

# Gas Semiconducting Sensors Based on Metal Oxide Nanocomposites

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Received: December 5, 2011    Accepted: December 26, 2011    Published: April 1, 2012  
doi:10.5539/jmsr.v1n2p56    URL: <http://dx.doi.org/10.5539/jmsr.v1n2p56>

## Abstract

This paper reviews the important problems associated with the synthesis of metal-oxide nanocomposites, charge transfer phenomena in these composites, their conductive and sensory properties, modeling of sensory effect and the role on this sensory effect of the electronic structure of the metal oxide. The size of metal particles and temperature significantly influence the efficiency of such systems. However, the electronic interactions between the different components of the nanocomposite films play the dominant role in the exploitation of the properties of such sensory systems. Depending on the chemical nature of the analyzed gas and the electronic structure of the semiconducting metal oxides, such interactions can result in either an increase or a decrease of the sensory effect. Thus, by varying the electronic structure of the metal oxide composite sensors as well as the temperature and size of the metal-oxide nanoparticles, the inherent characteristics of the sensor can be changed and tailored for detection of various gases. Such findings clearly open up new opportunities for development of novel selective sensors.

**Keywords:** Conductivity, Electron affinity, Electron transport, Electronic structure, Gas detection, Indium oxide, Metal-oxide, Nanocomposite, Nanoparticle, Semiconductor, Sensor, Sensory properties, Tin oxide

## 1. Introduction

The rapid growth in industrial production and the attendant environmental impact have made it imperative to develop highly sensitive and selective sensors for the detection of various pollutants in the atmosphere.

Conductometric chemical sensors based on nanocrystalline metal-oxide semiconductors are currently the most promising among solid-state gas detectors due to their reliability, and ease of manufacture and application. Miniaturization and low price also enable their use as personal sensors.

The sensitivity of such systems is manifest by the change in conductivity resulting from chemical interaction of adsorbed analyzed gas with active centers on the surface of the sensor. The sensor characteristics, which include sensitivity, response time and selectivity, are largely determined by two factors: the reactivity of active centers of the sensor and the diffusion of gas to these centers.

Previous studies on conductometric metal oxide sensors have mostly focused on systems consisting of single semiconducting metal oxide, mostly SnO<sub>2</sub>. The disadvantage of such sensors is the rather low selectivity to gases that have similar chemical characteristics, for example, various reducing gases. A promising approach to improve conductometric sensors is the use of composite materials in which nanoparticles of metal oxide

semiconductor or metal are embedded in an organic polymer or inorganic (mainly semiconductors) matrix. The following sections describe such sensors and discuss the fundamental mechanism underlying the sensory phenomena.

## 2. Sensors Based on Polymer Composite

Various methods have been reviewed of synthesis and properties of polymer composites for sensor applications (Godovski, 1995; Woehrl, 1996; Pomogailo, *et al.*, 2000; Trakhtenberg & Gerasimov, 2005; Gerasimov & Trakhtenberg, 2007). The polymer matrix prevents aggregation of nanoparticles of metal and metal oxide embedded in the matrix to form composites with high particle concentration. Conductometric sensory properties are included in such systems by the change in the tunneling electron transfer between the nanoparticles under the influence of substances being sensed, penetrating into the composite film from the environment and adsorbed onto the nanoparticles (Godovski, 1995; Trakhtenberg & Gerasimov, 2005).

Vorontsov *et al.* (1998) observed sensor response to low hydrogen pressures at ambient temperature in poly-p-xylylene film containing Pd nanocrystals. The electrical resistance of the film was found to increase under the influence of hydrogen presumably because of dissociative adsorption of hydrogen molecules on the Pd nanocrystals which increases the electron work function of these nanocrystals and consequently increases the barrier to the tunnel electron transfers between the nanocrystals. After removal of the hydrogen the film resistance returns to its initial value within 30-60 seconds, indicating that such films can be used as reversible sensors for hydrogen detection. It was also found that the polymer matrix properties and the concentration of stabilized metal oxide nanoparticles influence the sensitivity of composite films to strongly polar substances. It was shown that this effect depends on the type and structure of the analyte (Sergeev, *et al.*, 1997; Trakhtenberg, *et al.*, 1999; Du & Ilegbusi, 2004). Thus, the use of polymer composites with semiconductor metal oxide nanoparticles embedded in polymer matrix provides some opportunities to improve the selectivity of metal oxide sensors.

## 3. Sensors Based on Mixed Metal Oxides

Mixed metal oxide systems containing metal oxides of different electronic structure which interact with each other offer much more promise than single oxides for sensitive and selective detection of various gases in the environment (de Lacy Costello, *et al.*, 2002; Tang, *et al.*, 2006; Shouli, *et al.*, 2010; Ivanovskaya, *et al.*, 2003). Interaction between the component of metal oxide systems can lead to a change in the electronic structure of the nanocrystals and, hence, affect their reactivity. It is remarkable that the selectivity of the sensor response can be significantly improved by varying the composition, structure and work functions of such nanocomposite sensors (Yu & Choi, 2001; Kima, *et al.*, 2007; Shouli, *et al.*, 2008). In particular, the effect of temperature on the sensitivity of metal oxide nanocomposite sensor to gases in the air varies with sensor composition and type of gas.

A typical example is the data of Yu & Choi (2001), in which a small amount of ZnO, when added to 1 mol % CuO doped SnO<sub>2</sub>, shifted the H<sub>2</sub> gas-sensing curve in the presence of CO to a higher temperature. This trend resulted in selective CO detection in a mixture with H<sub>2</sub> at relatively low temperature (SCO/SH<sub>2</sub> ~ 5 at 160°C), and selective H<sub>2</sub> detection at high temperature (SH<sub>2</sub>/SCO ~ 2 at 310°C).

