Gas-sensitive properties of thin film heterojunction structures based on Fe_2O_3–In_2O_3 nanocomposites

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Abstract

This paper reports an investigation of the gas-sensitive properties of thin film sensors based on the double-layers Fe_2O_3–In_2O_3 and Fe_2O_3–In_2O_3/In_2O_3 towards gases of different chemical nature (C_2H_5OH, CH_4, CO, NH_3, NO_2, O_3). As it was found, the γ-Fe_2O_3–In_2O_3 composite (Fe:In = 9:1, mol) is more sensitive to O_3; on the contrary, the α-Fe_2O_3–In_2O_3 (9:1) system, possesses a higher sensitivity to NO_2. The optimal temperature for detecting of both gases is in the range of 70–100 °C. Sensors based on the γ-Fe_2O_3–In_2O_3 heterostructure show the maximum response to C_2H_5OH at considerably higher temperatures (250–300 °C), but this layer is practically insensitive to other reducing gases like CH_4, CO and NH_3 in the same temperature range.

An explanation of the different gas-sensitive behavior for the these samples resulted from the particular features of their structure and phase state.

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Keywords: Gas sensor; Oxide heterojunction; Fe_2O_3; In_2O_3; Nanosized composite

1. Introduction

The existing literature reports that the sensitivity of ceramic sensors based on Fe_2O_3 layers to reducing gases is rather low [1–3]. However, the doping of Fe_2O_3 with quadrivalent metal ions (Sn, Ti, Zr) as well as the modification of this material with SO_4^{2-} ions can significantly enhance the gas-sensitive properties of the corresponding sensors towards ethanol and hydrocarbons [3]. In particular, the addition of Fe_2O_3 to SnO_2 thick films leads to an increasing response to ethanol [4]. There are also some papers concerning the effect of Fe_2O_3 additives on the properties of In_2O_3 based sensors; for example, the sputtering of a Fe_2O_3 layer over In_2O_3 thin film increases its sensitivity to O_3 and reduces the optimal operating temperature [5].

A considerable improvement of In_2O_3 thin film sensors with respect to O_3 by doping with γ-Fe_2O_3 is reported by Gutman et al. [6]; the influence of α-Fe_2O_3 additives on In_2O_3 behavior is negligible. The high activity of γ-Fe_2O_3–In_2O_3 composite in the O_3 detection can be associated with the specific features of γ-Fe_2O_3 structure, like the presence of metal cation vacancies within the crystal lattice and the readiness of $Fe^{2+} \leftrightarrow Fe^{3+}$ transformation under exposure by gaseous species. Nevertheless, the available data are not sufficient in order to realize if iron oxides are suitable materials for gas sensing applications.

As it is known, γ-Fe_2O_3 is characterized by a comparatively low thermal stability with respect to γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$ phase transformation that ordinarily occurs at 485 °C. This peculiarity of γ-Fe_2O_3 limits its use as long-term stable gas-sensitive material.

The gas-sensitive properties of thin film layers of complex structure based on both γ-Fe_2O_3 and α-Fe_2O_3 have been extensively characterized in this paper. The use of systems with complex composition allows us to

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64 increase significantly the thermal stability of γ-Fe$_2$O$_3$
65 phase (up to 650 °C) in γ-Fe$_2$O$_3$–In$_2$O$_3$ composite and
66 to modify its gas-sensitive characteristics by imparting
67 to the sensors the required sensitive and dynamical fea-
68 tures.

2. Experimental

70 The gas-sensitive properties of thin film double-layer
71 sensors based on Fe$_2$O$_3$, and Fe$_2$O$_3$–In$_2$O$_3$ (Fe:In = 9:1
72 and 1:1, mol) were investigated; sensor response values to
73 CH$_3$OH, C$_2$H$_5$OH (100–500 ppm), CH$_4$, CO (50 ppm) ozone
74 (200 ppb) and NO$_2$ (0.5–5 ppm) were obtained.

75 The sensitive elements were formed from the stabilized
76 sols of the corresponding metal hydroxides which were
77 prepared by the sol-gel technique. The procedure of sol
78 preparation used in this study consisted of the following
79 steps:

81 (i) forced hydrolysis of inorganic metal salt solution
   (FeCl$_2$, In(NO$_3$)$_3$) with a basic agent (NH$_3$),
83 (ii) precipitation of metal hydroxide followed by its
   separation,
85 (iii) formation of sol through peptization of the depo-
   sit with a peptizing agent or as a result of self-
86,87 peptization.

88 The α-Fe$_2$O$_3$–In$_2$O$_3$ composite was prepared by com-
89 bined precipitation of Fe(OH)$_2$ and In(OH)$_3$ hydroxides
90 followed by their oxidation with oxygen. A flow of air
91 was passed through the corresponding suspension during
92 5–6 h at 30 °C to perform the material oxidization. In
93 contrast, γ-Fe$_2$O$_3$–In$_2$O$_3$ sample was obtained by mixing
94 of individual sols of γ-Fe$_2$O$_3$ and In(OH)$_3$ in the required
95 proportions.

