Gas Semiconducting Sensors Based on Metal Oxide Nanocomposites

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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 SnO₂. 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; Woehrle, 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 SnO2, shifted the H2 gas-sensing curve in the presence of CO to a higher temperature. This trend resulted in selective CO detection in a mixture with H2 at relatively low temperature (SCO/SH2 ~ 2 at 160ºC), and selective H2 detection at high temperature (SH2/ SCO ~ 2 at 310ºC).

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 ZnSnO3 and Zn2SnO4 compounds formed in the ZnO-SnO2 system (Shen & Zhang, 1993), and the crystal CdIn2O4 which is an effective sensor for CO, produced by the interaction of CdO with In2O3 (Szkolarski, et al., 1989). The phase \( \alpha \)-SnWO4, sensitive to small amounts of CO and NO, was observed in the system SnO2-WO3 (Solis & Lantto, 1995). The second category includes mixed oxides, which form solid solutions. An example of such a system is the mixture of TiO2 and SnO2, 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, In2O3-SnO2, TiO2-WO3 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 metal oxide 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 TiO₂-SnO₂ 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 SnO₂ and In₂O₃ 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 SnO₂ even at low concentrations of In₂O₃ in the composite (Manoj, et al., 2007). This result indicates the introduction of In³⁺ ions in the crystal lattice of SnO₂ with ions Sn⁴⁺, 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 SnO₂ (n-type). It has been shown that the work function of SnO₂ is increased significantly by loading with p-type metal oxides, for example, PdO (about 0.1 eV), Ag₂O (0.3 eV) and CuO (0.5 eV). The data in parentheses show how much the SnO₂ work function increases due to electron transfer from SnO₂ to the p-type metal oxides cited (Matsushima, et al., 1988), which is accompanied by lowering of the Fermi level of SnO₂ (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 In₂O₃ + SnO₂ 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°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% In₂O₃, significant positive chemical shifts have been observed, of 0.6 eV and 0.5 eV in the Sn 3d5/2 and O 1s peaks, respectively, relative to pure SnO₂. Such shifts are caused by the transition of electrons from In₂O₃ particles to SnO₂ particles, accompanied by the formation of charged In₂O₃⁺ and SnO₂⁻ nanocrystals contacting each other. The increasing concentrations of electrons and the existence of negative charge on the SnO₂ 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 SnO₂ 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 In₂O₃⁺ lattice due to lowering of the electron density in the In₂O₃⁺ crystals.

6. Sensory Phenomena in Composites

The interaction between the composite components produces significant sensory effect. Klein, et al., (2010) shows that the In₂O₃ + SnO₂ composite containing 20% to 40% In₂O₃ has a much higher sensitivity to CO compared with sensors based on pure nanocrystalline In₂O₃ and SnO₂. Mutual charging of the components of the metal oxide In₂O₃ + Ag₂O nanocomposite has been found (Mehta & Singh, 2005). The Ag₂O oxide is a
p-semiconductor and forms pn junction with In\textsubscript{2}O\textsubscript{3}. The conduction electrons of In\textsubscript{2}O\textsubscript{3} are drawn toward Ag\textsubscript{2}O, producing an electron-depleted layer in the In\textsubscript{2}O\textsubscript{3} nanoparticle resulting in an increased electrical resistance. It is important to note that In\textsubscript{2}O\textsubscript{3}-Ag\textsubscript{2}O composite containing 15% Ag\textsubscript{2}O is significantly more effective in detecting ethanol than pure In\textsubscript{2}O\textsubscript{3}.

The modification of nanocrystalline In\textsubscript{2}O\textsubscript{3} with rubidium carbonate (Rb\textsubscript{2}CO\textsubscript{3}) has been observed to increase the sensitivity in the detection of CO and H\textsubscript{2}. This finding is associated with the change in the electronic structure of the nanocomposite. Semiconducting crystals of Rb\textsubscript{2}CO\textsubscript{3} relate to p-type semiconductor. The p-n-contacts between the Rb\textsubscript{2}CO\textsubscript{3} and In\textsubscript{2}O\textsubscript{3} in this system result in the transfer of electrons from In\textsubscript{2}O\textsubscript{3} to Rb\textsubscript{2}CO\textsubscript{3}. As a result, XPS spectroscopy indicates that the binding energies of indium and oxygen ions in the lattice of In\textsubscript{2}O\textsubscript{3} decrease, while the binding energy of the Rb ions in the Rb\textsubscript{2}CO\textsubscript{3} lattice increases (Yamaura, et al., 1996).

