

Modelling and simulation of tin oxide based thick-film gas sensors using Monte Carlo techniques

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Abstract

An advanced model has been developed to explain the experimental results obtained from tin oxide sensors in the presence of carbon monoxide and/or water vapor. The basic principles of the proposed model applied to the simulation are that (a) there is a reduction of the tin oxide surface by both CO and water vapor, (b) at low temperatures, the oxygen vacancies cannot be refilled, (c) in the presence of both CO and water vapor, formate species are formed which, when they desorb, increase the sensor's resistance, and (d) hydroxyl species increase the electron availability and thus the sensitivity in CO. Simulation results are in excellent qualitative agreement with the experimental ones.

1. Introduction

Tin dioxide thick films have been widely accepted during the last few years as one of the most important tools to detect inflammable or toxic gases [1]. Measurements obtained in our laboratory and by other researchers [1, 2] demonstrate that thick-film sensors based on tin dioxide in carbon monoxide, ethanol, methane and butane show a significant response. All the tests were performed at different levels of relative humidity.

In the case of resistive-type solid-state gas sensors, the reactions on the surface cause a charge transfer which modulates the sensor's resistance and the kinetics of these reactions characterize the response of the sensor. Given that the simulation of chemical reactions on solid surfaces using Monte Carlo techniques has been successfully used for the study of the catalytic oxidation of carbon monoxide [3, 4], we decided that the development of an advanced simulation package based on Monte Carlo techniques would give us the opportunity to test different models of surface reactions and to explain the behavior of our sensors in the presence of CO and water vapor.

Moreover, a model based on the dependence of oxygen adsorption on the availability of electrons in the crystal [1, 2] and the contribution of intermediate species in the presence of both CO and water vapor [5] is proposed.

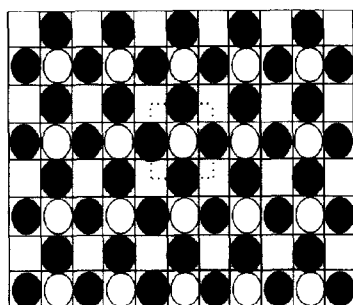
2. The simulation package

The simulation algorithm is achieved by considering an active surface, which is represented by a two-dimensional matrix. Each site of the matrix may be occupied by a surface species. The active sites form a cluster, in which the simulation is applied. In this way, different surface models may be considered. As shown in Fig. 1, the ratio of tin to oxygen atoms may be taken as a parameter in the simulation. The surface shown in Fig. 1(a) has been adopted for all simulation runs in this work. Moreover, fractals of desirable dimension may be constructed in order to study poisoning or island formation [3].

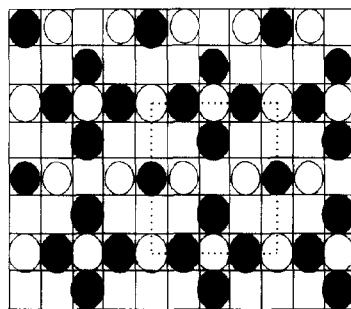
To obtain size-independent results within a short computation time, periodic boundary conditions were adopted so that the simulation could be run on a 486 personal computer.

In the proposed model, the reactions that occur on the surface are considered to have a finite rate, which is defined as a probability. The decision as to which reaction must happen is taken by considering the relative probabilities of all reactions. Of course, there is always the probability that nothing happens.

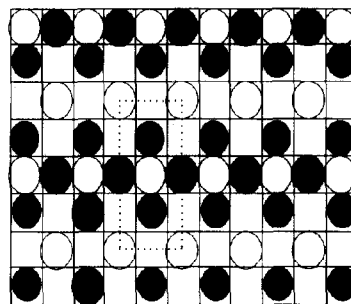
In addition to the set of possible reactions, a number of parameters that influence the reaction probabilities, such as the local availability of electrons (which modifies the adsorption rate of oxygen), or the electrostatic forces between charged adsorbed species, have also been included in the proposed model. Every reaction may or may not depend on a specific parameter. This



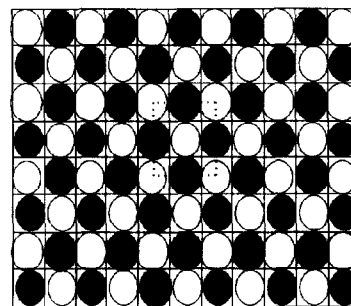
(a)



(b)



(c)



(d)

Fig. 1. Different types of surfaces on which the simulation is applied (●, oxygen atoms; ○, tin atoms): (a) Sn:O=1:2; (b) Sn:O=4:5; (c) Sn:O=2:3; (d) Sn:O=1:1.

