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Gas-Sensitivity Properties of Nanoscale Au–In_2O_3 Materials

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Abstract—A possibility was demonstrated of producing the chemical sensors based on Au–In_2O_3 obtained using a sol–gel technology. The sensors exhibit high sensitivity and selectivity toward CO. The differences in gas-sensitivity properties of In_2O_3 sensor with respect to CO and CH_4 at different ways of doping with Au(III) was examined. The effect of the gold nanoparticles size and the state of the indium oxide surface on the characteristics of Au–In_2O_3 and Au/In_2O_3 sensors at the detection of CO and CH_4 was examined.

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Solving the problem of registration of low concentrations of carbon monoxide in residential, public and industrial buildings is a relevant task. Due to its high toxicity, permanent monitoring of CO is needed in the areas where there are conditions for its appearance due to incomplete combustion of carbon-containing organic compounds. In most situations, carbon monoxide is a by-product of incomplete combustion of hydrocarbons. For the detection of CO can be used chemical sensors based on the semiconducting oxides, the signal is registered as a change in their electrical conductivity at the presence of the gas to be detected [1]. However, the threshold sensitivity and selectivity toward CO of the most sensors is not satisfactory. Therefore, the development of sensors for monitoring CO in the air to create safety systems requires to focus efforts on improving the sensitivity threshold (50×10^{-4}%) and selectivity of detection on the background of the other gases, primarily methane and other hydrocarbons of the natural gas. From the published data follows that the major semiconductor oxides (tin, indium, iron, and zinc) used in gas sensors have almost the same and not a high sensitivity toward CO and CH_4 [2, 3]. Therefore is required their doping with the additives increasing adsorption-catalytic properties of these oxide materials [4]. Solving the problem of selectivity of the metal oxide sensors is rather a complex task because adsorption of particles of different chemical nature often causes the same type of change in electrophysical state of semiconductor [5, 6]. There are several empirical approaches that in some cases allow to achieve selective determination of one of the gases in the two-component system [3, 7]. Among them the most effective are maintaining a certain temperature regime of the sensor and the introduction of additives active in adsorption and catalysis, that provide a change of sensitivity and the optimal temperature for the detection of individual gases. Among the heterogeneous oxidation catalysts, the most active are the noble metals, primarily palladium and platinum. However, these versatile oxidation catalysts based on platinum and palladium, as a rule, enhance sensitivity in respect of both CO and CH_4, as well as other gases having reducing properties. Therefore, to achieve the selectivity toward CO is necessary to use a catalyst with specific adsorption and catalytic properties. The substances with such properties include ruthenium and gold. Ruthenium is known as a highly active catalyst in the Fischer–Tropsch reaction due to its ability to form complexes with CO [8]. Catalytic reactions that include formation of intermediate complexes proceed by an associative mechanism, at lower temperatures than the direct oxidation reaction [9]. There is information about using this property of ruthenium for producing thermocatalytic sensors [10, 11]. It was shown that Ru–Al_2O_3 sensors induce maximum output signal toward CO at a much lower temperature (300°C) than toward methane (560–600°C). However, the magnitude of the threshold CO sensitivity (5×10^{-2}%) of

