength of this dipole layer at the surface depends on the surface relaxation (ionic polarization) and electronic polarization, especially of tin(II) ions, at the surface.

4.1. Dipole layers at distorted surfaces

In an infinite (or periodically repeated by the Born-von Karman boundary conditions) solid, the crystal potential U^{inf} can be expressed as a sum of contributions from Wigner-Seitz cells about each lattice point [23]:

$$U^{inf}(\mathbf{r}) = \sum_{\mathbf{R}} v(\mathbf{r} - \mathbf{R}) \quad (4)$$

where

$$v(\mathbf{r}) = -e \int_C \rho(\mathbf{r}') \frac{d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \quad (5)$$

$\rho(\mathbf{r})$ is the total charge density from ions and electrons and the integration is over a Wigner-Seitz cell C . From the multipole expansion of electrostatics for $1/|\mathbf{r} - \mathbf{r}'|$ it is possible to obtain

$$v(\mathbf{r}) = -e \frac{Q}{r} - e \frac{\mathbf{p} \cdot \mathbf{r}_0}{r^2} + O\left(\frac{1}{r^3}\right) \quad (6)$$

where $Q = \int_C \rho(\mathbf{r}') d\mathbf{r}'$ is the total charge of the cell and $\mathbf{p} = \int_C \mathbf{r}' \rho(\mathbf{r}') d\mathbf{r}'$ is its total dipole moment. In a periodic crystal, each primitive cell is neutral and $Q = 0$ and in a crystal with inversion symmetry also $\mathbf{p} = 0$. For instance, in a cubic symmetry the quadrupole potential (coefficient of the $1/r^3$ term) will also vanish. If we cut a finite crystal from an infinite crystal by a surface V and suppose that the charge density in the Wigner-Seitz cell about each ion remains undistorted, even in the cells near the surface, the crystal potential [23]

$$U^{fin}(\mathbf{r}) = \sum_{\mathbf{R} \text{ in } V} v(\mathbf{r} - \mathbf{R}). \quad (7)$$

A schematic illustration of the situation is shown in FIG. 3a. The work function, $\mathcal{W}_i$, and the electron affinity, $e\chi_i$, are also shown for the ideal surface in the case of an n -type semiconductor in FIG. 3a.

However, the actual charge distribution in cells near the surface of a finite crystal differs from the charge distribution of interior cells. The surface relaxation is a reason for that and, furthermore, the electronic charge distribution in surface cells need not have

