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Humidity Sensing Elements Based on Silica-Graphene Surface Layers

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Abstract. **The paper presents humidity sensing elements based on silica-graphene surface layers, prepared via a sol-gel method. The samples were sintered at temperatures of 400 °C, 600 °C and 800 °C. Tetraethoxysilane was used as a precursor of SiO_2 and as a dopant - graphene aggregates of nanoplatelets. A description of the sample preparation procedure is provided. Using a precise impedance analyzer and a calibrator for humidity and temperature, the changes in their resistance R were investigated with variations in relative humidity in the range of 30% to 90% at a temperature of 25 °C and at a frequency of 20 Hz. Morphological observations and map data analyses were carried out by Scanning Electron Microscopy (SEM) and Energy Dispersion Spectroscopy (EDX).**
The developed sensor elements have a good sensitivity to the humidity, and the resistance change reaches two orders of magnitude. Additions of graphene improve the sensitivity of the elements.
The characteristics of the sensing elements at different sintering temperatures and different amounts of graphene dopant were modeled using an artificial neural network.

Keywords: graphene, humidity sensing elements, silica, sol-gel method.

I. INTRODUCTION

The development of measurements of non-electrical quantities using electrical methods and devices necessitates continuous improvement of sensing elements that respond to changes in various non-electrical quantities.

One of the area in which intensive work is being done is the development of sensor elements for measuring and controlling humidity [1], [2]. This is necessary due to the fact that the amount of moisture in one form or another in the raw materials can have both positive and negative effects on end products in various human activities. Research on humidity sensors is usually aimed at improving their parameters and characteristics [2]. For this reason, humidity sensing elements are developed, operating on different physical principles.

A significant part of the research in this field is based on the development of new materials to achieve goals depending on the specified application. One of the direction is the development of thin-film sensing elements based on oxide materials such as TiO_2 [3], [4], SnO_2 [5] – [7], ZnO [8] – [11], Fe_2O_3 [12], [13], SiO_2 [14] – [18], and others, along with the use of various dopants. The sol-gel method is suitable for developing such sensing elements, allowing the synthesis of nanostructured layers.

Graphene and silicon dioxide are materials widely used. The graphene/silicon dioxide composite has good properties and promising future prospects in various fields [19]. The application of this composite is discussed in various areas such as adsorbents in wastewater purification [20], [21], energy storage, biomedicine, catalysts, etc. [19].

In the present work, thin-film humidity sensing elements based on SiO_2 and graphene, prepared via a sol-gel method and sintered at temperatures of 400 °C, 600

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°C, and 800 °C, are proposed. The influence of the amount of graphene dopant on the change in the active resistance R and the properties of the developed sensor elements concerning humidity for the respective sample groups at different sintering temperatures has been investigated.

II. MATERIALS AND METHODS

To prepare the sol-gel systems, the following materials were used: Tetraethoxysilane (TEOS) with a purity of 99%, produced by MERCK, graphene aggregates with submicron particles of 500 m^2/g from Alfa Aesar, 1-butanol 99%, and nitric acid 65%.

In two identical glass vessels, 30 ml of butanol, 30 ml of TEOS, and 3 ml of nitric acid are mixed. To one vessel, 6.0599 g of graphene is added, creating the two main solutions: TEOS (reference) and graphene-containing. Both solutions were subjected to vigorous shaking and left for 1 hour in an ultrasonic bath.

In the next stage, different amounts of the two main solutions are taken into four test tubes, resulting in the following compositions: SiR – 20 ml solution of TEOS (reference), SiG1 – 15 ml solution of TEOS and 5 ml of graphene-containing solution, SiG2 – 10 ml solution of TEOS and 10 ml of graphene-containing solution, and SiG3 – 5 ml solution of TEOS and 15 ml of graphene-containing solution. The obtained compositions are then left to stand for 2 hours at a temperature of 75 °C.

