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Flexible Humidity and Temperature Sensor Based on Film Structures of Polymer Nanocomposites with Carbon Nanotubes

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Abstract: **A brief review of humidity and temperature sensors based on film structures of nanocomposite materials is presented. The possibilities and prospects of sorption-impedance humidity sensors and resistive temperature sensors based on polymer nanocomposites with carbon fillers are considered. The studies results of the electrical conductivity dependences of nanocomposite films based on polyvinyl alcohol with magnetically sensitive multi-walled carbon nanotubes on humidity and temperature are presented. The structure and electrical circuit of a flexible two-parameter humidity and temperature sensor are proposed, in the form of two series-connected nanocomposite film resistors placed on a flexible silicone substrate, one of which is protected by a moisture-proof coating. Issues of sensor calibration are discussed.**

Keywords: **flexible sensor, polymer nanocomposites, film structures, carbon nanotubes**

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CONTENTS

1. INTRODUCTION

Determining the temperature and humidity of gaseous media, liquids, solids and granular bodies is an actual task for almost all areas of industry, economic and scientific activities. All methods for determining the humidity indicators are divided into direct and indirect. Direct methods involve the direct separation of the dry matter in the material under study from the moisture. The principle of indirect methods is to measure physical quantities that have a functional relationship with the humidity of a substance or material [1,2]. The need to monitor and regulate the moisture content of various substances has contributed to the design and development of compact humidity sensors. Modern sensors, in addition to high accuracy, sensitivity and speed of operations, must have a wide operating range and stability of readings.

For many applications in robotics, medicine, animal science, etc., it is required to place the sensor on non-planar surfaces, on the surface of objects that change their shape, while ensuring tight contact and maintaining the integrity of the sensing element. In this case, as a rule, it is necessary to simultaneously measure the humidity and temperature of the controlled environment or object. In this paper, we show the possibility of creating and propose the design and electrical circuit of a flexible two-parameter humidity and temperature sensor based on polymer nanocomposite films with various conductive fillers, including carbon nanotubes (CNTs).

2. HUMIDITY AND TEMPERATURE SENSORS BASED ON POLYMER NANOCOMPOSITES

Sorption type sensors are used to determine insignificant moisture concentrations. The main functional element of such sensors is the sorption layer, which is able to absorb water vapor. Often this layer is a polymer film or a material based on highly porous inorganic oxides. The simplest and most common type of humidity sensors are sorption-impedance type sensors. The advantages of these sensors are high sensitivity, ease of manufacture, and compactness. The operation of such a sensor is based on the dependence of the complex resistance of the sorption layer on the volume of moisture absorbed by it. The time constant has a value of 1-2 s for a relative humidity sensor and from 10 to 180 s for a micro-humidity sensor. By heat treatment of the humidity sensor, the measurement error can be reduced to 2% [1].

Characteristics of sorption-impedance humidity sensors depend on the sorption material. Previously, hygroscopic salts, such as lithium chloride, beryllium fluoride, etc., were used as a sorption layer. Such sensors are characterized by low stability, low sensitivity and large errors. Currently, impedance sensors with polymeric sorbents based on metal oxides, graphene oxide, electrically conductive polymers, polymers with fullerenes, etc., are being actively developed, including thin-film sensors [2].

In [3], the design of a thin-film resistive-type humidity sensor in the form of electrically conductive tracks of graphene oxide on a flexible polymer film, formed by a semiconductor laser from a dried aqueous suspension of graphene oxide deposited on a substrate, with contacts based on a conductive paste, was proposed. The conductivity of graphene oxide with an increase in relative humidity RH from 30 to 70% increases almost 3 times. When sweeping RH in the opposite direction, the phenomenon of weak conductivity hysteresis is observed. Such a thin film sensor does not allow simultaneous measurement of humidity and temperature, and is shown to exhibit a phenomenon of weak conductivity hysteresis.

