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Models for the Chemo-Physical Reactions at the Sensitive Layer of Semiconductor Gas Sensors and their Application in the Simulation of these Devices

Z. Gergintschew and D. Schipanski

Institut für Festkörperelektronik, Technische Universität Ilmenau
Weimarer-Straße 32, D-98684 Ilmenau, GERMANY

Abstract

In this paper we consider models for some adsorption effects, the resulting change of the work function at metal-oxide-semiconductor sensitive layers of gas sensors and their implementation in a two dimensional device simulator, which solves the Poisson equation. An example for the application of this simulation program is given with a Suspended Gate Field Effect Transistor.

1. Introduction

The importance of the development tools like the numerical device simulation in the sensor technics increases with the introduction of microelectronic sensor devices and manufacture methods. In order to regard the modelling of sensor devices as complete, apart from the common electrical description, the interaction of the sensor with the detected enviroment has to be taken into account in the simulation. That's why, we consider in our paper a model for the adsorption effects and the resulting work function change at the metal-oxide-semiconductor gas sensitive layers of microsensors.

2. Theoretical description of the adsorption effects for O_2

One of the main reactions of the metal-oxide-semiconductor sensitive layers (we consider here only n-type materials like ZnO, SnO_2) is the interaction with oxygen. Neglecting the reaction with instationar metal ions we have at the oxide surface the following effects:

$$\begin{array}{rcl} O_2(g) & \rightleftharpoons & O_2 \quad \} physiosorption \\ O_2 + e & \rightleftharpoons & O_2^- \\ O_2^- + e & \rightleftharpoons & 2O^- \end{array} \Big\} chemiosorption$$

To work out the models for these reactions we have used 'The Electron Theorie of Catalysis on Semiconductors' by Volkenstein [1]. He distinguishes between the 'weak' (^{o}) and the strong ($^-$) chemiosorption in dependance on the wave function interaction between the binding electron of the adsorbed particle and the oxide lattice. For the

further considering we assume a monocrystal oxide and an adsorption without dissociation. After complicated operations with the equation for the steady-state adsorption equilibrium (like Volkenstein [1] and Geistlinger [2]) we have for the fractional surface coverage θ with O_2^- the following expression:

$$\theta = \frac{N}{N_0} = \frac{\beta P_{O_2}}{\beta P_{O_2} + 1} \tag{1}$$

with:

$$\beta = \frac{s_0}{\nu(\sqrt{2\pi MkT}) \exp\left(\frac{-Q^o}{kT}\right)} \cdot \frac{1}{f^o(1 + \exp\left(\frac{E_f - E_c}{kT}\right)} \tag{2}$$

Here are: N the density of the occupied surface states; N_0 the density of the maximal available surface states; P_{O_2} the oxygen partial pressure; s_0 adhesion coefficient; M the mass of the adsorbed particle; k the Bolzmann constant; T the temperature; ν the phonon frequence of the adsorbed particle; Q^o the weak chemosorption energy; E_c the energy of the conduction band edge; E_f the Fermi energy. E_s is the energy difference between the strong and the weak chemiosorbed particles. f^o and f^- are the occupation probabilities for the weak and strong chemiosorption (eq.3):

$$f^o = \frac{1}{0.5 \exp\left(\frac{E_f - E_s}{kT}\right) + 1}; \quad f^- = \frac{1}{2 \exp\left(\frac{E_s - E_f}{kT}\right) + 1} \tag{3}$$

In eq.2 the fractional coverage depends additionally on the energy difference $(E_f - E_c)_s$ at the sensitive layer surface, that means on its doping, on the external electrical fields and on the number of the already adsorbed particles. The electron exchange between the adsorbed molecules and the oxide (mainly due to strong chemiosorption) leads to a charging of the surface:

$$Q_s = e\ N_0\ \theta^- = e\ N_0\ f^-\ \theta \tag{4}$$

e is the elementary electronic charge.
The changing of the work function $\Delta\varphi \cdot e$ (eq.5) of the sensitive layer, which the sensor effect of many devices is based on, is defined by the band bending $\Delta V_s \cdot e = \Delta(E_f - E_c)_s$ due to Q_s and by the electron affinity changing $\Delta\chi$ at the surface caused by dipol effect of the polarised adsorbed particles [3].

$$\Delta\varphi = \Delta V_s + \frac{\Delta\chi}{e} = \Delta V_s + \frac{\mu_{ad} N_0 \theta}{\varepsilon_s \varepsilon_0} \tag{5}$$

$\varepsilon_s\varepsilon_0$ is the permittivity at the surface of the sensitive layer and μ_{ad} the dipol moment of one adsorbed particle.