## 4. Synthesis of Metal Oxide Nanocomposites

Mixed metal oxide systems can be classified into three groups. The first category includes chemical compounds resulting from the chemical interaction between various oxides. Examples include ZnSnO<sub>3</sub> and Zn<sub>2</sub>SnO<sub>4</sub> compounds formed in the ZnO-SnO<sub>2</sub> system (Shen & Zhang, 1993), and the crystal CdIn<sub>2</sub>O<sub>4</sub> which is an effective sensor for CO, produced by the interaction of CdO with In<sub>2</sub>O<sub>3</sub> (Szklarski, *et al.*, 1989). The phase α-SnWO<sub>4</sub>, sensitive to small amounts of CO and NO, was observed in the system SnO<sub>2</sub>-WO<sub>3</sub> (Solis & Lantto, 1995). The second category includes mixed oxides, which form solid solutions. An example of such a system is the mixture of TiO<sub>2</sub> and SnO<sub>2</sub>, which form solid solutions over the entire range of compositions but only above a certain critical temperature (Edelman, *et al.*, 2000; Arakawa, *et al.*, 1997). The third group consists of systems that give neither individual compounds nor solid solutions. These systems contain mixtures of metal oxide nanocrystals interacting with each other such as, In<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub>, TiO<sub>2</sub>-WO<sub>3</sub> and many others (Chowdhuri, *et al.*, 2002; Neri, *et al.*, 2008; Xu, *et al.*, 2010). In fact, only mixed metal oxides of the third group can be regarded as composite materials. It is such systems that will be discussed in this chapter.

A variety of methods are used for producing mixed metal oxide nanocomposites. These methods include sol-gel technique using codeposition of mixed oxides from corresponding salt solution (Arbiol, *et al.*, 2006), aerosol spraying of salt solutions with subsequent heat treatment (Thangaraju, 2002), the deposition by reactive metal

sputtering from composite targets in the presence of oxygen (Comini, *et al.*, 2002; Nanto, *et al.*, 1996), and the blending of individual metaloxide nanopowders (Yu & Choi, 1998). It should be noted that the structure of the nanocrystalline components in the composite may differ significantly from that of individual substances which form the base of the composite. The formation of mixed metal oxide nanocomposites may probably produce nanoparticles with high volume defects resulting mainly from the incorporation of ions of one component in the lattice of another.

Such crystalline particles are produced, for example, in the synthesis of nanocomposite  $\text{TiO}_2\text{-SnO}_2$  by RF-sputtering and by molecular beam. In this case, initially formed amorphous system containing a mixture of titanium and tin ions (Edelman, *et al.*, 2000) transforms into a nanocrystalline composite upon further annealing. When spraying a mixture of Sn and In salt solutions on the surface of the heated substrate by aerosol method, the synchronous joint growth of crystals of  $\text{SnO}_2$  and  $\text{In}_2\text{O}_3$  with different crystal lattices produces the composite film, in which the size and state, and in particular, crystal defects strongly depend on the composition of the film and the spraying conditions. Aerosol synthesis has been used to produce composite films in which the conductivity sharply decreases compared to that of pure nanocrystalline  $\text{SnO}_2$  even at low concentrations of  $\text{In}_2\text{O}_3$  in the composite (Manoj, *et al.*, 2007). This result indicates the introduction of  $\text{In}^{+3}$  ions in the crystal lattice of  $\text{SnO}_2$  with ions  $\text{Sn}^{+4}$ , accompanied by the formation of electron accepting centers (see, eg, (Yu & Choi, 2001)). The formation of formation of sensor films by mixing individual nanocrystalline oxides also precludes the introduction of ions from one oxide into the volume of the other. This method of synthesizing composite films can only change the surface layers of contacting particles. Such a structure of mixed metal oxide films allows us to distinguish among other factors, the effect of contacts between individual crystallites on the conductivity of the composite film and its sensory properties and thus to gain a new insight into the mechanism of sensory mechanism in these systems.

Mixtures consisting of nanocrystalline semiconducting metal oxides with different work function and electron affinity are of special interest among the composites of this type. In such systems contacts between the nanocrystals of different electronic properties lead to the mutual charging of these contacting particles as a result of electron transfer between them. A typical example of such effect is the charge transfer in sensors consisting of semiconductor particles of p- and n-type (Gleiter, *et al.*, 2001). Charge transfer processes, as will be shown below, have a strong influence on the sensory effect.

### 5. Charge Transfer Processes

Many p-type oxides form p-n junctions with  $\text{SnO}_2$  (n-type). It has been shown that the work function of  $\text{SnO}_2$  is increased significantly by loading with p-type metal oxides, for example,  $\text{PdO}$  (about 0.1 eV),  $\text{Ag}_2\text{O}$  (0.3 eV) and  $\text{CuO}$  (0.5 eV). The data in parentheses show how much the  $\text{SnO}_2$  work function increases due to electron transfer from  $\text{SnO}_2$  to the p-type metal oxides cited (Matsushima, *et al.*, 1988), which is accompanied by lowering of the Fermi level of  $\text{SnO}_2$  (Klein, *et al.*, 2010)

The X-Ray Photoelectron Spectroscopy (XPS) method allows the interaction between the components of nanocomposite systems and charge transfer between them to be readily established. XPS analysis was used to determine the surface electronic states of Sn and In ions in  $\text{In}_2\text{O}_3 + \text{SnO}_2$  composite (Aifan, *et al.*, 2006). The composite was obtained by co-deposition mixture of chlorides of tin and indium, followed by annealing in air at  $600^\circ\text{C}$ .

It should be noted that the two components in this composite are both n-type semiconductors, but they differ significantly in the work function and electron affinity. In such a system containing 40%  $\text{In}_2\text{O}_3$ , significant positive chemical shifts have been observed, of 0.6 eV and 0.5 eV in the Sn 3d<sub>5/2</sub> and O 1s peaks, respectively, relative to pure  $\text{SnO}_2$ . Such shifts are caused by the transition of electrons from  $\text{In}_2\text{O}_3$  particles to  $\text{SnO}_2$  particles, accompanied by the formation of charged  $\text{In}_2\text{O}_3^+$  and  $\text{SnO}_2^-$  nanocrystals contacting each other. The increasing concentrations of electrons and the existence of negative charge on the  $\text{SnO}_2$  particles lead to downward bending of the conduction and valence bands. This result is accompanied by an increase in bonding energy of Sn and O ions in the lattice of  $\text{SnO}_2$  with a corresponding shift of the bands in the XPS spectra (see, e.g., (Yang, *et al.*, 2006, Aifan, *et al.*, 2008)). Correspondingly, a decrease in the binding energy of the In and O ions should be observed in the  $\text{In}_2\text{O}_3^+$  lattice due to lowering of the electron density in the  $\text{In}_2\text{O}_3^+$  crystals.

