Choice of technological conditions for synthesis of sensing materials based on polyacrylonitrile on flexible substrates

T.V. Semenistaya, A.V. Ivanenko
Southern Federal University, Engineering-technological Academy, Institute of Nanotechnologies, Electronics, and Equipment Engineering, Str. Shevchenko, 2, Taganrog, Russia, 347922

semenistayatv@sfedu.ru

Abstract. Cd-containing PAN films with modifying additive CdCl$_2$ have been fabricated by pyrolysis under the influence of incoherent infrared radiation under low vacuum conditions using different temperature and time of heat treatment. The influence of modifying additive concentration and of technological conditions on the films electrical and gas sensitive properties have been investigated. AFM-investigation of the films surface morphology has been fulfilled. The technological conditions for the formation process of the sensitive layer material for hydrogen sulphide sensor have been revealed experimentally.

1. Introduction
Currently, portable electronic devices such as mobile phones, computers, digital cameras, various sensors, are becoming more and more multifunctional and tend to reduce size, weight, the ability to flex and twist to meet the demands of today's market. The development of technologies related to the creation of portable power sources and energy storage is still at a rather low level. Technologies for creating gas sensors on flexible media are actively developing all over the world.

Flexible portable sensors that detect dangerous gases (hydrogen, nitrogen dioxide, hydrogen sulphide), as well as high levels of ultraviolet radiation are in demand. These electronic devices can be attached to the body in the form of patches or sewn into clothing and special equipment [1]. The use of such sensors will make it possible to more effectively monitor toxic and explosive gases in transport, industrial plants and thermal power plants, inaccessible places (mines, caves), thereby reducing risks for workers and the public [2-5].

Polyacrylonitrile (PAN) is a promising material for creating such flexible sensor devices. The technology of fabrication gas sensitive PAN films that does not require high-tech equipment and the ability to exhibit gas-sensing properties at room temperatures opens the prospect of creating flexible sensors. The gas-sensitive metal-containing PAN thin films have been fabricated [6] that are sensors for detecting to CO, NO$_2$, Cl$_2$, NH$_3$, H$_2$S [7-10].

2. Experiment
To form cadmium-containing PAN films pyrolysis method under the influence of IR radiation under low vacuum conditions was used. Electrically conductive films were obtained from film-forming solutions of PAN with a modifying additive content of cadmium chloride (CdCl$_2$) 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 [6]. Halogen lamps KG-220 with high radiation in the area of 0.8 µm – 1.2 µm were used as the source of radiation. Uniform heating of the samples was supplied with up and down position of the halogen lamps along the longitudinal perimeter outside the quartz reactor. The sample in the graphite cassette was fixed on special quartz holders inside the reactor. The thermoelectric couple chromium-aluminium inside the graphite cassette was used to control the intensity of IR-radiation. The intensity of the radiation in the first stage of IR annealing corresponded to temperatures of 250 °C, 300 °C for 20 min, and the intensity of the radiation in the second stage of IR annealing varied 350 °C, 400 °C, 450 °C for 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.

Thickness measurement of the films was carried out using MII-4 interferometer.

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 Terraommetr. Sensitivity is a change of measured resistance per analyte concentration unit. The gas sensitivity coefficient (S) was defined as the ratio $S = (R_0 - R_g)/R_0$, when $R_0 > R_g$, where $R_0$ is the films resistance in air, $R_g$ is the films resistance in the atmosphere of analyte.

3. Results and discussion

Influence of cadmium compounds concentration in the organic matrix of the film is obvious: the film thickness increases with the concentration of the modifying additive (Fig. 1).

![Figure 1](image1.png)

**Figure 1.** Thickness of the Cd-containing PAN films vs. weight concentration of modifying additive

As observed from Fig. 2 the Cd-containing PAN films have a dense homogeneous structure and developed surface morphology.
Figure 2. AFM-images of surface of Cd-containing PAN films, weight concentration of the modifying additive (ω, %): a) 0.0, b) 0.25, c) 0.5, d) 0.75, e) 1.0

For the Cd-containing PAN film (ω(Cd) = 0.25%) the highest peak-to-peak value of 300.5 nm and the highest average roughness value of 31.9 nm were obtained, corresponding to such film surface morphology, which creates the necessary energy background for the adsorption of the detected gas.

The measured values of resistance of the obtained samples are in the range $10^8$-$10^{10}$ Ω. Fig. 3 depicts there is reduction in resistance of cadmium-containing samples with concentration of the modifying additive.

Figure 3. Dependence of the Cd-containing PAN films resistance on weight concentration of modifying additive

The presence of transition metal compounds affects the electrical conductivity of the samples. The films become more electrically conductive with an increase in the number of charge carriers.

Temperature dependences of the resistance of cadmium-containing PAN films in the range from 18 °C to 100 °C were studied. A typical relation between the resistance and temperature of the fabricated films is shown in Fig. 4. The value of the determination coefficient $R^2$ is close to 1, which means that the approximation curve best describes the experimental dependence of the Cd-containing PAN film resistance on temperature. The experimental curve gives the approximating function $y = f(x)$, where $x$ corresponds to the heating temperature of the film.

