1. INTRODUCTION

Conductometric gas sensors (chemiresistors) have a simple structure and their operating principle is based on the fact that their electrical conductivity (or resistance) can be modulated by the presence or absence of some chemical species that comes in contact with the device [1]. Chemiresistors consist of three elements, a sensitive conducting layer, heater and contact electrodes. These electrodes are often interdigitated and embedded in the sensitive layer. To make the measurement, a DC voltage is applied to the device and the current flowing through the electrodes is monitored as the response. The chemical species interact with the sensitive layer and thus modulate its electrical conductivity. This can be measured as a change in the current, which is correlated to the concentration of the chemical species. The main advantages of these sensors are easy fabrication, simple operation, and low production cost, which means that well-engineered metal-oxide conductometric sensors can be mass produced at reasonable cost. Moreover, these sensors are compact and durable. As a result, they are amenable to being used for in situ monitoring [1].

The main processes controlling gas sensing effect are shown in Fig. 1. As it is seen, many various processes and factors influence the operating parameters of conductometric gas sensors. The change in resistance is observed under the effect of reactions such as adsorption, desorption, chemical reactions, surface reconstruction, diffusion, and catalysis, taking place on the surface of the sensing layer.

The most accepted mechanism, explaining sensitivity of n-type metal oxide–based sensors, includes consideration of the role of the chemisorbed oxygen [2-4]. Oxygen chemisorption means the formation of $O_2^-$, $O^-$, $O^2-$ species on the surface. Among these, $O^-$ proved to be more reactive than $O_2^-$, while $O^2-$ is not stable. So the dominant species is the $O^-$ species. It was established that $O^-$ species start to be dominant on oxide surface, in particular SnO$_2$, at $T>150$-$220$°C [3, 5]. However, it is necessary to note that some controversy on this subject still persists [4]. The oxygen chemisorption results in a modification of the space charge region toward depletion. At that the amount of charged adsorbates determines both the height of the surface potential $\phi_s$, as well as the width $d_s$ of the depletion layer. The resistance corresponding to this state is considered the base resistance. The appearance of a reducing gas leads to partial consumption of the adsorbed oxygen, resulting in a decrease in resistance, while the appearance of oxygen increases the surface oxygen coverage, and hence the resistance. The above mechanism suggests the existence of a grain boundary with the space charge region modified by environment [6].

According to Brynzari et al. [7], the influence of some adsorption/desorption parameters on the surface potential

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The study of other MOXs is a subject of interest to advance various parameters of conductometric sensors. For example, WO3-based gas sensors have excellent selective response to NH₃, H₂S, and NO₂. Moreover, the larger range of sensing materials is required to tailor sensitivity and cross-sensitivity profiles to particular applications and to develop multisensor arrays [1, 9]. More detail comparison of metal oxides tested for gas sensor application is given in Table 2 and Table 3.

As summarized in Table 1, MOX gas sensors exhibit broad-range sensitivity to a wide variety of analyte molecules. In all cases a maximum sensitivity occurs in the case of NO₂ and O₃, which competes with O₂ in forming negative surface ion species.

2. BINARY METAL OXIDES

Early works on chemisorption-type sensors (chemiresistors) focused mostly on studying SnO₂ and ZnO. Sensors based on these oxides have high sensitivity and rather low operating temperatures, 250-400°C. These oxides have negligible concentration of electron states in the band gap and high reactivity to many gaseous species. More recently, other oxide materials, such as WO₃, TiO₂, In₂O₃, Ga₂O₃, etc. have been used successfully to design conductometric gas sensors as well [9, 11-15] (see Table 1).

Theoretical there are no limitations for using any materials for chemiresistive gas sensor design independently of their either physical, chemical, structural or electrical properties [1, 8, 9]. At present, gas sensor’s prototypes on the base of covalent semiconductors, semiconducting metal oxides, solid electrolytes, polymers, ionic membranes, organic semiconductors, and ionic salts have been already tested [10]. However, there are no evidences for assertion that all materials are equally effective for gas sensor applications. Therefore, the selection of optimal sensing material becomes key problem in both design and manufacturing of gas sensor with required operation parameters. At present polymers and metal oxides are the most applied materials for manufacturing chemiresistive gas sensors [10]. However, only metal oxides possess required thermal and temporal stability [9, 10]. Therefore, in this paper only metal oxides will be discussed.

