Fabrication of gas-sensitive tin-containing polyacrylonitrile thin films to create a household carbon monoxide sensor

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Abstract. Sn-containing PAN films with modifying additive SnCl₂ have been fabricated by pyrolysis under the influence of incoherent infrared radiation under low vacuum conditions using different temperature and time of heat treatment. AFM-investigation of the films surface morphology has been fulfilled. The technological conditions for the formation process of the sensitive layer material for carbon monoxide sensor have been revealed experimentally.

1. Introduction
To date, the acute task is to strengthen and improve the systems that ensure the safety of the human dwelling. Monitoring systems, fire safety systems are being modernized and improved. Nowadays, the creation of "Smart House" systems becomes urgent and necessary.

Air inside the living quarters is usually different from the outside, as there are sources in the rooms that affect the chemical composition of the air and the physical condition of the person. Such sources are mainly household appliances: the allocation of significant amounts of heat, moisture, toxic fumes, gases and dust in the premises, ozonizing and ionizing radiation. Unfavorable conditions of the air environment, in addition to disturbing human health and reducing labor productivity, can adversely affect the condition of equipment and building structures.

A person can be poisoned by breathing in toxic fumes. Carbon monoxide poisoning often causes death. Carbon monoxide is very insidious, it has absolutely no smell. And can be formed wherever there is a burning process, even in the oven. The main reason for its formation is the lack of oxygen in the combustion zone. And then, instead of a completely harmless carbon dioxide - a product of high-grade fuel burn-out - carbon monoxide is formed. A significant number of cases of carbon monoxide poisoning is associated with the inhalation of engine exhausts of cars operating in poorly ventilated rooms.

The mechanism of exposure of carbon monoxide to a person is that it enters the blood, binds hemoglobin cells. The longer a person breathes carbon monoxide, the less oxygen the body receives. For example, if the concentration of carbon monoxide in the air is 0.02-0.03%, then for 5-6 hours of inhalation of such air a concentration of carboxyhemoglobin 25-30% will be created, if the concentration of CO in the air is 0.3-0.5%, then the lethal content of carboxyhemoglobin at the level of 65-75% will be achieved after 20-30 minutes of human presence in such an environment.

Thus, the creation of a portable, inexpensive household sensor of carbon monoxide is an actual and in-demand task [1].

Analysis of publications on research and study of the properties of Sn-based materials showed that polycrystalline tin films are widely used as a gas sensitive material for detecting carbon monoxide. It is
known that polycrystalline tin films are widely used to create sensors for both oxidant gases and reducing agents (table 1): CH₄, C₂H₅OH, NH₃, H₂S, CO [2-10].

Table 1. Sn-containing gas sensitive material and some carbon monoxide sensors based on organic polymers.

| Gas sensitive material                                  | Detected gas | Reference |
|---------------------------------------------------------|--------------|-----------|
| Pd-doped SnO₂/reduced graphene oxide                    | CH₄          | [2]       |
| Ag / SnO₂                                               | CH₄          | [3]       |
| SnO₂ thin film loaded with Pd clusters                  | CH₄          | [4]       |
| SnO₂                                                    | C₂H₅OH      | [5]       |
| SnO₂                                                    | NH₃, C₂H₅OH | [6]       |
| SnO₂                                                    | H₂S          | [7]       |
| Polypyrrole / (FTMA-I)                                  | CO           | [8]       |
| Polypyrrole / Ferrocene                                 | CO           | [9]       |
| Polyaniline / TiO₂                                      | NH₃, CO      | [10]      |

The aim of this work is to obtain gas sensitive thin films of tin-containing polyacrylonitrile (PAN). A feature of this material is the possibility of obtaining sensor elements that function at room temperature, using technology that does not require high-tech equipment [11].

2. Experiment

Sn-containing PAN films were prepared according to known technology [12]. With the purpose of working out the technology of obtaining Sn-containing PAN films and selecting films with the best gas sensitive characteristics, a series of samples of films with different tin content in film-forming solutions was synthesized with varying temperature-time regimes for their preparation in the first and second stages of IR annealing. Preliminary experiments were conducted to determine their gas sensitivity characteristics and it was found that the samples obtained had a response to such gases as: CH₄, CO, NO₂.