To study the dependence of the gas sensitivity coefficient of the films on the concentration of the detected gas, the films with the best characteristics were selected. Investigating the sensor properties of the films, we tested the samples with different contents of the modifying additive (Fig. 5). As it can be
seen, samples with a cadmium concentration of 0.25% turned out to be the best. This can be explained by the fact that the ratio of the amount of the modifying additive and the organic matrix makes it possible to form the structure of the composite material and the morphology of the film surface which meets the conditions for the best sorption of the detected gas. To determine the range of concentrations of the gas to be detected in which the film material is sensitive, the measurements shown in Fig. 6 were done.

Temperature dependences of gas sensitivity coefficient of the obtained samples showed that the maximum values of the gas sensitivity coefficient are reached at room temperature.

Polyacrylonitrile is the prospective material as gas-sensing layer of sensors as it offers low cost and relative simple structure. The design of environmentally-sensitive products involves selecting appropriate materials, technology and manufacturing equipment. Advantage of PAN-based material is the possibility of obtaining films with functional properties and there is no need to use complex technological equipment.

4. Conclusi
Thin cadmium-containing PAN films (h = 0.09 μm – 0.17 μm) with a resistance of \(7 \cdot 10^6\) to \(3 \cdot 10^{10}\) Ω were obtained by pyrolysis method. It has been found that the temperature dependence of the resistance of the films has an exponential character.

It is known that doping gas sensitive materials with cadmium compounds allows achieve sensor sensitivity to H\(_2\)S [11], formaldehyde (CH\(_2\)O) [12], ethanol (C\(_2\)H\(_5\)OH) [13], trimethylamine (CH\(_3\))\(_2\)N [14], liquefied petroleum gas (LPG), [15]. H\(_2\)S sensor based on polyaniline–CdS nanocomposites that demonstrated maximum response for 100 ppm at room temperature (300 K) has been fabricated [16]. It has been created [17] the 3.0 wt% Cd-doped SnO\(_2\) based sensor that showed selectivity toward H\(_2\)S at 275 °C, giving a response of about 31–10 ppm.

In our work it has been found that the cadmium-containing PAN films are sensitive toward H\(_2\)S at room temperature, which is not worse than the sensors presented in [11-17]. The best gas sensitivity at concentrations of the detected gas of 0.17 -3.9 ppm showed a sample of 0.25% Cd. Potential applications of the Cd-containing PAN films include environmental monitoring of gas emissions as non-heated semiconductor sensor.

Acknowledgments
This work was performed with the financial support of the Ministry of Education and Science of the Russian Federation, agreement No. 14.575.21.0126 (identification number of the project RFMEFI57517X0126). The equipment of the Research and Educational Center of "Nanotechnologies" and of the Research and Educational Center "Microsystem Technology and Multisensory Monitoring Systems" of Southern Federal University was used for this study.

References

[1] Honda W, Harada S, Arie T, Akita S and Takei K 2014 Adv Funct Mater 24 3299–3304
[2] Kenry Y J C and Lim C T 2016 Microsys Nanoeng 2 16043
[3] Kahn N, Lavie O, Paz M, Segev Y and Haick H 2015 Nano Lett 15 7023–7028
[4] Gutruf P, Walia S, Sriram S and Bhaskaran M 2015 Adv Electron Mater 1 1–6
[5] Wang C 2016 Flex Electron Mater Dev 1–44
[6] Semenistaya T V 2016 Springer Proc Phys 175 61–77
[7] Semenistaya T V, Plugotarenko N K and Petrov V V 2015 Appl Mech Mater 727–728 145–149
[8] Valovega G and Semenistaya T 2016 Solid State Phenom 257 175–178
[9] Semenistaya T V, Petrov V V, Bednaya T A and Zaruba O A 2015 Mater Today Proc 2 77–84
[10] Semenistaya T V, Petrov V V and Lu P 2013 Adv Mater Res 804 135–140
[11] Merdrignac-Conance C, Bercicot Y, Guyader J 2000 Sens. Actuators, B 63 86-90
[12] Zeng W, Liu T, Wang Z, Tsukimoto S, Saito M, Ikuhara Y 2009 Sensors 9 9029-9038
[13] Sivalingam D, Gopalakrishnan J B, Rayappan J B B 2012 Mater. Lett. 77 117-120
[14] Chua X, Zhoua S, Donga Y, Suna W, Ge X 2011 Mater. Chem. Phys. 131 27-31
[15] Bulakhe R N, Lokhande C D 2014 Sens. Actuators, B 200 245-250
[16] Raut B T, Godse P R, Pawar S G, Chougule M A, Bandgar D K, Patil V B 2012 Meas 45 94-100
[17] Sun P, Zhou X, Wang Ch, Wang B, Xua X, Lu G 2013 Sens. Actuators, B 190 32–39