Gas-sensitive properties of thin and thick film sensors based on Fe$_2$O$_3$–SnO$_2$ nanocomposites

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Abstract

Influence of phase composition, structural peculiarities and grain size of Fe$_2$O$_3$–SnO$_2$ nanocomposites prepared by sol–gel technology on gas-sensitive properties of the corresponding gas sensors has been studied in the paper. The characteristics of thin film sensors were obtained with regards to NO$_2$ and C$_2$H$_5$OH. Behaviour of thick film sensors was estimated in humid C$_2$H$_5$OH ambient. High sensitivity of Fe$_2$O$_3$–SnO$_2$ samples containing highly dispersive Fe$_2$O$_3$ phase has been revealed. The composites consisting of poorly crystallised α-Fe$_2$O$_3$ along with Sn(IV)–α-Fe$_2$O$_3$ solid solution demonstrate maximum sensitivity to ethanol. Structural and functional distinctions of the Fe$_2$O$_3$–SnO$_2$ composites obtained by using different Fe-precursors (Fe$^{3+}$ and Fe$^{2+}$ inorganic salts) have been revealed. Mechanisms of the processes, which determine gas-sensitive behaviour of the composites, are considered.

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1. Introduction

SnO$_2$-based composites are commonly used materials for gas sensing application. Simple SnO$_2$ is characterised by low sensitivity and unsuitable selectivity to most of toxic and explosive gases [1–3]. This objective causes the necessity of SnO$_2$ modifying by various additives like noble metals (Pd, Pt, Au) [4] and metal ions of variable valency (Mo, Ni, Fe, Sb). One of the most prospective ways to achieve good sensor performance is the obtaining sensitive layers of complex composition, where the functions of receptor and transducer are divided between different phases [5]. As it has been established by Yamazoe [6], metal cations, which are characterised by electronegativity lower than electronegativity of Sn(IV), increase the sensitivity of SnO$_2$-based sensors to ethanol.

The analysis of the existing literature shows that the layers based on the Fe$_2$O$_3$–SnO$_2$ composites possess high sensitivity to ethanol and suitable response to NO$_2$, CO and CH$_4$.

Tan et al. [7] reported good ethanol sensitivity values of Fe$_2$O$_3$–SnO$_2$ thick film as high as 850 at 1000 ppm in air. The sensor is selective to ethanol over carbon monoxide and hydrogen. The functional parameters are also found to be very stable.

The introduction of Fe in SnO$_2$ thin films by means of RGTO technique leads to the formation of the new ternary compound Sn$_x$Fe$_{1-x}$O$_2$, which shows high response to CO [8]. Maximum sensitivity (3.2 for 500 ppm) was observed for Fe content of 1.8%.

Suitable low-temperature detection of CH$_4$ by α-Fe$_2$O$_3$ (SO$_4^{2-}$, Sn) thick films as compared to other metal oxides was achieved by Chung and Lee [9]. As it was found, α-Fe$_2$O$_3$ (SO$_4^{2-}$, Sn) powders precipitated at different pH values exhibited different microstructures.

Remarkably, that structural peculiarities of oxide materials such as phase composition, dispersity and morphology, influence strongly the functional features (sensitivity, selectivity, long-term stability) of the corresponding gas sensors [1,10]. Moreover, type of sensitive layer (ceramic, thin film, thick film) determines substantially a sensor performance as well. But the fine structural features of an oxide system and its activity in reduction–oxidation reactions are not commonly taken into consideration.

This paper reports an investigation on structural and functional features of the Fe$_2$O$_3$–SnO$_2$ composites prepared by different variations of the sol–gel technology. An attempt to establish correlation between the fine structural peculiarities...
of the complex oxide systems and their gas-sensitive properties regarding NO₂ and C₂H₃OH has been made.