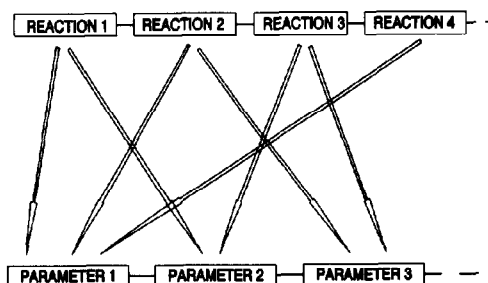


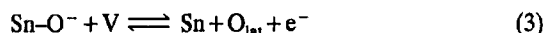
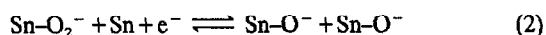
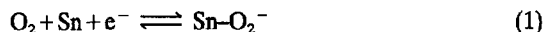
Fig. 2. Representation of the information included in the model file.

kind of information is stored in a file which is called the *model* file, as shown in Fig. 2. In this way, different models can be tested as well as the contribution of a specific parameter to the sensing mechanism.

3. Applications

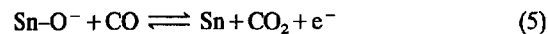
3.1. The effect of oxygen vacancies in CO and in water vapor

Beyond the chemisorbed oxygen atoms on a tin dioxide surface, oxygen lattice atoms play the main role in the sensing mechanism. The removal of these atoms increases the conductivity because the ratio O:Sn is decreased. More specifically, the oxygen vacancies diffuse to the bulk where they can act as electron donors [6]. This oxygen mechanism is included in the simulation by the reactions



Reaction (4) describes the fact that an oxygen vacancy must first diffuse into the bulk in order to become an electron donor. Reactions (1) and (2) describe the chemisorption of oxygen. Finally, reaction (3) describes the filling of oxygen vacancies by chemisorbed oxygen. This reaction is considered to have a high activation energy because of the tight bonding between oxygen and tin atoms. So, at low temperatures this reaction has a very low probability. The probability is increased with temperature. The oxygen mechanism is shown in Fig. 3.

Reactions (5) and (6) describe the mechanism by which CO is included in the simulation, and reactions (7)–(9) show the water vapor mechanism:



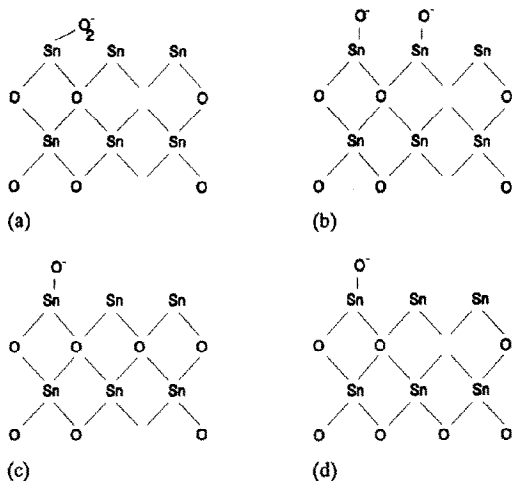
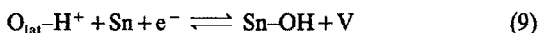
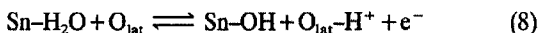


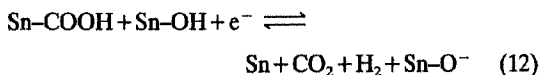
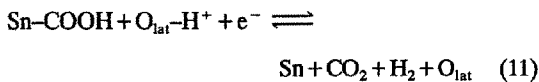
Fig. 3. The proposed oxygen mechanism.



Both CO and water vapor remove lattice oxygen. At low temperature, the removed lattice oxygen creates vacancies that cannot be filled by chemisorbed oxygen. So, after the removal of CO or the water vapor, the resistance of the sensor must be lower than before the entrance of the gas. This phenomenon does not take place at higher temperatures because the chemisorbed oxygen can refill the vacancies. Both experimental and simulation results in the presence of CO at low and high temperature are presented in Fig. 4. The results for water vapor are shown in Fig. 5.

3.2. The synergetic effect of CO and water vapor

When both CO and water vapor exist in the sensor's environment, a synergetic effect between the two gases takes place [5]. This mechanism is included in the simulation by reactions (10)–(12):



Both experimental and simulation results are presented in Fig. 6.

