Gas-Sensitivity Properties of Nanoscale Au–In$_2$O$_3$ Materials

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Received December 24, 2009

Abstract—A possibility was demonstrated of producing the chemical sensors based on Au–In$_2$O$_3$ obtained using a sol–gel technology. The sensors exhibit high sensitivity and selectivity toward CO. The differences in gas-sensitivity properties of In$_2$O$_3$ 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$_2$O$_3$ and Au/In$_2$O$_3$ sensors at the detection of CO and CH$_4$ was examined.

DOI: 10.1134/S1070363211100069

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 (5×10$^{-4}$%) and selectivity of detection on the background of 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$_2$O$_3$ 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...
such sensors is not sufficient for the monitoring CO at low concentration (10⁻³%), which is hazardous to human health and safety.

There is 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/Al₂O₃, Au/MgO and Au/Fe₂O₃ [13–15]. However, these materials cannot 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 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-In₂O₃) the gold ions were introduced into the indium hydroxide sol in the form of HAuCl₄ (0.5 wt % of Au relative to In₂O₃). In another experiment (sample Au/In₂O₃) the gas-sensitive layer was prepared by applying a solution of HAuCl₄ on the In₂O₃ ceramic layer with subsequent thermal treatment.

**Gas-sensitivity properties.** Figure 1 shows the dependence of relative magnitude of the output signals of In₂O₃ and Au/In₂O₃ 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/In₂O₃ sensors is typical almost the same temperature range of optimum detection of CO and CH₄, which corresponds to the power consumption P = 0.08 to 0.10 W (Fig. 1b).

At the introduction of HAuCl₄ to the indium hydroxide sol occurs a more significant change in the properties of sensors toward CO than at the application of Au(III) on the indium oxide ceramic layer (Fig. 2a). The CO detection occurs as an increase