2. Experimental

Simple oxides/hydroxides of iron and tin were prepared by hydrolysis of the corresponding inorganic precursors by using base agent (aqueous solution of NH₃). The precipitate then was washed thoroughly and transformed into colloidal solution (sol). The Fe₂O₃–SnO₂ composites (Fe:Sn = 1:9, 1:1, 9:1) were formed by mixing iron and tin oxides/hydroxides in the required proportions followed by annealing of the dried species at different temperatures (300, 500, 600, 800 °C) [5]. Fe²⁺ precursors (FeCl₂, FeSO₄) were used along with more common Fe³⁺ inorganic salts (FeCl₃, Fe(NO₃)₃, Fe₂(SO₄)₃). Using Fe³⁺ precursors leads to the formation of α-Fe₂O₃ species; meanwhile, hydrolysis of Fe²⁺ salts under certain conditions allows to obtain metastable γ-modification of iron oxide [10]. Thus, two types of the composites were prepared: α-Fe₂O₃–SnO₂ (by mixing α-Fe₂O₃ and SnO₂ sols) and γ-Fe₂O₃–SnO₂ (by mixing γ-Fe₂O₃ and SnO₂ sols).

Structural investigations were carried out by XRD, EPR, TEM and Mössbauer spectroscopy. The sensing layers were heated at 550 °C in air during 20 h. High-temperature treatment provides measurable range of the layer resistance. Measurements of the temperature-dependent conductivity of the oxide layers were carried out in the region of temperature 100–500 °C at RH 30%. Gas-sensitive properties of thin film species were mostly studied regarding 1 ppm NO₂ (RH 40%). Thick film sensors were measured in humid ethanol vapours (RH 98%) within the range 0.025–1.0‰ (0.1‰ corresponds to 45 mg/m³ of ethanol), thus modelling alcohol content in human’s expired air. A flow of gas was obtained by commercial ethanol generator GS-1 (Analitpribor, Kiev). The construction of the sensors is described elsewhere [11]. The sensor response was calculated as \((I_{\text{gas}} - I_{\text{air}})/I_{\text{air}}\) at fixed \(U\)-value for thin films and as \((R_{\text{gas}} - R_{\text{air}})/R_{\text{air}}\) in the case of thick film layers at detection of reducing gases and as \((I_{\text{air}} - I_{\text{gas}})/I_{\text{gas}}\) and \((R_{\text{air}} - R_{\text{gas}})/R_{\text{gas}}\) when detecting oxidising ambient, correspondingly; where \(I_{\text{gas}}\) and \(I_{\text{air}}\) are current and layer conductivity in gas ambient; \(I_{\text{air}}\) and \(R_{\text{air}}\) are current and layer conductivity in air.

3. Results and discussion

The Fe₂O₃–SnO₂ composites of the same Fe:Sn ratio prepared via Fe²⁺ and Fe³⁺ precursors differ considerably regarding their phase composition (Fig. 1a and b). The sharpest distinctions are observed when the samples been heated at temperatures below 500 °C. It is important to note, that all the oxide systems mentioned in this paper are characterised by high system dispersity and relatively low degree of crystallinity (Table 1). The grain size of the samples annealed at 500 °C does not exceed 6 nm.

The XRD reflections assigned to the α-Fe₂O₃–SnO₂ composites within the whole series of the applied component ratios (Fe:Sn = 9:1, 1:1, 1:9) appear to be broad and low-intensive. This can be explained by very small size of SnO₂ grains (about 2 nm) and poor crystallinity of α-Fe₂O₃ phase. The composites with Fe:Sn ratio 1:9 and 1:1 have the structure of Fe(III)–SnO₂ solid solution; in the case of the Fe₂O₃–SnO₂ (Fe:Sn 9:1), Sn(IV)–α-Fe₂O₃ solid solution is typical.

Fast removal of water and crystallisation of α-Fe₂O₃ occurs at temperatures above 500 °C: the reflections of this phase become narrow. Noticeable SnO₂ particle agglomerate accompanying the crystallisation processes was only observed at 800 °C. High-temperature treatment results in partial decomposition of the sample structure and isolation of simple oxide phases—SnO₂ and α-Fe₂O₃; the samples become heterogeneous.

