

Kinetic Monte Carlo simulation of oxygen exchange of SnO₂ surface

Ulla Pulkkinen^a, Tapio T. Rantala^{b,*}, Tuomo S. Rantala^c, Vilho Lantto^c

^a Department of Process Engineering, University of Oulu, FIN-90014 Oulu, Finland

^b Department of Physical Sciences, University of Oulu, FIN-90014 Oulu, Finland

^c Microelectronics Laboratory, University of Oulu, FIN-90014 Oulu, Finland

Abstract

Oxygen adsorption, dissociation and desorption kinetics at the SnO₂ surface is simulated. Both the temperature dependence of equilibrium coverages of various forms of oxygen and their transient behavior in varying temperature are considered. The model is based on our earlier work on rate equation simulations of ionosorbed oxygen, but now refined to include the “bridging” lattice oxygen atoms on the surface. Model for the electrical conductance of porous SnO₂ material as a function of temperature and in terms of the effects from surface coverages of different oxygen components is presented. With the present model, we are able to simulate the essential features in the experimental conductance dependence. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Oxygen chemistry at the SnO₂ surface is sensitive to the surrounding gas atmosphere, a reason why it is used in gas sensor applications [1,2]. The operation principle of these type of sensors is usually based on the measurable conductance response in the bulk material, which is understood in terms of reactions of the gas molecules with O₂⁻ and O⁻ ions adsorbed onto the surface. The role of lattice oxygen, the subsurface and the bridging oxygen atoms on the surface, in particular, is also active. The main mechanism that couples the bulk conductivity of the porous SnO₂ and its surface reactions is the formation of the surface charge dependent Schottky barriers that control the conduc-

tivity of the grain contacts [1–3]. This explains the central role of the charged surface species that react with the gas components of the surrounding gas atmosphere. Detailed understanding of these mechanisms is important, as it offers a way to the development of sensitivity and selectivity of the sensors.

Ideal SnO₂ crystal is an insulator with a bandgap of 3.6 eV, but in practice, the “intrinsic” oxygen vacancies are donors (or double donors) with donor levels at 0.03 eV (0.15 eV) below the conduction band and make the material a wide bandgap semiconductor. The temperature plays an important role in the conductivity and at higher temperatures, where the donors become mobile, the surface and bulk oxygen chemistry become coupled in a subtle way.

In our earlier work, we studied the kinetics of ionic oxygen components at the SnO₂ surface using rate equation simulations [4]. There we developed detailed models for the adsorption, desorption and dissociation of oxygen molecules coupled to the capture of bulk

* Corresponding author. Present address: Institute of Physics, Tampere University of Technology, P.O. Box 692, FIN-33101 Tampere, Finland.

E-mail address: tapio.rantala@tut.fi (T.T. Rantala).

conduction electrons and leading to the reaction rates of these elementary steps. We also modeled formation of the Schottky barrier due to the surface charge and its temperature dependence through physically motivated activation energies. With these models we were able to simulate the temperature dependence of O_2^-/O^- balance, and especially the transition at about 450 K, where O^- becomes dominant. The experimental observations, though largely variant, generally support these models.

Skafidas et al. [5,6] have carried out kinetic Monte Carlo simulations of SnO_2 surface reactions that are quite similar to our present study. These simulations relate to their experimental work on CO and H_2O sensitivity of SnO_2 sensors and qualitatively account for the role of oxygen. In fact, their model of oxygen reactions is very close to ours, but their interpretation differs, and especially, the relation of surface species to the conductivity is simpler. They have not, however, published the model parameters and the evaluation procedure, that does not make a detailed comparison possible.

Papadopoulos and Avaritsiotis [7] extended the above simulations to the study of effects from metallic surface additives, Pd and Pt. They model the surface conductivity in two parts, the conventional contribution from the bulk SnO_2 and another from the tunneling current between the metal particles. They do not, however, consider the effects of metal particles on the surface chemistry.

