IOP Conference Series: Materials Science and Engineering



# Electro-physical properties of thin films based on metal-containing polyacrylonitrile for application in low temperature gas sensors

To cite this article: T.V. Semenistaya and A.V. Ivanenko 2017 *IOP Conf. Ser.: Mater. Sci. Eng.* **220** 012003

IOP Conf. Series: Materials Science and Engineering **220** (2017) 012003 doi:10.1088/1757-899X/220/1/012003

# Electro-physical properties of thin films based on metal-containing polyacrylonitrile for application in low temperature gas sensors

**Semenistaya T.V.[1*], Ivanenko A.V.[1]**

[1]Engineering-technological Academy of the Southern Federal University, 44 Nekrasovskiy Lane, Taganrog 347928, Russia

*E-mail: semenistayatv@sfedu.ru

**Abstract.** The metal-containing (Cu, Co, Ag, Cr) polyacrylonitrile (PAN) thin films were fabricated using IR-pyrolysis under low vacuum conditions in different temperature and time modes. The thickness of the fabricated films was between 0.01÷0.68 μm. The metal-containing PAN films had the resistance values in the range from $2.9{\cdot}10^2$ to $5.1{\cdot}10^{11}$ Ohm. It has been investigated that the film thickness, resistance and gas sensitivity of the samples depends on the composition of the initial solution and on the process parameters of the film material's fabrication. It has been studied that the samples demonstrate gas-sensing properties to CO, $NO_2$, $Cl_2$ and gasoline vapours at room temperature.

## 1. Introduction

Polymeric materials have gained a wide theoretical interest and can be used for very different purposes and may offer unique possibilities [1-3]. Recent advances in polymer science and film fabrication have made polymeric material films useful, practical and economical in a wide range of sensor designs and applications [4, 5].

Conducting polymers have attracted considerable attention for room temperature gas sensing applications.

PAN is extremely popular and has attracted much attention due to its unique structure and ability to change it under heating, tolerance to most solvents and commercial availability [6]. PAN, which is a polymer with a chain of carbon atoms connected to one another, is turned into a semiconductor material under pyrolysis without changing its basic structure. PAN being subjected to carbonization under controlled conditions is known to be transformed into polymer with conjugated bonds and semiconductor properties. The method of fabrication of the electroconductive structure of PAN, hardware peculiarities and synthesis conditions ambiguously exert influence on the properties of the formed material. There are some methods of manufacturing the electroconductive structure of PAN such as: thermal pyrolysis and IR-radiation pyrolysis. Under the pyrolysis proceeding at temperatures higher than 300 °C , PAN is transformed into a polymer with a cyclic structure, containing the conjugated double bonds. Due to the π -orbital overlap of the neighbouring molecules of the conjugated structure, the π -electrons are delocalized along the entire chain, which provides semiconducting properties of PAN polymer. This method enables to manufacture films with a developed surface morphology and provides uniform distribution of modifying additives in a film. The presence of a transitional metal and its compounds completely excludes a stage of cyclization of PAN's nitrile groups. Being formed as a result of dehydrogenation of the main polymeric chain the sequence of conjugated bonds has greater length in comparison with the areas, fabricated in the absence of salts of transition metals, which increases the material conductivity [7, 8].

We are interested in PAN as the conjugated conducting polymer. PAN films can be considered as one of the most promising material in order to obtain chemoresistive sensors for environmental applications.

The composite films of metal-containing PAN, representing an organic matrix, which structure and properties change at influence of various temperatures, and the particles of a modifying additive dispersed in it, are a perspective material for microelectronics [9-14].

## 2. Experimental

The metal-containing PAN films were fabricated by pyrolysis method under the influence of incoherent IR-radiation under low vacuum conditions [14-17]. The following components were used: PAN (Aldrich 181315) as a conductive polymer matrix, copper chloride (II) $CuCl_2$, silver nitrate (I) $AgNO_3$, chrome chloride (III) $CrCl_3$ and cobalt chloride (II) $CoCl_2$ as a modifying additives for increasing the selectivity and adsorption activity of the films, dimethylformamide (DMF) as a solvent. The film-forming solutions were deposited on to polycrystalline aluminum oxide substrates using centrifugation method. Time-temperature modes of IR-annealing were selected experimentally, since the intensity and duration of infrared radiation provides an opportunity to control the properties of the film's material by changing the molecular structure of the PAN polymer. The radiation intensity at the first stage of IR-annealing corresponds to temperatures varying from 150 to 350 ℃ during a 5-60-minute time period, and the intensity of radiation at the second stage of the IR-annealing corresponds to temperatures of 350 – 800 ℃ during a 2-60-minute period.