### 6. Sensory Phenomena in Composites

The interaction between the composite components produces significant sensory effect. Klein, *et al.*, (2010) shows that the  $\text{In}_2\text{O}_3 + \text{SnO}_2$  composite containing 20% to 40%  $\text{In}_2\text{O}_3$  has a much higher sensitivity to CO compared with sensors based on pure nanocrystalline  $\text{In}_2\text{O}_3$  and  $\text{SnO}_2$ . Mutual charging of the components of the metal oxide  $\text{In}_2\text{O}_3 + \text{Ag}_2\text{O}$  nanocomposite has been found (Mehta & Singh, 2005). The  $\text{Ag}_2\text{O}$  oxide is a

p-semiconductor and forms pn junction with  $\text{In}_2\text{O}_3$ . The conduction electrons of  $\text{In}_2\text{O}_3$  are drawn toward  $\text{Ag}_2\text{O}$ , producing an electron-depleted layer in the  $\text{In}_2\text{O}_3$  nanoparticle resulting in an increased electrical resistance. It is important to note that  $\text{In}_2\text{O}_3$ - $\text{Ag}_2\text{O}$  composite containing 15%  $\text{Ag}_2\text{O}$  is significantly more effective in detecting ethanol than pure  $\text{In}_2\text{O}_3$ .

The modification of nanocrystalline  $\text{In}_2\text{O}_3$  with rubidium carbonate ( $\text{Rb}_2\text{CO}_3$ ) has been observed to increase the sensitivity in the detection of CO and  $\text{H}_2$ . This finding is associated with the change in the electronic structure of the nanocomposite. Semiconducting crystals of  $\text{Rb}_2\text{CO}_3$  relate to p-type semiconductor. The p-n-contacts between the  $\text{Rb}_2\text{CO}_3$  and  $\text{In}_2\text{O}_3$  in this system result in the transfer of electrons from  $\text{In}_2\text{O}_3$  to  $\text{Rb}_2\text{CO}_3$ . As a result, XPS spectroscopy indicates that the binding energies of indium and oxygen ions in the lattice of  $\text{In}_2\text{O}_3$  decrease, while the binding energy of the Rb ions in the  $\text{Rb}_2\text{CO}_3$  lattice increases (Yamaura, *et al.*, 1996).

Lee *et al.*, (2001) investigated nanocomposite sensor in which the  $\text{In}_2\text{O}_3$  particles were covered by layers of cobalt oxide. XPS was used to establish charge transfer between contacting nanocrystals of CoO (p-semiconductor) and  $\text{In}_2\text{O}_3$  (n-semiconductor), which leads to a significant increase in sensitivity of the composite sensor for detection of CO in comparison with the sensitivity of pure  $\text{In}_2\text{O}_3$ . The interaction between the nanocrystalline components of a mixed metal oxide system, accompanied by electron transfer, was also observed in a composite, consisting of electron donor  $\text{In}_2\text{O}_3$  particles and electron accepting  $\text{CeO}_2$  particles (Xu, *et al.*, 2010). Nanocomposite containing 25%  $\text{CeO}_2$ , produced a three-fold greater sensitivity to  $\text{H}_2\text{S}$  and ethanol than pure  $\text{In}_2\text{O}_3$ .

A detailed study has been done of sensory properties of semiconducting  $\text{SnO}_2 + \text{In}_2\text{O}_3$  metal oxide systems for detection of  $\text{H}_2$  and CO (Belysheva, *et al.*, 2010b, 2011). In these studies, the composite films were obtained by mixing nanocrystalline powders of individual oxides in aqueous media in a ball mill and subsequently annealing at 550-600°C. X-ray data indicate that the average size of  $\text{SnO}_2$  crystals in the film was 50-70 nm, and the size of the  $\text{In}_2\text{O}_3$  crystals was 30-40 nm.

There may be a variety of paths leading to conductivity with the participation of nanocrystals in mixed metal oxide semiconductor nanocomposite systems. Sensory effect depends on which path the current flows in the mixture. Therefore, the conductivity was investigated in nanocrystalline  $\text{SnO}_2 + \text{In}_2\text{O}_3$  system with varying concentration of the components over a wide temperature range (Belysheva, *et al.*, 2010a). The following section describes the modeling of sensory phenomena based on such data.

## 7. Modeling Sensory Phenomena

In reviewing the data on the conductivity and sensory effects in Belysheva *et al.*, (2010a, b, 2011), a common model of nanocrystalline sensor (Yamazoe & Shimano, 2008) has been used whereby the conductivity of a film consisting of metal oxide particles is due to the transfer of electrons between the particles and determined by the conduction electrons concentration ( $n_s$ ) on the surface of the particles. Chemisorption of molecular oxygen from the air at the particle surface is accompanied by the capture of semiconductor conduction electrons and the formation of negatively charged surface oxygen centers ( $\text{O}_2^-$ ,  $\text{O}^-$ ). It is assumed that these centers form the averaged uniform electric field, which creates a barrier to exit conduction electrons on the surface, resulting in sharp reduction of  $n_s$ , and respectively, decreased sensor conductivity. Sensor effect for reducing gases is attributed to the reaction of such gases with surface oxygen centers, leading to the consumption of the oxygen adsorbate, accompanied by a corresponding mitigation in barrier and an increase in conductivity. This model allows ready description of many of the sensory phenomena. Unfortunately, it remains unclear whether enough electrons are trapped by oxygen atoms to form a barrier for the transfer of conduction electrons between the nanoparticles.

## 8. Conductivity of Composite Films

The conductivity of  $\text{SnO}_2$  films increases with temperature in the temperature range 200 - 550°C according to the Arrhenius law, with the conductivity activation energy being 10.8 kcal/mol. The conductivity of  $\text{In}_2\text{O}_3$  films increases slightly with temperature in the range 150 - 250°C, drops sharply in the range 250-400 °C, and subsequently increases at temperatures above 400 °C. A similar trend was also observed in a previous study of  $\text{In}_2\text{O}_3$  film synthesized by the spray method (Korotcenkov, *et al.*, 2001, 2004). The decrease in the conductivity of  $\text{In}_2\text{O}_3$  films with increasing temperature can be explained within the framework of the model described above. Specifically, it is associated with the change in the nature of the oxygen centers, chemisorbed on the surface of metal oxide nanoparticles and creating a barrier to electron transfer between the particles of the film.

