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Application of linear chain carbon films for sensitive elements of humidity sensors

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Abstract. The technologies for synthesizing and the results of investigating novel relative humidity sensors are described. Films made of various metals in combination with linear-chain carbon films were used as electrodes. The study presents the results of testing the sensors for sensitivity and recovery time. Multifactor computational models were created using neural networks based on the obtained data to solve both direct and inverse experimental problems.

Keywords: linear chain carbon film, film electrodes, silver films, tin films, aluminum films, sensor, relative humidity

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Применение пленок линейно-цепочечного углерода для чувствительных элементов датчиков влажности

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Аннотация. Описаны технологии синтеза и результаты исследований новых датчиков относительной влажности. В качестве электродов использовались пленки из различных металлов в сочетании с линейно-цепочечными углеродными пленками. В исследовании представлены результаты тестирования датчиков на чувствительность и время восстановления. На основе полученных данных были созданы многофакторные вычислительные модели с использованием нейронных сетей для решения как прямых, так и обратных экспериментальных задач.

Ключевые слова: пленки линейно-цепочечного углерода, пленочные электроды, серебряные пленки, пленки олова, пленки алюминия, сенсор, относительная влажность

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Introduction

Relative humidity sensors are widely used in various fields (agriculture, medicine, industry) and are designed to control optimal conditions (storage of agricultural products 85–95%, living quarters 40–45%, etc.).

For example, a higher humidity value around electronic devices increases the conductivity of insulators; in turn, this can change the operating properties of semiconductor devices and lead to dangerous situations. That is why proper timing of its detection, measurement and control is essential. There are several applications of humidity sensors in many sectors of our modern life and these sectors include pharmaceuticals and healthcare, automotive, household appliances, food and beverages, and agriculture.

Currently, several technologies are used to measure relative humidity, using the property of various structures to change their physical parameters (capacitance, resistance, conductivity, etc.) depending on the degree of saturation with water vapor. For existing humidity sensors, there are such disadvantages as a long surface recovery time after several cycles of adsorption-desorption of water molecules, relatively low sensitivity. Therefore, it is important to search for new materials that expand the capabilities of humidity sensors.

Materials and Methods

The moisture sensor structure was prepared as follows. On a ceramic substrate with Ag and Me (Sn, Ti, Al) deposited on two film electrodes with different electrochemical potentials, spaced on the substrate relative to each other at a distance of 0.1–2.0 mm, made by thermoresistive vacuum deposition. The second layer covered the surface with a film of linear chain carbon (LCC) with a thickness of 2000 Å. After that, the substrate with the electrodes deposited on it and the LCC film is annealed in a muffle furnace at a temperature of 400 °C for 10 min. The sputtering structure is shown in Fig. 1.

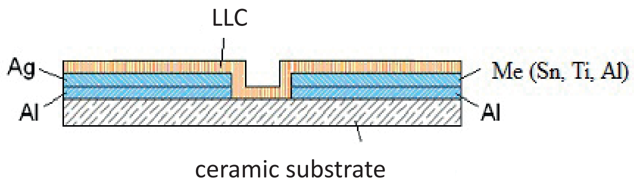


Fig. 1. Humidity sensor coating structure

LCC films were obtained by plasma deposition of graphite evaporated by a pulsed arc discharge in a vacuum, moreover, the plasma is created outside the region of the arc discharge discharge gap in the form of compensated currentless carbon plasma bunches with a density of $5 \cdot 10^{12}$–$1 \cdot 10^{13}$см$^{-3}$, a duration of 200–600 μs, repetition rate of 1–5 Hz, while in the process of carbon material deposition, carbon plasma is stimulated with an inert gas in the form of an ion flow with an energy of 150–2000 eV, which is directed perpendicular to the carbon plasma flow.

The structure of LCC films consists of many layers, each of which consists of chains of carbon atoms in sp1 hybridization, oriented normal to the layer surface. The chains are united by van der Waals forces into a hexagonal structure with a distance of about 5 Å between them. The presence of delocalized electrons belonging to the entire LCC molecule ensures metallic conductivity along the chain. The absence of a connection between the chains makes the film a dielectric in the perpendicular direction.

