Distinguishing feature of metal oxide films’ structural engineering for gas sensor applications

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Abstract. The different methods of structural engineering, used for improvement of solid state gas sensors parameters are reviewed in this paper. The wide possibilities of structural engineering in optimization of gas sensing properties were demonstrated on the example of thin tin dioxide films deposited by spray pyrolysis.

1. Introduction
At present, structural engineering of metal oxide films is one of the most effective methods used for optimization of solid state gas sensors. The considerable improvement of such operating parameters as gas response, selectivity, stability and rate of gas response can be achieved due to optimization of bulk and surface structure of applied metal oxide films. However, the technological potentialities of structural engineering have not been studied sufficiently.

In this report we have analyzed the peculiarities of structural optimization of SnO2 films deposited by spray pyrolysis. The choice of this method was stipulated by its wide possibilities for deposition of SnO2 films with various electro-physical and crystallographic properties [1-5].

2. Possibilities of structural engineering for optimization gas sensing characteristics of SnO2-based gas sensors
The different aspects of structural engineering have been studied in many papers both theoretically [6-8] and experimentally [1-5,9-16]. Basing on the obtained results we tried to formulate the some general conclusions.

The grain size and area of active surface are the main parameters, controlling gas sensing effects in metal oxide films. Usually it is displayed through so-called “dimension effect” e.g. comparability of the grain size with Debye length. Its influence on gas sensitivity is now considered as well known and may be attributed to the fundamentals of gas sensor operation [6-8]. However, both film thickness and agglomeration play important role in gas response as well. These parameters control the response time of solid state gas sensors. For instance, SnO2 sensors on the base of thin films with minimum agglomeration have maximum rate of response [9]. Possible processes, which can control the gas response properties, are shown in figure 1. At that, for strongly agglomerated
structures, the small size of grains (crystallites) is not an advantage. Agglomerates from smaller grains are denser packed, i.e. they have smaller gas penetrability [8]. Such example demonstrates that gas sensing phenomena is a many-factor effect, and therefore we have to control a great number of various parameters of metal oxide matrix (see figure 2) [6,8].

Analysis, carried out in [7,8], has shown that influence of above mentioned parameters on gas sensing characteristics takes place through the change of parameters such as effective area of intergrain and interagglomerate contacts; energetic parameters of adsorption/desorption processes; number of surface sites; concentration of charge carriers; initial surface potential; coordination number of metal atoms on the surface, etc.

From uncontrolled impurities, influencing on gas sensitivity, it is required to highlight carbon and its compounds; various forms of water; and chemisorbed species formed jointly by water and carbon-contained species [4,10]. For example, results presented in [15] showed that, from one hand, the concentration of carbon is high enough for blockage of many centers of adsorption at SnO2 surface, and, from other hand, the carbon concentration is being restored fast enough after treatments, targeted to carbon removal from SnO2 surface. Initial carbon concentration on SnO2 surface is being restored already after keeping in the air at $T=300\,^\circ\text{C}$ during 10 min.

The different processes affecting parameters of oxide sensors are summarized in the diagram shown in figure 3. One can see that there are a great number of methods for optimization of sensor structure [2,9,11-16]. However, the choice of both method and technological parameters for structure optimization must be determined by the requirements, presenting to sensor.

During the optimization of film structure it is necessary to take into account device destination, environmental conditions of exploitation, required rate of gas response, gas response selectivity, compatibility with peripheral measuring devices, the nature of detected gas, and the mechanism of gas detection in designed gas sensor. For example, the minimizing of grain size is a compulsory condition for achievement of high gas sensitivity of SnO2-based GS [6-8]. However, for In2O3-based GS, designed for detection of reducing gases such condition is not obligatory [14]. Developing of ozone detectors implies that O3 species easily dissociate on the surface and therefore application of thin films would be preferred solution for designing of such devices.

During the selection of temperature parameters of film deposition we have to remember, that the change of deposition temperature is accompanied generally by the change of both grain faceting [1,5], and surface stoichiometry of crystallites, forming gas sensing matrix. For example, we established that SnO2 nanocrystallites in dependence on deposition parameters and film thickness may have different shape with different crystallographic planes such as (110), (111), (200), (011), (-1-12), and (210). The

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**Figure 1.** Diagram illustrating the processes limiting the kinetics of gas response.

**Figure 2.** Diagram showing structural parameters, which influence on metal oxide’s gas sensing properties.
predomination of different crystallographic planes, participating in gas sensing reactions, caused corresponding changes in atomic and electronic structure along with surface energy parameters.

Figure 3. Diagram illustrating methods of structural engineering used for optimization of solid state gas sensors’s parameters.

The examples of some crystallographic planes observed in SnO$_2$ films deposited by spray pyrolysis [1,5] are shown in figure 4.

Figure 4. The models of unrelaxed rutile SnO$_2$ surfaces: (a) - (110); (b) – (100); (c) - (001); (d) – (101). The light large balls represent tin atoms and the dark small balls oxygen atoms.

