Modeling of a p-type resistive gas sensor in the presence of a reducing gas

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ABSTRACT

The detection mechanism in gas sensors based on semiconductor materials is mainly due to charge-transfer. The interaction between the semiconductor surface and the gas is approached by the theory of chemisorption. Based on the Wolkenstein adsorption model, we propose a model simulating the reaction between the ionized oxygen species adsorbed at the surface of a p-type semiconductor with a reducing gas as a function of: (i) work temperature; (ii) oxygen pressure; (iii) gas concentration; and (iv) characteristic properties of the semiconductor/gas interaction. The influence of the main parameters of the model on sensor performance is analyzed through the response curve as a support tool for the design and optimization of suitable materials for a desired sensing application.

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1. Introduction

Up to now, most devices have been based on n-type metal oxide such as ZnO, SnO_2, WO_3, TiO_2 and on p-type metal oxide such as Cr_2O_3, Cu_2O and CuO [1–6]. An interesting theoretical model for gas adsorption on semiconductors, which has been proposed by Wolkenstein, takes into account the effect of electronic coupling between the semiconductor and the adsorbate species [7,8].

In this model, the adsorption of gas species is carried out with two successive steps: 'weak or neutral chemisorption' and 'strong or ionized chemisorption' [9–13]. Localized electronic states are created by chemisorbed species. These states serve as traps for electrons or holes (acceptor-like or donor-like states, respectively) depending on their nature, which yield a charge transfer between the semiconductor and chemisorbed species (change of the electrical properties of semiconductor layer). Avner Rothschild et al., according to Wolkenstein's model, presented a computational method for numerical calculations of the amount of chemisorbed species and the resultant electrostatic potential barrier as a function of the semiconductor/gas interaction and the operating conditions. They focus on simulating the depletive chemisorption of oxygen on n-type semiconductor. They found that the chemisorption induced potential barrier is proportional to the logarithm of the ambient oxygen pressure which induces a change in the electrical conductivity in the semiconductor [14]. Different models are simulated to describe and optimize the sensor response.

In this paper we present our new numerical model to simulate the detection behavior of a gas sensor based on a p-type semiconductor under reducing gas. The ultimate goal of this work is to find the best material for a given gas and reciprocally, to find the best suited gas for a given material.

This model aims to simulate quantitatively the sensor response to different gases as a function of the sensor properties and operating conditions. This sensor response can be controlled primarily by the conduction mechanism and the chemical interactions between the sensor and the ambient gas.

In this work we first apply the Wolkenstein model on p-type semiconductor gas sensor operating under oxygen and reducing gases.

We then present how a variation of operating conditions such as: temperature, reducing gas pressure, etc. can influence the electronic properties of the sensor (coverage degree, resistance, sensitivity).

Finally, we describe the applications of the model as a tool to assist in sensor design, including selection of suitable materials, for desired application with optimal response.

2. Interaction semiconductor/gas

The sensor layer model consists of a continuous thin film of crystalline grains in contact with the atmosphere as schematically presented in Fig. 1a. According to the Wolkenstein's model, the adsorbed neutral oxygen molecules O_2 at the semiconductor

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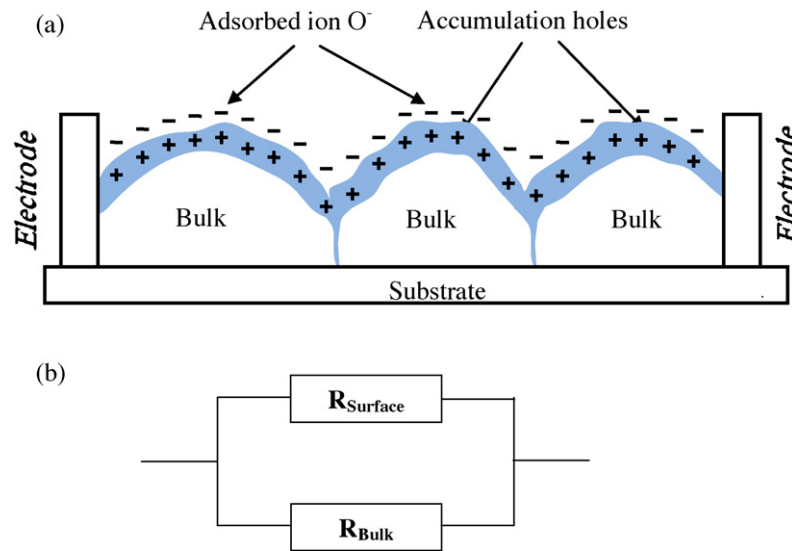
**Fig. 1.** Sensor scheme (a) sensor structure (b) equivalent electrical circuit.