3. COMPLEX METAL OXIDES AND COMPOSITES

Except for binary oxides, chemisorption-type conductometric sensors employ complex oxides such as CdIn₂O₄, NiTa₂O₆, CoTa₂O₆, CuTa₂O₆, BaSnO₃, LnFeO₃, CdFe₂O₄, Bi₃SnO₉, YBa₂Cu₃O₇₋ₓ, Bi₂Mo₄O₁₁, Sn₀.₇Fe₂O₇, NiFe₂O₄ and nanocomposites [1, 16, 17]. It was established that highly sophisticated surface-related properties important for gas sensor applications such as optical, electronic, catalytic, mechanical, and chemical can be obtained by advanced nanocomposites synthesized from various materials. For example, metallic and metal-oxide nanoparticles incorporated in various matrixes are capable of increasing the activities for many chemical reactions due to the high ratio of surface atoms with free valences to the cluster of total atoms. As a result, we can obtain an ideal platform for gas sensor design. More complicated metal oxides, for example such as Li-SnFe₂O₄, Ni₀.₉⁵Co₀.₀⁵Mn₀.₀¹Fe₁.₉⁹O₄, BaSn₀.₉⁵Zr₀.₀⁵O₃, Na₀.₁Nb₀.₁W₀.₈O₃, Cs₂SiW₁₂O₄₀, or...
CoMn$_{0.65}$Fe$_{1.35}$O$_4$, can be used as well. Such complex oxide-based sensors exhibit both $n$-type and $p$-type responses to gases under different operating temperatures. Experiments shown that composites or multicomponent metal oxides may sometimes be promising materials for a specific applications. In particular, Gadkari et al. [16] believe that nickel ferrite (NiFe$_2$O$_4$) can be promising for detection chlorine and acetone, zinc ferrite (ZnFe$_2$O$_4$) for detection ethanol, whereas magnesium ferrite (MgFe$_2$O$_4$) and cadmium ferrite (CdFe$_2$O$_4$) could be used for design LPG and ethanol sensors.

However, experiment has shown that sensors based on such complex oxides usually do not have better gas-sensing performance compared to sensing materials based on binary oxides. As a rule, the improvement of sensor response was observed only for specific gases such as H$_2$S [18]. The complex nature of these materials also limits their use for integrated gas sensors. The large number of elements in these metal oxides makes it hard to deposit thin films with good and repeatable stoichiometric ratios.

One should remember also that the complication of the composition of gas sensing matrix is always being accompanied by deterioration of sensor parameters’ reproducibility. Too many additional factors, which can affect gas sensing properties of materials, appear in nanocomposites. Moreover, one should take into account that sometimes the increase of the sensitivity of devices, elaborated on the base of nanocomposites, is being attained at the expense of worsening other exploitation parameters of sensors. For example, Tamaki et al. [18] have shown that sensors used SnO$_2$-CuO composite had higher sensitivity to H$_2$S in comparison with the SnO$_2$ sensors. However, SnO$_2$-CuO gas sensing matrix contains CuO phase, which does not have high thermodynamic stability as compared with SnO$_2$. This fact undoubtedly adversely affects temporal and thermal stability of such sensors’ parameters [9, 19]. The same could be said about SnO$_2$-Fe$_2$O$_3$, In$_2$O$_3$-Fe$_2$O$_3$ or SnO$_2$-AgO$_x$ composites, showing high sensitivity to several specific gases and vapors.

