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Atomistic understanding of semiconductor gas sensors

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Abstract

Oxide semiconductors form a group of compounds whose specific properties of surfaces and interfaces are used for gas sensing. Our fundamental understanding of the operation principles of these devices is still insufficient. The abundance of phenomena on open oxide–semiconductor surfaces at elevated operation temperatures of the sensors is a central reason for the situation, in addition of the effects originating in the electrode–semiconductor contacts. The exchange of lattice oxygen with the surrounding atmosphere and a possible diffusion of oxygen through oxygen–vacancy donors in *n*-type oxides, especially at elevated temperatures, have also strong effects on the behaviour of semiconductor gas sensors. Atomistic understanding of surfaces is the basis for the understanding of both the receptor and transducer functions of semiconductor gas sensors. The rutile structure tin dioxide, SnO_2, together with its most stable (110) face is the example material here. Especially, we consider the oxygen chemistry at the SnO_2 (110) surface together with its connection to dipole layers and band-gap surface states. For example, the role of tin (II) ions at the reduced SnO_2 (110) surface is discussed. A "transistor model" is also given to describe the transducing properties of semiconductor gas sensors. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Chemical properties; Electrical conductivity; Sensors; SnO_2; Surfaces

1. Introduction

Electronic structure of the material is responsible for most of its properties. This is true for surfaces, too. In semiconductor gas sensors, the chemical information is transduced through the electronic structure of the material and its surfaces 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] Therefore, we concentrate here to the rutile structure *n*-type semiconductor SnO_2 (cassiterite). Atomistic understanding of surfaces is the basis for the understanding of the chemical phenomena in gas–surface interactions (the receptor function) and the mechanisms which transduce these phenomena to a conductivity change of the material. This transducer function 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. Oxygen chemistry at oxide semiconductor surfaces has the key role for the operation of these ceramic gas sensors. The most stable surface of SnO_2 is (110) which is the surface which we mainly consider here.

A lot of experimental research has been done on rutile SnO_2 and TiO_2 surfaces.[2,3] Experimentally, the surface electronic structure of SnO_2 has been investigated with various spectroscopies,[4] the surface topology with LEED and latest with STM.[5] Modern computer codes based on accurate first-principles calculations permit theoretical investigations of these surfaces.[6–9] 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 350°C), the changes introduced by temperature stimulated surface reconstruction may strongly influence chemisorption and

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catalytic processes at the surface. The use of molecular dynamics (MD) methods for the calculation, e.g. of the (110) surface of SnO_2 and rutile TiO_2 allows one to perform simulations at elevated temperatures, and therefore, to complement ab initio calculations with temperature effects. For example, the universal force field (UFF) of Rappe et al.[10] 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 SnO_2 (110) surface. The atomic and electronic structures of the surface change with a change in the lattice oxygen content at the surface. 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 reflect in its electrical conductivity. Grain contacts together with electrode-ceramic interfaces play also an important role for the transducer function in the structure of a porous ceramic gas sensor. Here 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 SnO_2 (110) surface is discussed.

2. Models

2.1. Slab model for SnO_2 (110)–1×1 face

The rutile structure of SnO_2 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 SnO_2 (110) face with these three planes is possible, since it does not leave a net dipole moment in the structure and the cleavage cut between these layers of planes breaks the least number of cation–anion bonds. This is called the stoichiometric surface [see Fig.1(b), top face]. Therefore, the (110) face is the most stable and most dominant surface of the crystallites in porous SnO_2 ceramics. Removal of the topmost bridging-oxygen atoms from the stoichiometric surface 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.[7] However, this kind of termination creates a dipole layer at the surface and leads to a relaxation of the surface.[7,9]

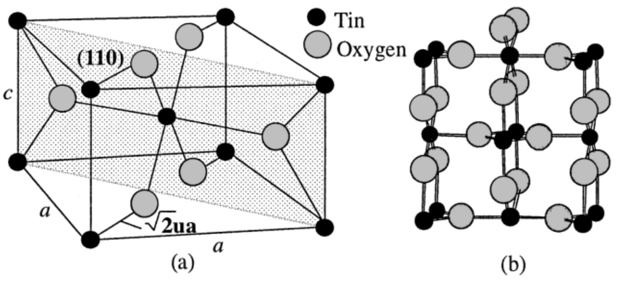

Fig. 1. (a) The primitive tetragonal unit cell of the bulk SnO_2. The lattice parameters are $a = 4.737$ Å, $c = 3.186$ Å and $u = 0.306$. (b) An example of an orthorhombic supercell of the SnO_2 used in the slab model. The top face models stoichiometric and the bottom face reduced (110) face, respectively.