3. Implementation of the models in the simulator CADI-CHEM

For the calculation of the band bending at the sensitive layer surface and in this way of the work function changing in dependance on the gas adsorption, doping and external fields, it is necessary to solve the Poisson equation (eq.6). For the interface sensitive layer/atmosphere the following equation system is valid:

$$\frac{d^2\varphi}{dz^2} = -\frac{1}{\varepsilon}[Q_s(E_f, P_{O_2}) + eV_o^{\cdot} + eV_o^{\cdot\cdot} + N_A^+ - N_D^- - en(z) + ep(z)] \quad (6)$$

$$Q_s = -eN_0 f^- \theta(E_f, P_{O_2}) \quad (7)$$

Here are: φ the electrical potential; $V_o^{\cdot}, V_o^{\cdot\cdot}$ the density of the singly and doubly ionised oxygen vacancies; N_A, N_D the acceptor and donator doping density; n, p the electron and hole density of the sensitive layer. This equation system is solved by the 2-dimensional device simulator CADI-CHEM, which solves additionally the Poisson equation in the Si-area and the Laplace equation in the insulator areas with a Finite Difference Method.

4. Application on a SGFET gas sensor

The simulator CADI-CHEM is applied for the modelling of a Suspended Gate Field Effect Transistor (SGFET) [4]. As shown in Fig.1, it is a MISFET with an air gap between the gate electrode and the gate insulator (100 nm SiO_2, 100 nm Si_3N_4). A ZnO sensitive layer is located over the air gap. The changing of its work function due to gas adsorption leads to a changing of the transistor threshold voltage.

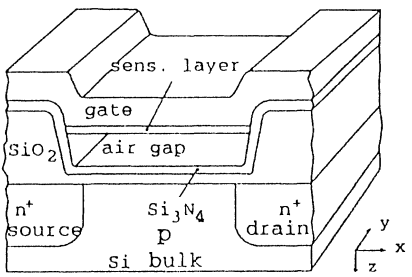

Figure 1: Schematic plot of a SGFET gas sensor

The gate area of a SGFET was calculated with the program CADI-CHEM. Fig.2 shows the energy band diagram of this stucture with and without gas adsorption.

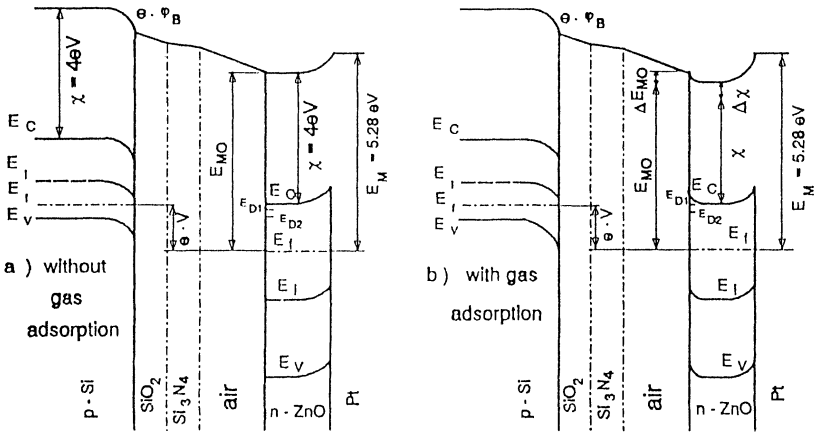

Figure 2: Energy band diagram of the gate structure of a SGFET with ZnO as sensitive layer

In this case the changing of the work function $\Delta\varphi$ is caused mainly by the band bending. Its modeled dependance on O_2 partial pressure is shown in Fig.3. Further on we use the calculated $\Delta\varphi$ for the simulation of the drain current dependance of a SGFET sensor on the O_2 partial pressure (Fig.3) with the 2-dimensional device simulator TOSCA [5] which solves the basic semiconductor equations with the Finite Element Method.

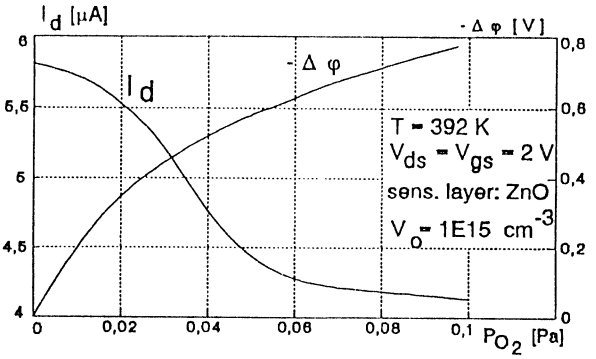

Figure 3: Threshold voltage and drain current dependance of a n-channel SGFET on the O_2 partial pressure

5. Summary

The introduced model describes the reaction of O_2 with n-type metal-oxide-semiconductors. This way the influences of the sensitive layer doping, the external voltage, the temperature and the geometry can be taken into account in the sensitive effect simulation. Further research should be done on the extension of these models by the reactions with reduction gases like H_2 or NH_3. For that it is necessary to determine a lot of unknown model parameters. The description of the chemo-physical reactions on the sensitive layers by the Electron Theory and the band model allows the implementation of these effects in the basic semiconductor equation system and so the extension of common device simulators with these models. An important condition for that is the possibility to define and to describe also a second semiconductor material in these simulation programs.

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