### 4. METAL OXIDE COMPARISON AND SELECTION

As it follows from Tables 2 and 3 there is no single metal oxide which can satisfy all possible requirements for efficient elaboration of gas sensors [1, 9-12]. This means that we do not have ideal sensing material. All materials have both advantages and shortcomings. Some sensing materials have poor selectivity, some are highly sensitive
to humidity, some are stable only at low temperatures, some degrade while interacting with ozone, some ones require high temperatures for operating, and so on [10]. Therefore, in choosing a sensing material for a particular application, the selected material should capitalize on its advantages, while its shortcomings should minimally influence the characteristics of the final device. For example, it was established that SnO2-based sensors have better sensitivity to reducing gases, and better stability during operation in reducing atmospheres. However, In2O3-based sensors have better conductivity response to oxidizing gases, and are less affected by changes in air humidity. Moreover, In2O3-based ozone sensors have shorter recovery time [12]. Which is better, high response to reducing gases, or to oxidizing gases? Only the designer can answer this question, depending on the requirements for a particular sensor.

The same can be said for other pairs of metal oxides, for example, SnO2-CTO or SnO2-WO3. Titanium-substituted chromium oxide, Cr2-xTixO3+z (CTO), with 0.01 < x < 0.45, has high chemical stability at its operating temperature, an easily measurable range of resistance, and good conductivity response [8]. In contrast to SnO2-based sensors, the effect of water vapor on the parameters of CTO-based sensors, such as the baseline and sensitivity, is much less than that on the parameters of SnO2-based devices operating at the same temperatures. This has been the key to the successful use of CTO-based sensors for detection of carbon monoxide and volatile organic compounds in the air. On the other hand, CTO sensors,

Table 2. Advantages and disadvantages of MOXs for conductometric gas sensor applications

<table>
<thead>
<tr>
<th>Material</th>
<th>Advantage</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO2</td>
<td>High sensitivity</td>
<td>Low selectivity</td>
</tr>
<tr>
<td></td>
<td>Good stability in reducing atmosphere</td>
<td>Dependence on air humidity</td>
</tr>
<tr>
<td>WO3</td>
<td>Good sensitivity to oxidizing gases</td>
<td>Low selectivity</td>
</tr>
<tr>
<td></td>
<td>Good thermal stability</td>
<td>Low sensitivity to reducing gases</td>
</tr>
<tr>
<td>Ga2O3</td>
<td>High stability</td>
<td>Low selectivity</td>
</tr>
<tr>
<td></td>
<td>Ability to operate at high temperatures</td>
<td>Average sensitivity</td>
</tr>
<tr>
<td>In2O3</td>
<td>High sensitivity to oxidizing gases</td>
<td>Low selectivity</td>
</tr>
<tr>
<td></td>
<td>Fast response and recovery</td>
<td>Low stability at low oxygen partial pressure</td>
</tr>
<tr>
<td>CTO (CrTiO)</td>
<td>High stability</td>
<td>Low selectivity</td>
</tr>
<tr>
<td></td>
<td>Low sensitivity to air humidity</td>
<td>Moderate sensitivity</td>
</tr>
</tbody>
</table>

Source: Reprinted with permission from Ref. [9]. Copyright 2007 Elsevier.

Table 3. Operating parameters of metal oxide conductometric gas sensors and particulars of their fabrication