Recently, we have investigated the detailed structure of the (110) face of SnO_2 with ab initio-DFT calculations using both the local density approximation (LDA)[7] and the generalized-gradient approximation (GGA).[9] In our calculations based on both linear combination of atomic orbitals (LCAO) and plane wave pseudopotential (PWPP) approaches, we adopted the slab model of the (110) surface with an orthorhombic supercell with 16 atoms (reduced, Sn_6O_{10}) or 18 atoms [stoichiometric, $(SnO_2)_6$] oriented as shown in Fig. 1(b). With LCAO, however, we found it necessary to double the unit cell in the smallest dimension (3.186–6.372 Å) resulting in 32 and 36 atom supercells. Vacuum between the surfaces was chosen to occupy half or 2/3 of the slab supercell.

2.2. 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 the electron depletion in the grains participate in transducing the chemical surface phenomena to conductivity changes. We have introduced a transistor model to describe the transducing properties of semiconductor gas sensors.[11] The model bears a resemblance to the model of the bipolar transistor. The injection current density of trapped electrons from the surface (e.g. in oxygen ions) into the bulk forms the base current density $J_b = -eKN_t$ in the transistor model [see the schematic band drawing in Fig. 2(a) where arrows show the direction of electron movements at the surface]. N_t is the density of trapped electrons at the surface and K is the fraction of electrons N_t injected in a unit time. The current density from the average flux of conduction electrons impinging against the surface from the bulk is the emitter current density $J_e = 1/4\ ev_{th}n_s$ (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 conduction electrons. The concentration $n_s = n_b\exp(-eV_s/kT)$ for an *n*-type semiconductor at temperature T with a Schottky barrier (band bending) eV_s at the surface and bulk electron concentration n_b. 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 are captured by the surface traps (e.g. adsorbed oxygen). At a steady state, the current density from this captured fraction, γJ_e, is equal to $-J_b$. The rest of the electrons impinging against the surface are assumed to continue to a neighboring grain at a grain contact (Fig. 2) and now the current density crossing the grain contact (the collector current density) is $J_c = (1-\gamma)J_e$ and the current gain

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

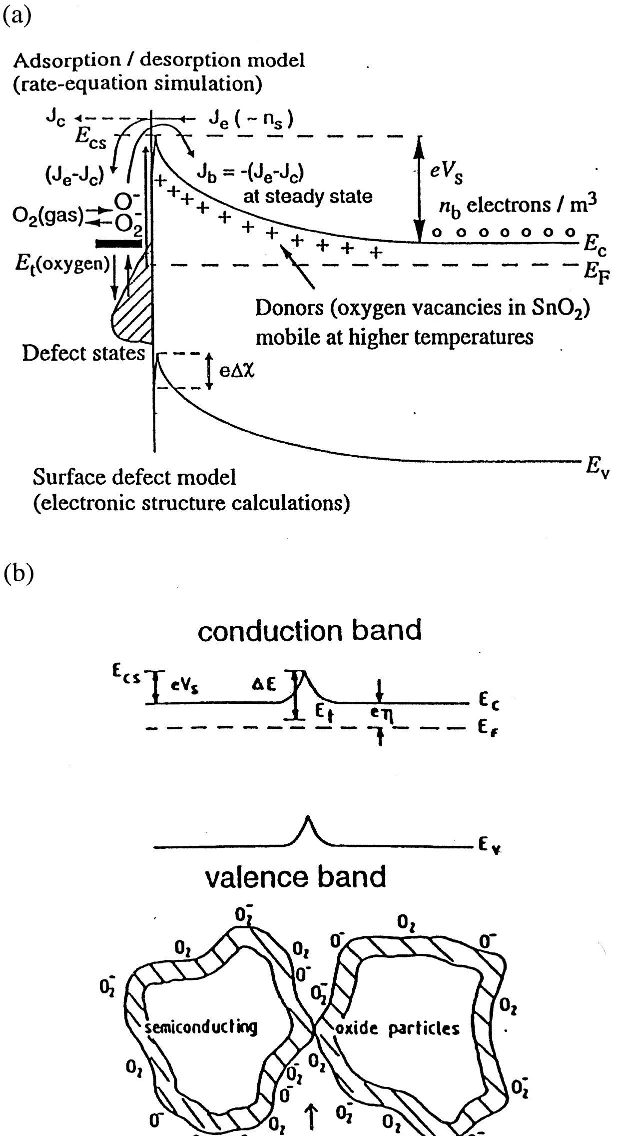

Fig. 2. (a) Schematic band drawing describing some possible phenomena at the surface and in the bulk of an *n*-type oxide semiconductor like SnO_2, and (b) a schematic picture of a grain contact where oxygen ions generate a depletion layer and a Schottky surface barrier eV_S as is sketched in the band picture above the grains. The current densities J_b, J_e 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.