3.3. The sensitivity in CO in the presence of water vapor

The proposed model for the synergetic effect between CO and water vapor, introduces the formation of

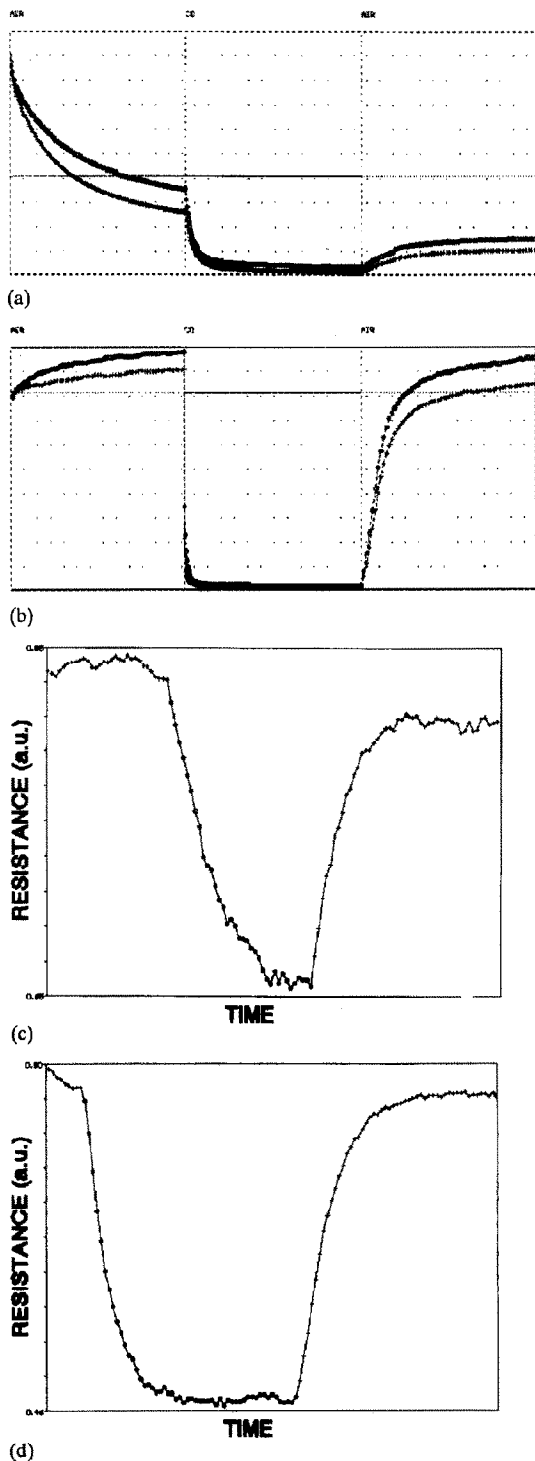


Fig. 4. Experimental results in CO ((a) and (b): [CO]=1000 ppm; total flow=300 ml/min; +, sample D1; O, sample D2) and simulation results ((c) and (d): +, Zero Grade Air; O, CO) for low ((a) and (c)) and high ((b) and (d)) temperature, 150.0 °C and 299.8 °C, respectively.