The dependence of conductivity on temperature for nanocrystalline composite films with low concentration (up to 20%) of  $\text{In}_2\text{O}_3$  crystals in crystalline  $\text{SnO}_2$  medium (Figure 1a) is similar to the smooth curve observed for

films of pure SnO<sub>2</sub>. The data obtained lead to the conclusion that the electrical current induced in these films flows through the SnO<sub>2</sub> nanocrystals, however, additives of In<sub>2</sub>O<sub>3</sub> nanocrystals produce an increase in film conductivity. A similar effect was also observed for the SnO<sub>2</sub> + In<sub>2</sub>O<sub>3</sub> system in the In<sub>2</sub>O<sub>3</sub> concentration range 0 - 20% (Neri, *et al.*, 2008).

The observed effect of composition of the mixed metal oxide SnO<sub>2</sub> + In<sub>2</sub>O<sub>3</sub> film on conductivity is due to mutual charging of the SnO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub> particles, similar to the hole and electron conductivity in a mixture of semiconductor particles (Gleiter, *et al.*, 2001): SnO<sub>2</sub> particles are negatively charged, and In<sub>2</sub>O<sub>3</sub> particles acquire a positive charge. A schematic representation of electron movement in SnO<sub>2</sub> + In<sub>2</sub>O<sub>3</sub> nanocomposite system is shown in Figure 2. It should be noted however, that the charges in contacting particles are not distributed uniformly over the volume of particles, but are concentrated near the contact zone. Belysheva *et al.* (2010a) have shown that as a first approximation, the conductivity through the SnO<sub>2</sub> particles in films containing low concentrations of In<sub>2</sub>O<sub>3</sub> particles can be represented as the sum of the conductivities along two parallel tracks: (BI) through the neutral particles of the nanocrystalline SnO<sub>2</sub> matrix (away from contact with In<sub>2</sub>O<sub>3</sub>) and (BII) through the negatively charged SnO<sub>2</sub> particles contacting with positively charged In<sub>2</sub>O<sub>3</sub> particles.

Conductivity (BII) occurs when the percolation threshold of the charged SnO<sub>2</sub> clusters has been overcome. Estimates made in Belysheva *et al.* (2010b) suggest that this threshold must be overcome even when the concentration of In<sub>2</sub>O<sub>3</sub> particles is about 3%. However, judging from the data (Belysheva, *et al.*, 2010a), the contribution of the second conduction path to the total conductivity at low concentrations of In<sub>2</sub>O<sub>3</sub> particles in the composite is not readily visible and indeed becomes significant only at In<sub>2</sub>O<sub>3</sub> concentrations about 10%. Following the explanation provided in Belysheva *et al.*, (2010a), the activation energy of conduction through a negatively charged SnO<sub>2</sub> in the nanocomposite is probably lower than that through usual neutral matrix. This is due to downward bending of the SnO<sub>2</sub> conduction band as a result of enrichment with electrons of the SnO<sub>2</sub> particles contacting with In<sub>2</sub>O<sub>3</sub> particles. The existence of two paths of conductivity through the SnO<sub>2</sub> particles with different activation energies leads to the deviation of the temperature dependence of the conductivity from Arrhenius law (Figure 1a).

There is a remarkable change in the temperature dependence of composite film conductivity at In<sub>2</sub>O<sub>3</sub> concentration of about 20%. Specifically, the conductivity decreases with temperature in the range 250-400 °C, which is characteristic of a nanocrystalline film of pure In<sub>2</sub>O<sub>3</sub> (Figure 1b). This result indicates there is a new path for current flow through the conducting cluster of In<sub>2</sub>O<sub>3</sub> nanocrystals, pervading the entire space between the electrodes within the film. Considering that the conductivity of In<sub>2</sub>O<sub>3</sub> is three orders of magnitude higher than that of SnO<sub>2</sub>, the In<sub>2</sub>O<sub>3</sub> particles can be regarded as quasimetallic inclusions in the SnO<sub>2</sub> matrix. According to the theory of percolation in a random close-packed mixture of metallic and dielectric spheres, metallic conductivity occurs when the metal concentration is approximately 25 vol.% (Efros, 1982). Thus the data of Belysheva *et al.* (2010a) as a first approximation is consistent with the theory. The reduction in resistance with further increase in In<sub>2</sub>O<sub>3</sub> concentration in the composite is due to the branching of the conducting cluster and increase in the number of paths for current flow (Efros, 1982).

## 9. Sensory Mechanism

Conductivity largely determines the sensory phenomena observed in nanocrystalline SnO<sub>2</sub> + In<sub>2</sub>O<sub>3</sub> films. The effect of composition on sensory characteristics of such films had been investigated for the detection of hydrogen and carbon monoxide (Belysheva, *et al.*, 2010b, 2011). The temperature dependence of the sensitivity  $S$  ( $S = R_0/R$ , where  $R_0$  and  $R$  are the sensor resistance in pure air and in air containing analyzed gas, respectively) has been shown to be typical for such sensors, and characterized by a maximum ( $S_{max}$ ) at a certain temperature ( $T_{max}$ ). It is remarkable that the sensitivity of In<sub>2</sub>O<sub>3</sub> nanocrystalline films reaches a maximum value at a much lower temperature than that of SnO<sub>2</sub> film for the detection of the hydrogen and carbon monoxide gases.

The sensitivity of SnO<sub>2</sub> films for the detection of CO in air is considerably lower than the sensitivity of In<sub>2</sub>O<sub>3</sub> film (Belysheva, *et al.*, 2011). The temperature dependence of  $S_{max}$  on the In<sub>2</sub>O<sub>3</sub> concentration for detection of CO with the SnO<sub>2</sub> + In<sub>2</sub>O<sub>3</sub> nanocomposite films investigated is shown in curve 1 of Figure 3. Introduction of a small quantity (up to 20%) of In<sub>2</sub>O<sub>3</sub> nanocrystals to nanocrystalline SnO<sub>2</sub> film leads to an increase in  $S_{max}$ . Considering that in these composite films, as noted above, the current flows through the SnO<sub>2</sub> nanocrystals, this phenomenon is due to increase in film sensitivity to CO of the conducting cluster of negatively charged SnO<sub>2</sub> particles in contact with positively charged In<sub>2</sub>O<sub>3</sub> particles (Figure 2a). Based on the data of Haouas *et al.* (1993), one of the reasons for this increase in sensitivity can be the increase in CO adsorption capacity of the contact zone between the charged particles of SnO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub>.