The thickness of the films was measured by the interferential microscopy using interferometer MII-4. The electrical characteristics of the prepared samples were carried out in a setup equipped with heating element. Ag contacts were deposited on the film surface in order to investigate the electrical properties of the samples.

The steady-state gas distribution method was used for testing gas-sensing properties. A specially made setup equipped with a quartz chamber, sensor holder, gas and purge lines was used to maintain the desired level of detected gas concentration. Sensing characteristics were examined on basis of the measurement of the film resistance. The quartz chamber volume was around 700 $cm^3$ so that the changes in gas concentration was immediate. The gas sensitivity (S) was defined as the ratio $S = R_o – R_g/R_o$, when $R_o > R_g$, where $R_o$ is the resistance in air, $R_g$ is the resistance in the atmosphere of the detected gas. Operating temperature was chosen experimentally.

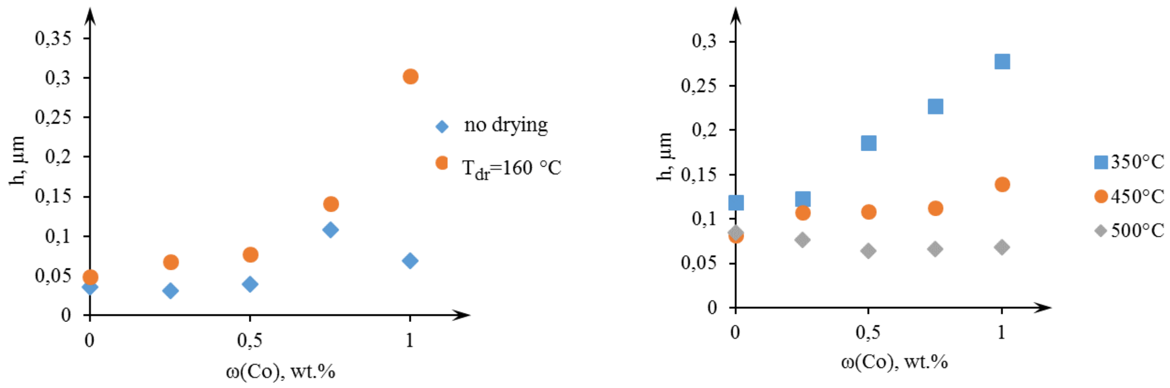
## 3. Results and discussion

The films growth was observed in accordance with the technological parameters and different weight concentration and type of a modifying additive in the initial solutions.

As observed from figure 1a, the preliminary drying stage ($T_{dr}$ = 160 ℃ , $t_{dr}$ = 30 minutes) leads to a considerable decrease in the Co-containing PAN film thickness values (20 - 40 %). The effect of the increase in temperature of the second stage of IR-annealing (350 ℃, 450 ℃, 500 ℃) on the Co-containing PAN film thickness was showed on figure 1b. The PAN film thickness were between 0.01 ÷ 0.12 μm and the Co-containing PAN film thickness were in the range from 0.03 to 0.28 μm.