Results and Discussion

For the measurement, a stand was assembled (Fig. 2) to saturate the samples with water vapor. A Keithley digital programmable multimeter is connected to the electrodes of the sensing element.

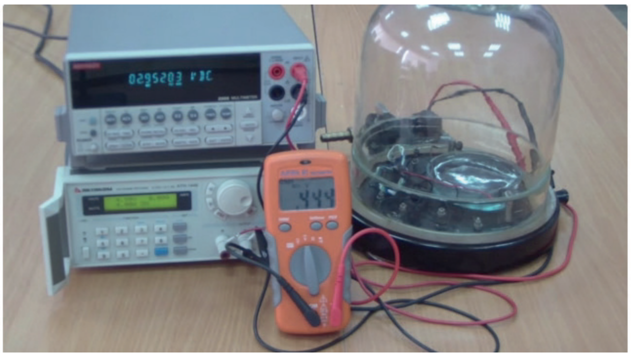


Fig. 2. Stand for measuring the output signal of the humidity sensor

At the first stage of adsorption, the H_2O molecule is chemically adsorbed on the active layer of the sensor with the formation of an adsorption complex, then an OH- group is formed on the surface. Then another water molecule reaches the surface and binds to neighboring hydroxyl groups through a hydrogen bond.

The results of measurements of the electromotive force (EMF) depending on the relative humidity were investigated and presented in Fig. 3. LCC films increase the generated EMF by an order of magnitude. The sensor generated a voltage of 715 mV at RH = 80% of the sensor with Ag, Sn electrodes with LCC and NaCl films.

To measure the surface recovery time after the adsorption of water molecules on a metal carbon sensor, the sample is placed under a vessel preliminarily saturated with moisture to RH = 95% and then exposed to RH = 25% humidity under ambient conditions. For all humidity sensors, the estimated recovery time was 50–60 seconds. The sensitivity of our sensor with NaCl exceeds the results obtained in [2, 3]. Below is a Table that presents the results of measuring the sensitivity of film structures with a combination of electrodes Ag and Me (Sn, Ti, Al), and a sample with Ag and Al electrodes with additional application of a NaCl film.

The nonlinear nature of the series in some parts of the graph is associated with a complex mechanism from the effect of physisorption and chemadsorption of water molecules. The best

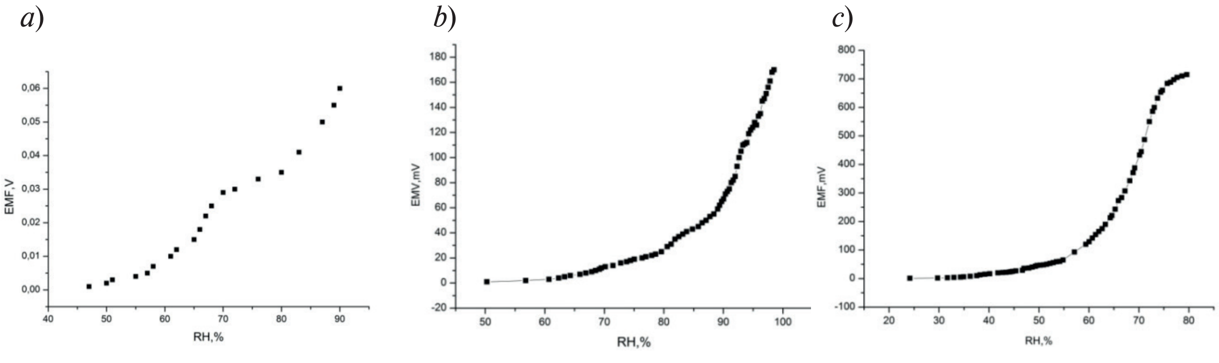


Fig. 3. The dependence of generated EMF on related humidity for elements: (Al(k)-Ag)/(Sn-Al(k)) on substrate (*a*); Al(k)-(Ag-LCC)/(Sn-LCC)-Al(k) on substrate (*b*); Al(k)-(Ag-LCC)/(Sn-LCC)-Al(k) on substrate with NaCl films (*c*)