The examples of some crystallographic planes observed in SnO$_2$ films deposited by spray pyrolysis [1,5] are shown in figure 4.
The catalytic activity of atomic faces to a large extent is determined by surface concentration of non-saturated cations and weakly bound bridging oxygen. The (110) face, shown in figure 4(a), is the most stable and therefore most extended surface in SnO$_2$ films. However, the contribution from the other faces may be rather important at certain conditions. The (110) surface is not atomically flat. Symmetric rows of ‘bridging’ O ions lie an equal distance above and below the surface plane. The bridging O ions can be easily removed and replaced, depending upon surface treatment. In the case of stoichiometric surface, the 5-fold coordinated surface tin atoms are of particular interest in providing active sites for adsorbates. (100) plane shown in figure 4(b) is rather rough surface, with O rows lying above the surface plane. All of the cations on this surface are five-fold coordinated with O ligands and therefore may serve as surface sites for adsorbates. Formation of bridging oxygen vacancy results in arising of 4-fold coordinated tin ions. Deep reducing of the surface may lead to appearance of 3-fold coordinated cations. The (001) surface shown in figure 4(c), in spite of the high symmetry of the lattice in that direction, is the least stable of the low-index faces. The nearest-neighbor ligand coordination of the surface cations has been reduced from six to four. Although this surface is non-polar, the low ligand coordination of the surface cations favors reconstruction to increase that coordination. The ideal cleavage of (101) atomic face, shown in Fig.4(d), is also a non-polar, microscopically rough surface, with non-symmetrically coordinated O rows lying above the surface plane and forming a rectangular pattern. The surface concentration of such two-fold ‘bridging’ oxygen is higher and they located closer to the atomic plane than at (110) face. All of the cations on this surface are five-fold coordinated with O-ligands and therefore may serve as surface sites for adsorbates. The involving of weakly bound bridging oxygen in surface reaction results in arising of 4-fold coordinated tin ions.

The conducted analysis allowed to propose the following rank of catalytic activity (CA) of ideal atomic planes: CA$_{(110)}$<CA$_{(001)}$, CA$_{(100)}$<CA$_{(101)}$. On the other hand, simple estimations show that dissociative chemisorption on the SnO$_2$ surface is orientation dependent as well. Various crystallographic planes have different distance between Sn atoms, which form following rank $d_{(110)}$<d$_{(100)}$<d$_{(101)}$<d$_{(001)}$ [1]. Tin atoms are centers of oxygen chemisorption, and therefore the change of indicated distance must influences on the rate of dissociative oxygen chemisorption, which in many cases is a main process of gas sensing phenomena [6]. So, we have cogent confirmations that optimization of SnO$_2$ crystal faceting really may be effective method for improvement of gas sensing characteristics of SnO$_2$-based gas sensors. Results of experimental research presented in [1,3,5,7,9] give the same conclusion.

![Figure 5](image)

**Figure 5.** Formation of segregation layer on the surface of SnO$_2$ grains in dependence on the nature of doping elements.

Analyzing the method of composition modification of metal oxides during their preparation we established that this method of structural engineering is the most unpredictable one, saying about results. Depending on both the concentrations of additives and crystallization modes, it can take place a simultaneous structure modification, accompanied by grain size change, appearance of second phase in base oxide, i.e. heterostructures of various forms (see figure 5), and the change of electrophysical...
and surface properties of metal oxides [13]. If we did not take into account such a complex influence on metal oxide properties, one can make a false conclusion. Therefore, trying to find parameters of metal oxide modification for achievement optimal gas sensing characteristics, we should consider the change of all parameters of controlled films. Only in this case we would be able to understand that often a changes observed on gas sensing characteristics do not connected with appearance of additional active catalytic centers. They are a consequence of a change of grain size, or concentration of free charge carriers.

Taking into account above-mentioned reasoning we have to admit that at present there is no universal solution for simultaneous optimization of all sensor parameters. As a rule improvement of one parameter is accompanied by change of other characteristics to worse. Therefore, basing on the desired characteristics of sensor to be developed it is necessary to search compromise between demands on high sensitivity, stability and selectivity of designed devices, see figure 6. At that we need to take into account that response signal in semiconductor gas sensor is based on conductivity changes, and therefore the priority should be given to the method of modification, which provides gas-metal oxide surface interaction with the most effectively conversion to conductivity changes.

Combine application of several technical decisions, i.e. using more than one method of structural engineering and more than one additive in metal oxide, allowed one to achieve better results due combination of different effects. However, success in this way is unpredictable to a great extent and depends on the ability of designer to find correct combination of additives and methods of structural engineering for goal achievement.

3. Conclusions

The presented results demonstrate that methods of structural engineering open a wide possibilities for control of gas sensor parameters and therefore can be used for optimization of their sensing properties. This approach allows to improve selectivity, to increase sensitivity, to decrease the response and recovery times, to shift the maximum of sensitivity in the range of lower operation temperature, and design nanostructured gas sensors with new consumer properties. However, we have to recognize that possibilities of structural engineering are not used completely in real developments of gas sensors.

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