Influence of Structural Features of Fe_2O_3-In_2O_3 and Fe_2O_3-SnO_2 Thin Films on their Gas-Sensitive Behaviour

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As it was found, chemical and phase compositions as well as dispersion and morphology of Fe_2O_3-In_2O_3 and Fe_2O_3-SnO_2 composites has a clear influence on their gas-sensitive properties. The required peculiar properties was imparted to the systems by varying of synthesis conditions, component ratio and mode of the obtained film thermal treatment. Structural features of the samples were studied by XRD, TEM, ESR and Mössbauer spectroscopy. Gas-sensitive parameters of the corresponding thin film sensors were estimated with regards to CH_4, CO, NH_3, O_3, NO_2, C_2H_5OH and CH_3OH.

Table 1 represents phase composition and average grain size of the most promising nanocomposites.

The sensitive elements were formed from the stabilised sols of the corresponding metal hydroxides which were prepared by sol-gel technique. The composites based on α-Fe_2O_3 were prepared by two procedures. The concept of the first approach is using of Fe^{3+} salts. The second method of α-Fe_2O_3 phase preparation assumes using of Fe^{2+} and In^{3+} salts, which being co-precipitated, give non-stable γ-Fe_2O_3 phase. This phase transforms completely into fairly well crystallized α-Fe_2O_3 under heating at 300°C.

It was found that all Fe_2O_3-In_2O_3 sensors are characterized by negligible sensitivity to CH_4, CO, NH_3, but demonstrate good response when detection of O_3 and NO_2 is mentioned. Both sensitivity and optimal operating temperature appeared to be considerably distinct for the thin film sensors of different composition (Table 2). The mentioned distinctions will probably make possible the selective detection of certain gases in gas mixture using Fe_2O_3-In_2O_3 sensors. Doping of SnO_2 with Fe_2O_3 leads to increasing of SnO_2 sensor response to alcohols. In contrast, Fe_2O_3-SnO_2 sensors are less sensitive to NO_2 and CO than simple SnO_2.

It is important to note that Fe_2O_3-In_2O_3 thin film sensors are more sensitive than already known oxide composites based on SnO_2, NiO and MoO_3. Fig. 1 shows the comparison of thin film sensor of various composition response values versus operating temperature. With regards to O_3, Fe_2O_3-In_2O_3 nanocomposite consisting of γ-Fe_2O_3 phase is the most sensitive material.

Maximum response values to NO_2 demonstrate the composites which are characterized by irregularity of Fe(III) environment and the presence of highly dispersive α-Fe_2O_3 phase with anisotropic shape of grains. Mössbauer spectroscopy data allows us to distinguish three types of Fe(III) ions which differ by coordination environment.

For efficient course of alcohols detection, heterojunction films with great phase interface (Fe_2O_3/In_2O_3, Fe_2O_3/SnO_2) are required.

ESR data give evidence that gas molecule adsorption is going effectively at Fe(III) ions in the environment which differs from cubic one.

Nanocomposite	Phase Composition	Grain Size, nm
γ-Fe_2O_3-In_2O_3 (9:1)	γ-Fe_2O_3 C-In_2O_3	25 25
α-Fe_2O_3-In_2O_3 (9:1) via Fe(II)	α-Fe_2O_3	8×15
γ-Fe_2O_3-In_2O_3 (1:1)	C-In_2O_3 γ-Fe_2O_3	7-8 5
α-Fe_2O_3-In_2O_3 (1:1) via Fe(III)	Amorphous Fe_2O_3 C-In_2O_3	- 8
α-Fe_2O_3-In_2O_3 (9:1) via Fe(III)	Amorphous Fe_2O_3	
α-Fe_2O_3-SnO_2(1:1) via Fe(III)	SnO_2 α-Fe_2O_3	4 -
γ-Fe_2O_3-SnO_2(1:1)	SnO_2 γ-Fe_2O_3	2 7-10

Table 1. Structural features of Fe_2O_3-In_2O_3 and Fe_2O_3-SnO_2 composites annealed at 300°C.

Sensor	T, °C	Detected Gas	Gas conc., ppm
γ-Fe_2O_3-In_2O_3(9:1)/ In_2O_3	135	O_3	0.060
α-Fe_2O_3-In_2O_3(9:1)/ In_2O_3 via Fe(II)	70-100	NO_2	0.5
γ-Fe_2O_3-In_2O_3(1:1)/ In_2O_3	70-100 300	NO_2 C_2H_5OH	0.5 50
α-Fe_2O_3-SnO_2(1:1) via Fe(III)	300	C_2H_5OH	50

Table 2. The most promising thin film sensors based on Fe_2O_3-In_2O_3 and Fe_2O_3-SnO_2 composites.

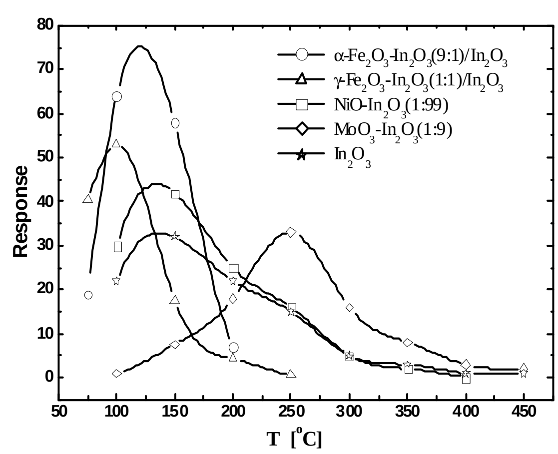

Fig. 1. Comparison of sensitivity of In_2O_3 based sensors doping with different metal oxides to 1 ppm NO_2.

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