<table>
<thead>
<tr>
<th>Material</th>
<th>SnO2</th>
<th>WO3</th>
<th>In2O3</th>
<th>ZnO</th>
<th>CTO</th>
<th>Ga2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optimal gases for detection</td>
<td>Reducing gases (CO, H2, CH4, etc.)</td>
<td>O3, NOx, H2S, SO2</td>
<td>O3, NOx</td>
<td>CH4, O2, C6H10, NOx</td>
<td>H2S, NH3, CO, VOCs</td>
<td>O2, CO</td>
</tr>
<tr>
<td>Operating temperature, °C</td>
<td>200-400</td>
<td>300-500</td>
<td>200-400</td>
<td>250-350</td>
<td>300-450</td>
<td>600-900</td>
</tr>
<tr>
<td>Stability</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Moderate</td>
<td>Satisfactory</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Compatibility with silicon technologies</td>
<td>Imperfect</td>
<td>Low</td>
<td>Good</td>
<td>Good</td>
<td>Imperfect</td>
<td>Good</td>
</tr>
<tr>
<td>Complexity of fabrication</td>
<td>Acceptable</td>
<td>Moderate</td>
<td>Acceptable</td>
<td>Acceptable</td>
<td>Acceptable</td>
<td>Acceptable</td>
</tr>
<tr>
<td>Sensitivity to air humidity</td>
<td>High</td>
<td>Reduced</td>
<td>Reduced</td>
<td>High</td>
<td>Low</td>
<td>Acceptable</td>
</tr>
<tr>
<td>Stability in reducing atmosphere</td>
<td>Good</td>
<td>Good</td>
<td>Moderate</td>
<td>Excellent</td>
<td>Moderate</td>
<td>Moderate</td>
</tr>
<tr>
<td>Readiness of synthesis and deposition</td>
<td>High</td>
<td>Medium</td>
<td>High</td>
<td>High</td>
<td>Medium</td>
<td>Medium</td>
</tr>
</tbody>
</table>

Source: Data from Ref. [9].
unlike SnO₂ sensors, are not sensitive to methane, though they are sensitive to the higher hydrocarbons and to carbon monoxide, H₂S, NH₃, and a wide range of solvents.

Considering the pair SnO₂-WO₃, SnO₂ shows both large and fast response to ozone at sufficiently low temperature (~200-300°C), though there are problems of baseline stability at such low temperatures. The effect decreases with increasing temperature, to virtually zero at 400°C. WO₃ shows particularly large resistivity increase at high temperatures (400-500°C) in response to the presence of ozone. However, the response to ozone is relatively slow, as is the recovery when the gas is removed. In addition, the signal depends on the flow rate of the gas to the surface, and on the partial pressures of water vapor and oxygen [8]. At the same time, however, experiments carried out by Solis et al. [13] showed that WO₃-based sensors have unique and excellent sensitivity to low concentrations of H₂S in air at room temperature.

Hoefer et al. [14] believe that Ga₂O₃-based sensors also have certain advantages in comparison with SnO₂-based sensors. Ga₂O₃ sensors are high-temperature devices (T_{oper} = 600-900°C) and therefore show faster response and recovery and lower cross-sensitivity to humidity than SnO₂-based sensors. Ga₂O₃ sensors also show stable long-term sensing properties and good reproducibility even in sulfur-containing atmospheres. This last property makes these sensors suitable for use in domestic burner controls. No cleaning cycles are necessary, and smut or other organic residues are burned off. Additionally, no pre-aging is necessary (compared to SnO₂). On the other hand, the sensitivity of Ga₂O₃ sensors to a number of gases is lower compared to SnO₂-based sensors, and the power consumption of Ga₂O₃-based sensors is comparably high due to their high operating temperatures.

Grimes and co-workers [15] found that TiO₂ nanotubes were excellent room-temperature hydrogen sensors not only with a high sensitivity but also with an ability to selfclean photoactively after environmental contamination. The hydrogen-sensing capabilities of the sensors were largely recovered by ultraviolet (UV) light exposure after being completely extinguished by a rather extreme means of sensor contamination: immersion of the sensor in motor oil. SnO₂ does not possess such properties.

All these factors mean that the choice of a metal oxide for gas sensor design is determined by the type of gas sensor to be designed, the apparatus or device in which the sensor will be used, the structure chosen for the sensor’s fabrication, and conditions of exploitation. However, any competition between potential materials can be ignored if the device is to become part of an “electronic nose.” Different behavior during interaction with the same gas is one of the most important requirements for sensors designed for this application [9, 10].

5. IMPROVEMENT OF GAS SENSING PARAMETERS THROUGH MATERIAL OPTIMIZATION

5.1. Conventional Approaches

Conducted research have shown that gas sensing effect in metal oxides is very complicated phenomenon, which depends on all metal oxide parameters, such as thickness, grain size, porosity, grain faceting, agglomeration, bulk conductivity, surface architecture, grain network, surface stoichiometry, catalytic reactivity, band gap and so on (see Fig. 2) [1, 20-23]. Analysis carried out has shown that the 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, gas penetrability of sensing matrix, etc. [24, 25].