96 Sols were deposited onto polycrystalline Al$_2$O$_3$ substrates
97 (3 mm × 3 mm × 0.25 mm size) with Pt interdigital elec-
98 trode deposited on the front side and Pt meander heater on
99 the back side.

100 An In$_2$O$_3$ sub-layer was preliminary deposited onto the
101 substrate in order to form the heterojunction structure and
102 provide suitable sensor conductance. A single-layer sensor,
103 consisting only of In$_2$O$_3$ or Fe$_2$O$_3$ also were studied in
104 parallel for comparison. The samples were dried at 25 °C
105 and annealed at 300 °C in air.

106 The sensors were then mounted on a TO8 standard cases
107 and were put inside the a chamber for the DC electrical
108 measurements in presence of fixed gas concentrations and
109 RH levels.

110 The sensor response was calculated as $\Delta G/G_{air}$ at CH$_3$OH,
111 C$_2$H$_5$OH, CH$_4$, CO detection and as $\Delta G/G_{gas}$ at NO$_2$ and O$_3$
112 detection, where G is the electrical conductance of sensitive
113 layer.

114 The structure of the single oxides (Fe$_2$O$_3$, In$_2$O$_3$) and
115 nanocomposites (Fe$_2$O$_3$–In$_2$O$_3$) were characterized by means
116 of X-ray diffraction (XRD), transmission electron micros-

117 copy (TEM) and Mössbauer spectroscopy. The resonance
118 spectra were recorded and processed in a commercial
119 SM2201 Mössbauer spectrometer. The measurements repor-
120 ted here were performed at 298 K using a 15 mCi ^{57}Co (Rh)
121 source.

3. Results and discussion

3.1. Gas-sensitive properties

124 As it was found, γ-Fe$_2$O$_3$–In$_2$O$_3$ (9:1)/In$_2$O$_3$ and α-
125 Fe$_2$O$_3$–In$_2$O$_3$ (9:1)/In$_2$O$_3$ sensors are characterized by
126 high sensitivity to O$_3$ and NO$_2$, respectively, over a low
127 temperature range (70–135 °C), as it is reported in Fig. 1a
128 and b. These response values are greater than those ones
129 typical for a single-layer sensors based on In$_2$O$_3$ and
130 Fe$_2$O$_3$.

131 The response values of α-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$ samples
132 to O$_3$ and NO$_2$ at various operating temperatures are
133 reported in Table 1. It is clearly seen from these data
134 that γ-Fe$_2$O$_3$–In$_2$O$_3$ (9:1)/In$_2$O$_3$ sensor shows a high con-
135 ductance variation in the O$_3$ atmosphere at 135 °C, while
136 its response to NO$_2$ at the same temperature is negligible.
137 In contrast, α-Fe$_2$O$_3$–In$_2$O$_3$ (9:1)/In$_2$O$_3$ sample shows a
138 good response to NO$_2$ in the temperature range 50–100 °C
139 together with a rather low one to O$_3$. These distinctions,
140 observed in the behavior of both composites, can be used
141 for a selective analysis of O$_3$ and NO$_2$ in the gas mix-
142 ture.

143 Generally, the sensitivity of In$_2$O$_3$ and SnO$_2$ films to O$_3$ is
144 lower in comparison with its sensitivity towards NO$_2$ [7,8].
145 In contrast, Fe$_2$O$_3$–In$_2$O$_3$ layers are characterized by a
146 higher sensitivity to O$_3$ than to NO$_2$. Moreover, the indicated
147 compositions show better NO$_2$ detection performances than
148 the previously investigated sensors based on In$_2$O$_3$–NiO [9]
149 and In$_2$O$_3$–MoO$_3$ thin films [7].

150 It should be noted that the sensors show insufficiently
151 rapid response and rather long recovery time at low operat-
152 ing temperatures. Isothermal response of α-Fe$_2$O$_3$–In$_2$O$_3$
153 (9:1)/In$_2$O$_3$ double-layer to 5 ppm NO$_2$ is represented in

Table 1
The comparison of response values of sensors based on both α-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$ to O$_3$ and NO$_2$