As opposed to α-Fe₂O₃, γ-Fe₂O₃ phase obtained by using the mentioned synthesis technique after drying at 150 °C is characterised by rather well crystallinity and absence of constitutional water. However, annealing the sample based on metastable γ-Fe₂O₃ phase at 400–500 °C results in its transforming into α-Fe₂O₃ one. Thus, the XRD patterns of both α-Fe₂O₃–SnO₂ and γ-Fe₂O₃–SnO₂ species of the same component ratio become similar after heating at 800 °C.

Besides, according to Mössbauer study, small areas of amorphous and highly dispersive Fe₂O₃ phase are also preserved within the α-Fe₂O₃–SnO₂ and γ-Fe₂O₃–SnO₂ (Fe:Sn = 9:1, 1:1) samples up to 400 °C. EPR and Mössbauer studies give evidence that the α-Fe₂O₃ phase obtained through the amorphous Fe₂O₃ (via Fe³⁺ precursor) and by the thermally stimulated transformation of γ-Fe₂O₃ (via Fe²⁺ precursor) are significantly different: the motive of γ-Fe₂O₃ structure (cubic symmetry) preserves within the latter species [5]. This phenomenon is also typical of highly dispersive α-modifications of iron oxides/hydroxides (trigonal symmetry). Note, that in the case of the γ-Fe₂O₃–SnO₂ composites the grain size of both oxide phases (Fe₂O₃ and SnO₂) is greater as compared to the α-Fe₂O₃–SnO₂. This effect is typical of all series of component ratios and annealing temperatures. Consequently, one can expect that the samples based on γ-Fe₂O₃ and α-Fe₂O₃ will demonstrate different gas-sensitive behaviour.

3.1. Electrical measurements in air

Electrical conductivity of the Fe₂O₃–SnO₂ thin film layers with Fe:Sn = 1:9 and 1:1 is found to be considerably lower as compared to the Fe₂O₃–SnO₂ (Fe:Sn = 9:1) composite and simple oxides in air (Fig. 2). The Fe₂O₃–SnO₂ (Fe:Sn = 9:1) and SnO₂ demonstrate minimum resistance values. The conductivity of the Fe₂O₃–SnO₂ (Fe:Sn = 1:9, 1:1) films is approximately equal at 100–500 °C; however, the trends of the curves are quite dissimilar within the indi
Fig. 1. XRD patterns of α-Fe₂O₃–SnO₂ (a) and γ-Fe₂O₃–SnO₂ (b) composites (Fe:Sn = 9:1, 1:1, 1:9), annealed at different temperatures for 1 h.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>SnO₂ d (nm)</th>
<th>Fe₂O₃ d (nm)</th>
<th>α-Fe₂O₃–SnO₂ (Fe:Sn = 1:1)</th>
<th>γ-Fe₂O₃–SnO₂ (Fe:Sn = 1:1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>2</td>
<td>–</td>
<td>SnO₂</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>α-Fe₂O₃</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SnO₂</td>
<td>γ-Fe₂O₃</td>
</tr>
<tr>
<td>500</td>
<td>6</td>
<td>15</td>
<td>SnO₂</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>α-Fe₂O₃</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SnO₂</td>
<td>(α + γ)-Fe₂O₃</td>
</tr>
<tr>
<td>800</td>
<td>40</td>
<td>70</td>
<td>SnO₂</td>
<td>10</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>α-Fe₂O₃</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SnO₂</td>
<td>α-Fe₂O₃</td>
</tr>
</tbody>
</table>

Table 1
Phase composition and grain size of simple Fe₂O₃ and SnO₂ oxides and Fe₂O₃–SnO₂ nanocomposites depending on annealing temperature
The thin film layers based on the Fe$_2$O$_3$–SnO$_2$ composites and simple oxides demonstrate the same regularities that intrinsic to the corresponding thin films, but absolute conductivity values appear to be significantly lower in the case of the thick films (Fig. 3). It is probably explained by poor contact between separate particles of the powder. Because of the indicated point we were not able to perform the functional characterisation of some samples at low operating temperatures in both air and gas ambient. The sample with Fe:Sn ratio 1:9 appeared to be of extremely high resistance in air.