Our previous model behind the rate equations [4] have been used as a basis of our present simulation of adsorption, dissociation and desorption steps. The reactions of ionosorbed oxygen was modeled on a sound physical basis and appeared to be applicable here without changes. The physisorption step has been refined and made more explicit, but most importantly, the oxygen exchange between the adsorbed ionic form and bridging lattice atoms has been included. Furthermore, new suggestions for the relationship between the surface coverages and conductivity of porous bulk is given here. With these ingredients, we are able to give new insight to both stationary and transient processes of oxygen chemistry at the SnO_2 surface and account for related experiments [3].

The next section reviews the kinetic model of the surface oxygen reactions and resulting reaction rate constants, and in the third section we discuss the con-

ductivity models. The two last sections give results and conclusions.

2. Reaction rates

Our kinetic model is presented in Fig. 1. It consists of four different oxygen species coupled by the elementary reaction steps. The physical parameters for writing reaction rate constants k_1 – k_4 are taken from our earlier rate equation simulation [4], but k_1 is decomposed to k_{in} , k_{out} and k_1 . This is done to model the physisorbed O_2 explicitly assuming a stationary balance with the surrounding gas phase oxygen.

We now write

$$k_{in} = p_{O_2} Z(T) \frac{S(T)}{N_s}, \quad (1)$$

where p_{O_2} is the oxygen partial pressure, $Z(T) \propto T^{-1/2}$ is the collision frequency of gas phase oxygen molecules onto the unit surface in unit time, $S(T)$ is the sticking coefficient and $N_s = 9.17 \times 10^{18} \text{ m}^{-2}$ is the surface site density. For the sticking coefficient $S(T)$ we use the temperature independent value 0.01.

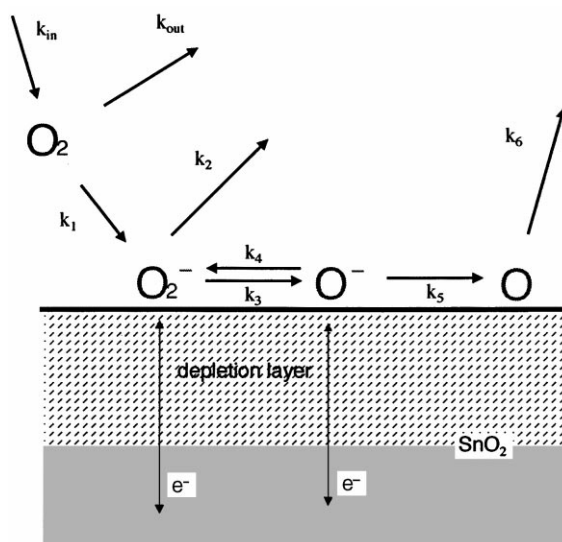


Fig. 1. The model of oxygen exchange at the SnO_2 surface. From left to right the oxygen species are physisorbed, molecularly and atomically ionosorbed, and neutral chemically bound oxygen atom. The k_i are reaction rate constants.

The desorption rate constant

$$k_{\text{out}} = \nu_{\text{O}_2} \exp \left[\frac{-E_{\text{ph}}}{k_{\text{B}}T} \right], \quad (2)$$

is inverse of the dwell time of a physisorbed molecule (t_{ph}), and depends on the frequency factor ν_{O_2} and activation energy E_{ph} .

Thus, for the chemisorption step the reaction rate constant becomes as

$$k_1 = \sigma_{\text{O}_2} \nu_{\text{th}}(T) n_{\text{s}}(T), \quad (3)$$

which involves a capture of an electron from bulk with a cross section σ_{O_2} . The capture depends on the thermal velocity of electrons $\nu_{\text{th}}(T) = (3k_{\text{B}}T/m^*)^{1/2}$ and the density of electrons close to the surface

$$n_{\text{s}}(T) = n_{\text{b}} \exp \left[\frac{-eV_{\text{S}}}{k_{\text{B}}T} \right] \quad (4)$$

and available for the process. Here m^* and n_{b} are the effective mass and the bulk density of conduction electrons, respectively. Thus, n_{b} relates also to the bulk donor concentration.