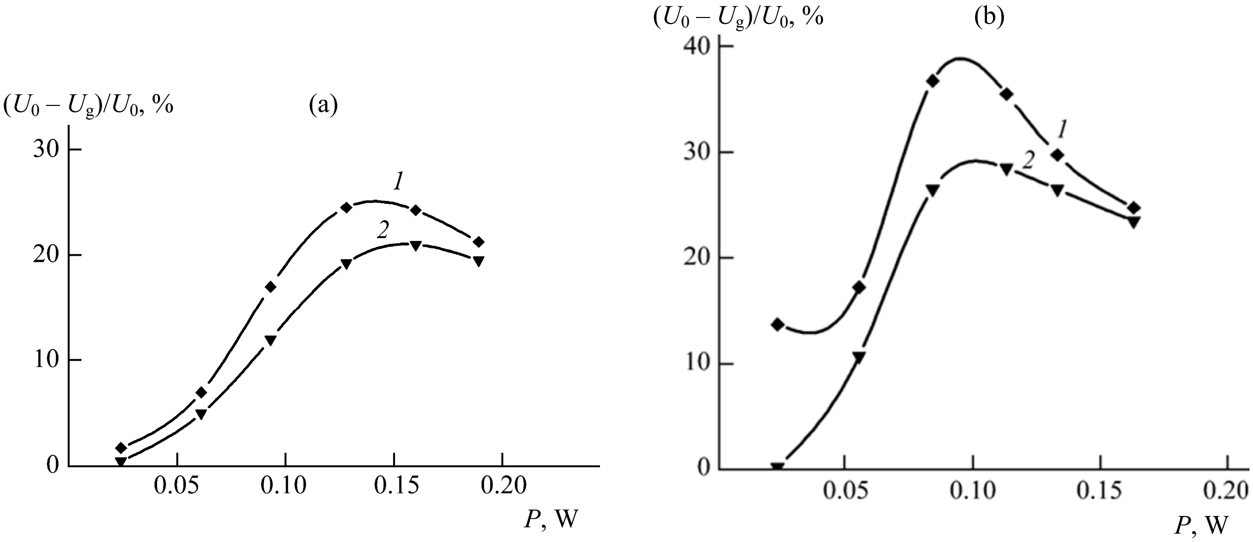

Fig. 1. The dependence of the output signal of the sensors (a) In_2O_3 and (b) Au/In_2O_3 on the power consumption at the determination of (*1*) CO and (*2*) CH_4. The concentration of gases in the air-gas mixture 20×10^{-2}%.

such sensors is not sufficient for the monitoring CO at low concentration (10^{-3}%), which is hazardous to human health and safety.

There is an evidence of activity of gold in the low-temperature oxidation of CO [12]. The following systems have been investigated as the catalysts for low temperature CO oxidation: Au/Al_2O_3, Au/MgO and Au/Fe_2O_3 [13–15]. However, these materials can not be used as sensitive elements of semiconductor sensors because of the low conductivity or absence of conductivity in these oxides. It is hoped that doping the oxides possessing the semiconductor conductivity with ruthenium or gold can lead to efficient detection of CO due to specific adsorption of the latter and catalysis at low temperature. In this case, as we know, gold and ruthenium catalysts are not effective in the methane oxidation at low temperatures.

It should be noted, however, that the present state of research in the field of semiconductor sensors does not allow to predict in advance, without an experimental study, the chemical and structural–phase composition of a semiconductor material effective for the CO detection in the presence of other gases with similar reductive properties, especially methane and hydrogen [16].

The purpose of this work is to investigate the possibility of obtaining chemical sensors based on indium oxide with a high sensitivity toward CO due to the introduction of gold into the gas-sensitive material.

As the semiconductor material we used indium oxide, which has high electrical conductivity and the highest sensitivity toward CO (among the investigated oxides) [17]. Synthesis of oxide material and producing the gas-sensitive layer was carried out using the sol-gel method [18]. In one experiment (the sample denoted as Au–In_2O_3) the gold ions were introduced into the indium hydroxide sol in the form of $HAuCl_4$ (0.5 wt % of Au relative to In_2O_3). In another experiment (sample Au/In_2O_3) the gas-sensitive layer was prepared by applying a solution of $HAuCl_4$ on the In_2O_3 ceramic layer with subsequent thermal treatment.

Gas-sensitivity properties. Figure 1 shows the dependence of relative magnitude of the output signals of In_2O_3 and Au/In_2O_3 sensors on the consumed power. The Au(III) application on the surface of the indium oxide sensor increases output signal toward both methane and CO. Therewith, there is a slight reduction in the power consumption. However, for the Au/In_2O_3 sensors is typical almost the same temperature range of optimum detection of CO and CH_4, which corresponds to the power consumption P = 0.08 to 0.10 W (Fig. 1b).

At the introduction of $HAuCl_4$ to the indium hydroxide sol occurs a more significant change in the properties of sensors towards CO than at the application of Au(III) on the indium oxide ceramic layer (Fig. 2a). The CO detection occurs as an increase