3.2. Electrical measurements in gas ambient

Thin and thick Fe$_2$O$_3$–SnO$_2$ films of different structure and chemical composition are characterised by dissimilar behaviour in gas ambient of different chemical nature—oxidising (NO$_2$) and reducing (C$_2$H$_5$OH) gases. Humid ethanol vapours (RH 98%) were used that caused by great importance of control the alcohol concentration in human’s expirations. It is obvious, that great humidity influences strongly the sensitive layer behaviour. As it was established by Kappler et al. [16], humidity growth leads to an increase in the number of oxygen vacancies that enhances the chemisorption of oxygen and forms specific oxygen sites. In synthetic air an increase of oxygen ions occurs at the sensor surface when humidity is increased. The rise in the number of available oxygen partners for ethanol in the oxidation reaction causes enhancement of the sensor signal. The thin film sensors are found to be more suitable for detection of NO$_2$; meanwhile, the thick films demonstrate good performance when detecting ethanol vapours. Note, that the response values (dG/G) to oxidising gases of all the sensors are very low as compared to individual oxides like SnO$_2$ and In$_2$O$_3$. The response of the best material to 1 ppm NO$_2$ does not exceed 0.5 r. u. At lower NO$_2$ concentration the signal is unstable and poorly reproducible (Fig. 4). The only α-Fe$_2$O$_3$–SnO$_2$ samples show measurable response values to NO$_2$ among the thin film layers. The α-Fe$_2$O$_3$–SnO$_2$ (Fe:Sn = 1:1) composite demonstrates maximum sensitivity at 100°C. It is important, that NO$_2$ molecules proceed as electron donors within low-temperature region. It can be connected with the point that the conductivity of
the Fe₂O₃–SnO₂ composites (up to 150°C) is determined by the presence of surface OH-groups, which desorbs at 150–400°C. Besides, the response of the α-Fe₂O₃–SnO₂ sensors of all series of compositions to NO₂ reaches its maximum value at temperatures, at which maximum layer conductivity drop in air is observed.

In the case of thick films, the α-Fe₂O₃–SnO₂ and γ-Fe₂O₃–SnO₂ (Fe:Sn = 9:1) composites show maximum sensitivity to humid C₂H₅OH vapours. As it was noted above, the layers were annealed at 550°C in order to provide measurable sensor conductivity. Thus prepared samples have the structure of Sn(IV)–Fe₂O₃. However, certain insignificant differences are observed in the α-Fe₂O₃–SnO₂ and γ-Fe₂O₃–SnO₂ behaviour that can be caused by certain distinctions in grain size and microstructure of the samples. Thus, the composites obtained via Fe³⁺ precursor (α-Fe₂O₃–SnO₂) are characterised by higher response and increased optimal detecting temperature (Fig. 5).

Maximum response to ethanol of the Fe₂O₃–SnO₂ (Fe:Sn = 9:1) layer appears to be greater than that one demonstrated by simple oxides (SnO₂, Fe₂O₃) (Fig. 6). We failed to measure the Fe₂O₃–SnO₂ (Fe:Sn = 1:9) sensor because of its extremely high resistance. Remarkably, that the optimal operating temperatures of the whole series of the thick film sensors lie in narrow-temperature range (280–320°C).

