Optimization of thin film gas sensors for environmental monitoring through theoretical modeling

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ABSTRACT

The task of optimization of gas sensor characteristics such as absolute value and temperature range of sensitivity, time response and selectivity is one of the most important problems of gas sensor design. Unfortunately, at present time the decision of this problem has empirical character, which is not effective, because of multi-factor task. We propose another approach to GS optimization, which is based on the theoretical modeling of gas sensing characteristics in the framework of chemisorptional views. Such approach is more effective as it permits both to understand and to predict the influence of surface and bulk parameters of metal oxide films on sensing characteristics.

The conclusions about optimum parameters combination of SnO_2 thin films were made. Many of these conclusions have experimental confirmation.

Keywords: SnO_2; thin film; gas sensors; simulation; chemisorption; optimization.

1. INTRODUCTION

Problem of optimization is a key factor in design and fabrication of any electronic sensor. In the case of gas sensors (GS) it has some specific moments and peculiarities due to absence of strict quantitative theory, which would describe GS operation. Some of these semi-quantitative approaches one can find elsewhere[1-4]. Since the number of physical and chemical parameters, which characterize the sensor properties are large, and some of them are controlled with difficulty, the problem of optimization today has empirical character and remains a kind of an art. Therefore, present situation in the field of gas sensorics[5] is characterized by searching of adequate theoretical models, which can promote GS optimization. Here the term optimization means the achievement of necessary or the most available values of sensitivity, selectivity and transient times of GS at given conditions. In our previous works[6-8] we developed thin film GS quantitative model, based on chemisorptional theory of Volkenstein[9]. This model allowed both to understand the main moments of GS behavior and to give some recommendations to optimization of GS technology.

2. TREATMENT OF GS PARAMETERS AND CHARACTERISTICS

2.1. Integral parameters determining gas sensitivity characteristics

One can select the following main physical parameters, which influence on GS characteristics, and that are needed to control both during manufacturing process and after various treatments. They are:

1) geometric and structural parameters of the film:

-length, width, thickness and porosity of the film;
-effective size of grains or crystallites, area of inter-grain contacts ;
-crystallographic structure and orientation of grains, crystallites (energetic parameters of adsorption/desorption (**A/D**) processes are closely connected with these parameters)

2) electronic parameters of chemisorbed species (number of surface sites; **A/D** energies; positions and distributions of local electronic levels in band gap of semiconductor due to chemisorption and so on)
3) composition or bulk and surface stoichiometry of the film (these parameters determine the electron concentration, initial surface potential, own surface charge through the number of oxygen vacancies)
4) parameters of the impurities and additives: type of impurity; effective size and surface density of clusters; bulk and surface concentration; electrical activity, etc. Metal catalysts particles are the main controlled additives. From uncontrolled impurities it is required to isolate carbon and its compounds, various forms of water and interfering chemisorbed species between water and carbon-contained species.

Part of the SPIE Conference on Chemical Microsensors and Applications II
Boston, Massachusetts • September 1999
SPIE Vol. 3857 • 0277-786X/99/$10.00

Anyhow these parameters must be taken into account at theoretical consideration.

2.2. Base Model of Gas Sensitivity. Rate Equations

The GS operation mechanism can be conditionally divided into two steps: receptor function, when the appearance of active impurities in gas phase leads to some chemical changes on semiconductor surface, and transducer function, when these chemical changes are transformed into output signal (in our case - conductivity) due to electrophysics of film. The main difficulties in description and modeling arise on the first step.

Our model is based on existence of two forms of chemisorbed species: neutral and charged. Neutral form of chemisorbed species can trap the conduction band electrons and become charged or ionosorbed form. Basis of our treatment is kinetic equations within Gleston theory of absolute rates of **A/D** reactions. The kinetic equations for carbon monoxide interaction with SnO_2 surface (as a well-known example) may have the following forms:

$$dN_O^0/dt = \alpha_O P_{O_2}(N^* - N_O)^2 - \beta_O (N_O^0)^2 - \beta_1 N_O^0 + \beta_2 N_O^- \tag{1}$$

$$dN_O^-/dt = \beta_1 N_O^0 - \beta_2 N_O^- - \alpha_{CO} P_{CO} N_O^- + \beta_{CO} N_{CO_2}^- \tag{2}$$

$$dN_{CO_2}^0/dt = -\beta_3 N_{CO_2}^0 + \beta_4 N_{CO_2}^- - \gamma N_{CO_2}^0 \tag{3}$$

$$dN_{CO_2}^-/dt = \alpha_{CO} P_{CO} N_O^- + \beta_3 N_{CO_2}^0 - \beta_4 N_{CO_2}^- - \beta_{CO} N_{CO_2}^- \tag{4}$$

where N_O, N_O^0, N_O^- - the surface concentrations of total number of oxygen atoms and its number in neutral and single charged form correspondingly; N_{CO_2}, $N_{CO_2}^0$, $N_{CO_2}^-$ - similar designations for CO_2 molecules; P_{O_2}, P_{CO} - partial pressure of O_2 and CO; α_O, α_{CO}, β_O, β_{CO}, γ - coefficients of adsorption and desorption; β_1, β_3 - coefficients of charging of particles; β_2, β_4 - coefficients of particles neutralization; N^* - total number of surface sites.

Here we assumed that reaction of CO conversion goes by Redeal-Eley mechanism[10], thus only two chemisorbed species are on the SnO_2 surface: oxygen and carbon dioxide (the product of detection reaction). At given temperature range (T>200°C) only atomic form of oxygen exists on surface due to dissociation. At low temperatures one must take into account molecular form of oxygen too. In principle, molecular oxygen does not interact with CO, but it can influence sensitivity due to occupation and competition for surface sites with atomic oxygen. Schematic illustration of rate balance in (1)-(4) is given in Fig.1.

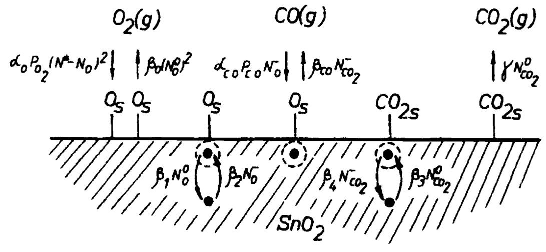

Fig.1. Schematic illustration of gas particle balance on the SnO_2 surface in the presence of carbon monoxide in air.

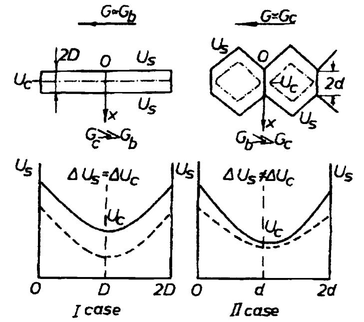

Fig.2. Schematic illustration of grain geometry, corresponding two mechanisms of electron transfer in polycrystalline film. G_c and G_b are contact and bulk conductance.

In the absence of active gas one can consider GS behavior in oxygen atmosphere. Studying this mode one can answer on most questions, connected with active mode of GS operation.

2.3. Steady-State Consideration

It was demonstrated[7], that in steady-state condition, associated with active mode of gas detection, equations (1)-(4) can be reduced to one equation, that is to N_O^-. Algorithm of this solution is connected with relation between surface charge N_S and surface potential U_S. Total surface charge is defined as

$$N_S = N_O^- + N_{CO_2}^- + N_{ss}^{+,-} \tag{5}$$