Note, that the explicit surface coverage θ dependencies do not enter into the reaction rate probabilities explicitly. These become implicitly included in the kinetic Monte Carlo simulation through the nearest neighbor structure of the two dimensional lattice gas model. Thus, the reaction rate constants k_2 – k_4 , taken from [4], become

$$k_2 = \nu_{\text{O}_2^-} \exp \left[\frac{-E_{\text{O}_2^-}}{k_{\text{B}}T} \right] \quad (5)$$

for desorption,

$$k_3 = \sigma_{\text{O}_2^-} \nu_{\text{th}}(T) n_{\text{s}}(T) \exp \left[\frac{-E_{\text{diss}}}{k_{\text{B}}T} \right] \quad (6)$$

for dissociation and

$$k_4 = \nu_{\text{O}^-} \exp \left[\frac{-E_{\text{O}^-}}{k_{\text{B}}T} \right] \quad (7)$$

for recombination. The presently used frequency factors and activation energies are given in Table 1. Diffusion of the surface species is not essential in our model, except for the ionosorbed atoms who need to find a partner for the recombination reaction k_4 , Eq. (7). For the diffusion rate we write

$$k_{\text{diff}} = \nu_{\text{O}^-} \exp \left[\frac{-E_{\text{diff}}}{k_{\text{B}}T} \right], \quad (8)$$

where E_{diff} is the related activation energy.

The most significant development of the model is incorporation of the neutral oxygen atoms, which can be considered to be a part of the lattice in the oxidized or stoichiometric form of the surface. Neutral oxygen becomes removed in the reduction process. For the formation reaction rate constant we write

$$k_5 = \nu_{\text{O}^-} \exp[-E_{\text{O}^-}/k_{\text{B}}T]. \quad (9)$$

The rate constants k_4 and k_5 are equal, as they both are activated by the electron release from the surface O^- to bulk. The reaction rates, however, differ essentially as the nearest neighbor and coverage dependencies are different, the reaction steps are of second and first order, respectively.

Desorption of neutral oxygen is allowed only in form of O_2 molecules, see k_6 (and k_2). As the neutral atoms are assumed to be relatively tightly bound to their lattice sites, diffusion is not modeled and desorption process becomes effective only when two neutral atoms occupy adjacent lattice sites. Thus, the desorption rate constant of lattice oxygen can be written as

$$k_6 = \nu_{\text{O}} \exp \left[\frac{-E_{\text{O}}}{k_{\text{B}}T} \right]. \quad (10)$$

The essential values of the parameters in the model are collected in the Table 1. Highest frequency factors have their origin in the atomic and molecular vibrations, whereas the lowest ones include other phenomena, e.g. electron capture from bulk to surface species in k_1 and k_3 . The temperature dependencies

Table 1

The model parameters: frequency factors ν_i (Hz) and activation energies E_i (eV) for the reaction rate constants k_i ^a

k_i	Freqf. ν_i	Freqf. T-dep.	E_i	Controlling factors
k_{in}	$Z(T)$	$T^{-1/2}$	–	Pressure
k_{out}	10^9		0.1	
k_1	10^{-21}	$T^{1/2}$	eV_{S}	
k_2	10^7		0.9	
k_3	10^{-21}	$T^{1/2}$	$0.4 + eV_{\text{S}}$	
k_4	10^2		0.4	Surface diffusion
k_5	10^2		0.4	
k_6	10^{12}		1.5	Neighborhood
k_{diff}	10^2		0.35	

^aTemperature dependencies of the total frequency factors are given in the third column and “ eV_{S} ” denotes the explicit activation energy dependence on the Schottky barrier. The controlling factors are explained in the text.

of the phenomena included into the frequency factors are also given in Table 1. Activation energies of k_1 and k_3 include the surface charge dependent Schottky barrier eV_S , which we will consider in the next section. See further details of the frequency factors and activation energies in [4].