We assume here, in fact, that the oxygen traps are present also inside the grain contact (pressed ceramic). The gain factor $\beta = 1/\gamma$ in the case where electron traps are missing inside small grain contacts.

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, K and β, respectively, are the two important factors in the model. The model is ideal for small ideal contacts between grains [see Fig. 2(b)] and also for small grains without band bending (flat-band situation).

The Schottky barrier at the surface, eV_s in Fig. 2(a), is very sensitive to the surface density of trapped electrons N_t. According to the well-known Weisz limitation,[12] N_t is practically constant during the adsorption/ desorption phenomena and temperature. 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 K for the electron injection from the surface traps, if we assume a weaker temperature-dependence for the gain factor β. Then, the Arrhenius plot of current versus inverse sensor temperature describes the temperature behaviour of the activation energy of the rate constant K.

3. Results and discussion

3.1. Dipole layers at SnO_2 (110) surfaces

The ionosorption of oxygen (electron trapping) on oxide surfaces is important for the gain factor β in the transistor model. On the other hand, the injection-rate factor K 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 that can change due to lattice–oxygen exchange between the surface and ambient atmosphere (Fig. 2). The affinity changes originate in surface dipoles, e.g. from the removal of lattice oxygen at an ionic surface. Similar dipoles also result from the adsorption and dissociation of water on the surface.

The removal of the bridging oxygen to form the reduced 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.[11] A potential difference of about 2 V follows from the release of the bridging oxygens at the SnO_2 (110)–1×1 surface without ionic and electronic polarizations[13] (see Fig. 3). The ionic polarizations through the surface relaxation, respectively, of the stoichiometric and reduced SnO_2 (110) surfaces were calculated in Ref. 7. The most prominent feature in the relaxation at the reduced surface is that the oxygen in the surface plane moves outwards about 0.4 Å with respect to the surface tin atoms,[7,9] as illustrated in Fig. 3(b). This relaxation decreases the potential difference of the dipole layer at the reduced surface by about 0.6 V.[13] 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 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 Sn5s-5p hybrid lone-pair electrons pointing outwards of the surface, as shown in the sketch in Fig. 3(b).

The electronic polarization of tin (II) ions decreases the potential difference in the surface dipole layer to a large extent. A preliminary value for this potential difference at the reduced SnO_2 (110) surface from the first-principles calculations was about 0.2 V.[13] This means that the electron affinity of the (110) surface changes by about 0.2 eV when the bridging oxygen leaves the surface ($e\Delta\chi$ in Fig. 2). An affinity change of about 0.2 eV was found also by Cox et al.[4] from their ultraviolet photoelectron spectroscopy (UPS) measurements upon heating an oxidized (stoichiometric) SnO_2 (110) surface in vacuum up to 700 K. Their results also show that the 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.

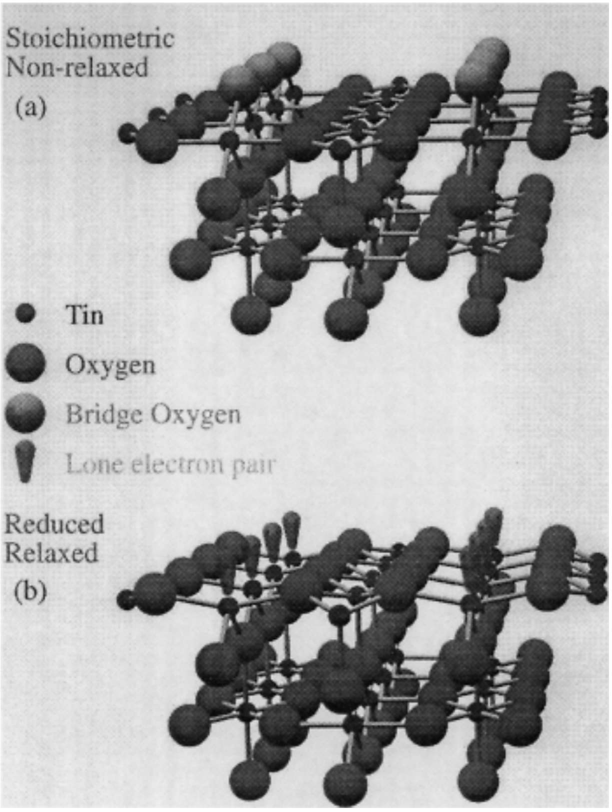

Fig. 3. Perspective view (a) of stoichiometric SnO_2 (110)–1×1 surface without relaxation and (b) of the same surface in the reduced and relaxed form where Sn5s-5p hybrid lone-pair electrons of tin (II) ions occupy stereochemical positions upwards of the surface.