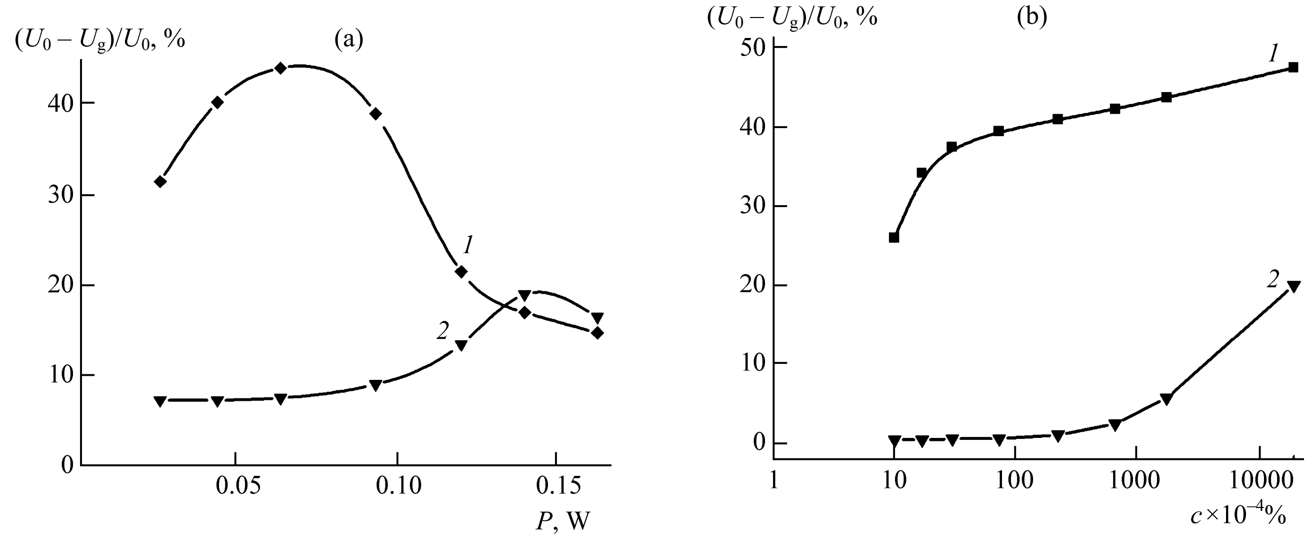

Fig. 2. The dependence of the output signal of Au–In_2O_3 sensors at the determining (*1*) CO and (*2*) CH_4 on the power consumption at the gas concentration (a) 20×10^{-2}% and (b) on the gas concentrations at a power consumption 0.06 W.

in the output signal and a significant shift of the maximum sensitivity to low power consumption (P = 0.06 W), where the sensitivity toward methane is practically absent. By sensitivity toward methane the Au–In_2O_3 sensors differ little from the In_2O_3 sensors, and the maximum of their output signal toward CH_4 is achieved at P = 0.14 W. From the data obtained follows that at low values of the power consumption, when sensitivity of Au–In_2O_3 toward methane is low, the output signal toward CO reaches its maximum. The value of the minimum concentration of CO determined by the Au–In_2O_3 sensors is 10^{-3}% (Fig. 2b). In the concentration range that is most important for the analysis (30×10^{-4}% and higher), the sensor output is a linear function of the logarithm of CO concentration. Such dependence and low power consumption is important for practical use of the Au–In_2O_3 sensors in the handheld devices for detecting CO [19].

In the case of Au–In_2O_3 sensors the dynamic parameters are reduced compared with the In_2O_3 sensor. This is an expectable sequence of decrease of the gas detection temperature and is a result of the slowdown of the surface adsorption-catalytic processes. Thus, the duration of reaching equilibrium value of the output signal at detecting CO in the range of high concentrations ($5–200\times10^{-4}$%) is 30–40 s for the Au–In_2O_3 sensors and 5–10 s for In_2O_3 sensors. This response time for the appearance of gas is acceptable for the use of the Au–In_2O_3 sensors in gas detectors [20].

Our results demonstrate that the introduction of Au(III) in an amount of 0.5 wt % in the indium oxide gas-sensitive material increases the output signal, improves the threshold sensitivity of the semiconductor sensors toward CO, and reduces significantly the power consumption (to 0.05–0.06 W). When Au(III) is applied on the surface of the indium oxide ceramic layer, such positive influence on the gas-sensitivity properties of sensors in relation to CO does not occur. The observed difference in the properties of the Au–In_2O_3 and Au/In_2O_3 samples may be due to the unequal state of the gold in them, as well as due to the influence of gold on the formation of the active surface of indium oxide.

State of gold and indium oxide. Using transmission electron microscopy, we revealed a difference in the size of gold particles in the samples of Au–In_2O_3 and Au/In_2O_3. Figure 3 shows the images of the carbon replicas from the samples surface doped with gold: the gold particles size is 3–6 nm in the Au–In_2O_3 and 7–15 nm in Au/In_2O_3. The size of the indium oxide globules is from 20 to 60 nm. Note that the observed replicas of large indium oxide globules do not allow to reveal their fine structure. A study by electron microscopy of powder samples shows that in them dominate the indium oxide particles with a diameter of 30–40 nm.