The involved reactions are of zeroth or first order, except for k_4 and k_6 , where the nearest neighbor interaction is involved. These reactions involve two nearest neighbors, which for reaction k_4 are created by diffusion. The reaction rate, however, should not be sensitive to the details of diffusion, except if the diffusion is very slow.

3. Conductance

Most of the experiments, which give direct or indirect information about the surface chemistry of SnO_2 , relate to the gas sensor activity of this material [1–4]. Thus, modeling of the material conductivity is an essential part of simulation and allows the most direct way to compare simulations with experiments. The conventional conductivity models are based on the effect of Schottky barriers at the grain contacts [2] formed indirectly as a consequence of surface reaction related surface charge. On the other hand, the Schottky barrier is involved in the reaction rates (3) and (6) through the surface charge (4) and, therefore, must be included into the simulation self-consistently.

We assume that there is not only the Schottky barrier eV_S , that leads to the activation energy of conduction electrons, but also other mechanisms adding up to a contribution eV_D . Hence, the total “thermal” activation barrier of current carrying electrons is

$$E_A = eV_S + eV_D \quad (11)$$

and the consequent observed temperature dependent conductance is

$$G(T) = G_0 \exp \left[\frac{-E_A}{k_B T} \right], \quad (12)$$

where G_0 is considered to be a constant. In addition, there may be other mechanisms, which effect on the conductance through the conduction electron surface concentration n_s or mobility. These may relate to the differences in the electronic structures of reduced and stoichiometric surfaces.

The simplest model of the Schottky barrier is a solution of the one dimensional Poisson equation [2]:

$$eV_S = C_S \frac{N_t^2}{N_d}, \quad (13)$$

where $C_S = e^2/(2\epsilon_s)$ is a constant, N_t the surface charge density of the ionosorbed oxygen species and N_d the bulk donor concentration. This model was found to be reasonable, at least, at low temperatures. Another, more sophisticated model includes the mobility and redistribution of donors close to the surface where the electric field is considerable [8].

The surface charge formation in reactions k_1 and k_3 has a strong feed-back through the Schottky barrier, that results in a relatively constant charge in the coverage. In the next section, it will be seen to adjust itself around 0.25–0.3%. This leads to a linear Arrhenius plot of the conductance that allows direct experimental determination of eV_S .

The emergence of eV_D is related here to the transition from the reduced surface to the stoichiometric. Experimentally it is known to be about 0.2 eV [3]. This is also supported by our ab initio calculations [11], where the one-electron levels are found at about 0.2–0.3 eV lower in energy in the stoichiometric case. This indicates that also the conduction electrons may have an additional barrier eV_D to overcome at the grain boundaries.

4. Simulations and results

Simulations were carried out using the kinetic Monte Carlo method on a two dimensional lattice gas model. We describe the surface with a square lattice, usually 100 by 100 or 200 by 200 identical cells with periodic boundary conditions, where only the four nearest neighbor interactions were considered. In simulations, we modeled the reduced surface as “empty” or unoccupied (by adsorbates), and the stoichiometric surface as one oxygen atom occupying each cell. All other occupation configurations fall in between these two limiting cases. No detailed atomic structure [10] was included in the model.

The Fig. 2 presents the equilibrium coverages simulated with the Schottky potential model, Eq. (13). The coverage of physisorbed oxygen depends trivially on