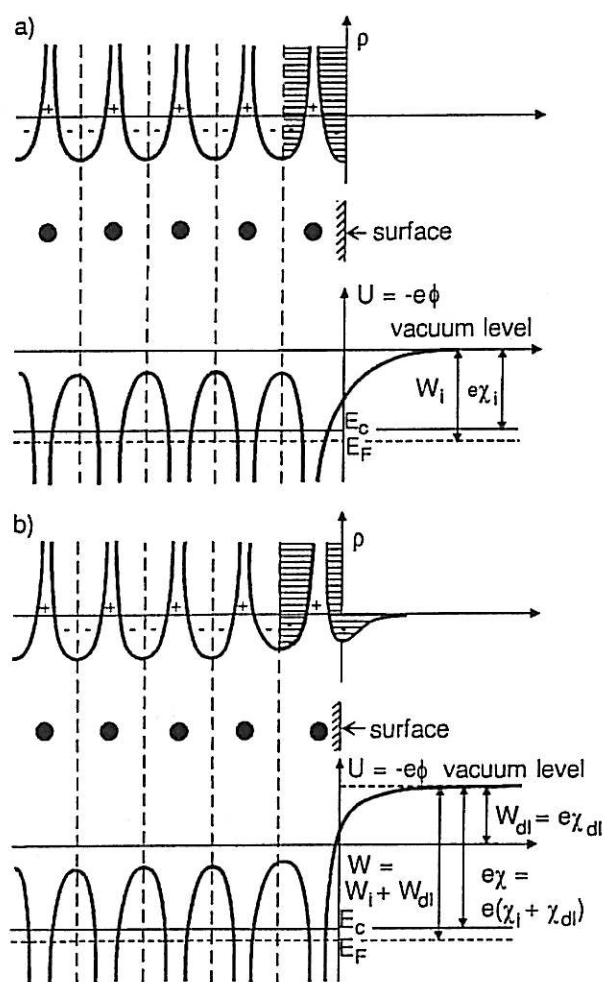


FIG. 3. Schematic description of the work function, W , and electron affinity, $e\chi$, for an undistorted surface (a) and a distorted surface (b) of an n -type semiconductor. ρ and U describe the charge and crystal potential, respectively, in the 1-dimensional crystal. Both electronic and ionic (relaxation) distortions are shown in the surface cell in (b).

the symmetry of the Bravais lattice. Such cells will have a nonvanishing electric dipole moment and may even yield a nonvanishing net electrical surface charge. The situation is illustrated in FIG. 3b for the case where the distortion of the surface cells does not result in a net macroscopic charge at the surface (no band bending at the semiconductor surface). Within the surface layer in which the cells are distorted (with both an ionic displacement and electronic polarization in FIG. 3b), this distortion will give rise to an electric field E against which an amount of work $W_{dl} = e\chi_{dl} = \int eE \cdot dz$ must be performed, to move an electron through the layer. The correct work function and electron affinity for the surface are now given by $W = W_i + W_{dl}$ and $e\chi = e(\chi_i + \chi_{dl})$, respectively.

4.2. Dipole layers at $\text{SnO}_2(110)$ faces

The ideal (non-relaxed) stoichiometric $\text{SnO}_2(110)$ surface, shown in FIG. 4a, is non-polar, but a removal

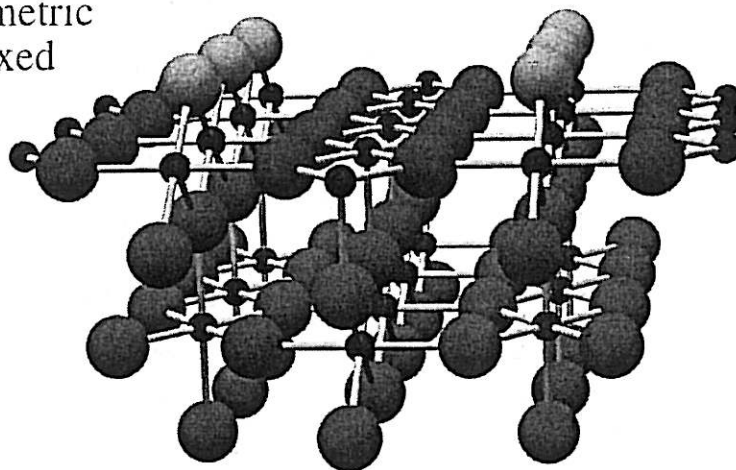
of the bridging oxygens from the surface will give rise to a surface dipole layer. It is possible to represent the distortion in the charge of surface cells as a uniform macroscopic surface density of dipoles. When the two electrons of each bridging oxygen vacancy are trapped by the tin(II) ions in the $(2\text{Sn} + 2\text{O})$ surface plane, it is possible to express, with the density of $[(2+)(2-)]$ dipoles at the reduced (110) surface, the potential difference, U , over the dipole layer by the equation: $U = 2eN < d > / \epsilon_s$, where N is the surface density of the tin(II) ions ($= 4.7 \cdot 10^{18} \text{ m}^{-2}$), $< d >$ is the average distance between opposite charges in the dipole and ϵ_s is the permittivity at the surface. If the value of the atomic distance between tin(II) and O^{2-} ions is used in the case of the non-relaxed reduced (110) surface, 0.129 nm, for $< d >$ and the bulk permittivity ($\sim 12 \epsilon_0$) for ϵ_s (thus neglecting the decrease of ϵ_s from the bulk value at the interface between air and SnO_2), a value 1.81 V for the potential difference, U , is obtained. The obtained surface relaxation (ionic polarization) for the reduced (110) surface in [24] decreases, from calculations as above, the potential difference over the dipole layer at the surface by about 0.6 V. In the relaxation, the oxygen in the $(2\text{Sn} + 2\text{O})$ surface plane of the reduced surface (FIG. 1b) moves outwards about 0.04 nm with respect to the tin atoms in the same plane. It was also found in [12, 24] that the electrons from the bridging oxygen vacancies reduce the tin atoms below the bridging oxygen vacancies at the surface plane to tin(II) ions which have a high polarization from the $\text{Sn}5s-5p$ hybrid lone-pair electrons pointing outwards of the surface, as shown in FIG. 4b. This electronic polarization of tin(II) ions may, of course, decrease the potential difference, U , to a large extent. A preliminary value for the potential difference, U , at the reduced $\text{SnO}_2(110)$ surface from the first-principles calculations [24] was about 0.2 V. This means that the electron affinity and work function of the (110) surface decrease by about 0.2 eV when the bridging oxygen leaves the surface ($e\Delta\chi$ in FIG. 2). An affinity decrease of about 0.2 eV was found also by COX ET AL. [6] from their ultraviolet photo-electron spectroscopy (UPS) measurements upon heating an oxidized (stoichiometric) $\text{SnO}_2(110)$ surface in vacuum up to 700 K. From their ion-scattering spectroscopy (ISS) and UPS measurements they further concluded that the bridging oxygen disappeared from the oxidized surface during heating up to about 700 K in vacuum. The results in [6] show also that the $\text{SnO}_2(110)$ surface can remain reduced in air at low temperatures, but oxidizes to the stoichiometric form during heating up to 700 K in an atmosphere having sufficient oxygen.