The above conductivity data on mixed oxide films indicate that for  $\text{In}_2\text{O}_3$  concentration greater than 20%, the  $\text{In}_2\text{O}_3$  particles connecting to one another form a conducting path spanning the entire sample and in so doing, the percolation threshold for these particles is overcome. Since the conductivity and sensitivity to CO of  $\text{In}_2\text{O}_3$  clusters are significantly higher than the corresponding properties for the surrounding  $\text{SnO}_2$  matrix, the sensory properties of the  $\text{In}_2\text{O}_3$  clusters largely govern those of the  $\text{SnO}_2 + \text{In}_2\text{O}_3$  composite. Figure 3 shows that, with increasing concentration of  $\text{In}_2\text{O}_3$  in the film from 20 to 50% the value of  $S_{\text{max}}$  of the composites investigated remains mostly constant, and differs very little from the  $S_{\text{max}}$  for a film of pure  $\text{In}_2\text{O}_3$ .

It should be noted that  $S_{\text{max}}$  depends on the cluster surface on which oxygen and the analyzed gas are adsorbed. Probably, with increasing  $\text{In}_2\text{O}_3$  concentration in the film, the total surface of  $\text{In}_2\text{O}_3$  clusters grows to a certain limit beyond which any increase of the surface area due to formation of new clusters is balanced by the surface diminution resulting from their aggregation. Similar effects were observed during the formation of a new phase (see, e.g., (Zaporojchenko, *et al.*, 1999; Blackman, 1995)). This finding explains why  $S_{\text{max}}$  of the mixed oxide composite film remains unchanged over the range of indium concentration from 20 to 50%.

The value of temperature  $T_{\text{max}}$  corresponding to  $S_{\text{max}}$  for the  $\text{SnO}_2 + \text{In}_2\text{O}_3$  sensors applied for detection of CO does not depend on the  $\text{In}_2\text{O}_3$  concentration in the range 20% to 37% and it is significantly higher than the  $T_{\text{max}}$  ( $\text{In}_2\text{O}_3$ ) for pure  $\text{In}_2\text{O}_3$ . Calculations based on the established model of metal oxide sensor conductivity (Yamazoe & Shimano, 2008) considering the influence of Langmuir adsorption on sensory effect, discussed in (Ahler, *et al.*, 2005), shows that the  $T_{\text{max}}$  value increases with increase in the heat of gas adsorption on the surface of the sensor (Belysheva *et al.*, 2011). As noted above the contacts between  $\text{SnO}_2$  and  $\text{In}_2\text{O}_3$  particles in the composite film lead to their mutual charging:  $\text{SnO}_2$  particles become negatively charged, and  $\text{In}_2\text{O}_3$  particles acquire a positive charge. It is reasonable to assume that the heat of adsorption of polar CO molecules on charged particles of  $\text{In}_2\text{O}_3$  and  $\text{SnO}_2$  is higher than that on neutral particles. Therefore, until  $\text{In}_2\text{O}_3$  clusters which determine the conductivity and sensitivity of the  $\text{SnO}_2 + \text{In}_2\text{O}_3$  composite sensor to gas, are surrounded by a matrix of  $\text{SnO}_2$ , the  $T_{\text{max}}$  value for such sensors would be higher than  $T_{\text{max}}$  ( $\text{In}_2\text{O}_3$ ). When the concentration of  $\text{In}_2\text{O}_3$  in the composite reaches 50%, there is, apparently, a reorganization of the composite, and clusters of  $\text{In}_2\text{O}_3$  form a separate phase. Consequently, the influence becomes negligible of  $\text{SnO}_2$  on the sensory phenomena in these clusters. In addition, the  $T_{\text{max}}$  of the composite sensor becomes equal to  $T_{\text{max}}$  ( $\text{In}_2\text{O}_3$ ) as depicted in Figure 4.

The sensitivity of  $\text{In}_2\text{O}_3$ -sensor applied for  $\text{H}_2$  detection is significantly lower than the sensitivity of  $\text{SnO}_2$ . The introduction to the  $\text{SnO}_2$  film of up to 20% of  $\text{In}_2\text{O}_3$ -nanocrystals results in a significant increase in sensitivity of the composite sensor. A further increase  $\text{In}_2\text{O}_3$  concentration in the composite up to 50% is initially accompanied by a decrease in sensitivity, and subsequently remains constant at a value equal to the sensitivity of pure  $\text{In}_2\text{O}_3$  (Figure 3, curve 2).

Sensor response to hydrogen, as indicated in the study (Kohl, 1989) is due to the dissociative chemisorption of hydrogen on the surface of the nanocrystalline sensor films with subsequent migration of hydrogen atoms formed along the sensor surface and their reaction with oxygen centers. This reaction lowers the barrier to electron transfer between the particles in the film. Published data (Chowdhuri, *et al.*, 2004) suggest that the dissociation of hydrogen proceeds more efficiently when its chemisorption occurs in the charged boundary regions formed as a result of contact between the  $\text{SnO}_2$  and  $\text{In}_2\text{O}_3$  particles. This explains the increase in sensitivity to  $\text{H}_2$  with  $\text{In}_2\text{O}_3$  concentration in the composite sensor containing up to 20%  $\text{In}_2\text{O}_3$ . Specifically, the increase in conductivity is due to increase in charged regions involved in the conduction process.

As indicated earlier, at higher concentration of  $\text{In}_2\text{O}_3$  particles (above the percolation threshold) the current flow path in the composite film is through the conductive clusters of  $\text{In}_2\text{O}_3$  nanocrystals. It should be noted that these clusters (threads) have a small diameter, roughly equal to the diameter of the particles (50 nm), and at low concentrations of  $\text{In}_2\text{O}_3$  in the composite film the number of threads is quite small. Therefore, the transition from conduction through  $\text{SnO}_2$  particles to conduction through  $\text{In}_2\text{O}_3$  particles with increasing concentration of  $\text{In}_2\text{O}_3$  in the film, occurs gradually in the region from 20 to 50%, where there are parallel paths of conduction through threads of  $\text{In}_2\text{O}_3$  particles and through surrounding  $\text{SnO}_2$  matrix, as shown in the a previous study (Manoj, 2007).