Electrically conductive films were obtained from film-forming solutions of PAN with a modifying additive content of cadmium chloride (SnCl₂) from 0.0% to 1.0% in dimethylformamide. The prepared film-forming solution was applied to the substrates by centrifugation. Then, the samples were dried in oven at T = 160 °C for 30 minutes. The temperature-time IR-annealing regimes were selected experimentally, because the intensity and duration of exposure to IR radiation makes it possible to control the properties of the film material, changing the molecular structure of the polymer [13]. The intensity of the radiation in the first stage of IR annealing corresponded to temperatures of 250 °C for 5-20 min, and the intensity of the radiation in the second stage of IR annealing varied 450°C, 500°C, for 2-5 min. Electrically conductive properties of PAN are manifested as a result of thermal treatment of the polymer. Further, the films were cooled down for 40-60 minutes.

The film surface morphology was observed by atomic force microscopy (AFM) using scanning probe microscope Solver P47 Pro (NT-MDT). The 5 × 5 μm² area AFM-images of the films are processed with Image Analysis program.

Resistance measurement was carried out using E6-13A Terrameter. Sensitivity is a change of measured resistance per analyte concentration unit. The gas sensitivity coefficient (S) was defined as the ratio S = (R₀ - R_g)/R₀, when R₀ > R_g, where R₀ is the films resistance in air, R_g is the films resistance in the atmosphere of analyte.

3. Results and discussion
The temperature dependences of the resistance of the obtained samples have been studied in the temperature range from 20°C to 95°C. The measured values of resistance of the obtained samples are in the range 1-30·10^6 Ω. The temperature dependences of the resistance of films of tin-containing PAN with different contents of tin are shown in figure 1.

**Figure 1.** Sn-containing PAN films resistance dependence on temperature

![Graph showing temperature dependence of resistance](image)

**Figure 2.** AFM-images of surface of Sn-containing PAN films, weight concentration of the modifying additive (ω, %): a) 0.25, b) 0.5, c) 0.75, d) 1.0

![AFM-images](image)
Regardless of the weight concentration of the modifying additive (ω, %) in the film-forming solution and the temperature-time regimes of film formation, a slight change in the resistance of the film material during heating is observed (Figure 1), caused by the relatively weak temperature dependence of the mobility of the current carriers, which is characteristic of organic semiconductors [14]. The tendency to decrease the resistance when the film is heated indicates the semiconductor nature of the conductivity of the sample material.

As observed from figure 2 the Sn-containing PAN films have a dense homogeneous structure and developed surface morphology.

According to the results of measuring the Hall effect, it is established that the material of the PAN films has a p-type conductivity [15]. It is known that for semiconductor gas sensors with a sensitive layer of inorganic p-type materials, the presence of reducing gases in the atmosphere leads to a decrease in its electrical conductivity, which is explained by a decrease in the electron concentration in the near-surface layer and an increase in the height of the intergranular barriers [16].

Figure 3. The resistance-time curves of Sn-containing PAN sensing film at c(CO) = 100 ppm

Thus, we should expect a reduction in the resistance of the investigated films in the atmosphere of the detecting oxidizing gas (NO₂, Cl₂) and the opposite result in the presence of a reducing gas (CO), which is clearly visible from graphs reflecting the kinetics of the adsorption response of the samples under periodic exposure to the corresponding gases.

It was established that the obtained samples of films based on tin-containing PAN show a gas sensitivity to a reducing gas CO. In figure 3 shows the characteristic responses of tin-containing PAN film. When the gas is injected, the film resistance increases; this does not contradict the theory of the reaction of the p-type semiconductor to the electron-donor gas. With periodic gas inlet into the chamber (every minute), a steady response of the gas-sensitive film is observed. The response time was determined experimentally and was 55 seconds, the recovery time was 5 seconds. Stopping the flow of the detected gas into the measuring chamber and blowing it with air leads to the restoration of the resistance values of the film.

Thus, the sensitivity of the obtained tin-containing PAN films was found at 100 ppm concentration of CO gas at 20-80 °C.

4. Conclusion

The Sn-containing carbon monoxide sensitive PAN films have been fabricated. The use of metal-containing PAN films as a gas-sensitive element of the sensor is based on the adsorption-resistive effect
– the ability to change resistance due to selective interaction with the molecules of the detected gas. The resistive properties of films are governed by the parameters of the synthesis of PAN films: the addition of transition metal salts in low concentrations to the film-forming solution or by changing the annealing temperature. The issues of the influence of concentrations of additives and other conditions on the sensitive properties of films require further research.

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