At present, material engineering of metal oxide films is one of the most effective methods used for optimization of solid state gas sensors [23, 24, 26]. The considerable improvement of operating parameters such as sensor signal, selectivity, stability and the rate of sensor response can be achieved due to optimization of chemical, structural, bulk and surface properties of applied metal oxides.

There are a great number of technological methods, which could be used for optimization of sensor parameters (see Fig. 3). It was shown that deposition parameter control, post deposition treatments and doping during synthesis and deposition processes really influence all properties of metal oxides important for gas sensor applications. For example, the increase of pyrolysis temperature during In₂O₃ and SnO₂ deposition reduces the influence of water vapor on the conductivity of these metal oxides and respectively on sensor response. The surface modification by noble metals promotes the improvement of sensitivity and decrease of response and recovery times. The use of one-dimensional metal oxides improves thermal stability of structure and
properties. The metal oxide doping by noble and transition metals modifies the catalytic reactivity and morphology of deposited films, etc. [1].

However, the same researches have shown that the elaboration of sensors with optimal gas sensing characteristics is really very complicated task. At that, 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, numerous investigations have shown that the decreasing crystallite size leads to an increase of gas sensitivity. A dramatic increase in sensitivity for metal oxides with grain size smaller than a Debye length has been demonstrated many times for various materials, such as SnO2, WO3, In2O3 etc. [24, 27-29]. For In2O3 this effect is illustrated in Fig. 4.

For In2O3, it was also found that sensors fabricated using thin films with minimal crystallite size had minimal response time in addition to maximum sensor response, especially to ozone [30]. Therefore, at present polycrystalline materials with nano-dimensional grains are most often considered as a basis for prospective gas sensors.

However, it was established that the decrease of grain size decreases thermal and temporal stability of designed gas sensor [28, 31]. It was shown that for SnO2 grains with size about 1-4 nm, grain growth process begins already at
temperatures equaled ~200-400 °C (see Fig. 5).

The similar situation takes place for materials, modified by catalitically active additives. As it was shown, catalytically active additives, especially noble metals, can essentially increase sensitivity. However, at the same time they might be one of the reasons of observed temporal instability of gas sensor parameters [19].

The same we can say about bulk doping of metal oxides, which can be used for improvement of sensitivity, selectivity and stability of gas sensors [11, 19, 23]. The process of bulk doping in very complicated one, which is accompanied by the change of all parameters of metal oxide matrix, even in the case of small concentration of additives (see Fig. 6).

Therefore, researchers have to be careful during the elaboration of technologies of gas sensing layers’ forming on the base of doped and multi-component materials. When you choose additives for film structure optimization or stabilization, one should take into account, that the optimization of sensor response takes place usually only for concentrations of additives in the range from 0.05-3 wt.% and the superfluous concentration of these additives sharply reduces the sensor response (see Fig. 7).

We need to take into account that for high concentration of additives we will observe the precipitation of second phase in the matrix of based metal oxide [33]. Moreover, in real situation, as a rule, the concentration of doping, which is optimal for improvement of gas sensing characteristics, is not sufficient for improvement structural stability of metal oxides [31]. Moreover, instead of anticipated improvement of structural stability you can obtain considerable worsening of this parameter [34]. The last one, as a rule, is a consequence of increase of fine dispersed phase contents in metal oxide matrix.
5.2. 1-D Metal Oxide Structures

At present many of researchers believe that the use of 1D nanostructures is one of the main trends in gas sensors design [10]. It is truth, because results obtained during study of one-dimensional metal oxide nanomaterials have great importance due to their potential for fundamental studies of gas sensing effects as well as for design low-cost, small-sized, and low-power consumption devices [1]. One-dimensional metal oxide nanomaterials have excellent crystallinity and clear facets (Table 4). Moreover one-dimensional structures can be synthesized using inexpensive, simple technology. It is expected that these nanomaterials will have less concentration of point defects and specific adsorption and catalytic properties, conditioned by a particular combination of crystallographic planes. In addition, one-dimensional metal oxide nanomaterials should be more thermodynamically stable in comparison to nanograins, promoting stable operation of gas sensors at higher temperatures.