4.3. Grain contacts with an interfacial layer

Grain contacts between two ceramic grains or between a ceramic grain and the electrode metal are the

Stoichiometric
Non-relaxed

(a)



- Tin
- Oxygen
- Bridge Oxygen
- ! Lone electron pair

Reduced
Relaxed

(b)

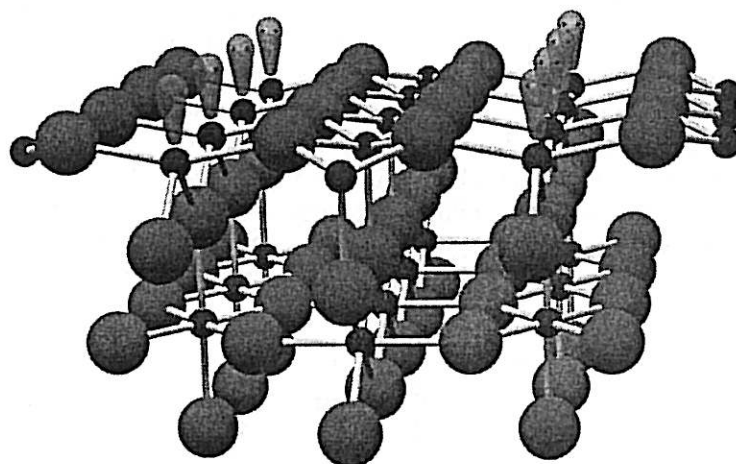


FIG. 4. Perspective view of stoichiometric $\text{SnO}_2(110)\text{-}1\times 1$ surface without relaxation (a) and of reduced and relaxed $\text{SnO}_2(110)\text{-}1\times 1$ surface (b) where the $\text{Sn}5s\text{-}5p$ hybrid lone-pair electrons of tin(II) ions occupy stereochemical positions upwards of the surface.