To operate in a wide range of humidity and temperature changes, the authors of [4,5] proposed a humidity sensor containing a glass substrate on which a two-layer multigraphene film of a given shape and size is deposited, with electrical contacts placed on the edges of the film. The rigid glass substrate does not allow the sensor to be placed on deformable surfaces, and the sensor cannot simultaneously measure humidity and temperature.

To measure the temperature of various media and objects, flexible temperature sensors of various types are also being actively developed: flexible thermal resistances, flexible thermocouples, flexible thermistors, flexible thermochromic elements, etc. [6]. Conductive polymer nanocomposites based on polymers with conductive carbon nanomaterials (carbon fiber, graphene, fullerenes, porous carbon, CNTs) as well as metal nanoparticles are widely used as sensitive materials in such sensors. The electrical resistance of such composites critically depends on the volume fraction of the conductive filler.

Nanocomposite thermal resistances have a positive temperature coefficient, since the conductive chains of conductive fillers are destroyed with increasing temperature. In addition, the volume expansion of the polymer matrix leads to a decrease in the volume fraction of conductive nanoparticles, which also leads to an increase in the electrical resistance of conductive composites.

In [7], a conducting composite based on a PMMA polymer with the addition of MWCNTs was proposed for flexible thermistors with a negative temperature coefficient of resistance. These sensors have high temperature coefficients reaching 0.0013°C^{-1} at 30-42°C.

3. DEPENDENCES OF THE ELECTRICAL CONDUCTIVITY OF POLYMER NANOCOMPOSITES WITH CNTs ON HUMIDITY AND TEMPERATURE

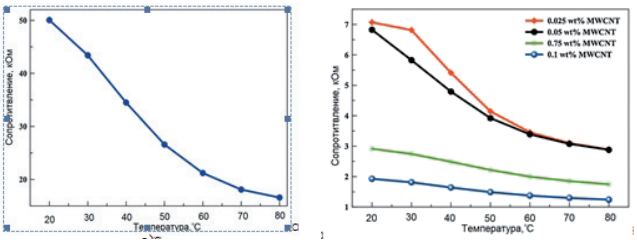
A large number of articles have been devoted to the study of the dependences of the electrical conductivity of polymer nanocomposites with SWCNTs and MWCNTs on humidity and temperature [8]. Based on numerous studies, it has been established [9] that the dependence of the electrical conductivity of polymer nanocomposites with CNTs on temperature in the temperature range from approximately –150°C to the glass transition temperature T_g of the polymer (for polyvinyl alcohol, for example, T_g = 85°C, for PPMA – 105°C) is described by the formula:

$$\sigma = A\exp\left(-\frac{T_1}{T+T_2}\right), \tag{1}$$

where A, T_1 and T_2 are some parameters determined by the properties of the polymer and CNTs.

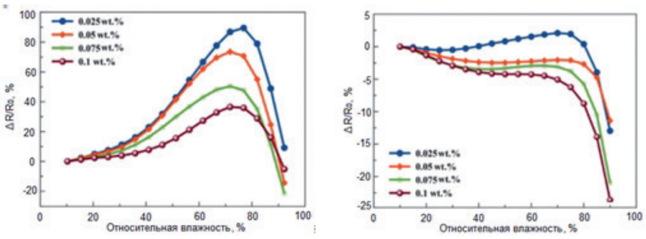
The dependence of the electrical conductivity or resistance of polymer nanocomposite films on humidity is more complex and cannot be described by a single expression. This dependence is explained by the absorption mechanism and is largely determined by the structure of the nanocomposite. At the same time, this dependence at a fixed temperature has a regular character and is reproduced with high accuracy in repeated measurements.