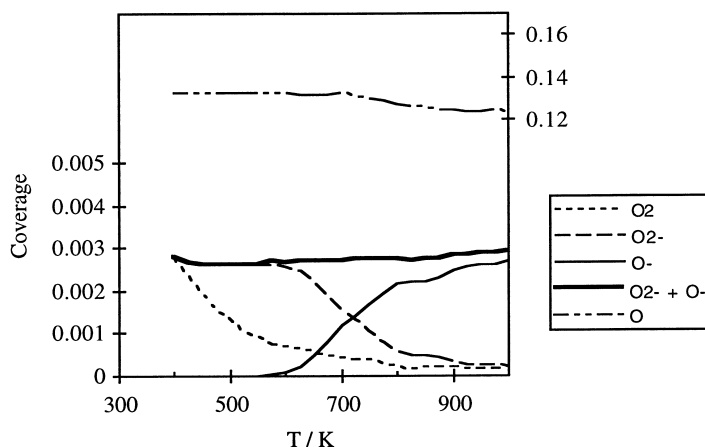


Fig. 2. The simulated equilibrium coverages of the oxygen species. Note that the neutral “bridging” oxygen coverage is down-scaled by a factor of 20.

the oxygen partial pressure and the collision rate of O₂ gas molecules onto the surface. This is only slightly effected by the small activation energy of desorption.

The coverage of neutral oxygen does not seem to depend much on the temperature, either. At low temperatures, it reaches the constant value of about 13.5%, which obviously is determined by the nearest neighbor structure of the model. It follows from the rule that no adjacent neutral oxygen atoms are allowed as they rapidly form a desorbing oxygen molecule. As this is clearly unphysical, the limiting maximum coverage cannot be considered to be realistic and comparable with the experimental ones [9,12]. At high temperatures the neutral oxygen coverage slightly decreases due to the rapidly diffusing O⁻ that following the step k_5 induces the reduction step k_6 .

The transition from O₂⁻ dominating the charged coverage to O⁻ occurs at 450 K, if the neutral oxygen is not included in the model [4]. But here, with neutral oxygen included this transition is seen to be shifted to about 700 K. The obvious reason for this is that the reaction k_5 consumes O⁻, thus decreasing its coverage, but as the surface charge should remain constant, this increases k_1 .

Next, we turn to consider the transient coverage simulations and aim at reproducing the data of [3]. Therefore, we start from the room temperature and reduced surface, raise the temperature with a constant rate of 0.04 K/s to a high enough temperature and equilibrium

situation, and finally, cool down back to the initial low temperature. The equilibrium is reached at about 720 K almost independent of the temperature raising rate, because the reaction rates become exponentially faster.

The coverages in the transient simulation in Fig. 3 do not essentially differ from those of the equilibrium case, except for the neutral oxygen. The transition from the O₂⁻ to the O⁻ dominance is seen to occur just below 700 K. Only the coverages from the heating simulation are shown, except for the neutral oxygen, as the cooling coverages are essentially the same.

The surface is seen to oxidize in heating between 600 and 700 K. As pointed out earlier the maximum value in the present model, around 14%, may be artifact of our model, and should be taken just as a “maximum”, what ever it is. In cooling process, the coverage still slightly increases, but essentially keeps its constant value. This obviously is behind the experimentally observed hysteresis in the conductance of SnO₂, see Fig. 4.

Fig. 4 presents the experimentally measured conductances as a function inverse temperature together with our simulated data. According to the Eq. (12) this should result in straight line in case where E_A is constant. In the experimental heating curve a wiggle is seen between 1.5 and 1.8, which corresponds to the temperature region where neutral oxygen coverage develops. Furthermore, in cooling phase the high