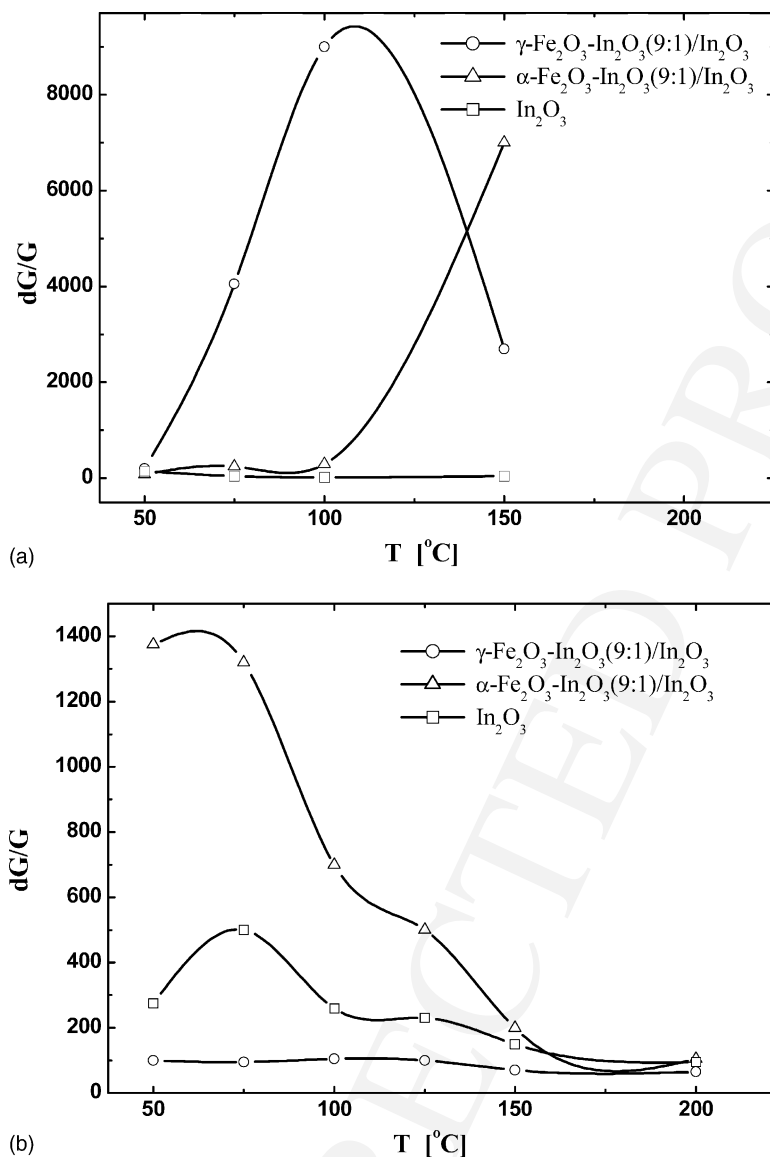| Detected gas	C_{gas} (ppb)	T (°C)	$\Delta G/G_{gas}$	
			α-Fe$_2$O$_3$–In$_2$O$_3$ (9:1)/In$_2$O$_3$	γ-Fe$_2$O$_3$–In$_2$O$_3$ (9:1)/In$_2$O$_3$
O$_3$	100	100	65	130
	100	135	450	8670
NO$_2$	500	100	65	15
	500	135	75	10
	5000	100	600	90
	5000	135	440	50

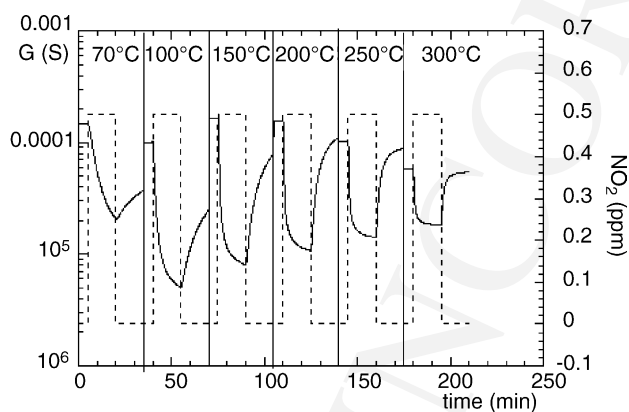Fig. 1. Temperature-dependent responses of In$_2$O$_3$ based sensors to (a) 200 ppb O$_3$ and (b) 5 ppm NO$_2$.

Fig. 2. Isothermal response of α-Fe$_2$O$_3$–In$_2$O$_3$ (9:1)/In$_2$O$_3$ thin film sensor between 70 and 300 °C to 5 ppm NO$_2$ in 50% RH.

Table 2
Responses and dynamical parameters of In$_2$O$_3$ and α-Fe$_2$O$_3$–In$_2$O$_3$ (9:1)/In$_2$O$_3$ thin film sensors to 5 ppm NO$_2$ vs. temperature in the range of 55–250 °C