critical points for the transducer function in porous ceramic gas sensors. An illustration of the contact together with an interfacial layer between the two grains is shown in FIG. 5. Consider first a metallic crystal (grain *B* in FIG. 5) with two inequivalent faces F_m and F_m' . Their work functions W and W' need not be the same, since the contributions W_{di} and W_{di}' (FIG. 3b) may arise from different dipole layers at the two surfaces. In moving an electron from the interior Fermi level around the loop *B* in FIG. 5 and back to the Fermi level, the total work done in such a cycle must vanish, if energy is to be conserved. This means that the two faces of the crystal must be at different electrostatic potentials ϕ and ϕ' (an electric field outside of the crystal from a macroscopic charge redistribution between the faces) satisfying the equation: $-e(\phi - \phi') = W - W'$. In the case of a semiconductor crystal (grain *A* in FIG. 5),

the compensating amount of work for the difference $e(\chi - \chi')$ in a corresponding cycle (loop *A*) needs, e.g., different barrier heights eV_s and eV_s' at the two faces F_s and F_s' , respectively, satisfying the equation: $e(V_s' - V_s) = e(\chi - \chi')$. However, a macroscopic charge redistribution between different faces of a semiconductor grain is also possible. Now, the sum $(e\chi + eV_s + e\phi)$ has the same value for each face of the grain. Then, Eqs. (1) and (2) for the Schottky barrier, based on the charge neutrality of the semiconductor surface, are no more valid.

Next, we assume that the two grains *A* and *B* in FIG. 5 are SnO_2 grains separated by a Schottky barrier eV_i due to electron traps in the interfacial layer F_i . A change $e\Delta\chi_{di}$ of the electron affinity of the (110) faces due to a change in the amount of the bridging oxygens will change the work function in the grains. If the electron

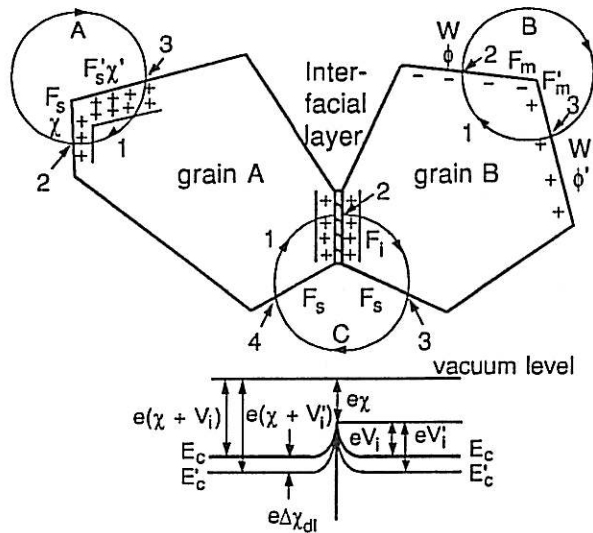


FIG. 5. Schematic picture of a contact with an interfacial layer between two crystal grains. Loops A and B refer to a semiconductor crystal and to a metallic crystal, respectively. In the case of loop C, grains A and B are semiconductor crystals and the schematic band picture at the bottom shows for a special case a change of bands around the contact during a change $e\Delta\chi_{dl}$ of the dipole layer at the surfaces of grains A and B.

affinity ($e\chi$) does not change in the interfacial layer during the affinity change of the (110) faces and there is no charge redistribution between the faces, the barrier, eV_i , across the layer will also change (by the amount $e\Delta\chi_{dl}$ in the band picture at the bottom in FIG. 5 for the special case where the change of the work function is also $e\Delta\chi_{dl}$). However, a charge redistribution between the faces may change the picture, to a large

extent. This is a possible model for the transducer function in the case where current is controlled through changes in the dipole layers at the grain surfaces.

