



Modeling of the influence of H₂O on metal oxide sensor responses to CO

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ABSTRACT

In this work a model able to predict the dynamic response of conductimetric SnO₂ sensors in presence of humid mixtures of a reducing gas and oxygen is presented. Sensors consisting of large-grained porous films are taken into account. For these sensors the conduction is given by the surface charge carriers, whose density is exponentially related to the height of the potential barrier that establishes at the surface of the grains. The barrier is due to the presence of some localized charge, trapped both on surface intrinsic defects and on chemisorbed species. In this perspective the complete dynamic model of sensor response is obtained by combining a set of differential equations describing the kinetics of surface species adsorption and ionization, the relationship between the density of the charge trapped at the surface and the potential barrier magnitude, and, finally, the relationship between film conductance and the potential barrier height.

The presented work is a development of some previous studies that led to the development of a model of the sensor behavior in dry mixtures of oxygen and CO. In the present study the influence of water on sensor response, in the same operating conditions previously considered, is treated, and a simple model of its effect is proposed. Water is accounted for as a further adsorbant interacting with the other two chemical species. A dissociative adsorption is considered, where adsorbed OH⁻ groups, by losing their electrons, behave as donors and inject a non-negligible (significant) amount of free electrons in the conduction band. The experimental results obtained with a set of 8 Taguchi sensors prove that the proposed model can predict the most important characteristics of the sensor behavior.

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1. Introduction

The interaction of water with solid surfaces was deeply studied by many authors [1–7]. E.g. [7] is a survey that diffusely treats also the adsorption of water on metal oxide. In [8] Goniakowski and Chernikov described the adsorption of water on metal oxide surfaces and proposed adsorption and desorption mechanisms. In [9], Korotchenkov et al. focused on the different adsorption mechanisms of water on semiconductor surfaces as a function of the involved measurement temperature. More specifically some authors studied the influence of water on SnO₂ or other Metal Oxide (MOX) conductivity sensor. In particular the authors of [10] and [11] studied the response of MOX sensor to CO in a humid environment, proposing some chemical reaction paths, whereas Koziej and al. in [12] studied the interaction with adsorbed oxygen. Others, as Sohn et al. in [13] tried to take into account the influence of water on the MOX sensor responses by means of simple correction functions describing the relationship between water concentration and conductance.

Despite the obtained results the water influence was not yet taken into account in a model able to predict the dynamical behavior of the sensor, and capable of predicting both thermal and chemical transients. In this work the authors tried to incorporate the influence of water in a previously developed simplified model [14–17], based on total charged surface state density, in order to obtain a description of the sensor conductance response to humid CO and O₂ mixtures.

The model was obtained starting from the chemical–physical description of the dynamic behavior of the sensor, under the hypothesis that it consists of a large-grained porous film. In this case the grains forming the film present a superficial electric field confined in a thin layer at the surface. For n-type metal oxides, in most operating conditions, the field is generated by a negative superficial charge, trapped over the grain on ionized intrinsic defects and on chemisorbed species, and by a depleted layer under the grain surface. The field gives rise to a potential barrier for the free bulk electrons. Hence, only the surface conduction is relevant, that is due to those electrons (for n-conduction) having a sufficient energy to overcome the grain surface barrier and to pass from one grain to the next. The surface carrier density depends linearly on the bulk carrier density and exponentially on the height of the potential barrier that establishes at the surfaces of the grains. In this perspective the proposed dynamic model is derived starting from the set

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of differential equations describing the kinetics of surface species adsorption and ionization, the relationship between surface charge density and potential barrier height, and finally the relationship between this latter and the film conductance.

The model was obtained by simplifying the above listed relationships, under some hypotheses justified by the specific operating conditions (temperature above 250 °C and below 400 °C). After this, a further simplification was obtained with successive steps based on experimental validations.

The influence of water is accounted for as an individual adsorbant interacting with the other adsorbed chemical species; a dissociative adsorption [7] is considered, for which adsorbed OH⁻ groups, by losing their electrons, behave as donors and inject a non-negligible (significant) amount of free electrons in the conduction band. The experimental results obtained with a set of 8 Taguchi sensors (TGS 26XX and TGS 24XX Figaro sensors [18]) with the system described in [19], prove that the proposed model can predict the most important characteristics of the sensor behavior.

2. Model derivation

2.1. Sensor conductance

For a porous layer, in the case of grains with small contact regions, the free conduction electrons have to overcome the surface potential barrier (V_s) when hopping from one grain to another. In this hypothesis the conductance of the sensing layer can be expressed by [14,20–23]

$$G(T, V_s) = G_0 \exp\left(\frac{-qV_s}{kT}\right) + G_C \quad (1)$$

where q is the electronic charge, k the Boltzmann constant, and T the absolute temperature. The pre-exponential factor in the left term can be written as follows:

$$G_0 = gq\mu_s N_d \quad (2)$$

where g is a constant determined by the semiconductor geometry, μ_s is the electron mobility, and N_d is the density of ionized donors. G_0 is a parameter weakly dependent on temperature, which varies with $T^{-3/2}$ as μ_s . G_C is a constant introduced to take into account different conduction phenomena [20].

In the case of porous layers whose grains are much larger than the Debye length λ_D , typically ranging from few to tens of nanometers [14], the potential barrier V_s is due to the negative charge localized at the surface of the grain related to the intrinsic charged surface state density and modulated by the ionosorbed molecules.