Effect of gold on the gas-sensitivity properties of indium oxide. The data obtained are in accordance with the published information that only the gold

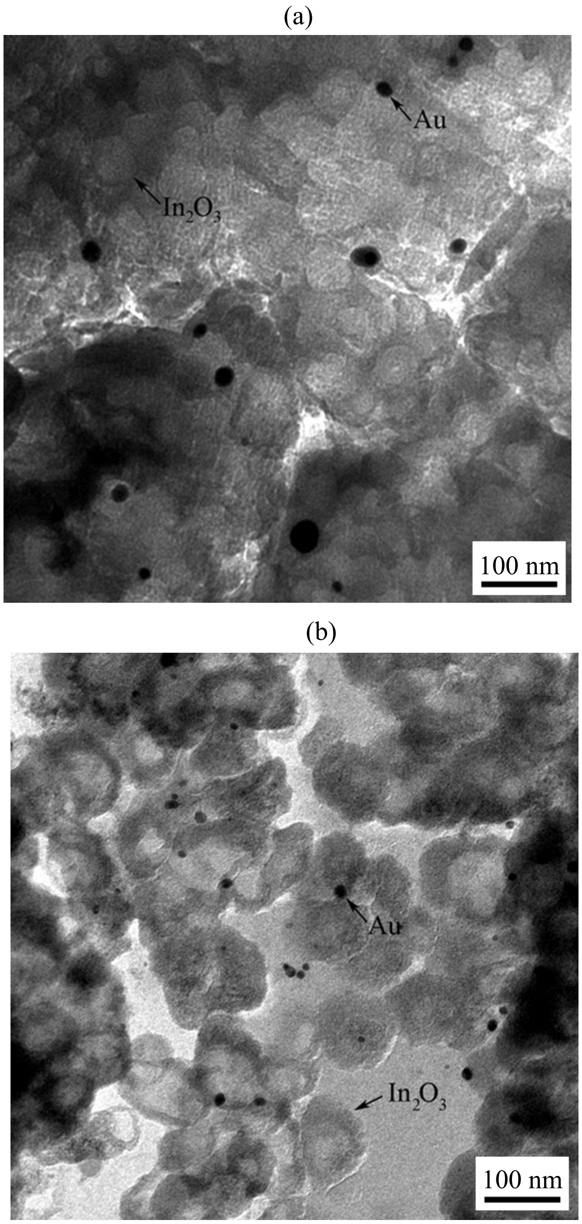

Fig. 3. Microphotographs obtained by electron microscopy of carbon replicas from the surface of the samples (a) Au/In$_2$O$_3$ and (b) Au–In$_2$O$_3$.

particles of small size (3.5–5 nm) exhibit catalytic activity at the low-temperature CO oxidation [12]. The CO oxidation at low temperature proceeds by the mechanism of associative type, which includes the CO adsorption on Au and the interaction between adsorbed particles and activated oxygen at the interface between gold particles and oxide matrix and the redistribution of bonds in the intermediate complexes. This causes a change in the charge carrier concentration in the indium oxide surface layer. The low-temperature charge transport requires the presence in the catalyst system of metal ions in a certain state of valence and coordination environment [12, 15]. In [13, 14] has been shown that the activity of the Au/Al$_2$O$_3$ and Au/MgO systems in the catalytic process depends on the size of gold particles and the ratio of the metallic (Au^0) and oxidized (Au^{3+}) states in them. Experiments with single-crystalline TiO$_2$ films showed that the high catalytic activity is typical for the two-dimensional gold particles on the titanium dioxide surface. There is an optimum particle size to achieve the maximum sensitivity toward CO of the semiconductor oxides, which can vary for various oxides [21]. These factors help to explain the observed differences in the gas-sensitivity properties of the systems Au–In$_2$O$_3$ and Au/In$_2$O$_3$ by the uneven state of the gold, as well as by changes in the state of indium oxide.

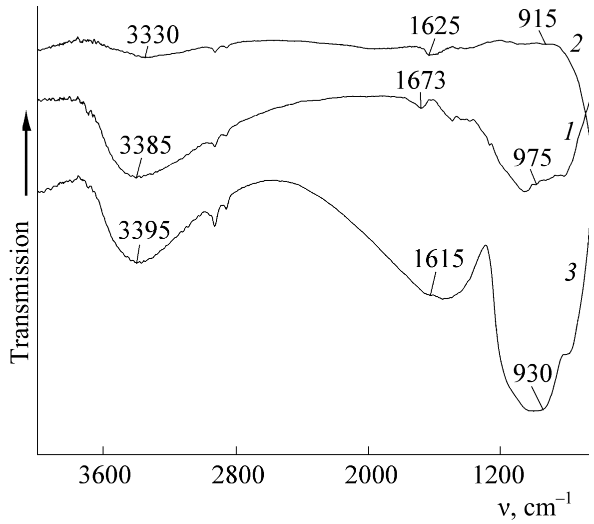

Fig. 4. IR spectra of the samples (*1*) In$_2$O$_3$, (*2*) Au/In$_2$O$_3$, and (*3*) Au–In$_2$O$_3$.