Lee et al., (2001) investigated nanocomposite sensor in which the In\textsubscript{2}O\textsubscript{3} particles were covered by layers of cobalt oxide. XPS was used to establish charge transfer between contacting nanocrystals of CoO (p-semiconductor) and In\textsubscript{2}O\textsubscript{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 In\textsubscript{2}O\textsubscript{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 In\textsubscript{2}O\textsubscript{3} particles and electron accepting CeO\textsubscript{2} particles (Xu, et al., 2010). Nanocomposite containing 25% CeO\textsubscript{2}, produced a three-fold greater sensitivity to H\textsubscript{2}S and ethanol than pure In\textsubscript{2}O\textsubscript{3}.

A detailed study has been done of sensory properties of semiconducting SnO\textsubscript{2} + In\textsubscript{2}O\textsubscript{3} metal oxide systems for detection of H\textsubscript{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 SnO\textsubscript{2} crystals in the film was 50-70 nm, and the size of the In\textsubscript{2}O\textsubscript{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 SnO\textsubscript{2} + In\textsubscript{2}O\textsubscript{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 (ns) 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 (O\textsubscript{2}-, O\textsuperscript{-}). 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 ns, 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 SnO\textsubscript{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 In\textsubscript{2}O\textsubscript{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 In\textsubscript{2}O\textsubscript{3} film synthesized by the spray method (Korotcenkov, et al., 2001, 2004). The decrease in the conductivity of In\textsubscript{2}O\textsubscript{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 In\textsubscript{2}O\textsubscript{3} crystals in crystalline SnO\textsubscript{2} medium (Figure 1a) is similar to the smooth curve observed for
films of pure SnO$_2$. The data obtained lead to the conclusion that the electrical current induced in these films flows through the SnO$_2$ nanocrystals, however, additives of In$_2$O$_3$ nanocrystals produce an increase in film conductivity. A similar effect was also observed for the SnO$_2$ + In$_2$O$_3$ system in the In$_2$O$_3$ concentration range 0 - 20% (Neri, et al., 2008).

The observed effect of composition of the mixed metal oxide SnO$_2$ + In$_2$O$_3$ film on conductivity is due to mutual charging of the SnO$_2$ and In$_2$O$_3$ particles, similar to the hole and electron conductivity in a mixture of semiconductor particles (Gleiter, et al., 2001): SnO$_2$ particles are negatively charged, and In$_2$O$_3$ particles acquire a positive charge. A schematic representation of electron movement in SnO$_2$ + In$_2$O$_3$ 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$_2$ particles in films containing low concentrations of In$_2$O$_3$ particles can be represented as the sum of the conductivities along two parallel tracks: (B) through the neutral particles of the nanocrystalline SnO$_2$ matrix (away from contact with In$_2$O$_3$) and (B) through the negatively charged SnO$_2$ particles contacting with positively charged In$_2$O$_3$ particles.

Conductivity (B) occurs when the percolation threshold of the charged SnO$_2$ clusters has been overcome. Estimates made in Belysheva et al. (2010b) suggest that this threshold must be overcome even when the concentration of In$_2$O$_3$ 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$_2$O$_3$ particles in the composite is not readily visible and indeed becomes significant only at In$_2$O$_3$ concentrations about 10%. Following the explanation provided in Belysheva et al., (2010a), the activation energy of conduction through a negatively charged SnO$_2$ in the nanocomposite is probably lower than that through usual neutral matrix. This is due to downward bending of the SnO$_2$ conduction band as a result of enrichment with electrons of the SnO$_2$ particles contacting with In$_2$O$_3$ particles. The existence of two paths of conductivity through the SnO$_2$ 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$_2$O$_3$ 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$_2$O$_3$ (Figure 1b). This result indicates there is a new path for current flow through the conducting cluster of In$_2$O$_3$ nanocrystals, pervading the entire space between the electrodes within the film. Considering that the conductivity of In$_2$O$_3$ is three orders of magnitude higher than that of SnO$_2$, the In$_2$O$_3$ particles can be regarded as quasimetallic inclusions in the SnO$_2$ 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$_2$O$_3$ 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$_2$ + In$_2$O$_3$ 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 $S$ ($S = \frac{R_0}{R}$, 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 ($S_{\text{max}}$) at a certain temperature ($T_{\text{max}}$). It is remarkable that the sensitivity of In$_2$O$_3$ nanocrystalline films reaches a maximum value at a much lower temperature than that of SnO$_2$ film for the detection of the hydrogen and carbon monoxide gases.