The dependence of the thick film sensor resistance vs. concentration of humid ethanol vapour (270°C) is presented in Fig. 7. There is a clear difference in the behaviour of the α-Fe₂O₃–SnO₂ and γ-Fe₂O₃–SnO₂ species. The α-Fe₂O₃–SnO₂ layers demonstrate suitable performance when detecting alcohol within the concentration range 0.05–1.0%. In contrast, the γ-Fe₂O₃–SnO₂ composites and simple oxides are characterised by unsuitably low ΔRlayer/ΔCGas ratio that makes the mentioned materials unusable for accurate registration of the gas concentration.

According to the available EPR data, two types of Fe(III) centres occur within the Fe₂O₃–SnO₂ composites obtained both via Fe³⁺ and Fe²⁺ precursors (Fig. 8): (I) g = 4.3, ΔB = 4 mT and (II) g = 4.3, ΔB = 4 mT. The signal I, which is observed in the case of SnO₂ doped with Fe³⁺ ions is assigned to isolated Fe(III) centres in strong crystal field of rhombic symmetry [17]. Strong crystal field can be caused by the distribution of Fe(III) ions within near-surface layers of SnO₂, as well as by the presence of oxygen vacancies in close environment of Fe(III) within SnO₂ matrix [18]. Both intensity and shape of the signal II (g ~ 2.0) depend on the recording temperature. The spectrum recorded at 77 K allows realising that the broadened resonance signal II contains two lines at g ~ 2.3 and ~2.0. The former
line is assigned to noncrystalline Fe$_2$O$_3$ nanoparticles, which consist of Fe(III) ions in cubic symmetry of oxygen close environment. Note, that the mentioned environment is similar to a greater extent to $\gamma$-Fe$_2$O$_3$/γ-FeOOH crystal structure (cubic symmetry) rather than to trigonal $\alpha$-Fe$_2$O$_3$. The second component of the signal II ($g \sim 2.0$) is assigned to the associates of Fe(III) ions; it is typical of superparamagnetic Fe$_2$O$_3$ clusters. This fact explains activity of the studied species in gas adsorption processes. Thus, gas-sensitive and electro-physical properties of the thin and thick film Fe$_2$O$_3$–SnO$_2$ are substantially determined by Fe(III) state.

Treating the Fe$_2$O$_3$–SnO$_2$ (Fe:Sn = 1:1) powder with NO$_2$ (120°C, 10 min) leads to the increase of the signal II only; the signal I remains unchanged. This fact gives evidence that only amorphous Fe$_2$O$_3$ can participate in NO$_2$ adsorption; the isolated Fe(III) ions within SnO$_2$ lattice are inactive. This explains greater sensitivity of the Fe$_2$O$_3$–SnO$_2$ (Fe:Sn = 1:1 and 9:1) films to NO$_2$ as compared to Fe$_2$O$_3$–SnO$_2$ (Fe:Sn = 1:9).

Mössbauer spectra of the $\alpha$-Fe$_2$O$_3$–SnO$_2$ and $\gamma$-Fe$_2$O$_3$–SnO$_2$ samples (annealing temperature 300–500°C) represent a broadened doublet, which is an evidence of superparamagnetic Fe$_2$O$_3$ particles ($d \sim 3$–4 nm) formation. Thus, the samples with Fe:Sn = 9:1 and 1:1 contain areas of highly dispersive and poorly crystallised Fe$_2$O$_3$. The parameters of the Fe$_2$O$_3$–SnO$_2$ spectra are different from the parameters, which are typical of the spectra of both $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$ bulk phases. However, the values of isomeric shift ($\delta$) and induction of magnetic field ($B$) of amorphous Fe$_2$O$_3$ are closer to the parameters of cubic $\gamma$-Fe$_2$O$_3$ rather than to trigonal $\alpha$-Fe$_2$O$_3$ that is in agreement with the EPR data (Table 2). The coordination of Fe(III), which is specific of cubic structure of unit cell ($\gamma$-FeOOH, $\gamma$-Fe$_2$O$_3$), preserves within the Fe$_2$O$_3$ amorphous phase. Considerable increase of the quadrupole splitting ($\Delta$) values as compared to the simple oxides is typical of the studied composites; it indicates that the crystal environment of Fe(III) points within the Fe$_2$O$_3$ matrix is strongly irregular in the presence of Sn(IV).