4.4. Surface conductivity

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. 6a. The line corresponds to a 1-dimensional crystal with the lattice constant c (of SnO_2). There is, in fact, 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. According to the first-principles calculations [12, 24], the electron 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. 6b 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. 6b 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 , as it is sketched in FIG. 6c for the case where the crystal is in vacuum. $e\Delta\chi$ in FIG. 6c shows the change

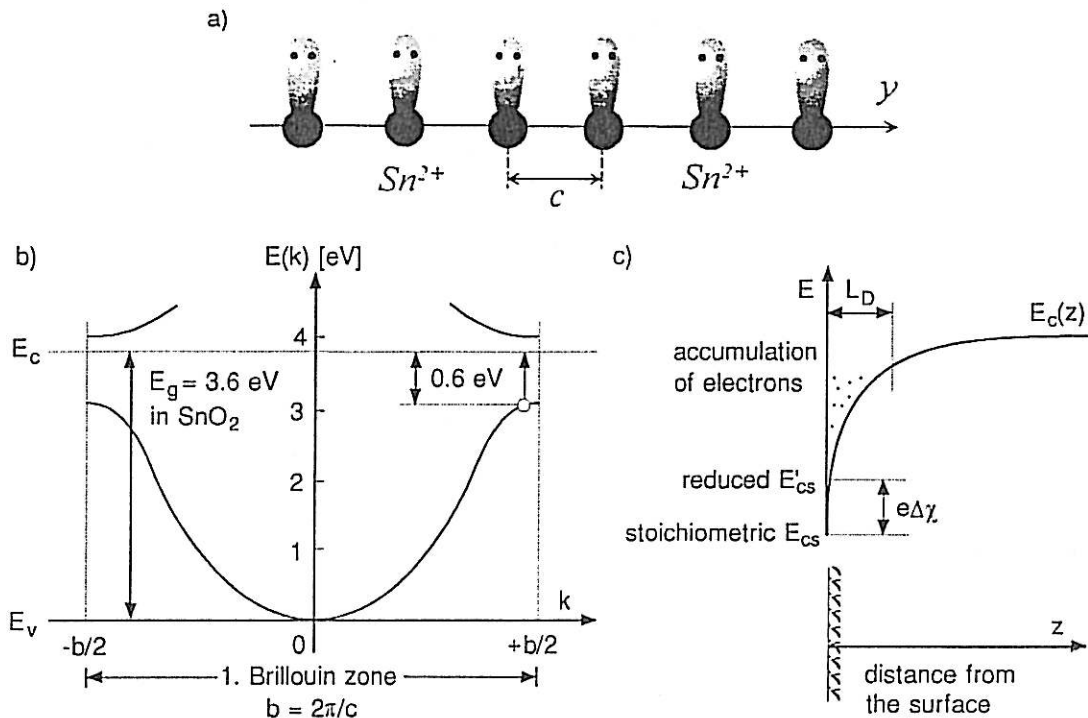


FIG. 6. a) Schematic description of a line of tin(II) ions with the spacing c and with their lone-pair electrons at the reduced $\text{SnO}_2(110)$ surface, b) a sketch of the band structure of this 1-dimensional crystal in the band gap of SnO_2 , c) a band picture for the case where a part of lone-pair electrons is released from tin(II) ions to the conduction band of SnO_2 . The Debye length L_D describes the width of the electron accumulation layer at the surface.

of the electron affinity between the stoichiometric and reduced $\text{SnO}_2(110)$ faces and the bands bend upwards in vacuum through the accumulation of electrons at the surface. The Debye length L_D is for the width of the accumulation layer. A band bending upwards from the surface by about 0.4 eV, similarly as in FIG. 6c, was also deduced in [25] on the basis of UPS (HeII excitation) and XPS (HeI and $\text{MgK}\alpha$ excitations) spectra measured from SnO_2 samples (see also the interesting discussion in [25]). The possible holes at the top of the 1-dimensional band (FIG. 6b) and the 2-dimensional electron gas at the surface (FIG. 6c) from a possible electron injection from the tin(II) ions to the conduction band of SnO_2 may have a strong effect on the surface conductivity of the $\text{SnO}_2(110)$ face at elevated temperatures, especially in vacuum. At higher injection rates, the 1-dimensional line, with its partially filled band in the band gap of SnO_2 , may change to an electron conductor instead of the hole conductor.