It is well known that humidity has an effect to increase the conductance of SnO_2 gas sensors. It is possible to understand this behaviour on the basis of the transistor model. First-principles calculations[8,14] show the different steps in the adsorption and dissociation of H_2O molecule on the SnO_2 (110) surface. Two OH^- groups follow from the dissociation of a H_2O molecule when a proton is captured by a bridging oxygen to form a ‘rooted’ OH^- group and the other OH^- group stays over the five-fold coordinated surface tin. As a result, there is a dipole layer at the surface with negative charge on the surface side. This increases the electron affinity of the surface and, respectively, decreases the activation energy of the injection-rate constant K. The increase in the injection rate of trapped electrons needs an increase in the conduction electron surface concentration n_s for a balance between the injection and capture rates and, therefore, the sensor current also increases.

3.2. Surface states at the reduced SnO_2 (110) surface

A schematic drawing of a line of tin (II) ions together with their lone-pair electrons at the reduced SnO_2 (110) surface is shown in Fig. 4(a). The line corresponds to a “one-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 one-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,[6,7] 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 this $E(k)$ band with a width of 3.0 eV starts from the valence band edge E_v of SnO_2 at the Brillouin-zone centre $k=0$ and reaches the maximum at the 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 “one-dimensional crystal” in Fig. 4(b) is above E_c and, therefore, a possible injection

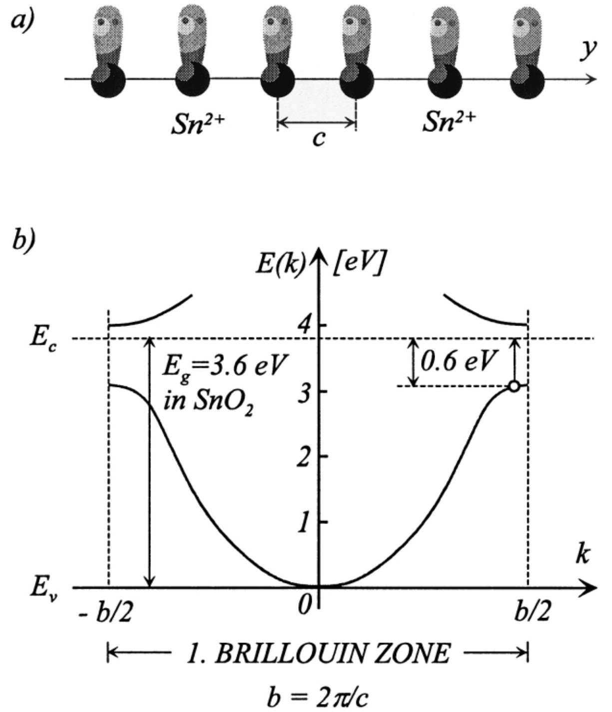

Fig. 4. (a) Schematic description of a line of tin (II) ions with the spacing c and with their lone-pair electrons at the reduced SnO_2 (110) surface and (b) a sketch of the band structure of this "one-dimensional crystal" in the band gap of SnO_2.

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 of great interest to know its exact position and structure in the band gap. Our recent ab initio–DFT calculations based on GGA[9] show that the valence bands of the stoichiometric surface are flat, whereas remowing the bridging oxygen atoms results in strong dispersion at the valence band maximum (VBM). In the symmetry line Γ-X' [the same as in Fig. 4(b)] the calculated surface state band in the band gap increases by about 2 eV from Γ to X'.[9]

4. Conclusions

An atomistic model with an analogy to the bipolar transistor is described for the transducer function of semiconductor gas sensors. The model gives a dynamic description for the operation of semiconductor gas sensors and explains the high sensitivity of these devices through a gain factor. The other factor in the model, the injection-rate factor, relates the operation of semiconductor gas sensors to specific surface properties, such as dipole layers at the surface and surface and other trap states in the band gap. For an atomistic understanding of tin-dioxide gas sensor, atomic and electronic structures of SnO_2 (110) face are considered on the basis of first-principles calculations in the case of lattice–oxygen exchange between the surface and ambient atmosphere (stoichiometric and reduced surfaces). Surface dipoles together with band-gap surface states follow from the removal of bridging oxygen at the (110) face.

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