Two ways of alcohol (in particular, ethanol) molecule conversion are possible at oxide surface—dehydrogenation (1) and dehydration (2) [6,19]:

\[
\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + \frac{1}{2}\text{H}_2 \quad \text{(dehydrogenation) (1)}
\]

\[
\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \quad \text{(dehydration) (2)}
\]

Besides, further oxidation of the formed products (foremost, oxidation of H atoms) is also possible; it should result in sensor response growth. Thus, the process (1) most often proceeds through the oxidising dehydrogenation mechanism:

\[
\text{CH}_3\text{CH}_2\text{OH} \overset{\text{O}^\cdot -\text{O}^\cdot}{\rightarrow} \text{CH}_3\text{CHO} + \text{H}_2\text{O} \quad \text{(oxidising dehydrogenation) (3)}
\]

As we established earlier [11], lattice oxygen is only participating in the indicated process at high operating temperatures (300–400°C). The role of adsorbed oxygen consists of regenerating of partially reduced oxide surface.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta$ (mm/s)</th>
<th>$\Delta$ (mm/s)</th>
<th>$B$ (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$–SnO$_2$</td>
<td>0.35 ± 0.02</td>
<td>0.72 ± 0.02</td>
<td>50.8</td>
</tr>
<tr>
<td>(Fe:Sn = 1:1) 300°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$_2$O$_3$–SnO$_2$</td>
<td>0.35 ± 0.02</td>
<td>0.87 ± 0.02</td>
<td>50.8</td>
</tr>
<tr>
<td>(Fe:Sn = 1:1) 500°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\gamma$-Fe$_2$O$_3$ (bulk)</td>
<td>0.34 ± 0.01</td>
<td>−0.053 ± 0.020</td>
<td>49.6</td>
</tr>
<tr>
<td>$\alpha$-Fe$_2$O$_3$ (bulk)</td>
<td>0.47 ± 0.03</td>
<td>0.23 ± 0.01</td>
<td>51.8</td>
</tr>
</tbody>
</table>

Recorded at 300 K.
The oxidising dehydrogenation is heterolytic catalytic reaction. The process involves both reductive–oxidative and acid–base steps. In particular, alcohol molecule adsorption at metal cations, which play role of Lewis centres, is related to acid–base reaction. The reactivity of oxides in acid–base reactions depends on the electronegativity of cations $M^{n+}$:

$$\chi = \chi_0(2n + 1)$$

(4)

where $\chi_0$ is the Pauling’s electronegativity, $n$ the ion charge. The electronegativity can be used as the measure of Lewis acid activity [20]. Adsorption of alcohol molecules at Lewis sites is going with great output. The relative measure of an oxide activity in the oxidation reactions can be oxygen–oxide surface bonding energy. Lesser energies of oxygen atom isolation from an oxide surface favour higher oxide oxidising ability. Complete oxidation of the intermediate products is possible at the surface of the oxide, which is characterised by small values of M–O bonding energy and electronegativity. Thus, due to the low Fe–O bonding energy and increased basicity of Fe$_2$O$_3$ in comparison to SnO$_2$ ($E_{\text{Fe-O}} = 56$, $E_{\text{Sn-O}} = 70$ kcal/g per atom; $\chi(\text{Fe}^{3+}) = 13.72$, $\chi(\text{Sn}^{4+}) = 17.64$) Fe(III) centres promote further oxidation of intermediate products of ethanol molecule transformation [21]. For the detailed mechanism of ethanol detection refer to [22].