Development of nanotechnology gives hope for realizing gas sensors based on one-dimensional metal oxide nanowires with parameters improved relative to devices based on polycrystalline materials [1, 10, 24]. Achievements in the field of gas sensor design are listed in Table 5.

Wide use of one-dimensional structures is however impeded by the great difficulties required for their separation and manipulation. During the synthesis process of one-dimension structures one may observe a considerable diversity in their geometric parameters. Therefore, reproducibility of performance parameters for sensors based on individual one-dimension structures would depend on the uniformity of those structures. Moreover, technological approaches used in manufacturing sensors based on individual 1-D structures differ fundamentally from the methods used in standard silicon technology. As a result, while working with individual 1-D structures we face great difficulties with integration in silicon technology [1, 10]. Unfortunately, the problem of separation, sizing, and manipulations of one-dimensional structures is not resolved yet. To achieve uniform sizing and orientation, new advanced technologies will need to be implemented, and these would be expensive and not accessible for wide use. Therefore, gas sensors based on individual one-dimension structures are not yet readily available commercially. Further, the manufacturing cost of sensors based on one-dimensional structures would far exceed that of polycrystalline devices. Based on what was said above, it becomes clear that in near future, polycrystalline materials would remain the dominant platform for solid-state gas sensors [24].

5.3. Mesoporous, Macroporous and Hierarchical Metal Oxide Structures

Mesoporous, macroporous and hierarchical metal oxide structures is other modern direction in design of sensing materials for conductometric gas sensors. It was established that the ability to create macroporous objects from nanoscaled components may create new resources for optimization of gas sensor parameters. The pores in 3-D MOX structures are developed in the submicrometer or nanodimensional domain. Therefore, these structures are frequently called mesoporous. These rather new materials with extremely high surface area offer a high degree of versatility in terms of structure and texture. The most successful approaches to developing mesoporous structures are based on synthesis of pore-containing particles via templating or via a facile wet-chemical approach combining with an annealing process [57].

The hierarchical nanostructures have also extremely high surface area and have little tendency to agglomerate, which allows one to employ them as high-performance gas sensor materials. A “hierarchical structure” means the higher dimension of a micro- or nanostructure composed of many, low dimensional, nano-building blocks [58]. The various hierarchical structures can be classified according to the dimensions of nano-building blocks and the consequent hierarchical structures, referring to the dimensions,
respectively, of the nano-building blocks and of the assembled hierarchical structures (see Fig. 8). For example, ‘1-3 urchin’ means that 1D nanowires/nanorods are assembled into a 3D urchin-like spherical shape and ‘2-3 flower’ indicates a the 3D flower-like hierarchical structure that is assembled from many 2D nanosheets. Under this framework, the hollow spheres can be regarded as the assembly of 1D nanoparticles into the 3D hollow spherical shape. Thus, strictly speaking, the 0-3 hollow spheres should be regarded as one type of the hierarchical structures.

Various methods have been considered for synthesizing such hierarchical hollow-particle structures, including spray drying [59, 60], sol-gel [61], layer-by-layer (LbL) templating [62, 63], electrodeposition [64], vapor-phase impregnation [65], interface growth, pulse laser deposition, and others [66]. However, the most promising technologies seem to be methods based on sol-gel, aerosol spray and
LbL deposition [58]. From our point of view electrochemical etching of metal films with following oxidation of fabricated porous structure is also very promising approach to design of mesoporous gas sensing matrix. Such approach was discussed with reference to TiO$_2$ and SnO$_2$ in Refs. [67-69] and [70], correspondingly.

