THEORETICAL BASES OF THE OPERATION
OF NANOSCALE SEMICONDUCTING GAS SENSORS
ON THE EXAMPLE OF TIN DIOXIDE

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The problem of phenomenological modeling of chemiresistive metal oxide gas sensors (GS), particularly SnO_2-based ones, has a rather long history and can be described through multiple approaches [1-3]. However, each of them may be conditionally divided into solution of receptor and transducer functions as suggested in [1]. Receptor function is understood as the conversion of a chemical signal (concentrations of gas impurities) into the changes in electron state of the surface (as a rule this is a change of surface charge Q_s and surface potential V_s), while the transducer function reflects how these changes are converted into electrical signal – sensor conductance G_{sen} (or resistance R_{sen}). Thus, these functions may be represented as:

$$Q_s = f(\,Air, C_a) \;\rightarrow\; V_s = f(\,Q_s\,) \qquad\qquad (1)$$

$$G_{sen} = f(\,V_s\,) \qquad\qquad (2)$$

where C_a is the concentration of analyte gas in air.

The majority of existing GS models are devoted to the consideration of the transducer functions and partially – to the second part of the receptor function, i.e. to the relationship between the surface charge and surface potential values. The most complicated treatment in the description of the receptor function is concerned with the first part of Eq. 1 and namely, with the behavior of the chemisorbed oxygen, which determines the initial state of the sensor surface. This state is a basis for further understanding of the gas sensing processes and mechanisms controlling them. The theoretical treatment of receptor function in the literature is generally limited to the use of simple chemical reactions and their rate constants between adsorbed species, where ionosorbed oxygen is usually introduced in the form of O^- [1-3]. Namely, this form of oxygen is considered to be paramagnetic and radically-active in surface interactions with target gases because it has an unpaired electron. Such an approach does not use statistical concept that considers a population by electrons of acceptor-like oxygen state and kinetic interaction with the conduction or valence bands (CB, VB), that is a required description of any electronic system. As a result, an idea of a neutral form of surface oxygen which is a covalent form free of CB electrons is not considered in these models. Moreover, as a rule, the energy position of this surface acceptor-like state relative the conduction band is out of consideration for the most models. Without specifying this parameter, it is impossible to calculate the initial position of the surface Fermi level and the corresponding band bending.

Strict consideration of the specific details characterizing receptor function is based entirely on the quantum-mechanical approach and implies the use of the modern computational programs and techniques like density functional calculations (DFT) and molecular dynamics. Several thorough attempts of adsorption calculations within DFT [4-7]

on stoichiometric surfaces with low indexes, including (110) surface as the most stable, showed that any form of oxygen (molecular or atomic in different conformations and on adsorption sites) turns out to be unstable for surface coverage of 0.5 and 1.0 ML Further achievements in DFT calculation on (110) surface [5, 6] showed that stable oxygen adsorption occurs only on reduced surface where some amount of bridging oxygen is removed. Adsorption occurs in such a way when one oxygen atom occupies the position near 5-fold Sn atom and the other one is embedded in a neighboring bridging vacancy site. After the introduction of extra electrons in SnO_2 slab [7] the atomic form accumulates additional negative charge (~0.5 electron per one O atom bounded to Sn-5f atom) and becomes more stable than neutral atomic form.

Many efforts were directed towards the studies of the structural and electronic properties of low indexes surfaces of SnO_2 by photoemission spectroscopy [8]. Unfortunately, these studies failed to provide the necessary data for constructing a phenomenological model of GS. According to the surface studies by TPD, XPS methods of metal oxides like SnO_2, TiO_2, the oxygen coverage on a metal oxide surface does not exceed 0.05-0.1 of ML. The detailed study found that the oxygen molecule uptake was determined by the number of bridging vacancies and the adsorption stoichiometry was 1:1 in a case of dissociative adsorption which corresponds to the number of particle of ~10^{14} cm^{-2}. Such surface coverage of oxygen adatoms is considerably larger than Weitz limitation for charged species on metal oxide surface. Thus, this fact leads to the conclusion on existence of the neutral forms of adsorbed oxygen.

The problem of adsorption description for chemiresistive sensor can be limited to the temperature range determined by the operation mode where dissociative form of oxygen does exist. Atomic oxygen is considered to be the most reactive form of oxygen at T>150ºC for undoped SnO_2.

Taking into account all aforementioned facts, an obvious question arises – what kind of atomic oxygen form (neutral or charged) is responsible for the direct interaction with a target molecule during a detection act. One should note that present situation is characterized

by the lack of a clear understanding of the nature of such typically applied and mentioned in the literature forms of atomic oxygen as O^0, O^-, O^{2-}, and their role in gas sensing effects. However, this is a central moment in the generalized gas sensing pattern of metal oxides.

Traditionally, the O^- form is considered to be responsible for the detection act with reducing gases. However, what does such a form mean from the point of view of O atom interaction with a conduction band? Is a CB electron captured on one of the two half-occupied *p*-orbitals after oxygen molecule rupture, or is this additional electron the result of a local charge redistribution near adsorption site (from dangling unsaturated Sn5f orbital)? It is very interesting to note, that

O^- form was found on such solid surfaces, which may be considered insulating surfaces (alkali metal halogenides, MgO, Al_2O_3 et al.). These materials have extremely low concentration of free electrons, which could be captured by oxygen. The latter indicates the existence of a "charged" form of O^- of local nature.

In this presentation we develop a phenomenological kinetic approach to the problem of receptor function of (110) SnO_2 surface and verify it by simulation of the typical sensing characteristics of undoped SnO_2 nanocrystalline film for O_2, CO and H_2O. This approach takes into account the results of above mentioned DFT studies but interprets the activity of neutral and charged form of atomic oxygen in a different way. The balance of adsorbed particles is presented by the means of the rate equations for neutral and charged forms. Transducer function was calculated in the framework of electron filtering model by double Schottky potential barriers between the nanograins.

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