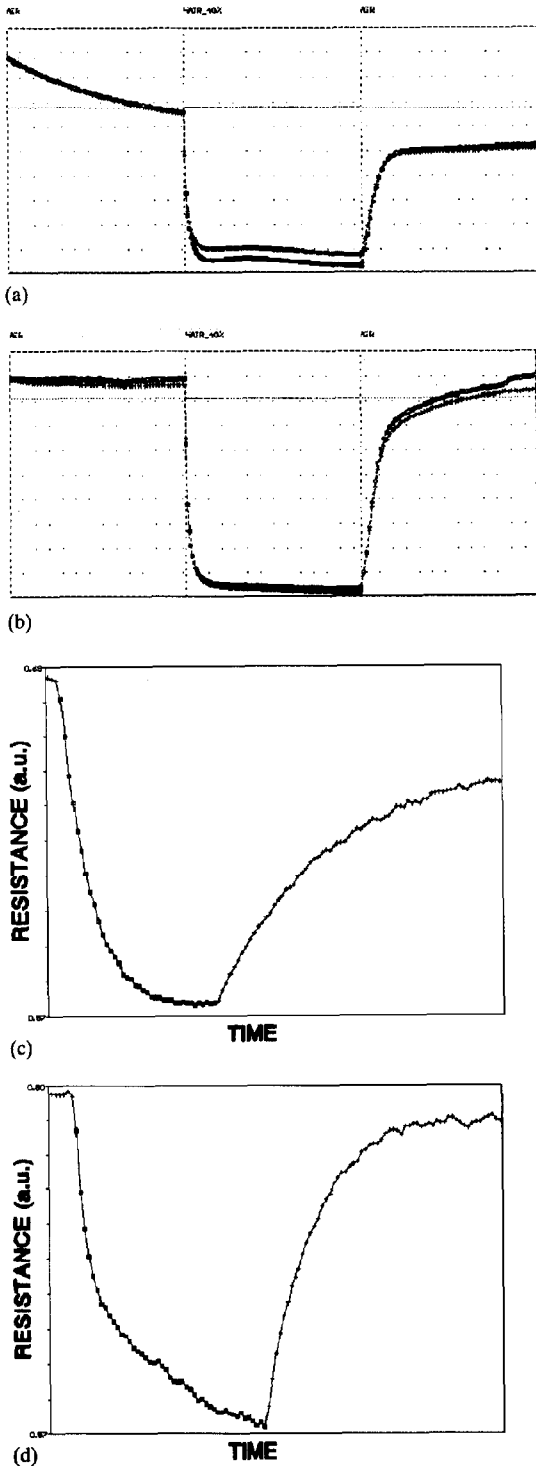


Fig. 5. Experimental results in water vapor ((a) and (b): total flow = 300 ml/min; +, sample D1; O sample D2) and simulation results ((c) and (d): +, Zero Grade Air; □, water vapor) for low ((a) and (c)) and high ((b) and (d)) temperature, 249.2 °C and 299.3 °C, respectively.

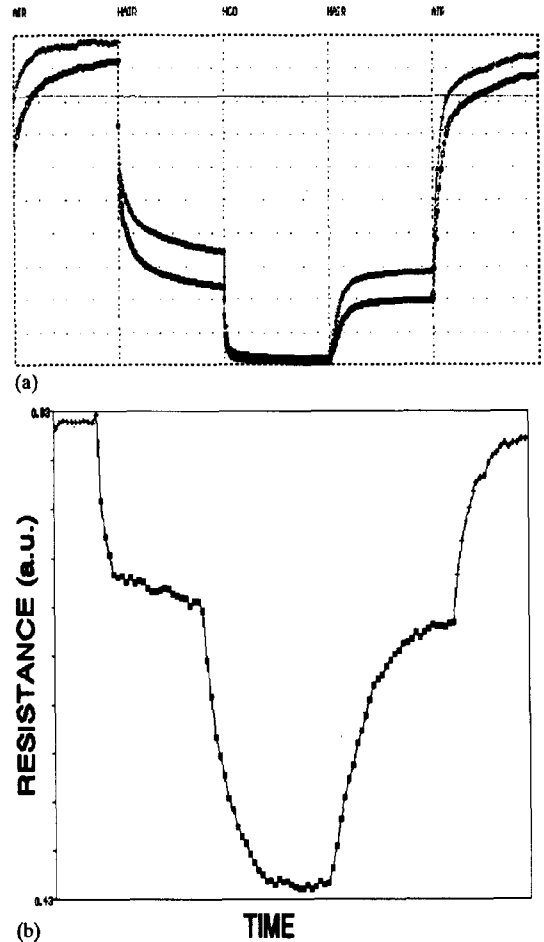


Fig. 6. Experimental (a) (total flow = 300 ml/min; +, sample D1; O, sample D2; temp. = 299.9 °C; relative humidity = 40%) and simulation (b) (+, Zero Grade Air; □, wet air; ■, wet CO) results in the presence of both CO and water vapor.

formate species on the tin oxide surface. The desorption of these species has the effect of taking electrons from the crystal and thus increasing the resistance of the sensor. The experimental results for the sensitivity of CO for different values of relative humidity are shown in Fig. 7. As the relative humidity is increased, the hydrogen atoms that are chemisorbed on oxygen lattice atoms each give one electron to the crystal. So, the availability of electrons in the vicinity of these species is increased and thus the oxygen adsorption rate is increased too. The sensitivity in CO depends on the number of oxygen adatoms. So the sensitivity is increased, as shown in area 1 of Fig. 7. A further increase in the relative humidity does not affect the sensitivity since this effect cannot contribute more, and consequently the sensitivity goes into saturation (area 2 in Fig. 7). At high levels of relative humidity, the aforementioned effect of formate desorption starts to de-

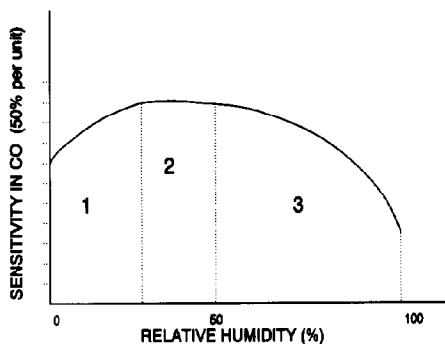


Fig. 7. Experimental curve showing the dependence of CO sensitivity on the level of relative humidity.

crease the sensitivity because it increases the sensor's resistance (area 3 in Fig. 7).

4. Conclusions

It has been shown that Monte Carlo simulation of the reactions occurring on the surface of tin oxide based sensors is a very powerful tool in the analysis of the kinetics of these reactions, and thus in the analysis of a sensor's response. The simulation results

are in excellent qualitative agreement with experimental results obtained with tin oxide thick-film resistive-type sensors in the presence of CO and water vapor.

Acknowledgement

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