It is necessary to note that technologies for fabricating mesoporous and hierarchical nanostructures have been developed for all the basic MOXs (SnO$_2$, In$_2$O$_3$, TiO$_2$, WO$_3$, Fe$_2$O$_3$, etc.) utilized to develop conductometric gas sensors [58]. The gas-sensing performance of sensors based on mesoporous and hollow nanostructures is well reviewed elsewhere [58, 71], and it is agreed that such structures are really attractive platforms for gas-sensing applications [65, 72, 73]. Mesoporous and hollow structures have been reported to show very high gas-sensing response [74-76] and fast response kinetics [77], which are attributed to their high surface area and well-defined porous architecture. Especially big difference in kinetics of sensor response was observed in comparison with sensors fabricated using agglomerated powders [78].

At that it was established that the hollow nanostructures follow the same basic trends as we mentioned for the thin-film layers. When the shells are rather dense and thick, the gas-sensing reaction occurs only near the surface of the hollow spheres, and the inner parts of these spheres are inactive. However, if the shell is sufficiently thin, the primary particles in the entire hollow sphere are able to participate in gas-sensing reactions even when the shells are less permeable. In addition, the rate of sensor response of hollow spheres increases with the thinner shell configuration due to the faster gas diffusion. It has been also found that the sensor response and response kinetics of the mesoporous sensing materials similarly to conventional metal oxide matrix can be improved further by surface modification [75] and doping by catalytic materials [79-81].

It is necessary to note that the problem of structural instability exists for all types of mentioned above structures independently of material used. Moreover, resolving this problem does not have universal approach. Unfortunately, every material used for mesoporous, macroporous and hollow structures fabrication requires specific approach to resolving. For example, Shimizu and co-workers [82] found that the most important key to the drastic improvement of thermal stability of mesoporous (m-) SnO$_2$ powders is to immerse them in a phosphoric acid aqueous solution before calcination and consequently loading of phosphorous-components on the surface of m-SnO$_2$ crystallites. Such treatment enabled to prepare the m-SnO$_2$ powders with small crystallite size (2~3 nm in diameter) and large specific surface area (>300 m$^2$/g) even after calcination at 600$^\circ$C.

5.4. Nanofiber

Of course, metal oxide nanofibers are not 1-D structures in classical understanding as nanotubes or nanowires. However, nanofibers, which usually have diameter in the range of 10-1000 nm and the length from several μm up to cm and meter, possess many unique properties since these fibers have also very large surface area per unit mass and small pore size. For preparing nanofibers can be used various methods, including drawing, hard and soft template synthesis, self-assembly, and electrospinning. Among these methods, electrospinning seems to be the simplest and most versatile technique capable of generating metal oxide nanostructures.

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Fig. 8. Nomenclature of hierarchical structures according to the dimensions of the nano-building blocks (the former number) and of the consequent hierarchical structures (the latter number). (Reprinted with permission from Ref. [58]. Copyright 2009 Elsevier.)
It is necessary to note that metal oxide nanofibers can be fabricated using various methods [83-87]. Electrospinning also can be used for metal oxide nanofibers fabrication [88, 89]. For example, there are reports related to nanofibers of TiO$_2$ [90-92], SnO$_2$ [91, 93, 94], WO$_3$ [95], TiO$_2$:LiCl [96], ZnO [97], SrTi$_{0.8}$Fe$_{0.2}$O$_3$-$\delta$ [98], etc. Usually for preparing metal oxide nanofibers a hybrid solution, which is a mixture of the metal oxide sol precursor, polymer, and solvent is used. In order to make the inorganic nanoparticles effectively disperse in polymer, sometimes a surfactant is needed. At that it is necessary to take into account that for preparing metal oxides fibers the sintering at elevated temperatures usually is required. This thermal treatment is necessary for both the transformation of hydroxides in oxides and decomposition and removing polymeric components used for electrospinning. Fig. 9 shows SEM images of In$_2$O$_3$-based nanofibers deposited using PVA/indium acetate composite with following annealing in oxygen containing atmosphere. As it is seen, metal oxides in nanofibers are polycrystalline.