The sensitivity of SnO$_2$ films for the detection of CO in air is considerably lower than the sensitivity of In$_2$O$_3$ film (Belysheva, et al., 2011). The temperature dependence of $S_{\text{max}}$ on the In$_2$O$_3$ concentration for detection of CO with the SnO$_2$ + In$_2$O$_3$ nanocomposite films investigated is shown in curve 1 of Figure 3. Introduction of a small quantity (up to 20%) of In$_2$O$_3$ nanocrystals to nanocrystalline SnO$_2$ film leads to an increase in $S_{\text{max}}$. Considering that in these composite films, as noted above, the current flows through the SnO$_2$ nanocrystals, this phenomenon is due to increase in film sensitivity to CO of the conducting cluster of negatively charged SnO$_2$ particles in contact with positively charged In$_2$O$_3$ 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$_2$ and In$_2$O$_3$. 

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The above conductivity data on mixed oxide films indicate that for In$_2$O$_3$ concentration greater than 20%, the In$_2$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 In$_2$O$_3$ clusters are significantly higher than the corresponding properties for the surrounding SnO$_2$ matrix, the sensory properties of the In$_2$O$_3$ clusters largely govern those of the SnO$_2$ + In$_2$O$_3$ composite. Figure 3 shows that, with increasing concentration of In$_2$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 In$_2$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 In$_2$O$_3$ concentration in the film, the total surface of In$_2$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., (Zaporojtchenko, 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 SnO$_2$ + In$_2$O$_3$ sensors applied for detection of CO does not depend on the In$_2$O$_3$ concentration in the range 20% to 37% and it is significantly higher than the $T_{\text{max}}$ (In$_2$O$_3$) for pure In$_2$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 SnO$_2$ and In$_2$O$_3$ particles in the composite film lead to their mutual charging: SnO$_2$ particles become negatively charged, and In$_2$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 In$_2$O$_3$ and SnO$_2$ is higher than that on neutral particles. Therefore, until In$_2$O$_3$ clusters which determine the conductivity and sensitivity of the SnO$_2$ + In$_2$O$_3$ composite sensor to gas, are surrounded by a matrix of SnO$_2$, the $T_{\text{max}}$ value for such sensors would be higher than $T_{\text{max}}$ (In$_2$O$_3$). When the concentration of In$_2$O$_3$ in the composite reaches 50%, there is, apparently, a reorganization of the composite, and clusters of In$_2$O$_3$ form a separate phase. Consequently, the influence becomes negligible of SnO$_2$ on the sensory phenomena in these clusters. In addition, the $T_{\text{max}}$ of the composite sensor becomes equal to $T_{\text{max}}$ (In$_2$O$_3$) as depicted in Figure 4.

The sensitivity of In$_2$O$_3$-sensor applied for H$_2$ detection is significantly lower than the sensitivity of SnO$_2$. The introduction to the SnO$_2$ film of up to 20% of In$_2$O$_3$-nanocrystals results in a significant increase in sensitivity of the composite sensor. A further increase In$_2$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 In$_2$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 for 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 SnO$_2$ and In$_2$O$_3$ particles. This explains the increase in sensitivity to H$_2$ with In$_2$O$_3$ concentration in the composite sensor containing up to 20% In$_2$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 In$_2$O$_3$ particles (above the percolation threshold) the current flow path in the composite film is through the conductive clusters of In$_2$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 In$_2$O$_3$ in the composite film the number of threads is quite small. Therefore, the transition from conduction through SnO$_2$ particles to conduction through In$_2$O$_3$ particles with increasing concentration of In$_2$O$_3$ in the film, occurs gradually in the region from 20 to 50%, where there are parallel paths of conduction through threads of In$_2$O$_3$ particles and through surrounding SnO$_2$ matrix, as shown in the a previous study (Manoj, 2007).

Since the sensitivity of SnO$_2$ to CO is much lower than that of In$_2$O$_3$ in the range of In$_2$O$_3$ concentrations above the percolation threshold for In$_2$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 In$_2$O$_3$ clusters and largely independent of the SnO$_2$ matrix.

By the same token, the sensitivity of SnO$_2$ to H$_2$ for is much larger than that for In$_2$O$_3$. Therefore, when SnO$_2$ + In$_2$O$_3$ composite sensors are used for detection of H$_2$ in air, a significant contribution of sensor phenomena in the SnO$_2$ matrix to overall sensory property is retained even with relatively minor contribution of SnO$_2$ conductivity.
to the overall composite conductivity at In$_2$O$_3$ concentration above the percolation threshold for In$_2$O$_3$ particles. With increasing concentration of In$_2$O$_3$ above 20%, the contribution of sensor phenomena in the 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 In$_2$O$_3$ is equal to or greater than 50% the conductivity of the composite proceeds completely through the In$_2$O$_3$ particles (Belysheva, et al., 2010a), and the sensitivity of the composite sensor is the same as in pure In$_2$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 SnO$_2$-In$_2$O$_3$ films on sensitivity to CO and H$_2$ is due to the electron transfer between contacting In$_2$O$_3$ and SnO$_2$ particles and the resulting mutual charging of these particles. This effect is more pronounced in the detection of 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 In$_2$O$_3$ and 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 (In$_2$O$_3$ with electron affinity of 3.7 eV (Klein, 2000)) embedded in electron accepting matrix (SnO$_2$ with the electron affinity of about 4.8 eV (Hoefer, et al., 2001)). The detection of hydrogen and CO was also investigated utilizing sensors consisting of electron donor matrix (In$_2$O$_3$) with inclusions of nanocrystals of electron accepting component (ZnO). Published data show that the electron affinity of In$_2$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 SnO$_2$- In$_2$O$_3$ nanocomposite sensors.

