Solid state gas sensors: improvement through material engineering

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Abstract

Different methods of material engineering, used for improvement of solid state gas sensors parameters are reviewed in this report. The wide possibilities of material engineering in optimization of gas sensing properties were demonstrated on the example of SnO₂, TiO₂ and In₂O₃-based sensors.

Key Words : gas sensors; metal oxides; SnO₂, In₂O₃, TiO₂ material engineering; optimization

1. Introduction

At present, material 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 sensor signal, selectivity, stability and the rate of sensor response can be achieved due to optimization of structural, bulk and surface properties of applied metal oxides. Different aspects of material engineering have been studied in many papers^[1-4]. In this report we have presented our view on above-mentioned problem. For discussing possibilities of material engineering for sensor response control we mainly used the results obtained for SnO₂, In₂O₃ and TiO₂-based devices. These metal oxides are materials mostly used for design of solid state gas sensor and therefore the determination of the nature of processes, controlling gas sensing effects with participation of those metal oxides, is very important for determination a real prospects of these materials for applications^[5-11].

There are many types of solid state sensors, which can be used for gas detection. However, we will focus on chemiresistors, or conductometric gas sensors, and on catalytic type gas sensors. It means that we will discuss sensors, which mainly operate on the base of surface reactions.

Despite some disadvantages of these sensors (Table 1), they have excellent sensitivity, very short response time, low cost, and very good suitability for design of portable

instruments, which compensate their disadvantages and open great possibilities for those sensors' application in alarm systems, portable instruments and electronic nose.

2. Parameters of metal oxides, which control their gas sensing properties

Conducted research have shown that gas sensing effect in metal oxides is very complicated phenomenon, which practically depends on all metal oxide parameters (Fig. 1)^[4,6,7].

Carried-out analysis has shown that influence of above mentioned parameters on gas sensing characteristics takes place through the change of such parameters as effective area of intergrain and interagglomerate contacts; energetic parameters of adsorption/desorption

Table 1. Gas Sensor Comparison

Parameter	Type of gas sensors				
	(1)	(2)	(3)	(4)	(5)
Sensitivity	e	g	g	b	e
Accuracy	g	g	g	g	e
Selectivity	p	b	g	b	e
Response time	e	g	p	g	p
Stability	g	g	b	g	g
Durability	g	g	p	g	e
Maintenance	e	e	g	g	p
Cost	e	e	g	g	p
Suitability to portable devices	e	g	g	g	b

e: excellent; g: good; p: poor; b: bad

(1) semiconductor; (2) catalytical combustions; (3) electrochemical; (4) thermal conductive; (5) infra-red adsorption.

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Fig. 1. Diagram showing metal oxide parameters, which control their gas sensing properties.

Fig. 2. The diagram illustrating approaches used for optimization of metal oxide properties.

processes; number of surface sites; concentration of charge carriers; initial surface potential; coordination number of metal atoms on the surface, etc^[7,12].

3. Methods of material engineering

Different processes affecting parameters of oxide sen-

sors are summarized in the diagram shown in Fig. 2. One can see that there are a great number of methods for optimization of sensor parameters^[13-17]. The effectiveness of above mentioned methods one can estimate on the base of the results is presented in Refs.^[4]. It was shown that deposition parameter control, post deposition treatments and doping during synthesis and depo-

Fig. 3. Diagram illustrating the factors, which determine the choice of sensor technologies.

sition processes really influence all properties of metal oxides, important for gas sensor applications.

For example, the increase of pyrolysis temperature during In_2O_3 deposition reduces the influence of water vapor on the conductivity of In_2O_3 and SnO_2 films and respectively on sensor response^[18]. The surface modification by noble metals promotes the improvement of sensitivity and decrease of response and recovery times^[19-23]. The use of one-dimensional metal oxides improves catalytic activity. The metal oxide doping by transition metal modifies the morphology of deposited films, etc.^[24] We established that the last method of material engineering is the most unpredictable one. Depending on both the concentrations of additives and crystallization parameters, it can take place a simultaneous structure modification, accompanied by the grain size change, appearance of second phase in base oxide^[24-26], i.e. heterostructures of various forms, and the change of electrophysical and surface properties of metal oxides^[6]. It means that trying to find parameters of metal oxide doping for achievement of optimal gas sensing characteristics, we should consider the change of all parameters of designed metal oxides.

4. What determines the selection of sensor technologies

Based on conducted research, it was established the following. The choice of either methods and technological parameters of metal oxide synthesis and deposition for achievement necessary electrophysical and structural properties should take into account a great number of requirements presented to designed sensor(Fig. 3)^[4].

The configuration of designed sensors is also important factor influencing our choice. For example one-electrode and two-electrode sensors have different requirements to material resistance for their optimal functioning^[27]. At the same time for catalytic combustion type sensors we do not have any requirements to the material resistance.

5. Remarks

The elaboration of sensors with optimal gas sensing characteristics is very complicate task. Besides, in spite of great technological possibilities, there is no universal decision for simultaneous optimization of all sensor parameters. As a rule, an improvement of one parameter is accompanied by worsening of another one.

For example, the smaller the crystallite size is, the higher the sensitivity is^[28], but at the same time the stability of gas sensor parameters is lower^[29]. It means that the decrease of the grain size improves sensitivity and decreases the thermal and temporal stability of designed gas sensor. Therefore on all stages of gas sensor design and fabrication one should seek a compromise between different parameters of designed gas sensors: between sensitivity and stability; between selectivity and sensitivity; between stability, sensitivity and sensor cost; and so on.

As the comparison of various metal oxides has shown, there is no universal material suitable for application in all types of gas sensors. For example, even analyzed tin and indium oxides have both advantages and disadvantages for application in different gas sensors^[30]. Therefore the choice of one or other material

would be also determined by exploitation conditions, and the requirements to sensors.

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