In an ambient atmosphere containing oxygen, however, the situation is very different. Now, the bands bend downwards through the depletion of electrons at the surface (oxygen ionosorption). The transistor model described in the Section 3 needs a revision since there is now an electron injection from both the oxygen ions and tin(II) ions to the conduction band. The Weisz limitation is no more valid and, in principle, a high increase can appear in the amount of oxygen ions on the surface. Then, the current density, J_b , in the model increases and the gain factor, β , in Eq. (3) amplifies the increase $|\Delta J_b|$ to an increase $\Delta J_c = \beta |\Delta J_b|$ of the current density J_c (the collector current density). Of course, the rate constant, K , for the electron injection from the surface traps (oxygen ions) to the conduction band may also change with the changing amount of the bridging oxygen vacancies. On the other hand, holes in tin(II) ions make it possible for mobile O^- ions on the surface to occupy the corresponding bridging oxygen vacancies. This is a possible mechanism for the occupation of empty bridging oxygen sites in an oxygen atmosphere at high enough temperatures, as was found to happen at the $\text{SnO}_2(110)$ surface by COX ET AL. [6]. A high dispersion of the band of lone-pair electrons in the band gap of SnO_2 (FIG. 6b) means that the occupation of the empty bridging oxygen sites with the proposed mechanism takes place over a broad temperature range. An increasing occupation of the bridging oxygen vacancies may decrease the electron injection rate from the tin(II) ions to the conduction band which leads to a decrease in the amount of oxygen ions on the surface and the sensor (collector) current also decreases through the transistor action. This may be an explanation for the observed conductance decrease of different SnO_2 thick-film sensors in FIG. 7 during heating the sensors in dry synthetic air over the temperature range between 290°C and 420°C [26]. The origin of the hysteresis in the conductance values between the

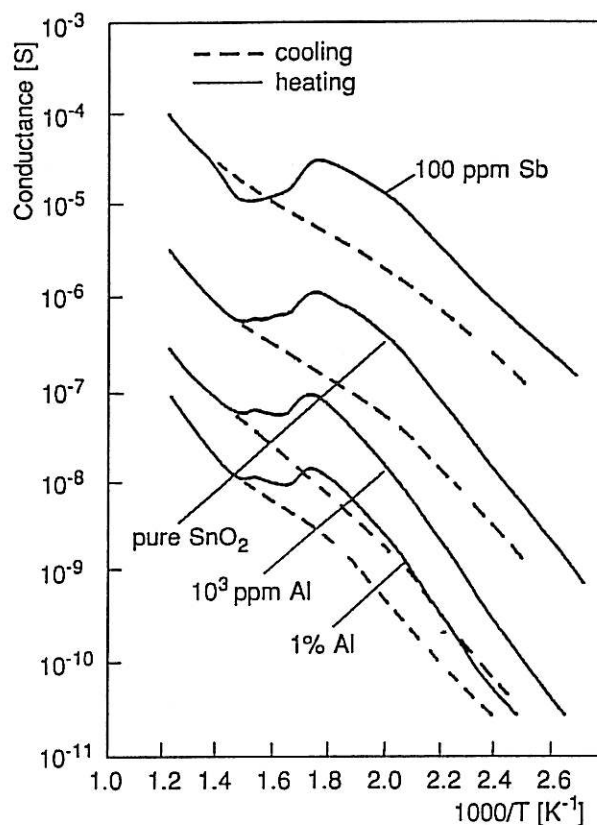


FIG. 7. Conductance of pure, Sb- and Al-doped SnO_2 thick-film samples with Au electrodes in dry synthetic air as a function of inverse temperature, measured at a cooling and heating rate of 2.4 Kmin^{-1} [26].

heating and cooling runs in FIG. 7 may also relate to the bridging oxygen. During a long stay in dry synthetic air at a low temperature, they may disappear from the $\text{SnO}_2(110)$ faces, but reappear again during heating in air at high enough temperatures. The transistor model will also be used to explain the different conductance values between the sensors with different doping in FIG. 7.