T (°C)	In$_2$O$_3$			α-Fe$_2$O$_3$–In$_2$O$_3$ (9:1)/In$_2$O$_3$		
	$\Delta G/G_{gas}$	τ_{res} (s)	τ_{rec} (s)	$\Delta G/G_{gas}$	τ_{res} (s)	τ_{rec} (s)
55	300	110	>900	1375	30	>900
75	500	35	>900	1375	30	>900
100	260	30	>900	560	25	>900
135	220	25	>900	440	20	>900
150	45	25	850	110	25	800
200	12	25	725	25	20	540
250	3	25	235	4	25	90
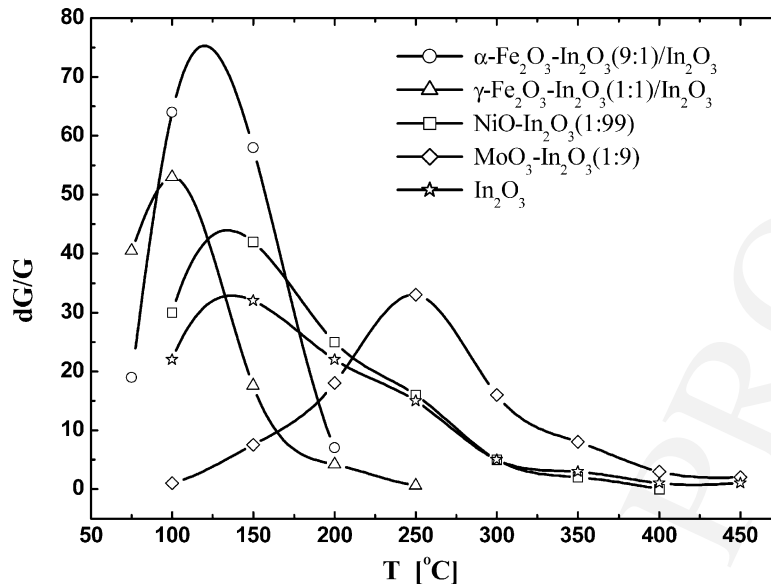
Fig. 3. Comparison of sensitivity of In_2O_3 based sensors doping with oxides of different metals to 1 ppm NO_2.

Fig. 2. The responses and dynamical characteristics of In_2O_3 and α-Fe_2O_3–In_2O_3 (9:1)/In_2O_3 thin film sensors are compared in Table 2.

Fig. 3 shows the dependence of the response values to NO_2 on the operating temperature for sensors with different composition of the sensitive layer. As it is seen from these curves, Fe_2O_3–In_2O_3 sensors have not only the greatest signals, but they can operate properly at relatively low temperatures.

Fe_2O_3–In_2O_3/In_2O_3 and Fe_2O_3–In_2O_3 sensors posses poor responses to low concentration of 50 ppm CO, as it is shown in Fig. 4; they are also almost insensitive both to CH_4 and NH_3.

It is important to note that all double-layer sensors are much more sensitive towards alcohol (C_2H_5OH, CH_3OH) vapors than single-layer In_2O_3 and Fe_2O_3 samples; the maximum response is showed by γ-Fe_2O_3–In_2O_3 composite. Temperature dependent responses of γ-Fe_2O_3–In_2O_3 and In_2O_3 sensors are represented in Fig. 5.

One should also point out that Fe_2O_3-containing films are insensitive to O_3 and NO_2 over the temperature range of the most efficient ethanol detection (250–400 °C); at the same time, their sensitivity regarding ethanol is negligible at 50–150 °C, when O_3 and NO_2 interaction with oxide surface has the maximum value. An increase of the In_2O_3 content within Fe_2O_3–In_2O_3 composite up to 50 mol%
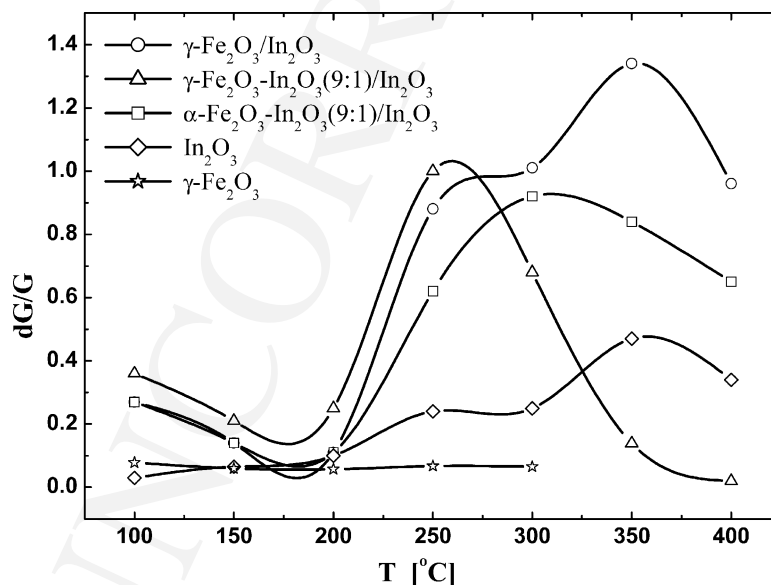