According to IR spectroscopy, when a solution of HAuCl$_4$ is applied to the In$_2$O$_3$ ceramic layer is, first of all occurs a change in the properties of the surface caused by the decrease in the content of hydroxyl groups and adsorbed water (Fig. 4).

Most sensitive to the changes in the surface state of the metal oxides obtained by thermal dehydration of related hydroxides is the region in the IR spectra of the deformation vibrations of hydroxyl groups bound to themetal cation ($\delta_{M–O–H}$). In the spectrum of indium oxide the absorption maximum of the band of these bonds vibrations is at 1050 cm^{-1} (Fig. 4, curve *1*). The content of adsorbed water on the surface of indium oxide can be revealed from the intensity of the absorption bands of stretching $\nu_{H–O–H}$ and bending $\delta_{H–O–H}$ vibrations located at 3385 and 1673 cm^{-1}, respectively. After applying $HAuCl_4$, the absorption bands in these areas of the IR spectrum becomes scarcely visible. Most likely, that in Au/In_2O_3 on the surface of indium oxide are formed the adsorbed complexes $[AuCl_3(OH)]^-$ and $[AuOCl_3]^{2-}$. At their thermal decomposition with the gradual removal of chloride ions appear the gold particles with the size distribution in a wide range (7–15 nm), which adversely affects the Au/In_2O_3 sensitivity toward CO. Decrease in the amount of hydroxyl groups on the surface of a semiconductor oxide, according to the literature [22], affects positively the efficiency of the methane detection, which is observed in the case of the Au/In_2O_3 samples.

In the IR spectrum of $Au–In_2O_3$ occurs a significant increase in the intensity of the absorption bands at 930–1030 cm^{-1} due to the deformation vibrations $\delta_{M–O–H}$, indicating an increase in the concentration of the hydroxyl groups on the sample surface (Fig. 4, curve *3*). At the introduction of $HAuCl_4$ into the $In(OH)_3$ sol apparently occurs the formation of the hydroxo-complexes $[Au(OH)_4]^-$ which can form mixed structures with the polynuclear cations such as $In_4(OH)_{10}^{2+}$, $In_5(OH)_{14}^{+}$ and thus promote the growth of indium oxide particles at the dehydration. At the thermal decomposition of the mixed In(III) and Au(III) hydroxo-complexes there is a mutual influence of the components on the formation and growth of particles of the end products, indium oxide and gold, resulting in the formation of small size gold particles (3–6 nm), therwith the concentration of hydroxyl groups on the indium oxide surface remains high. These structural features provide formation of the sensors based on $Au–In_2O_3$ characterized by good threshold sensitivity toward CO (10^{-3}%) and low power consumption (0.06 W).

EXPERIMENTAL

The study of gas-sensitivity properties was performed with the ceramic type sensors. The features of design and manufacturing methods with the use of the sol-gel technology are described in [18, 23]. The sensors sensitive elements and the powders for the research were annealed at 700°C for 2 h. The heating of ceramic sensor fixed on the platinum coil was performed by supplying stabilized electric current (I). The sensor output signal was measured as a difference (ΔU) of the voltage from the sensors in air (U_0) and in the gas-air medium (U_g) due to the change in the resistance of the semiconductor layer at the occurence of adsorption-catalytic processes on its surface. The power consumption (P) was determined as $P = I \cdot U_0$. To measure the gas-sensitivity characteristics of the sensors were used standard air-gas mixtures with a given concentration of gases (CO, CH_4) and 30% relative humidity. If necessary, the gas concentration was reduced by a generator 623GR-03M. Electron microscope LEO 903 was used to view the carbon replicas from the surface of samples, the latter were prepared by standard methods. The indium oxide from the carbon films was dissolved in nitric acid, while the gold particles remained in the film. The IR spectra of powdered samples were recorded on an Avatar 330 (Thermo Nicolet) spectrometer in a wavelength range $\lambda = 400–4000\ cm^{-1}$ using a Smart Diffuse Reflectance diffuse attachment.

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