Since the sensitivity of  $\text{SnO}_2$  to CO is much lower than that of  $\text{In}_2\text{O}_3$  in the range of  $\text{In}_2\text{O}_3$  concentrations above the percolation threshold for  $\text{In}_2\text{O}_3$  particles, the sensitivity of the mixed metal oxide system to CO is completely determined by the effect of CO on conductivity of the  $\text{In}_2\text{O}_3$  clusters and largely independent of the  $\text{SnO}_2$  matrix.

By the same token, the sensitivity of  $\text{SnO}_2$  to  $\text{H}_2$  for is much large than that for  $\text{In}_2\text{O}_3$ . Therefore, when  $\text{SnO}_2 + \text{In}_2\text{O}_3$  composite sensors are used for detection of  $\text{H}_2$  in air, a significant contribution of sensor phenomena in the  $\text{SnO}_2$  matrix to overall sensory property is retained even with relatively minor contribution of  $\text{SnO}_2$  conductivity

to the overall composite conductivity at  $\text{In}_2\text{O}_3$  concentration above the percolation threshold for  $\text{In}_2\text{O}_3$  particles. With increasing concentration of  $\text{In}_2\text{O}_3$  above 20 %, the contribution of sensor phenomena in the  $\text{SnO}_2$  matrix is reduced and, accordingly, in this composition range the sensitivity of the composite sensor to hydrogen gradually decreases (Figure 3). When the concentration of  $\text{In}_2\text{O}_3$  is equal to or greater than 50% the conductivity of the composite proceeds completely through the  $\text{In}_2\text{O}_3$  particles (Belysheva, *et al.*, 2010a), and the sensitivity of the composite sensor is the same as in pure  $\text{In}_2\text{O}_3$ .

The results obtained in the recent studied (Belysheva, *et al.*, 2010a, 2010b, 2011) therefore lead to the conclusion that the specific effects of the composition of mixed  $\text{SnO}_2$ -  $\text{In}_2\text{O}_3$  films on sensitivity to CO and  $\text{H}_2$  is due to the electron transfer between contacting  $\text{In}_2\text{O}_3$  and  $\text{SnO}_2$  particles and the resulting mutual charging of these particles. This effect is more pronounced in the detection of  $\text{H}_2$  than the detection of CO. This trend appears to be associated with the more efficient dissociative chemisorption of hydrogen in the charged surface areas on the border between the particles of  $\text{In}_2\text{O}_3$  and  $\text{SnO}_2$ .

#### 10. The Role of Electron Affinity

The results of the study (Belysheva, *et al.*, 2010a, 2010b, 2011) characterize the effect on sensory properties of the resulting composites of nanocrystalline electron donor additives ( $\text{In}_2\text{O}_3$  with electron affinity of 3.7 eV (Klein, 2000)) embedded in electron accepting matrix ( $\text{SnO}_2$  with the electron affinity of about 4.8 eV (Hoefler, *et al.*, 2001)). The detection of hydrogen and CO was also investigated utilizing sensors consisting of electron donor matrix ( $\text{In}_2\text{O}_3$ ) with inclusions of nanocrystals of electron accepting component (ZnO). Published data show that the electron affinity of  $\text{In}_2\text{O}_3$  matrix is much smaller than electron affinity of ZnO (4,35 eV (He, *et al.*, 2007)). These systems were synthesized using a technique similar to that used for the  $\text{SnO}_2$ -  $\text{In}_2\text{O}_3$  nanocomposite sensors.

In contrast to the  $\text{SnO}_2$ -  $\text{In}_2\text{O}_3$  system, a strong influence was observed of electron accepting additives of ZnO on sensory properties of  $\text{In}_2\text{O}_3$  nanocrystalline films even at low concentrations of ZnO in the film. For example, it was found that the addition of 1% ZnO in the  $\text{In}_2\text{O}_3$  film produces a sharp increase in sensitivity to  $\text{H}_2$  and a shift in  $T_{\text{max}}$  to lower temperatures, as well as significant reduction in sensitivity to CO (Figure 5). The additive introduced in this composite system, as indicated in (Yamazoe & Shimanoe, 2009), is likely in the form of small crystal clusters of ZnO, located at the surface of the  $\text{In}_2\text{O}_3$  crystals. Sensory reactions of hydrogen or carbon monoxide with the active O<sup>-</sup> centers proceeds both in the zone of contact between ZnO and  $\text{In}_2\text{O}_3$ , and on the surface of  $\text{In}_2\text{O}_3$  crystals free of ZnO. The redistribution of electrons between ZnO and  $\text{In}_2\text{O}_3$  results in negatively charged ZnO clusters and positively charged  $\text{In}_2\text{O}_3$  crystal zones, associated with the clusters. This in turn leads to a large potential barrier that prevents the transfer of electrons from the  $\text{In}_2\text{O}_3$ -ZnO contact zone to the free surface of  $\text{In}_2\text{O}_3$ . Therefore, in the contact zones the sensory reaction  $A + \text{O}^- = \text{AO} + e^-$ , where A is the analyzed gas, has little effect on the surface concentration of electrons in the ZnO-free areas of the  $\text{In}_2\text{O}_3$  particles. These electrons at low concentrations of additives also determine the conductivity of the composite sensor, and changes in surface electron density in the ZnO-free areas under the influence of the analyzed gas induce the conductometric sensor effect.

As mentioned above, the data from the study (Haouas, *et al.*, 1993) indicate that a significant proportion of polar carbon monoxide molecules adsorbed on the surface of  $\text{In}_2\text{O}_3$  can be assumed to be concentrated in areas of contact between electron donor  $\text{In}_2\text{O}_3$  and electron acceptor crystalline ZnO clusters. The reaction characteristics of the analyzed gas with the oxygen centers in these areas lead to the conclusion that the essential part of the adsorbed CO actually counteracts the sensory process. This explains the observed decrease in sensitivity to CO of  $\text{In}_2\text{O}_3$  nanocrystalline containing small additions of ZnO.

The existence of small clusters of ZnO on the surface of  $\text{In}_2\text{O}_3$  is not to significantly affect the adsorption capacity of these particles for non-polar  $\text{H}_2$  molecules. The enhancement of sensitivity to hydrogen in this case, as well as in the  $\text{SnO}_2$ -  $\text{In}_2\text{O}_3$  system, is probably due to an increase in the rate of dissociation of hydrogen in the charged contact zone between the ZnO clusters and  $\text{In}_2\text{O}_3$  particles. The hydrogen atoms generated migrate from the contact zone to the surface of the  $\text{In}_2\text{O}_3$  particle. This in turn leads to an increase in both the rate of sensory reaction and conductometric sensor response.