5. Conclusions

A discussion is given for the transducer function of porous SnO_2 gas sensors in two cases where the gas-surface interactions are based on the adsorption/desorption mechanism and on a surface defect mechanism, respectively. A possible connection between the two receptor mechanisms is also discussed. A transistor model with an analogy to the bipolar transistor is given for the transducer function in the case of the adsorption/desorption mechanism. A feature of the model is that the sensor response is insensitive to the bulk electron concentration, since the electron injection rate from the surface traps (oxygen ions) to the bulk conduction band controls the sensor current, and not *vice versa*.

The bridging oxygen vacancies at the $\text{SnO}_2(110)$ face are used as an example for the discussion of the surface defect mechanism. A dipole layer at the (110)

surface is a result of the removal of bridging oxygen from the surface. However, the relaxation of the surface together with a high polarization of tin(II) ions decrease effectively the strength of the dipole layer at the reduced $\text{SnO}_2(110)$ surface. Grain contacts with an interfacial layer are used to describe a possible transducer function which is based on changing dipole layers at the grain surfaces through changes in the amount of the bridging oxygen at the (110) surfaces. The role of the lone-pair electrons of tin(II) ions at the surface which form a wide 1-dimensional band in the band gap of SnO_2 is also considered. A possible release of these electrons to the conduction band of SnO_2 at higher temperatures may have remarkable effects on the surface conductivity, especially in vacuum, and also to the conductance behaviour and transducing properties of SnO_2 gas sensors in air.

Acknowledgement

The authors acknowledge the Academy of Finland for the financial support (Grants No. 29261 and No. 37778). The Centre for Scientific Computing (CSC) in Finland is acknowledged for the computational resources in Project No. oy1199.