Table

The results of measuring the sensitivity of film structures

Structure of humidity sensors	Sensitivity, mV/RH%
Al(k)-(Ag-LCC)/(Ti-LCC)-Al(k) on substrate	4.80
Al(k)-(Ag)/(Sn)-Al(k) on substrate	1.13
Al(k)-(Ag-LCC)/(Al-LCC)-Al(k) on substrate	5.28
Al(k)-(Ag-LCC)/(Sn-LCC)-Al(k) on substrate	1.74
Al(k)-(Ag-LCC)/(Sn-LCC)-Al(k) on substrate with NaCl films	12.91

sensitivity and linearity of the dependence is observed for samples Al(k)-(Ag-LCC)/(Sn-LCC)-Al(k) on substrate with NaCl films. The nature of the series in some parts of the graph is associated with a complex mechanism from the effect of physisorption and chemadsorption of water molecules. The best sensitivity is observed for samples Al(k)-(Ag-LCC)/(Sn-LCC)-Al(k) on substrate with NaCl films.

In [4], a potentiometric humidity sensor based on Pt/*n*-Si/SiO_2/LaF_3 was prepared by electron beam evaporation and high-frequency magnetron sputtering. The sensor generates EMF = 191.57 mV at RH 83.6%, and the sensitivity value was 5.4 mV at 1% RH, which is inferior in characteristics to the parameters obtained in our work.

The ratio of the increment of the output signal to the initial signal in the range of 50–90% is higher for potentiometric-type humidity sensors, obtained in this work is 16 units, in existing relative humidity sensors (output signals, respectively, the change in capacitance or electrical resistance of the sensitive elements is less than 0.1 units.

The obtained experimental data were generalized using neural networks [5, 6] in the form of a multifactor computational model that solves both direct problems (calculating the signal of different sensors for a specific humidity range) and inverse problems (determining which sensor needs to be taken to ensure given signal).

The models created in the framework of the research program to create the “Genome of hybrid metal-carbon materials” – by analogy with the “Genome of high-energy materials” [7, 8, 9].

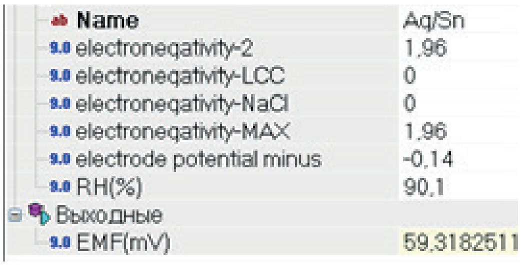
To create models, the analytical platform “Deductor” by BasegroupLab, located in Ryazan (www.basegroup.ru), was used. The platform allows presenting modeling results in the form of a calculator that enables instantaneous computation of numerical or categorical values of the objective function for any set of factor values. It also delivers graphs indicating the correlation between the objective function and any individual factor at fixed values of the other factors.

Examples and application technologies of the analytical platform “Deductor” are described in [6–8].

The results obtained are depicted on Fig. 4–7 (direct problem) and Fig. 8, 9 (inverse problem).

The direct problem factors included a categorical variable – the sensor composition (Name), the electro negativity values according to Pauling for the second metal elements (Sn, Ti, Al) that are part of the sensor composition (electronegativity-2), the maximum electro negativity value among these metals (electro negativity-MAX), the electrode potential, as well as the relative humidity (RH). The electro negativity of Ag was not included among the factors since Ag was present in all types of sensors considered. The target function was the EMF values.

One possible formulation of the inverse problem is as follows: what should be the sensor composition in order for the EMF value to be equal to 100 at RH = 80%. In this case, the factors of the inverse problem are the relative humidity values (RH) and the EMF values. The target function is the sensor composition (in the form of “yes” or “no” answers, indicating the presence of a particular component in the sensor composition: Sn, Ti, Al, NaCl, LCC). The results of the solution are presented in Fig. 8.