It should be emphasized that the sensor system consisting of  $\text{In}_2\text{O}_3$  nanocrystals with ZnO inclusions, fundamentally differs from the  $\text{SnO}_2$ -  $\text{In}_2\text{O}_3$  composite sensor described above. In the latter sensor with the relatively small (up to 20%) concentration of electron donor  $\text{In}_2\text{O}_3$  nanocrystals in  $\text{SnO}_2$  matrix, current flows through the set of electron accepting  $\text{SnO}_2$  crystals. Electron transfer from  $\text{In}_2\text{O}_3$  to  $\text{SnO}_2$  crystals does not diminish, but, on the contrary, increases the conductivity of the composite film. Correspondingly, the sensory

reaction occurring in the contact zone between the SnO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub> crystals and liberating electrons in this zone, as indicated above, leads to increased sensitivity of the sensor.

## 11. Conclusion

The data presented in this chapter indicate that the electronic interactions between the components of metal oxide semiconductor composite sensors play important role in the conductivity and sensory properties of these systems. Such interactions can result in both an increase and a decrease in the sensory effect, depending on the chemical structure of the analyzed gas and the electronic structure of the semiconducting metal oxides utilized in the composite. Thus, by varying the electronic structure of the metal oxide composite sensors their inherent characteristics can be changed and tailored for detection of various gases. Such findings clearly open up new opportunities for development of novel selective sensors.

## Acknowledgements

This study was partially supported by the US National Science Foundation under grant CMMI-1030689, Russian Fund of Basic Research (grants 10-03-00274 and 11-07-00191) and contract 16.513.11.3065 with Federal Agency of Science and Innovations of the Russian Federation.

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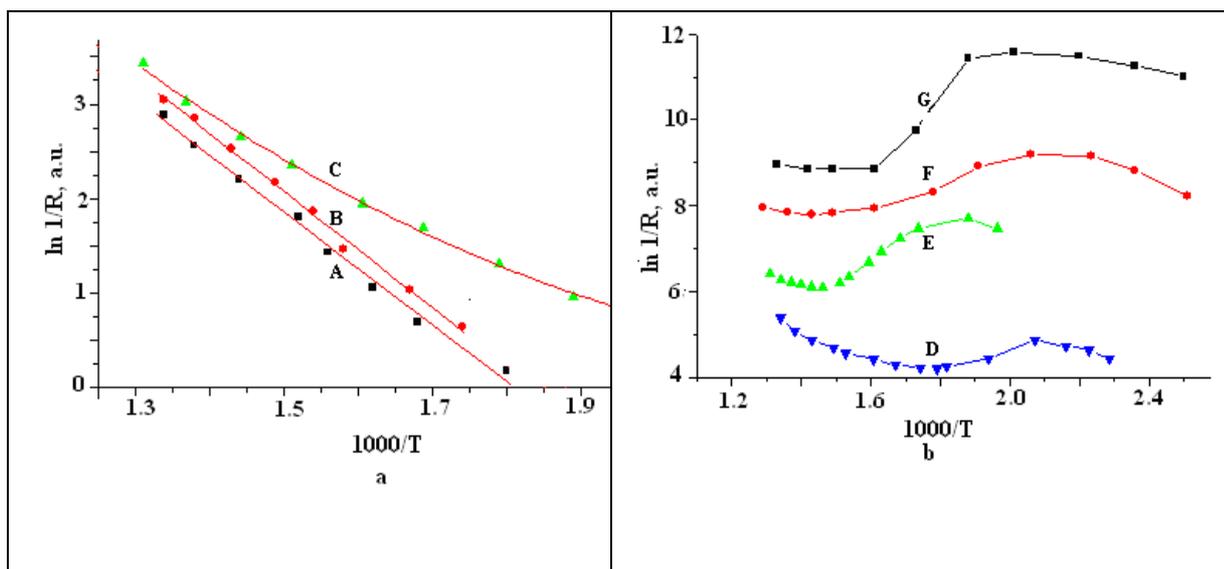


Figure 1. Temperature dependence of conductivity  $1/R$  in arbitrary units, where  $R$  is film resistance, for nanocrystalline  $\text{SnO}_2$  film (A);  $\text{SnO}_2 + \text{In}_2\text{O}_3$  composite films with different  $\text{In}_2\text{O}_3$  concentrations (wt.)- 6% (B); 12% (C); 20% (D); 37%(E); 50% (F); nanocrystalline  $\text{In}_2\text{O}_3$  film (G)

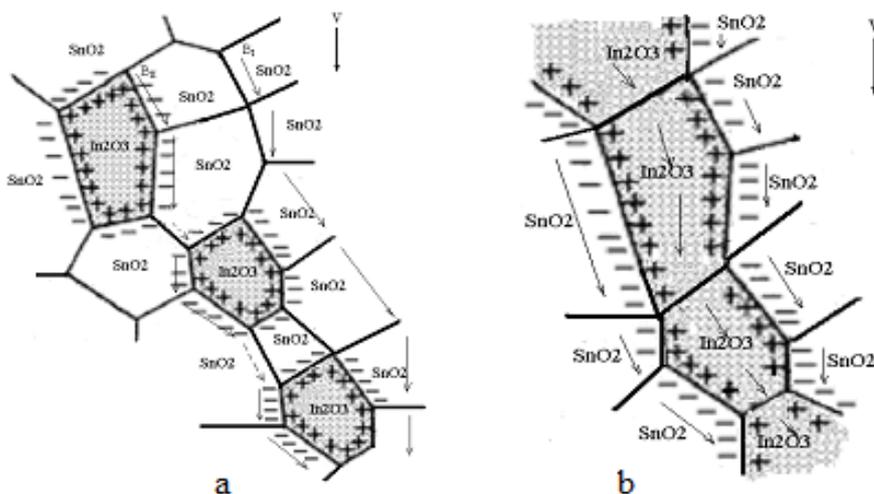


Figure 2. Schematic representation of electron movement in  $\text{SnO}_2 + \text{In}_2\text{O}_3$  composite film with concentration of  $\text{In}_2\text{O}_3$  below (a) and above (b) of the percolation threshold of  $\text{In}_2\text{O}_3$  particles in an electric field  $V$ . Arrows indicate the movement of electrons through a system of  $\text{SnO}_2$  nanocrystals, including uncharged region with conductivity BI and negatively charged region with conductivity BII, as well as through conducting  $\text{In}_2\text{O}_3$  cluster. The activation energy of the conductivity is determined by the barriers at the boundaries between nanocrystals such that electron transfer within the charged crystal in the path BII (dashed arrows) has no effect on the activation energy of conduction along this path