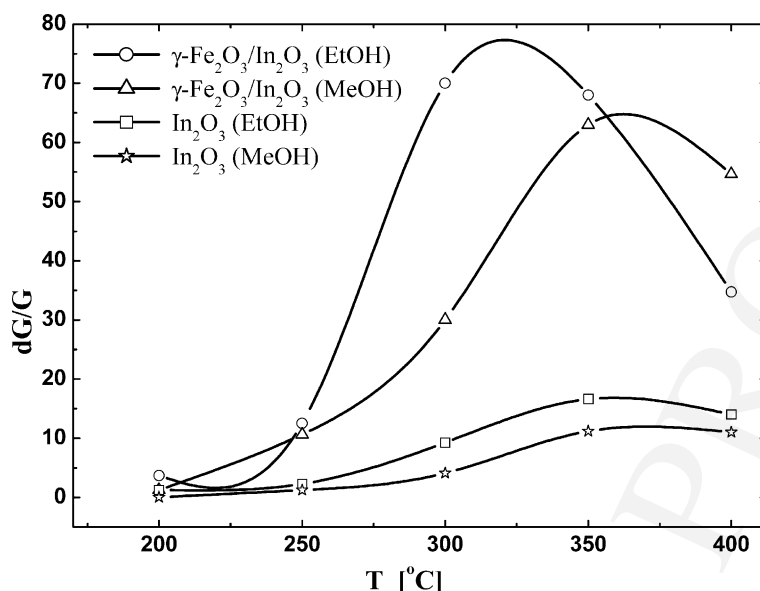Fig. 4. Temperature-dependent responses of the layers of different composition to 50 ppm CO.

Fig. 5. Temperature-dependent responses of In_2O_3 and Fe_2O_3 based single- and double-layer sensors to 100 ppm C_2H_5OH and 100 ppm CH_3OH.

leads to the growth of the sensor responses both to NO_2 and ethanol.

The comparison of gas-sensitive behavior of both single- and double-layer Fe_2O_3 species regarding NO_2, CO and ethanol is presented in Table 3. In the case of O_3, the response of single Fe_2O_3 layer was negligible and irreproducible.

Referring to the results of functional and structural investigations, we can recommend a series of Fe_2O_3–In_2O_3 samples with different structural and phase state to be used as advanced materials for O_3, NO_2 and C_2H_5OH detection. The particular compositions, dispersion, structural and phase features are listed in Table 4. The first three sensors appeared absolutely selective to O_3, NO_2 and C_2H_5OH at the indicated operating temperature. The fourth one can be used for NO_2 detection (low temperatures) as well as for C_2H_5OH analysis (higher temperatures).

3.2. Structural characterization

Both TEM and XRD data give evidence that all the films studied appear to be nanosized systems.

Table 4 displays the average grain size of the samples (300 °C) calculated from the corresponding XRD line broadening.

According to the XRD pattern, α-Fe_2O_3–In_2O_3 (9:1) composite consists of α-Fe_2O_3 phase with increased parameters of unit cell (see Fig. 6). The increasing of the cell parameters is caused by the substitution of part of Fe(III) ions with In(III) ones. Besides, the X-ray reflexes assigned to the α-Fe_2O_3 phase are strongly broadened; this fact can be explained both by the nano-dimension of particles and the high defectiveness of the crystalline structure.

It was also assumed that α-Fe_2O_3 phase, obtained through the oxidation of γ-Fe_2O_3 phase, is quite different from α-Fe_2O_3 phase prepared by thermal dehydration of α-modification of iron(III) hydroxide. The irregularity of Fe(III) state within α-Fe_2O_3–In_2O_3 (9:1) can be observed from the Mössbauer pattern recorded from the indicated sample.

Table 3
The comparison of gas-sensitive behavior of In_2O_3, Fe_2O_3 and Fe_2O_3–In_2O_3 thin films

Sensor	NO_2, 5 ppm		CO, 50 ppm		C_2H_5OH, 100 ppm	
	$\Delta G/G_{gas}$	T (°C)	$\Delta G/G_{air}$	T (°C)	$\Delta G/G_{air}$	T (°C)
In_2O_3	40	100	0.45	350	15	350
Fe_2O_3	5	100	0.1	250	15	350
Fe_2O_3–In_2O_3	65	135	1.25	350	65	300

Table 4
The most promising gas-sensitive materials recommended for fabricating of highly selective sensors and their structural peculiarities

Sample	T (°C)	Detected gas	Phase composition	Particle size (nm)
γ-Fe_2O_3–In_2O_3 (9:1)	135	O_3	γ-Fe_2O_3[a]	25
			C-In_2O_3	25
α-Fe_2O_3–In_2O_3 (9:1)	70–100	NO_2	α-Fe_2O_3	10–15
γ-Fe_2O_3	250	C_2H_5OH	γ-Fe_2O_3	25–30
γ-Fe_2O_3–In_2O_3 (1:1)	70–100	NO_2	C-In_2O_3[a]	7–8
	300	C_2H_5OH	γ-Fe_2O_3	5