One of the most promising materials for organic electronics due to its high chemical and thermal stability and the possibility of obtaining films based on it from aqueous solutions is PEDOT:PSS or poly(3,4-ethylene dioxythiophene)–poly (4-styrenesulfonate) [10-12]. As an example, **Fig. 1** shows the dependences of the resistance of a pure PEDOT:PSS film and a MWCNTs/PEDOT:PSS film on temperature at different contents of MWCNTs, and **Fig. 2** shows the dependences of the normalized change in resistance on the relative humidity



a *b*

Fig. 1. *Dependences of the resistance of a pure PEDOT:PSS film (a) and a MWCNTs/PEDOT:PSS film on temperature at different contents of MWCNT (b)* [12]



a *b*

Fig. 2. *Normalized change in resistance as a function of relative humidity of an MWCNTs/PEDOT:PSS film at different concentrations of MWCNTs at 50°C (a), at 70°C (b)*

of a MWCNTs/PEDOT:PSS film with different content of MWCNTs at 50°C and 70°C [12]. A feature of the presented characteristics is the nonmonotonic nature of the dependence of the film resistance increment on humidity.

In our works [13,14], magnetically sensitive MWCNTs (M-MWCNTs) decorated with Fe_3O_4 nanoparticles were obtained based on MWCNTs synthesized by the MOCVD method at the experimental setup of Ulyanovsk State Technical University. Based on such M-MWCNTs and polyvinyl alcohol (PVA) as a matrix, nanocomposite polymer films were obtained. The film fabrication technique is described in detail in [13].

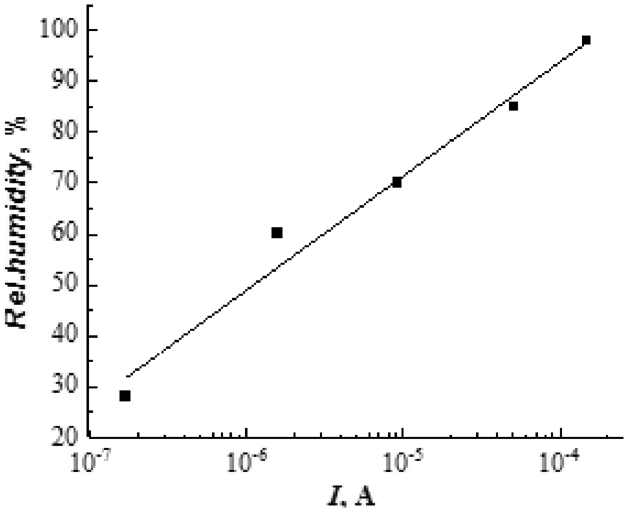


Fig. 4. *Dependence of the current through a PVA film with a 5% MWCNTs concentration at a voltage of 5 V on humidity; dots – experiment, line – approximation by a linear function.*

To measure the conductivity of the films, film samples 1×1 cm in size were glued to a glass substrate, and two rectangular copper contacts were applied to their working surface at a distance of 0.5 mm from each other. To obtain air with a given humidity, a set of flasks with a water-glycerol solution of a certain concentration according to GOST 29244-91 (ISO 483-88) was used [15].

Fig. 3 and **Fig. 4** show the current-voltage characteristics of one of the samples of the PVA/M-MWCNTs film at different relative air humidity.

The current-voltage characteristics of another PVA/M-MWCNT film sample at a relative air humidity (RH) of 56% and various temperatures are shown in **Fig. 5**.

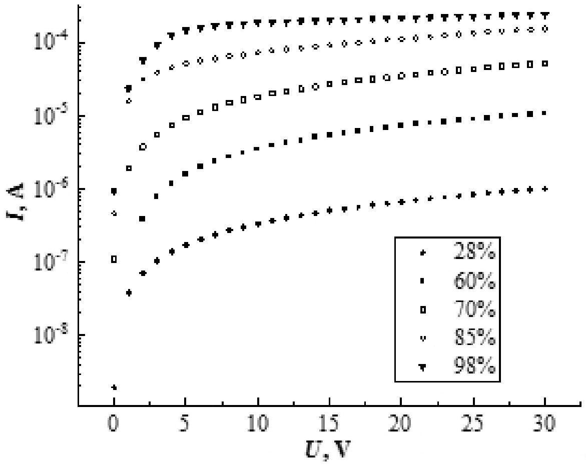


Fig. 3. *Current-voltage characteristics of PVA film with 5% MWCNTs concentration at different values of relative humidity (RH) of air and room temperature.*