Name	Ag/Sn
electronegativity-2	1,96
electronegativity-LCC	0
electronegativity-NaCl	0
electronegativity-MAX	1,96
electrode potential minus	-0,14
RH(%)	90,1
Выходные	
EMF(mV)	59,3182511

Fig. 4. An example of result of calculation of the model that solves the direct task for RH = 90%

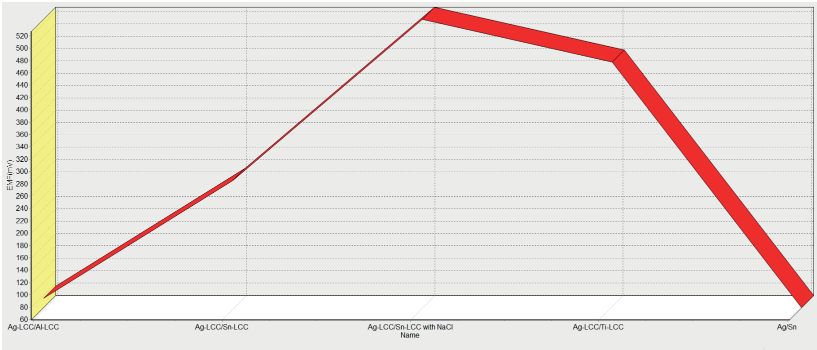
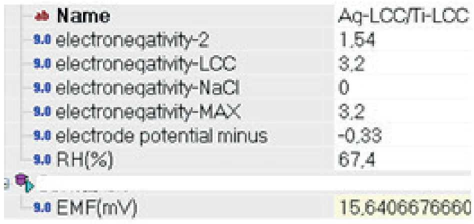


Fig. 5. Values of EMF for various kinds of sensors (Name) for RH = 90% in the view of graph



Name	Ag-LCC/Ti-LCC
electronegativity-2	1,54
electronegativity-LCC	3,2
electronegativity-NaCl	0
electronegativity-MAX	3,2
electrode potential minus	-0,33
RH(%)	67,4
EMF(mV)	15,6406676660

Fig. 6. Another example of result of calculation of the model that solves the direct task for RH = 67%

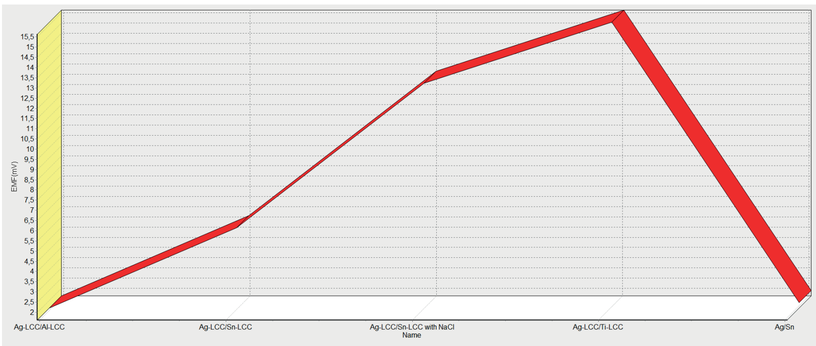
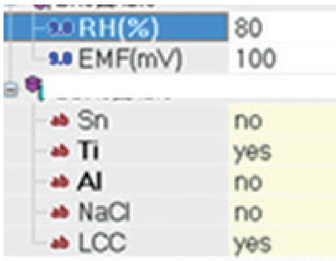


Fig. 7. Another values of EMF for various kinds of sensors (Name) for more less (than in Fig. 5) RH = 67% in the view of graph



RH(%)	80
EMF(mV)	100
Sn	no
Ti	yes
Al	no
NaCl	no
LCC	yes

Fig. 8. An example of result of calculation of the model that solves the inverse task for RH = 80% and EMF = 100 mV

The results presented in Fig. 4–8 depict only a small portion of the relationships between sensors found in the multifactor calculation models (MCM) obtained. Autonomous computer modules containing the instructions for use can be made available to the authors upon a reasonable request. These autonomous computer modules of MCM allow readers to study all the regularities within the models in detail and independently. Hundreds of graphs depicting these regularities are visualized to supplement the limitations on the article's length that prevented the authors from presenting them in the paper.

Conclusion

Thus, a sensitive element of a potentiometric type humidity sensor with an output signal – EMF between film electrodes was synthesized. The sensor showed good sensitivity and fast response. Due to the developed surface and structural features (bends of carbon chains with carbon atoms), the LCC film increases the sensitivity of the created structure. The usage of neural networks for the creation of MCM of the sensors, that solve the direct and inverse tasks, depict that these methods have the wide possibilities for sensors research.

Acknowledgments

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