REFERENCES

1. W. GÖPEL, K. D. SCHIERBAUM, *SnO₂ Sensors: Current Status and Future Prospects*, Sensors a. Actuators B, 1995, 26–27, 1–12.
2. V. LANTTO, *Semiconductor Gas Sensors Based on SnO₂ Thick Films*, [In:] G. Sberveglieri (Ed.), *Gas Sensors*, Kluwer, Dordrecht, 1992, 117–167.
3. M. J. MADOV, S. R. MORRISON, *Chemical Sensing with Solid State Devices*, Academic Press, San Diego, 1989.
4. F. H. JONES, R. DIXON, J. S. FOORD, R. G. EGDELL, J. B. PETHICA, *The Surface Structure of SnO₂(110)(4x1) Revealed by Scanning Tunneling Microscopy*, Surf. Sci., 1997, 376, 367–73.
5. T. J. GODIN, J. P. LAFEMINA, *Surface Atomic and Electronic Structure of Cassiterite SnO₂(110)*, Phys. Rev. B., 1993, 47, 6518–23.
6. D. F. COX, T. B. FRYBERGER, S. SEMANCIK, *Oxygen Vacancies and Defect Electronic States on the SnO₂(110)-1x1 Surface*, Phys. Rev. B, 1988, 38, 2072–83.
7. T. S. RANTALA, V. LANTTO, *Computational Approach for the Chemical Sensitivity of Oxide and Sulphide Semiconductor Surfaces*, Physica Scripta, 1997, T69, 259–63.
8. T. S. RANTALA, V. LANTTO, T. T. RANTALA, *A Cluster Approach for the SnO₂(110) Face*, Sensors a. Actuators B, 1994, 18–19, 716–19.
9. T. S. RANTALA, V. LANTTO, T. T. RANTALA, *A Cluster Approach for Modelling of Surface Characteristics of Stannic Oxide*, Physica Scripta, 1994, T54, 252–55.
10. T. S. RANTALA, V. GOLOVANOV, V. LANTTO, *A Cluster Approach for the Adsorption of Oxygen and Carbon Monoxide on SnO₂ and GdS Surfaces*, Sensors a. Actuators B, 1995, 24–25, 532–6.
11. I. MANASSIDIS, M. J. GILLAN, *First-Principles Study of SnO₂(110)*, Surf. Rev. a. Lett., 1994, 1, 491–4.
12. I. MANASSIDIS, J. GONIAKOWSKI, L. N. KANTOROVICH, M. J. GILLAN, *The Structure of the Stoichiometric and Reduced SnO₂(110) Surface*, Surf. Sci., 1995, 339, 258–67.
13. J. GONIAKOWSKI, J. M. HOENDER, L. N. KANTOROVICH, M. J. GILLAN, *Influence of Gradient Corrections on the Bulk and Surface Properties of TiO₂ and SnO₂*, Phys. Rev. B, 1996, 53, 957–60.
14. S. R. MORRISON, *Mechanism of Semiconductor Gas Sensor Operation*, Sensors a. Actuators, 1987, 11, 283–7.
15. D. KOHL, *Oxidic Semiconductor Gas Sensors*, [In:] G. Sberveglieri (Ed.), *Gas Sensors*, Kluwer, Dordrecht, 1992, 43–88.
16. V. LANTTO, T. S. RANTALA, *Computer Simulation of the Surface Energy Barrier of Oxidic Semiconductors with Mobile Donors*, Sensors a. Actuators B, 1994, 18–19, 711–15.
17. T. S. RANTALA, T. T. RANTALA, V. LANTTO, *Computational Studies for the Interpretation of Gas Response of SnO₂(110) Surface*, submitted to the Proceedings (Sensors and Actuators B) of the 7th Int. Meet. on Chemical Sensors, Beijing, China, July 27–30, 1998.
18. P. B. WEISZ, *Effect of Electronic Charge Transfer between Adsorbate and Solid on Chemisorption and Catalysis*, J. Chem. Phys., 1953, 21, 1531–8.
19. T. S. RANTALA, V. LANTTO, T. T. RANTALA, *Rate Equation Simulation of the Height of Schottky Barriers at the Surface of Oxidic Semiconductors*, Sensors a. Actuators B, 1993, 13–14, 234–7.
20. V. LANTTO, T. S. RANTALA, *Computer Simulation of the Surface Energy Barriers of Oxidic Semiconductors with Mobile Donors*, Sensors a. Actuators B, 1994, 18–19, 711–15.
21. T. S. RANTALA, V. LANTTO, *Some Effects of Mobile Donors on Electron Trapping at Semiconductor Surfaces*, Surf. Sci., 1996, 352–354, 765–70.
22. T. S. RANTALA, V. LANTTO, T. T. RANTALA, *Effects of Mobile Donors on Potential Distribution in Grain Contacts of Sintered Ceramic Semiconductors*, J. Appl. Phys., 1996, 79, 9206–12.
23. N. W. ASHCROFT, N. D. MERMIN, *Solid State Physics*, Holt-Saunders Japan, Tokyo, 1981.
24. T. T. RANTALA, T. S. RANTALA, V. LANTTO, *Surface Relaxation of the (110) Face of Rutile SnO₂*, Surf. Sci., 1999, 420, 103–9.
25. M. SCHWEIZER-BERBERICH, *Gas Sensors Based on Stannic Oxide: Material, Design, Performance, and Modeling Aspects*, Ph.D. Dissertation, Institute of Physical and Theoretical Chemistry, Eberhard-Karls-Universität Tübingen, Germany, 1998.
26. V. LANTTO, V. GOLOVANOV, *A Comparison of Conductance Behaviour between SnO₂ and CdS Gas-sensitive Films*, Sensors a. Actuators B, 1995, 24–25, 614–8.