Thus, substitution of Sn(IV) for the isolated Fe(III) ions in points of SnO$_2$ lattice considerably electrical conductivity of SnO$_2$ films and their sensitivity to both oxidising (NO$_2$) and reducing (C$_2$H$_5$OH) gases. As it was noted above, the Fe$_2$O$_3$–SnO$_2$ nanocomposites, which have a structure of Sn(IV)–α–Fe$_2$O$_3$ solid solution, show high response to ethanol vapours due to the presence of two types of adsorption centres—Sn(IV) and Fe(III). The two centres are characterised by different activity in the course of both reduction–oxidation and acid–base reactions.

Moreover, high dispersity of Sn(IV)–α–Fe$_2$O$_3$ solid solution provides efficient electron exchange between the cations: Fe(III) $\leftrightarrow$ Fe(II). All this produces greater conductivity drop of the active layer and, consequently, improves the sensor performance.

4. Conclusion

Sol–gel technology provides the obtaining of complex oxide systems, which differ by chemical composition (oxide nature, component ratio), structure (phase composition, peculiarities of microstructure) and dispersity. As it was found out, the studied composites are characterised by distinct electrical properties in both air and gas ambient. Besides, type of the used sensors (thin and thick film) influences strongly the functional features of the layers as well. The correlation between the indicated factors and gas-sensitive performance of the sensors has been established. Thus, doping SnO$_2$ with Fe$^{3+}$ ions leads to the sensor response decrease to most of gases, in particular NO$_2$ and C$_2$H$_5$OH, that is caused by the occurrence of separately distributed Fe(III) ions within SnO$_2$ matrix; no clusters of amorphous Fe$_2$O$_3$ are present. Good performance of the sensors is typical of the Fe$_2$O$_3$–SnO$_2$ composites with Fe:Sn $\geq$ 1. Advanced oxide gas-sensitive materials were obtained under the used conditions of synthesis and mode of thermal treatment of the layers. The highly defective α–Fe$_2$O$_3$ phase provides suitable sensor conductivity and high sensitivity. Besides, the occurrence of two types of adsorption centres (Sn(IV) and Fe(III)), which possess different activity in both reduction–oxidation and acid–base reactions results in additional improvement of the sensor sensitivity to ethanol vapours.

Certain distinctions were revealed in the behaviour of the Fe$_2$O$_3$–SnO$_2$ composites obtained either through the crystallisation of amorphous Fe$_2$O$_3$ or as a result of thermally induced transformation of γ–Fe$_2$O$_3$. The composites obtained via Fe$^{3+}$ precursors differ by slightly decreased response and unsuitable $\Delta$R$_{\text{layer}}$/$\Delta$C$_{\text{gas}}$ ratio as compared to the corresponding species prepared through the Fe$^{3+}$ salt hydrolysis.

Acknowledgements

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References

Biographies

Dzmitry Kotsikau graduated from the Belarus State University in 2001 with honours; in the same year he entered the post graduate courses; simultaneously, he is working at the Scientific Research Institute for Physical and Chemical Problems of Belarus State University in the field of solid state chemistry and semiconductor gas sensors. His main scientific interests are Fe₂O₃–In₂O₃ and Fe₂O₃–SnO₂ nanosized composites, their structural and gas-sensitive characterisation.

Maria Ivanovskaya received her degree in chemistry in 1980 from Belarus State University in the field of photochemistry. Since 1989 she has been working at the Scientific Research Institute of Physical and Chemical Problems (Belarus State University). Her main scientific interest is solid state chemistry in applications to catalysis and semiconductor gas sensors, structural features of nanosized oxides (SnO₂, MoO₃, In₂O₃, Fe₂O₃) and oxide composites. She is co-author of more than 200 papers on the indicated topics.

Dmitry Orlik received his PhD degree in chemistry in 1990 from Belarus State University with a thesis on gas sensors and structural characterisation of oxide systems. Now he is occupying the research position in the Scientific Research Institute for Physical and Chemical Problems (Belarus State University). Now he is working in the field of solid state chemistry and semiconductor gas sensors.

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