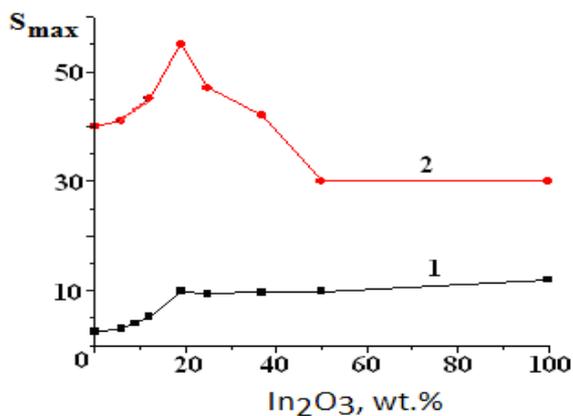


Figure 3. Variation of maximum sensitivity  $S_{\text{max}}$  of  $\text{SnO}_2 + \text{In}_2\text{O}_3$  composite sensor with  $\text{In}_2\text{O}_3$  concentration for detection of 0.46% CO (1), and 2%  $\text{H}_2$  (2)

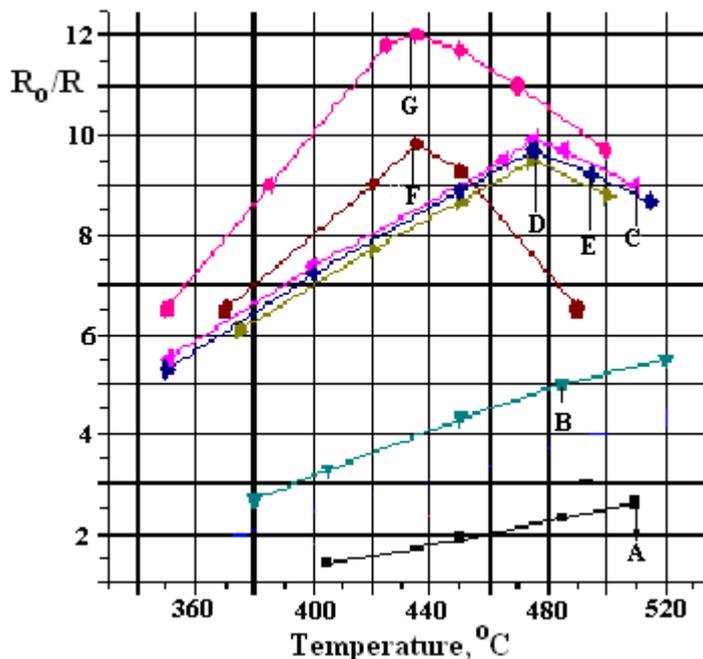


Figure 4. Temperature dependence of SnO<sub>2</sub> + In<sub>2</sub>O<sub>3</sub> composite sensor sensitivity  $S = R_0/R$  ( $R_0$  and  $R$  are the sensor resistance in pure air and air containing analyzed gas, respectively) in detecting 0.46% CO, for varying In<sub>2</sub>O<sub>3</sub> concentration (wt. %): 0 (A); 12% (B); 20% (C); 25% (D); 37% (E); 50% (F); 100% (G)

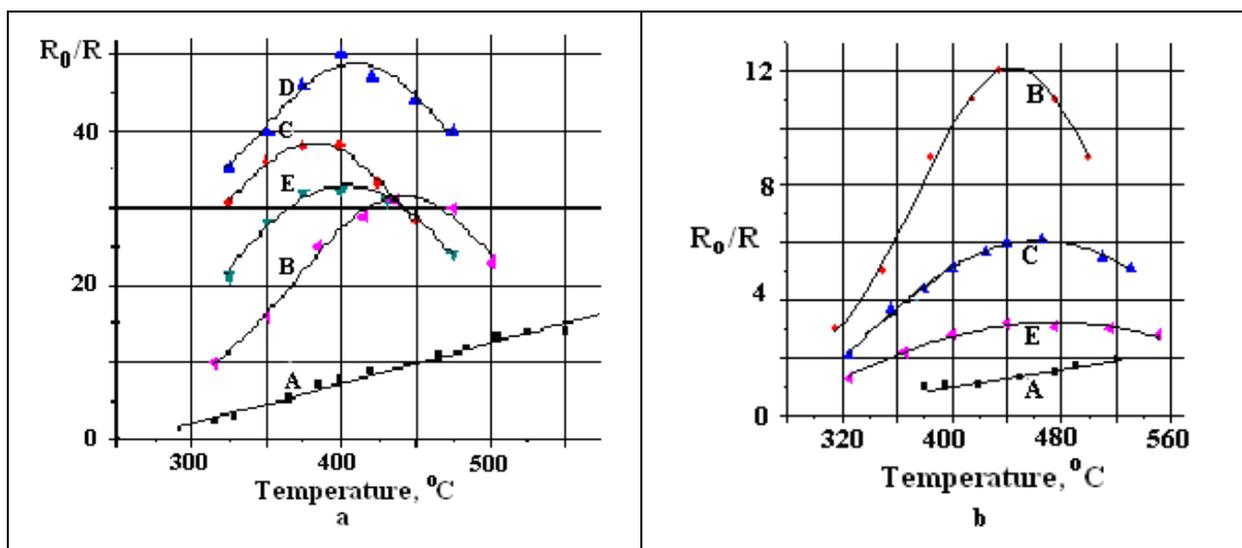


Figure 5. Temperature dependence of sensor sensitivity  $S = R_0/R$  ( $R_0$  and  $R$  are sensor resistance in pure air and in air containing analyzed gas, respectively) in detecting 2% H<sub>2</sub> (a) and 0.46 % CO (b) for a variety of films: ZnO (A); In<sub>2</sub>O<sub>3</sub> (B); In<sub>2</sub>O<sub>3</sub> + ZnO composite sensors with different wt. % of ZnO: 1% (C); 3% (D); 10% (E)