Research, however, has shown that feature of nanofiber configuration and dimensional factor play positive role during design of conductometric gas sensors. Extremely high porosity is the main advantage of these sensors, which show very good operating characteristics (great and fast response) in comparison with sensors based on conventional materials. Parameters of several gas sensors designed on the base of metal oxide nanofibers are listed in Table 6.

### 6. OUTLOOKS

Our discussion has shown that there is no universal material suitable for application in all types of conductometric gas sensors. For example, even mostly used metal oxides such as tin dioxide and indium oxides have both advantages and disadvantages for application in different gas sensors. Therefore, the choice of one or other material would be determined by exploitation conditions, and the requirements to sensors. Moreover, during the choice of either methods and technological parameters of metal oxide synthesis, deposition and modification, which should guarantee the achievement of necessary electrophysical and structural properties, we have to take into account a great number of requirements presented to

<table>
<thead>
<tr>
<th>Material</th>
<th>Array</th>
<th>Fiber diameter (nm)</th>
<th>Gases tested</th>
<th>$T_{\text{opt}}$ (°C)</th>
<th>Detection limit</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>N</td>
<td>200-500</td>
<td>NO$_2$</td>
<td>150-400</td>
<td>500 ppb</td>
<td>[90]</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>N</td>
<td>120-850</td>
<td>CO, NO$_2$</td>
<td>300-400</td>
<td>50 ppb</td>
<td>[92]</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>N</td>
<td>400-500</td>
<td>CO</td>
<td>200</td>
<td>&lt;1 ppm</td>
<td>[89]</td>
</tr>
<tr>
<td>LiCl-TiO$_2$</td>
<td>N</td>
<td>150-260</td>
<td>H$_2$O</td>
<td>RT</td>
<td>11%</td>
<td>[96]</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>S</td>
<td>70</td>
<td>H$_2$O</td>
<td>RT</td>
<td>N/A</td>
<td>[94]</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>N</td>
<td>~100</td>
<td>C$_2$H$_5$OH</td>
<td>330</td>
<td>10 ppb</td>
<td>[91]</td>
</tr>
<tr>
<td>MWCNT/SnO$_2$</td>
<td>N</td>
<td>300-800</td>
<td>CO</td>
<td>RT</td>
<td>47 ppm</td>
<td>[93]</td>
</tr>
<tr>
<td>In$_2$O$_3$</td>
<td>N</td>
<td>~100</td>
<td>CO</td>
<td>300</td>
<td>~1 ppm</td>
<td>[88]</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>N</td>
<td>20-140</td>
<td>NH$_3$</td>
<td>350</td>
<td>50 ppm</td>
<td>[95]</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>N</td>
<td>32-82</td>
<td>NO</td>
<td>300</td>
<td>30 ppb</td>
<td>[100]</td>
</tr>
<tr>
<td>V$_2$O$_3$</td>
<td>N</td>
<td>~10</td>
<td>NH$_3$</td>
<td>RT</td>
<td>30 ppb</td>
<td>[86]</td>
</tr>
<tr>
<td>SrTi$<em>{0.8}$Fe$</em>{0.2}$O$_3$-$\delta$</td>
<td>N</td>
<td>~100</td>
<td>CH$_3$OH</td>
<td>400</td>
<td>5 ppm</td>
<td>[98]</td>
</tr>
</tbody>
</table>
sensor designed. We have to take into account the device destination, the nature of detected gas, required sensitivity, exploitation conditions, required rate of sensor response and so on. The configuration of designed sensors is also important factor influencing our choice. For example, one-electrode and two-electrode gas sensors have different requirements to material resistance for their optimal functioning. At that we need to recognize that 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. 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 (see Fig. 10).

Good technological effectiveness and processibility (see Fig. 11), i.e., the ability to produce, under control and with reproducibility, powders, films, and ceramics with the required structural and morphological properties, is also an important criterion in selecting a material for a gas sensor. Both complicated techniques and the absence of a technological base for mass production can also considerably limit the application of a particular sensing material. This confirms again that, for practical use, considerations of stability, reliability, and technological effectiveness are determinative.

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