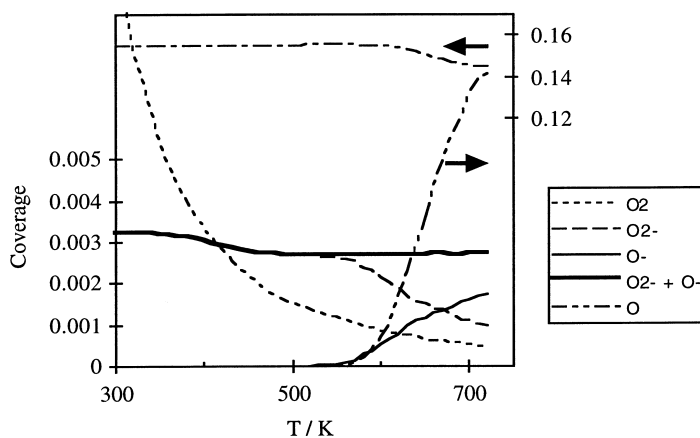


Fig. 3. The oxygen coverages in the transient simulation starting from the reduced surface at 300 K. The heating rate of 0.04 K/s has been applied until equilibrium coverages have been reached at high enough temperature. This is followed by cooling with the same rate. Only the neutral oxygen coverage is shown from the cooling run. Note that the neutral oxygen coverages are down-scaled by a factor of 20.

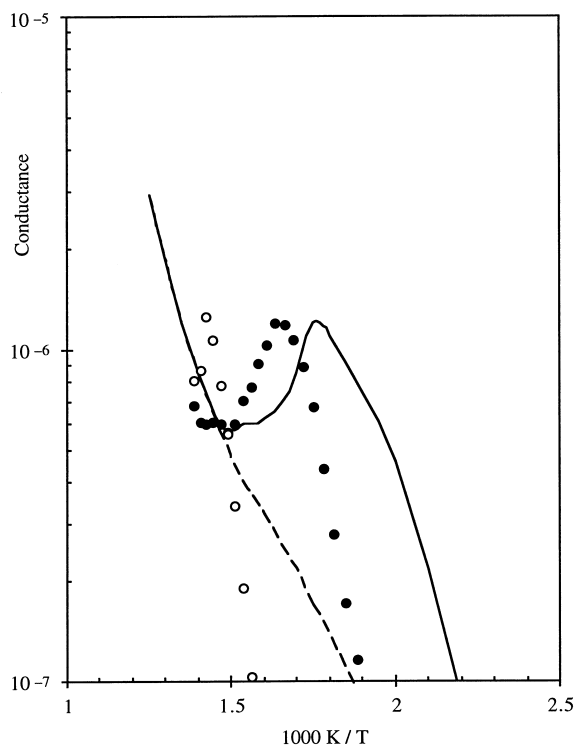


Fig. 4. Conductance during the heating and cooling of a SnO₂ thick film sample with the rate of 0.04 K/s. Experimental [3] heating is shown with the solid curve and cooling with the dashed one. The corresponding simulated data are shown with solid (heating) and open (cooling) circles. The units are not essential to define here.

temperature line is followed, indicating persistence of oxidation of the surface.

We are able to simulate this behavior with a simple model

$$eV_D = \frac{\theta_O}{\theta_O^{\max}} eV_D^{\max}, \quad (14)$$

where θ_O^{\max} is the maximum neutral oxygen coverage from our simulations and eV_D^{\max} was fitted to 0.22 eV to yield the correct wiggle size in Fig. 4. The prefactor G_0 in the conductance (Eq. (12)) was chosen to adjust the simulated data to the experimental.

The hysteresis in the measured temperature dependence of the conductance of the thick film sample of SnO₂ has been a puzzle [3]. Now, the simulated conductance presents the experimental features clear enough to allow us claim that we can explain it with the response from neutral lattice oxygen coverage.

5. Conclusions

We find that at low temperatures O₂⁻ dominates the ionic adsorbates at the SnO₂ surface, while at the higher temperature region oxygen ions are in the form of O⁻. The transition temperature from O₂⁻ to O⁻ is about 700 K depending on the details of the heating process.

The coverages in the transient simulation do not essentially differ from those of the equilibrium case, except for the neutral oxygen. The surface is seen to oxidize in course of heating between 600 and 700 K. During the cooling the surface remains oxidized (or stoichiometric).

The adsorption and presence of neutral oxygen is obviously behind the experimentally observed hysteresis in the conductance of SnO₂. Our simulated conductance presents the experimental features clear enough to allow us claim that we can explain it with the response from neutral lattice oxygen coverage.

Finally, we expect this simulation procedure to be applicable to various other surface chemical reactions.

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