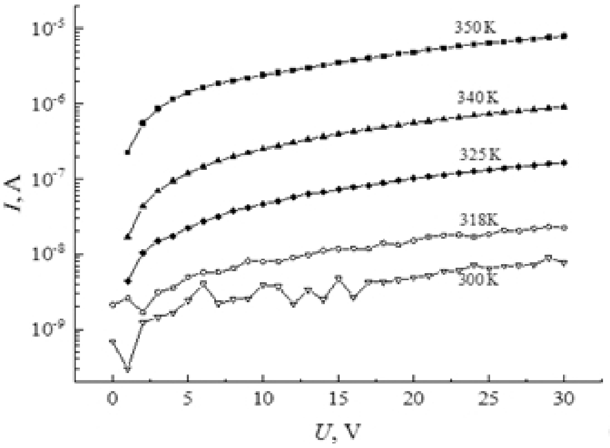


Fig. 5. *Current-voltage characteristics of PVA/M-MWCNTs nanocomposite films at relative air humidity 56% and different temperatures.*

As can be seen from the presented graphs, the resistance of PVA/M-MWCNTs films is significantly (by several orders of magnitude) higher than that of MWCNTs/PEDOT:PSS films, but the nature of its temperature dependences coincides: with increasing temperature, the resistance of films of both types decreases monotonically. At the same time, in contrast to MWCNTs/PEDOT:PSS films, PVA/M-MWCNTs films exhibit an almost linear dependence of the logarithm of the current at a constant voltage (that is, a monotonically decreasing exponential dependence of resistance) on relative humidity.

4. TWO-PARAMETER FLEXIBLE HUMIDITY AND TEMPERATURE SENSOR

Based on the analysis of the dependences of the resistance of polymer nanocomposite films on humidity and temperature, in order to provide the possibility of simultaneous measurement of temperature and humidity, the structure of a flexible two-parameter temperature and humidity sensor was proposed in [16] (**Fig. 6**). The sensor includes a substrate 1, for example, from a silicone elastomer with high elasticity and resistance to water, salt and acid solutions. Two polymer film resistors 2 and 3 are located on the surface of the substrate in the form of two polymer films with CNTs, made in the form of rectangular strips. The two edges of the strips are electrically connected by a thin metal contact pad 4, and on the other edges of the strips two separate metal contact pads 5 and 6 are created. Strips with contacts form an electrical circuit of two series-connected resistors 2 and 3 (**Fig. 7**). The resistor 3 is covered in a dry air atmosphere with a moisture-proof protective material 7, for example a lacquer or a compound. Flexible insulated conductors are attached to metal contact pads 4-6 by contact or ultrasonic welding.

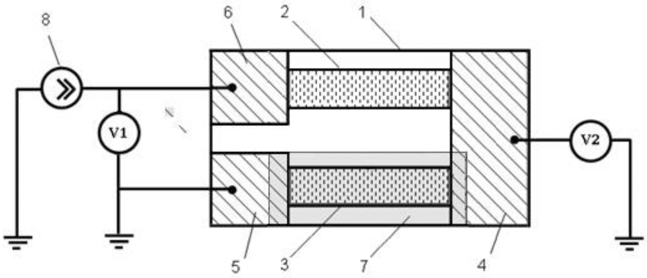


Fig. 6. *The structure of a flexible two-parameter temperature and humidity sensor.*