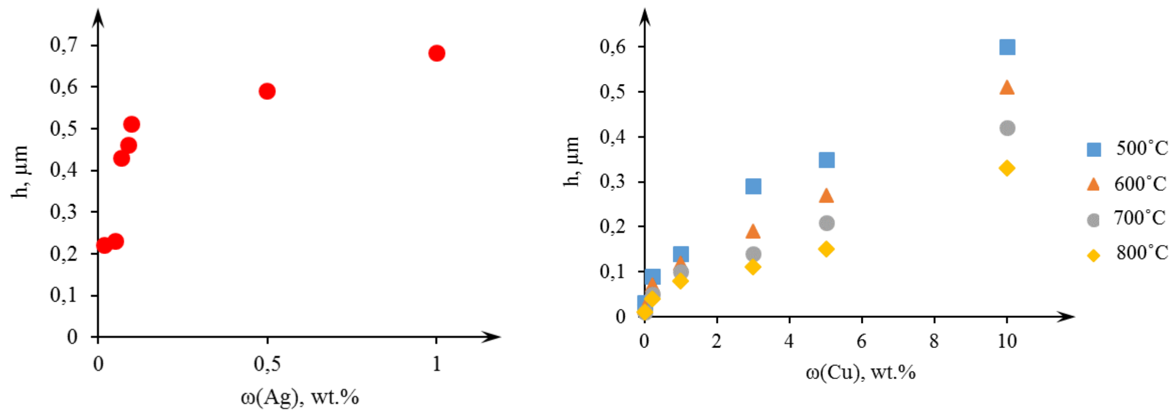
Figure 2 depicts the dependence of the Ag-containing PAN film thickness on different weight concentration of a modifying additive in the initial solutions that was between 0.22 ÷ 0.68 μm.

The Cu-containing PAN films were of the thicknesses in the range from 0.04 to 0.6 μm when fabricated in various temperature modes of the second stage of IR-annealing (figure 2b).




a) b)

**Figure 1.** The dependences of the PAN film thickness and the Co-containing PAN film thickness on the weight concentration of a modifying additive and drying stage (a): 1 – without drying, 2 – with drying; and on IR-pyrolysis temperature of the second stage of annealing (b): 1 – 350 ℃; 2 – 450 ℃; 3 – 500 ℃.

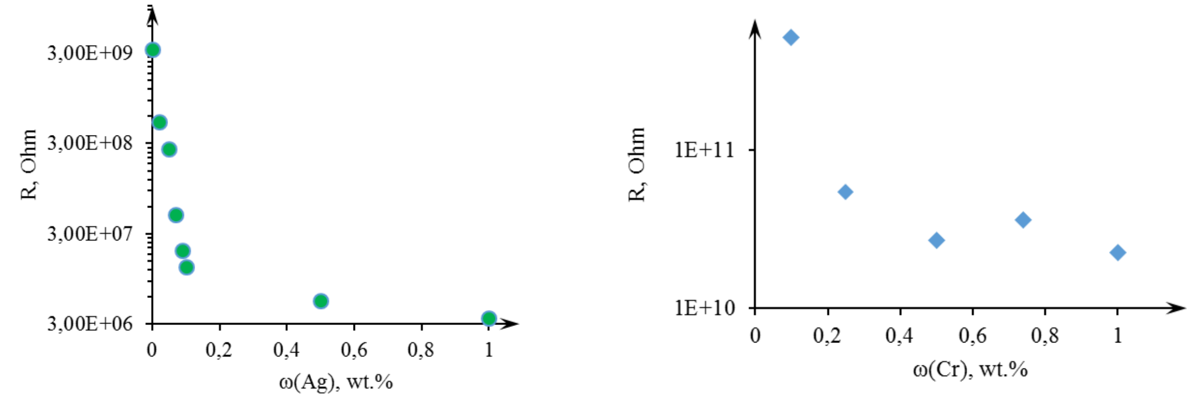



a) b)

**Figure 2.** The dependence of the Ag-containing PAN film thickness on the weight concentration of a modifying additive (a) and the dependences of the PAN film thickness and of the Cu-containing PAN film thickness on IR-pyrolysis temperature (b).

Prospects of the metal-containing organic polymer films' application as a gas-sensing layer of chemoresistive sensors is caused by PAN properties, which turned into a semiconductor material under pyrolysis [10]. In the work the influence of technological parameters of heat treatment on electrical properties of the fabricated films based on the metalorganic material were studied. The decrease in a modifying additive weight concentration in the initial solutions sharply worsened the conductivity of the Ag-containing PAN films (figure 3a), and it was not significantly reflected on the Cr-containing PAN film conductivity (figure 3b). The thin Cu-containing PAN films with the resistance values in the range from $4.0 \cdot 10^2$ to $2.7 \cdot 10^{11}$ Ohm were fabricated at various IR-annealing temperatures and using various weights of a modifying additive (figure 4). As observed from the figure 4 the films conductivity was improved significantly by the IR-annealing temperature growth and the increase of copper chloride (II) weight concentration in the initial solutions.