surface are partially ionized into O_2^- ions with a single negative electric charge by attracting an electron from the valence band of a p-type semiconductor [Eqs. (1.a)–(1.b)]. This electric surface charge induces an underlying positive accumulation zone formed by holes, which induces a lower resistance layer which extends from grain to grain covering the whole surface of the sensor. The surface resistance thus decreases by the presence of atmospheric oxygen (Fig. 2a).
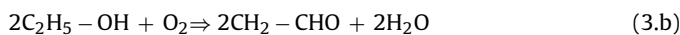
$$(O_2)_{gas} \Leftrightarrow (O_2)_{ads} \tag{1.a}$$

$$(O_2)_{ads} + e^- \Leftrightarrow (O_2^-)_{ads} \tag{1.b}$$

At high temperatures of ~473–523 K, the oxygen molecules O_2 dissociate into oxygen atoms which are adsorbed separately. The electric surface charge is then formed by O^- ions as shown in Eqs. (2.a)–(2.b).

$$(O_2)_{gas} \Leftrightarrow 2(O)_{ads} \tag{2.a}$$

$$(O)_{ads} + e^- \Leftrightarrow (O^-)_{ads} \tag{2.b}$$

The addition of a reducing gas in the atmosphere allows the capture of part of the adsorbed oxygen ions and the consequent return of trapped electrons in the valence band. This process reduces the electric charge of the accumulation zone and increases the layer resistance. This reaction scheme involves a dissociative adsorption of oxygen which is more favorable to a reaction with a reducing gas than molecular adsorption of O_2 and O_2^-. It is described in the specific case of ethanol by the reaction in Eq. (3.a):

$$C_2H_5-OH + O^-_{ads} \Rightarrow CH_2-CHO + H_2O + e^- \tag{3.a}$$
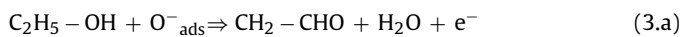
Eq. (3.a) is a part of the oxidation reaction

$$2C_2H_5-OH + O_2 \Rightarrow 2CH_2-CHO + 2H_2O \tag{3.b}$$

It is clear that this reaction scheme can be extended to other vapors or reducing gases (R) by Eq. (4)

$$R + O^-_{ads} \Rightarrow R_1-O + X + e^- \tag{4}$$

where X and R_1-O are the products of the reaction.

3. Wolkenstein adsorption theory and model

As previously mentioned, the Wolkenstein model considers the adsorption of an oxidizing gas species as carried out in two successive steps, namely 'weak or neutral chemisorption' and 'strong or ionized chemisorption'. During the first step, the bond between the adsorbate $(O)_{ads}$ and the substrate is weak and does not involve electronic transfer; in this case the electrons of the atom (or molecule) remain located in the vicinity of the adsorbate involving a simple deformation of the orbitals. The binding energy of the adsorbate is E_a and involves an equivalent loss of free energy from the initial level E_{init} of the system during the adsorption process. This neutral chemisorption does not change the electrical properties of the material; however, the perturbation created by the adsorbate induces surface states E_{ss} in the valence band that acts as an electron trap (Fig. 2a).

The second step (strong chemisorption) occurs when an electron of the valence band, whose energy is E_{vb}, is transferred from the semiconductor to the adsorbed species $(O^-)_{ads}$. The binding energy of the adsorbate is increased by $(E_{vb} - E_{ss})$, which represents the loss of free energy of the system during the ionization process. This process involves the creation of a negative superficial charge and a chemisorption induced surface energetic barrier $\Delta E_{(holes)} = -q \cdot \Delta V_s$, see Fig. 2b. where ΔV_s is the potential bending associated to the accumulation of the (positive) electric charge and q is the electron charge.

Let us name $E_{vs} = E_{vb} + \Delta E_{(holes)}$ the surface valence band level, one can then write $E_{vb} - E_{ss} = (E_{vs} - \Delta E_{(holes)}) - E_{ss}$, where the energy difference $(E_{vs} - E_{ss})$ is also the difference $\chi_{ads} - \chi_{sc} = E_{fort}$ between the electronic affinities of the neutral adsorbate and the semiconductor. The binding energy of the strongly adsorbed species can be written $E_a + (E_{vb} - E_{ss}) = E_a + E_{fort} - \Delta E_{(holes)}$. This expression shows that the binding energy of the strongly adsorbed species decreases when the adsorbed charge increases, which facilitates the desorption mechanism. Therefore, the binding energy of the strongly adsorbed species, $E_a + (E_{vb} - E_{ss})$, is also the activation energy of the strong desorption process allowing the return of the free energy of the system at E_{init}. The neutral chemisorption mechanism is only limited by the number of adsorption sites at the surface of the material, while the strong adsorption mechanism is limited by the upper band bending.