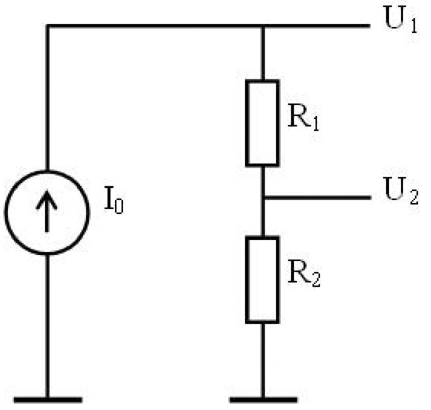


Fig. 7. *Sensor electrical connection diagram.*

During the operation of the sensor, the electrical circuit is connected to the current source 8. The voltage drops U_1 and U_2 across each film resistor are measured separately by voltmeters (V1 and V2 in Fig. 6) or by the analog-to-digital converter of the microcontroller.

In the electrical circuit (Fig. 7), the resistance R_1 corresponds to an unprotected film resistor 2, and the resistance R_2 corresponds to a film resistor 3 coated with a protective material, its electrical resistance depends only on temperature and does not depend on humidity. Accordingly, the resistance R_2 of the film resistor 3, covered with a protective material, will depend only on temperature, and this dependence can be written as

$$R_2(T) = R_{20}(T_0,0)\exp\left(\frac{T_1}{T+T_2}\right), \tag{2}$$

where $R_{20}(T_0,0)$ is the resistance value of the film resistor 3 at some given sensor calibration temperature T_0 (for example, at room temperature T_0 = 20°C) and zero humidity;

parameters T_1 and T_2 are determined during the preliminary calibration of the sensor by additionally measuring $R_2(T)$ at two more known calibration temperatures T_{K1} and T_{K2} and solving the resulting system of equations.

We write the dependence of the electrical resistance R_1 of the film resistor 2 on the temperature T and relative humidity Ψ of the ambient air in general form:

$$R_1 = R_{10}(T_0, 0)F(T,\Psi), \tag{3}$$

where $R_{10}(T_0,0)$ is the resistance of the film resistor 2 at temperature T_0 and zero humidity, and the function $F(T,\Psi)$ is determined during preliminary calibration of the sensor in the operating range of measured values and is specified either in the form of a formula or in the form of a table.

When the sensor is placed on a controlled object and (or) in a controlled environment with an unknown temperature T_x and humidity Ψ_x and when current I_0 is passed through the film resistors, the required values can be determined (calculated) by the results of measuring the voltage drops U_{1meas} and U_{2meas}. The voltage U_{2meas} across the resistor R_2, depending only on the measured temperature T_x, according to (2) will be equal to

$$U_{2meas.} = I_0 R_{20}(T_0, 0)\exp\left(\frac{T_2}{T + T_2}\right), \tag{4}$$

and on the resistor R_1, which depends on both temperature and humidity, respectively, will be equal to

$$U_{1meas.} = I_0 R_{10}(T_0, 0)F(T_x,\Psi_x). \tag{5}$$

From (2) we obtain an expression for determining the value of T_x

$$T_x = T_1[\ln(U_{2meas.}/I_0 R_{20})]^{-1} - T_2. \tag{6}$$

With a known value of T_x, the value of Ψ_x is found from the solution (by calculation or from a table) of the equation

$$F(T_x, \Psi_x) = \frac{I_0 R_{10}(T_0, 0)}{U_{1meas.}}. \tag{7}$$

Thus, the measured parameters of the sensor, the voltage drop U_1 across the film resistor R_1 and U_2 across the film resistor R_2, make it possible to simultaneously determine the current temperature of the object with which the flexible film sensor is combined, applied, glued, as well as the humidity of the environment surrounding the object.

4. CONCLUSIONS

Based on the analysis of the known dependences of the resistance of polymer nanocomposite films on humidity and temperature, a structure of a flexible two-parameter temperature and humidity sensor is proposed to provide the possibility of simultaneous measurement of temperature and humidity. The design of the flexible sensor allows it to be used on uneven and deformable surfaces without destroying the sensitive element and loss of performance. The sensor is characterized by simple manufacturing using available materials, techniques and equipment.

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