The investigations of the Co-containing PAN film resistance were carried out that revealed the specified dependence of the resistance values on the second stage IR-annealing temperature and on the weight concentration of a modifying additive. As observed from figure 5 the thin Co-containing PAN films had the resistance values in the range from $2.9{\cdot}10^2$ to $4.7{\cdot}10^{10}$ Ohm. The resistance values of Cd-containing PAN films were between $10^6 \div 10^9$ Ohm. Thus, the studied composite material based on thermally treated PAN and Cu, Co, Ag, Cr, Cd compounds show a rich evolution of electric properties that inspires the idea that the metal-containing PAN films can be good materials for high performance chemoresistive sensors.




a) b)

**Figure 3.** The dependence of the Ag-containing PAN film resistance (a) and the Cr-containing PAN film resistance (b) on the weight concentration of a modifying additive.

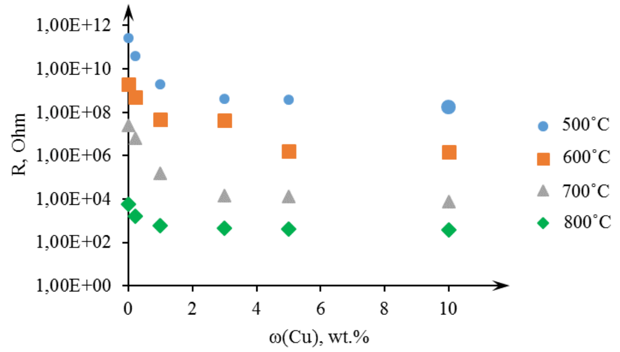



**Figure 4.** The dependence of the Cu-containing PAN film resistance on the weight concentration of a modifying additive and IR-pyrolysis temperature: 1 – 500 ℃; 2 – 600 ℃; 3 – 700 ℃; 4 – 800 ℃.

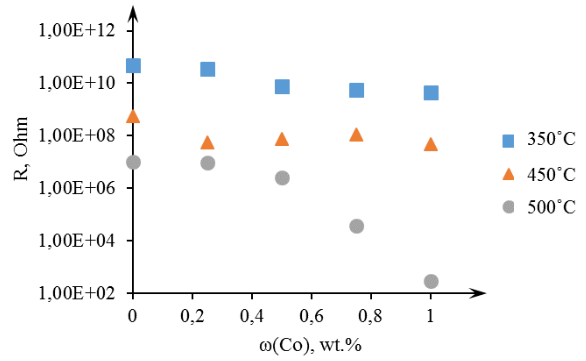
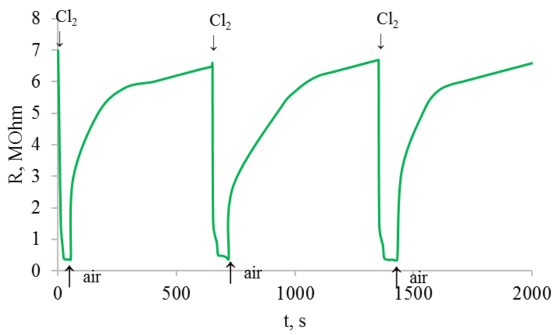


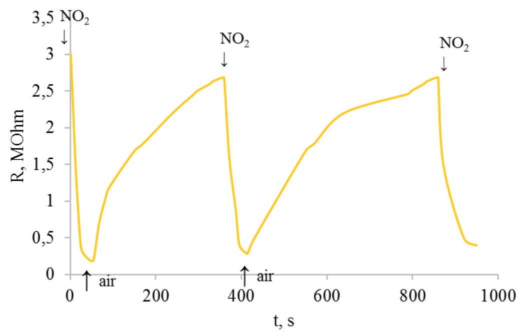

**Figure 5.** The dependence of the Co-containing PAN film resistance on the weight concentration of a modifying additive and IR-pyrolysis temperature of the second stage of annealing: 1 – 350 ℃, 2 – 450 ℃, 3 – 500 ℃.

As a result of the carried-out researches it was established that Co-containing PAN films with rather high degree of resistance ($10^9 - 10^{11}$ Ohm) were sensitive to CO (S = 0.44 ÷ 0.58 r.u.) at working low temperatures (18 ÷ 25 °C) and the concentration of detected gas being in an interval of 250 ÷ 400 ppm.