Temperature of annealing is 300 °C.
[a] Main phase.
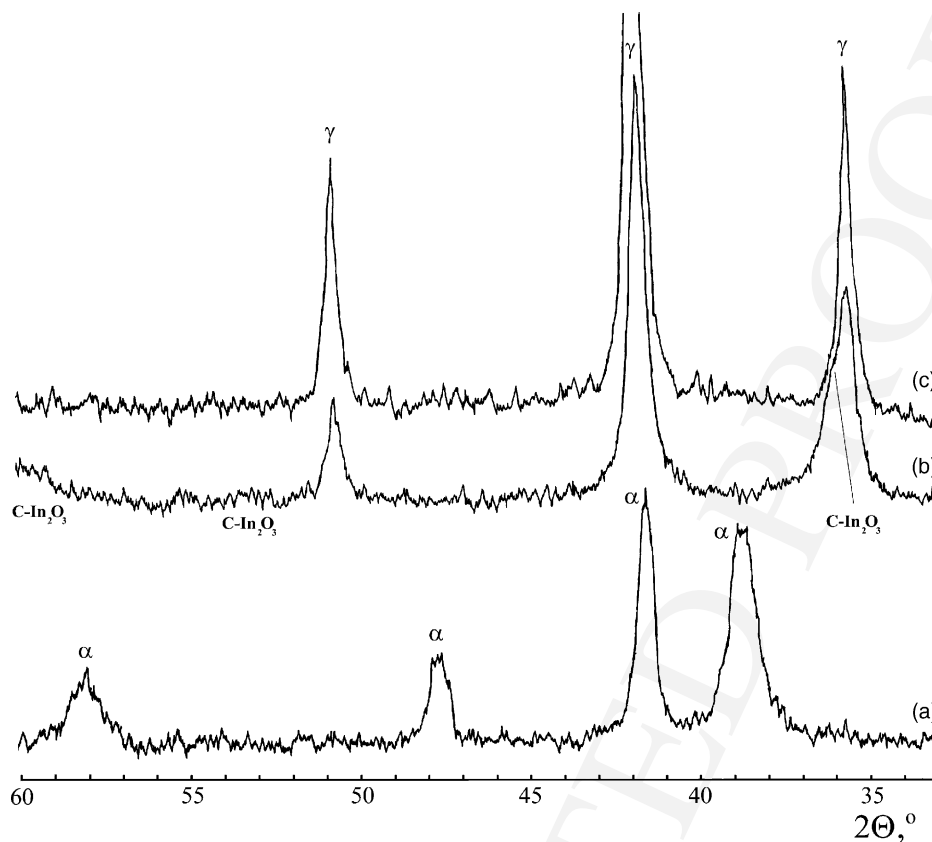
Fig. 6. XRD patterns recorded from (a) α-Fe_2O_3–In_2O_3 (9:1), (b) γ-Fe_2O_3–In_2O_3 (9:1) and (c) γ-Fe_2O_3 samples. Temperature of annealing is 300 °C.

Regarding to magnetic properties, the oxides prepared by the sol-gel technology differ from the corresponding standard sample (Fig. 7a and b). We can distinguish three types of Fe(III) ions with discriminate parameters in Mössbauer spectrum of α-Fe_2O_3–In_2O_3 composite (Table 5).

(i) About 78% of total amount of Fe(III) ions is characterized by magnetic parameters and coordination environment typical for Fe(III) ions within amorphous or poorly crystallized α-Fe_2O_3 phase.

Table 5
Parameters of Mössbauer spectra recorded from iron-containing samples at 298 K

Sample	δ (mm s^{-1})	Δ (mm s^{-1})	B (T)
α-Fe_2O_3–In_2O_3 (9:1) (300 °C)	0.38 (78)	0.08	50.7
	0.53 (15)	0	0
	0.22 (7)	0.69	0
γ-Fe_2O_3–In_2O_3 (9:1) (300 °C)	0.33	0.02	48.6
γ-Fe_2O_3 (sol) (300 °C)	0.34	−0.03	49.1
γ-FeOOH (300 °C)	0.33	0.78	0
α-Fe_2O_3 (amorphous) (300 °C)	0.39	0.09	50.7
γ-Fe_2O_3 (standard sample)	0.34	−0.05	49.6
α-Fe_2O_3 (standard sample)	0.47	0.24	51.8
	0.38	0.12	51.5

The values in parentheses are in percent.

(ii) About 15% of Fe(III) has a cubic coordination environment. This type of coordination can be assigned to isolated Fe(III) ions in octahedral environment of oxygen, which is typical for cubic In_2O_3 modification. Moreover, γ-Fe_2O_3 can possess cubic structure as well.

Under sample heating at 150–200 °C, the γ-Fe_2O_3 phase remains stable within α-Fe_2O_3–In_2O_3 (9:1) sample obtained from Fe(II) precursor, which was used in this study. The annealing of the composite at temperatures over 250 °C leads to the transformation of γ-Fe_2O_3 phase doped with In(III) ions into α-Fe_2O_3, whereas individual γ-Fe_2O_3 oxide remains stable regarding γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$ phase transformation up to 485 °C. Moreover, γ-Fe_2O_3 phase within γ-Fe_2O_3–In_2O_3 composite is stable at temperatures up to 700 °C depending on the component ratio. Thus, in the case of γ-Fe_2O_3–In_2O_3 (9:1) sample, the γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$ phase transformation occurs at about 500 °C.

(iii) A minor part of Fe(III) ions (7%) can be only assigned to γ-FeOOH structure.