In contrast to the SnO$_2$- In$_2$O$_3$ system, a strong influence was observed of electron accepting additives of ZnO on sensory properties of In$_2$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 In$_2$O$_3$ film produces a sharp increase in sensitivity to H$_2$ and a shift in Tmax 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 In$_2$O$_3$ crystals. Sensory reactions of hydrogen or carbon monoxide with the active O-centers proceeds both in the zone of contact between ZnO and In$_2$O$_3$, and on the surface of In$_2$O$_3$ crystals free of ZnO. The redistribution of electrons between ZnO and In$_2$O$_3$ results in negatively charged ZnO clusters and positively charged In$_2$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 In$_2$O$_3$-ZnO contact zone to the free surface of In$_2$O$_3$. Therefore, in the contact zones the sensory reaction $A + O^- = AO + e^-$, where A is the analyzed gas, has little effect on the surface concentration of electrons in the ZnO-free areas of the In$_2$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 In$_2$O$_3$ can be assumed to be concentrated in areas of contact between electron donor In$_2$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 In$_2$O$_3$ nanocrystalline containing small additions of ZnO.

The existence of small clusters of ZnO on the surface of In$_2$O$_3$ is not to significantly affect the adsorption capacity of these particles for non-polar H$_2$ molecules. The enhancement of sensitivity to hydrogen in this case, as well as in the SnO$_2$- In$_2$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 In$_2$O$_3$ particles. The hydrogen atoms generated migrate from the contact zone to the surface of the In$_2$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 In$_2$O$_3$ nanocrystals with ZnO inclusions, fundamentally differs from the SnO$_2$- In$_2$O$_3$ composite sensor described above. In the latter sensor with the relatively small (up to 20%) concentration of electron donor In$_2$O$_3$ nanocrystals in SnO$_2$ matrix, current flows through the set of electron accepting SnO$_2$ crystals. Electron transfer from In$_2$O$_3$ to 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$_2$ and In$_2$O$_3$ 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.

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References


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**Figure 1.** Temperature dependence of conductivity $1/R$ in arbitrary units, where $R$ is film resistance, for nanocrystalline SnO$_2$ film (A); SnO$_2$ + In$_2$O$_3$ composite films with different In$_2$O$_3$ concentrations (wt.%)- 6% (B); 12% (C); 20% (D); 37% (E); 50% (F); nanocrystalline In$_2$O$_3$ film (G)
Figure 2. Schemattic representation of electron movement in SnO$_2$ + In$_2$O$_3$ composite film with concentration of In$_2$O$_3$ below (a) and above (b) of the percolation threshold of In$_2$O$_3$ particles in an electric field V. Arrows indicate the movement of electrons through a system of SnO$_2$ nanocrystals, including uncharged region with conductivity BI and negatively charged region with conductivity BII, as well as through conducting In$_2$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 $S_{max}$ of SnO$_2$ + In$_2$O$_3$ composite sensor with In$_2$O$_3$ concentration for detection of 0.46% CO (1), and 2% H$_2$ (2).
Figure 4. Temperature dependence of SnO$_2$ + In$_2$O$_3$ composite sensor sensitivity $S = R_o/R$ ($R_o$ and $R$ are the sensor resistance in pure air and air containing analyzed gas, respectively) in detecting 0.46% CO, for varying In$_2$O$_3$ concentration (wt. %): 0 (A); 12% (B); 20% (C); 25% (D); 37% (E); 50% (F); 100% (G).

Figure 5. Temperature dependence of sensor sensitivity $S = R_o/R$ ($R_o$ and $R$ are sensor resistance in pure air and in air containing analyzed gas, respectively) in detecting 2% H$_2$ (a) and 0.46% CO (b) for a variety of films: ZnO (A); In$_2$O$_3$ (B); In$_2$O$_3$ + ZnO composite sensors with different wt. % of ZnO: 1% (C); 3% (D); 10% (E).