The results of the sensing tests of the Cr-containing PAN films revealed their sensitivity to 0.2% gasoline vapors in ambient air with 0.5 ÷ 0.9 r.u. of the gas sensitivity value at room working temperature. The Ag-containing PAN films were found to be a highly sensitive chemoresistive sensor (S = 0.68 ÷ 0.76 r.u.) for chlorine $Cl_2$. The films gave a stable response for a sufficiently long time in the range of concentrations of detected gas between 0.14 ÷ 107 ppm at working low temperatures (18 ÷ 25 °C). The fabricated Cu-containing PAN films used as a sensing layer for chemoresistive $NO_2$ sensor that operates at room temperature (figure 6). The sensor was found to detect nitrogen dioxide gas down to 36.5 ppm with a reversible and reproducible response (S = 0.6 ÷ 0.8 r.u.).




a)




b)

**Figure 6.** Typical time-dependant curves of the Ag-containing PAN film resistance (a) and the Cu-containing PAN film resistance (b) upon periodic exposure to gas.

## 4. Conclusion

Thus, the gas sensitivity of the fabricated semiconductor thin films based on metal-containing PAN depends on the composition of the initial solution and on the process parameters of film material's forming. The fulfilled research inspires the idea that metal-containing PAN films can be good materials for high performance low temperature multisensory system.

## Acknowledgments

This work was performed with the financial support of the research project No. VnGr-07 / 2017-21 within the framework of the internal grant of SFU. The equipment of the Centre of Collective Use of Equipment "Nanotechnologies" and Multi-Access Center of Microsystem Engineering and Integral Sensor Technology of Southern Federal University was used for this study.

## References

[1] Lange U, Roznyatovskaya N V and Mirsky V M 2008 *Anal. Chim. Acta*. **614** 1.
[2] Li X, Wang Y, Yang X, Chen J, Fu H and Cheng T 2012 *Trends in Anal. Chem*. **39** 163.
[3] Iwan A and Sek D 2008 *Prog. Polym. Sci*. **33** 289.
[4] Javadpour S, Gharavi A, Feizpour A, Khanehzar A and Panahi F 2009 *Sens. and Act.* B **142** 152.
[5] Srivastava S, Kumar S and Vijay Y K 2012 *Int. J. Hydr. En.* **37** 3825.
[6] Surianarayanan M, Vijayaraghavan R and Raghavan K V 1998 *J. Polym. Sci*. **36** 2503.
[7] Chatterjee N, Basu S, Palit S K and Maiti M M 1995 *J. of polymer science: Part B: Polymer physics* **33** 1705.
[8] Jing M, Wang C and Wang Q, Bai Y and Zhu B 2007 *Polymer Degradation and Stability* **92** 1737.
[9] Korolev A N, Semenistaya T V, Al-Hadrami I S, Loginova T P and Bruns M 2010 *Persp. Mat*. **5** 52.
[10] Semenistaya T V, Petrov V V and Lu P 2013 *Adv. Mat. Res*. **804** 135.
[11] Bednaya T A, Konovalenko S P, Semenistaya T V and Korolev A N 2012 *Persp. Mat*. **5** 39.
[12] Lu P, Gorbatenko Yu V, Semenistaya T V, Vorobjev E V and Korolev A N 2011 *J. Nano- and microsystem technique* **9** 5.
[13] Petrov V V, Plugotarenko N K and Semenistaya T V 2013 *Chaotic Modeling and Simulation* **4** 609.
[14] Semenistaya T V, Petrov V V, Bednaya T A and Zaruba O A 2015 *Materials Today: Proceedings* **2(1)** 77.
[15] Semenistaya T V, Plugotarenko N K and Petrov V V 2015 *Applied Mechanics and Materials* **727-728** 145.
[16] Plugotarenko N, Semenistaya T and Petrov V 2015 *Modern Applied Science* **9(11)** 213.
[17] Semenistaya T V, Petrov V V, Kalazhokov Kh Kh, Kalazhokov Z Kh, Karamurzov B S, Kushkhov Kh V, Konovalenko S P 2015 *Surface Engineering and Applied Electrochemistry* **51(1)** 9.