V_s can be expressed as a function of the total charged surface state density that hereafter will be named N_s as follows [14,20]:

$$V_s = \frac{qN_s^2}{2\varepsilon_r\varepsilon_0 N_d} \quad (3)$$

where $\varepsilon_r\varepsilon_0$ is the electrical permittivity of the semiconductor.

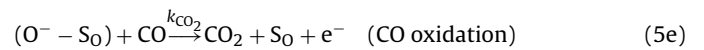
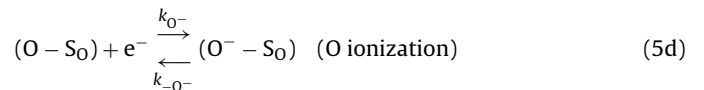
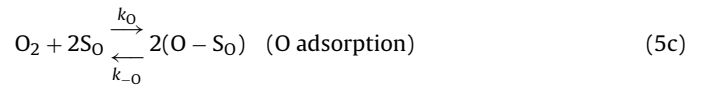
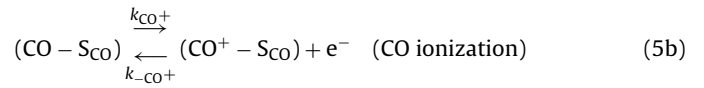
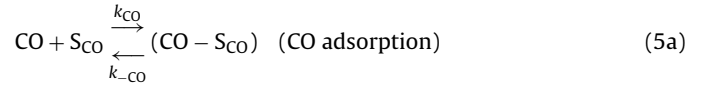
Eq. (3) can be replaced in Eq. (1), thus obtaining the conductance as a function of the total charged surface state density N_s . Moreover, the density n_s of surface electrons that can overcome the potential barrier V_s can be written as:

$$n_s = N_d \exp\left(-\frac{qV_s}{kT}\right) = N_d \exp\left(-\frac{q^2 N_s^2}{2k\varepsilon_r\varepsilon_0 N_d T}\right) \quad (4)$$

If all the donors are supposed to be ionized at the working temperatures, N_d can be considered constant, as it will be also discussed in what follows, and both n_s and G depend only on the total charged surface state density, and explicitly on temperature.

2.2. Model in dry mixtures of CO and oxygen

The film behavior in presence of dry gas mixtures containing CO and O₂ is described assuming the following reactions at the surface [14]:



where S_X indicates the surface adsorbing site for the specie X (e.g., oxygen or Sn atoms), whereas $(X - S_X)$ indicates the adsorbed species X ($X = \text{O}, \text{O}^-, \text{CO}, \text{CO}^+$), and k_X are the rate reaction constants.

As already stated, the total charged surface state density N_s , in Eq. (3), is given by the charged species that are formed at the surface from the adsorbed gases, but also by the density of ionized intrinsic superficial states (defects), hereafter named N_{si} , whose density can vary depending on the temperature. In particular, the following Eq. (6) can be written:

$$N_s = N_{si} + [\text{O}^- - S_{\text{O}}] - [\text{CO}^+ - S_{\text{CO}}] \quad (6)$$

It is considered that only the reactions involving charged species ((5b), (5d), (5e)) are relevant for the dynamic behavior. In fact, the adsorption reactions are assumed to be fast phenomena, so that, in practice, the adsorption reactions ((5a) and (5c)) are always at the equilibrium. Under this hypothesis, and assuming first order kinetics, the dynamics of the surface states N_s as a function of temperature and chemical condition variations can be described by three first order differential equations according to [14], where it is assumed to be far from saturation:

$$\begin{aligned} \frac{dN_{si}}{dt} &= k_i n_s N_i - k_{-i} N_{si} \\ \frac{d[\text{CO}^+ - S_{\text{CO}}]}{dt} &= k_{\text{CO}^+} [\text{CO} - S_{\text{CO}}]_0 - k_{-\text{CO}^+} [\text{CO}^+ - S_{\text{CO}}] n_s \\ \frac{d[\text{O}^- - S_{\text{O}}]}{dt} &= k_{\text{O}^-} [\text{O} - S_{\text{O}}]_0 n_s - k_{-\text{O}^-} [\text{O}^- - S_{\text{O}}] \\ &\quad - k_{\text{CO}_2} [\text{CO}] [\text{O}^- - S_{\text{O}}] \end{aligned} \quad (7)$$

The first equation, where N_i is the intrinsic superficial state density, describes the intrinsic sensor behavior, e.g., the intrinsic surface states ionization and neutralization, and it describes the dynamics of the sensor in an inert environment where no adsorption is possible. The second and third equations describe the extrinsic surface state contribution to sensor response in CO and oxygen, i.e., the ionization and neutralization of adsorbed species and the oxidation of CO. In these latter equations $[\text{CO} - S_{\text{CO}}]_0$ and $[\text{O} - S_{\text{O}}]_0$ are the steady state densities of the adsorbed CO and O, obtained imposing, starting from Eqs. (5a) and (5c), $(d[\text{CO} - S_{\text{CO}}])/dt = 0$ and $(d[\text{O} - S_{\text{O}}])/dt = 0$ (that is assuming that ionization is the rate determining process) [14]. The explicit expressions of $[\text{CO} - S_{\text{CO}}]_0$ and $[\text{O} - S_{\text{O}}]_0$ are reported in Table 1.

It is assumed that, when ionization occurs, the dominant effect is the variation of the potential barrier height V_s and on the other hand, the effect of the variation of the free electron number is

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