Therefore, the sample based on γ-Fe_2O_3–In_2O_3 (9:1) consists of γ-Fe_2O_3; a small amount of C-In_2O_3 phase is also present (See Fig. 6). In this case, the grain size is greater than in the case of α-Fe_2O_3 sample with the same composition. Mössbauer pattern of γ-Fe_2O_3–In_2O_3 system differs from that one recorded from the standard sample by broad-

Fig. 7. Mössbauer spectra recorded from (a) α-Fe$_2$O$_3$ standard, (b) α-Fe$_2$O$_3$–In$_2$O$_3$ (9:1) and (c) γ-Fe$_2$O$_3$–In$_2$O$_3$ (9:1) samples at 298 K.

ening and asymmetric shape of the resonance peaks (Fig. 7c). The distinctions in shape and parameters observed in Mössbauer spectra recorded from γ-Fe$_2$O$_3$–In$_2$O$_3$ and γ-Fe$_2$O$_3$ samples probably result from the following factors: γ-Fe$_2$O$_3$ cubic lattice distortion, irregularity of Fe(III) octahedral environment or Fe–O bond ionicity shift in the presence of In(III) ions within γ-Fe$_2$O$_3$ crystal lattice.

3.3. Regularities of certain gas detection

On the base of the obtained results we made an attempt to find the correlation between gas-sensitive behavior of Fe$_2$O$_3$–In$_2$O$_3$/In$_2$O$_3$ and Fe$_2$O$_3$–In$_2$O$_3$ active layers and their structural features.

3.3.1. Nitrogen dioxide

In order to obtain an advanced sensor for NO$_2$ detection, it is necessary to use materials which are characterized by high dispersion and defectiveness [10]. It is well known that doping of In$_2$O$_3$ with Ni(II) and Mo(VI) ions results in increasing of In$_2$O$_3$ based sensor sensitivity to NO$_2$ [7,9]. Addition of these ions leads to the formation of strongly defective In$_2$O$_3$ structure and favors the decreasing of oxide grains.

Similar changes were observed for α-Fe$_2$O$_3$ oxide doped with In(III) ions. In the case of α-Fe$_2$O$_3$–In$_2$O$_3$ (9:1) sample, together with α-In$_x$Fe$_{2-x}$O$_3$ solid solution, it is possible to distinguish other structural elements based on Fe$_2$O$_3$. We have yet not succeeded in identification of the supposed additional phases using XRD analysis, but the presence of several types of Fe(III) ions was confirmed by Mössbauer spectroscopy. An increased Fe–O bond length and the distortion of octahedral environment of Fe(III) ions favors the effective adsorption of NO$_2$, whereas the presence of two types of ions (Fe(III) and In(III)) within the α-In$_x$Fe$_{2-x}$O$_3$ solid solution facilitates to a certain extent the desorption of oxygen in comparison with the simple oxides. Thus, high sensitivity of α-Fe$_2$O$_3$–In$_2$O$_3$ films to NO$_2$ at low temperatures can be explained by high system dispersion and the presence of Fe(III) ions in irregular coordination environment which is evoked by doping of Fe$_2$O$_3$ phase with In(III) ions.

The growth of the response value of γ-Fe$_2$O$_3$–In$_2$O$_3$/In$_2$O$_3$ sensor with the increasing of In$_2$O$_3$ content from 10 to 50% within composite can be connected with grain size decreasing and the formation of highly defective sample with the high specific surface.

3.3.2. Ozone

The most important requirement for the efficient detection of ozone at low temperatures (70–100 °C) is the suitable catalytic activity of an oxide in reaction of ozone decomposition:

$$O_3 \rightarrow O_2 + O.$$
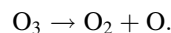
Iron oxide is known to be an active catalyst in this process; the main factors which influence the catalytic ability of Fe$_2$O$_3$ are oxidation state of a sample and its dispersion [11]. The oxidation level of the sample is closely related to its activity. Thus, α-Fe$_2$O$_3$ possesses better catalytic properties than γ-Fe$_2$O$_3$.

With regards to O$_3$, α-Fe$_2$O$_3$ phase demonstrates considerably higher sensitivity in comparison with γ-Fe$_2$O$_3$ species

[6]. However, the origin of different behavior of these systems is still unclear. In the case of γ-Fe$_2$O$_3$–In$_2$O$_3$ composite, the presence of separate γ-Fe$_2$O$_3$ phase probably provides an elevated activity of this sample towards O$_3$ at low temperatures. In contrast, α-Fe$_2$O$_3$–In$_2$O$_3$ sample consists of In(III)—α-Fe$_2$O$_3$ solid solution; catalytic ability of α-Fe$_2$O$_3$ phase in O$_3$ decomposition reaction is insignificant.

Since at low temperatures a limiting stage of the reaction is removing of chemisorbed oxygen, the presence of the second phase (In$_2$O$_3$) in γ-Fe$_2$O$_3$ is capable to facilitate the desorption of oxygen from the oxide surface.

At temperatures higher than 100 °C decomposition of ozone is passing effectively in gas phase according to the following equation:

$$O_3 \rightarrow O_2 + O$$
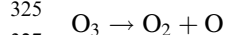
Detection of O$_3$ is going at Fe$_2$O$_3$–In$_2$O$_3$ through the adsorption of not molecular (O$_2$) but atomic (O) oxygen species. Thus, one can explain the observed differences in optimal detecting temperature of O$_3$ using α-Fe$_2$O$_3$–In$_2$O$_3$ and γ-Fe$_2$O$_3$–In$_2$O$_3$ composites by change of detection mechanism as a result of operating temperature variation.

3.3.3. Alcohol

The sensors based on heterojunction oxide structures show considerable response in alcohol (ethanol, methanol) media. The heterojunction between the oxide and the solid solution phases appears to be very active in course of both adsorption and oxidation of alcohol.

It is shown in [12] that the presence of two types of centers possessing the discriminate redox and acid–base properties and participating in transformation processes of alcohol molecule is an essential requirement to achieve high sensor response when alcohol detection is mentioned. Alcohol detection is considered as a multi-step process involving both reductive–oxidative and acid–base interactions. Oxide phases within the composite differ by oxygen–oxide surface bonding energy which can be the relative measure of oxide activity in the oxidation reactions. The reactivity of oxides in acid–base reactions depends on electronegativity of metal cation. The electronegativity is the measure of Lewis acid site activity. Thus, the centers of one type can mainly participate in adsorption–desorption processes of alcohol molecules, whereas complete oxidation of intermediates is going effectively at the centers of another type.

Increased response of γ-Fe$_2$O$_3$–In$_2$O$_3$ (1:1)/In$_2$O$_3$ sample as compared with γ-Fe$_2$O$_3$–In$_2$O$_3$ can be explained by the presence of an higher contact interface between In$_2$O$_3$ and γ-Fe$_2$O$_3$ phases within γ-Fe$_2$O$_3$–In$_2$O$_3$ composite.

4. Conclusions

The sensing characteristics of Fe$_2$O$_3$–In$_2$O$_3$ sensors towards gases of different chemical nature are found to be very promising. It is important to note that the most sensitive materials consist of two layers. In this case, the specific heterojunction is formed providing the differentiation between receptor and transducer functions. As it was established, γ-Fe$_2$O$_3$–In$_2$O$_3$ (9:1) composite is highly sensitive to O$_3$; on the contrary, the α-Fe$_2$O$_3$–In$_2$O$_3$ (1:1) system possesses the highest sensitivity to NO$_2$. The γ-Fe$_2$O$_3$–In$_2$O$_3$ sensor is sensitive to C$_2$H$_5$OH at considerably higher temperatures (250–300 °C) but it is practically inactive to detect the other reducing gases (CH$_4$, CO, NH$_3$).

An attempt to establish the correlation between particular structural features of the samples and their gas-sensitive behavior was made in this paper.

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Biographies

Maria Ivanovskaya received her degree in chemistry in 1980 from Belarus State University in the field of photochemistry. Till 1988 she carried out investigations in the field of solid state photochemistry (TiO$_2$, ZnO,

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Dzmitry Kotsikau graduated from the Belarus State University in 2001 with honors; in the same year entered the post graduate courses. Now he is working in the field of solid state chemistry and semiconductor gas sensors. His main scientific interests are Fe_2O_3–In_2O_3 nanosized composites, their structural and gas-sensitive characterization.

Guido Faglia has received an MS degree from the Polytechnic of Milan in 1991 with a thesis on gas sensors. In 1992 he has been appointed as a researcher by the Gas Sensor Laboratory at the University of Brescia. He is involved in the study of the interactions between gases and semiconductor surfaces and in gas sensors electrical characterization. In 1996 he has received the PhD degree by discussing a thesis on semiconductor gas sensors. In 2000 he has been appointed associate professor in Experimental Physics at University of Brescia. During his career Guido Faglia has published more than 60 articles on International Journals with referee.

Paolo Nelli received his MS degree in physics from the University of Pavia in 1987, after then he joined the Gas Sensor Laboratory at the University of Brescia, where at present he carries out his research activity on gas sensors. He held a permanent position at the Department of Chemistry and Physics for Materials of the University of Brescia; his interests are focused on the preparation and characterization of gas sensors based on semiconducting metal oxides. He is co-author of about forty papers on gas sensors and material science and 30 presentations at international congresses on the same topics.

Sobir Irkaev graduated from the Tadjik State University in 1965; then he entered the post graduate courses in Moscow State University in 1967. He received his Doctor of Science degree in 1994; Philosophy Doctor degree in 1971. Now he is working at Institute for Analytical Instrumentation of Russian Academy of Science, since 1971 up to now occupies the head of Resonance Laboratory position. He is the author of two monographs: ''Nuclear Gamma Resonance'', 1970 and ''Mössbauer Spectroscopy'', St. Petersburg, 1997, over 80 publications and 20 patents.