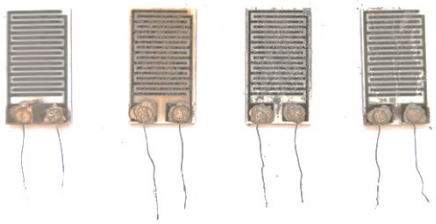


Fig. 1. Samples SiR, SiG1, SiG2, and SiG3, sintered at a temperature of 800°C.

The deposition of the surface layers was performed on Al_2O_3 substrates with deposited silver-palladium electrodes, which were previously cleaned and degreased with ether. The layer deposition procedure involved immersing the substrates in the respective solutions for 15 minutes, followed by drying for 15 minutes. This procedure was repeated six times, with the final drying lasting for 30 minutes. After depositing the gel onto the substrates, the samples were sintered at temperatures of 400 °C, 600 °C, and 800 °C, respectively, for 30 minutes. Groups of four samples from different compositions were thus obtained and sintered at the three temperatures. Samples prepared using the described procedure are presented in Figure.1

III. RESULTS AND DISCUSSION

A. Surface morphology characterization

To investigate the influence of graphene and different sintering temperatures on the surface morphology of the obtained sensor elements, SEM and EDX analyses were conducted. For this purpose, a Scanning Electron Microscope (SEM), combined with elemental analysis, was used, specifically the TESCAN SEM/FIB LYRA I XMU operating at 20 kV with a magnification of 5000, and an Energy Dispersion Spectrometer Quantax 200 of BRUKER detector.

The SEM and EDX images of the three groups of sensor elements sintered at temperatures of 400 °C, 600 °C, and 800 °C are presented in Figure 2.

In the SEM images of the samples, porosity in the deposited surface material is observed. The presence of porosity facilitates the penetration of moisture into the pores and enhances the sensitivity of the elements to humidity.

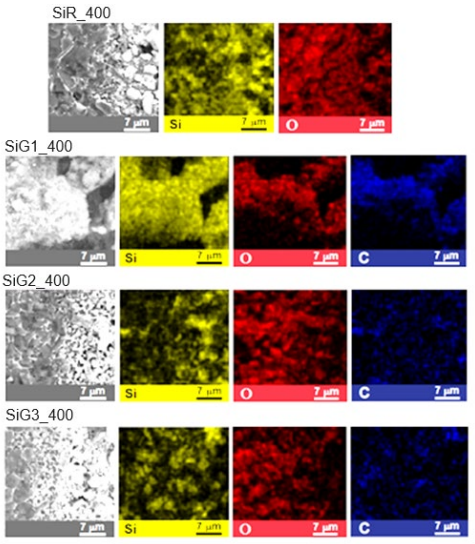
As the sintering temperature increases from 400 °C to 800 °C, the material increasingly penetrates into the intergranular spaces in the substrate of these samples. This is most pronounced in the reference sample, without the presence of graphene dopant, at a sintering temperature of 800 °C, where the material largely fills these spaces and has the least pronounced porosity in the surface material.

EDX images confirm the presence of Si and O in all the investigated samples, as well as the presence of traces of C in the samples, in the composition of the solutions for the preparation of which graphene is added.

A. Electrical measurements

The measurement of the active resistance R on the investigated samples under varying relative humidity was performed using the Impedance Analyzer Precision LCR Meter MIFA from Zurich Instruments AG, with the capability to measure with an accuracy of up to 0.05%. The measurements were conducted at a test signal amplitude of 500 mV and a frequency of 20 Hz. The samples were placed in the chamber of the humidity and temperature calibrator, HygroGen2-XL from Rotronic Instruments Ltd., providing controlled humidity in the range of 5% RH to 95% RH with an accuracy of 0.1% RH, and temperature in the range of 0 ºC to 60 ºC with a maximum deviation of 0.01 ºC.

The change in resistance R with varying relative humidity RH for the respective groups of samples sintered at temperatures of 400 °C, 600 °C, and 800 °C is presented in Fig. 3. The measurements were taken in the range of relative humidity variation from 30% to 90% RH at a temperature of 25ºC.



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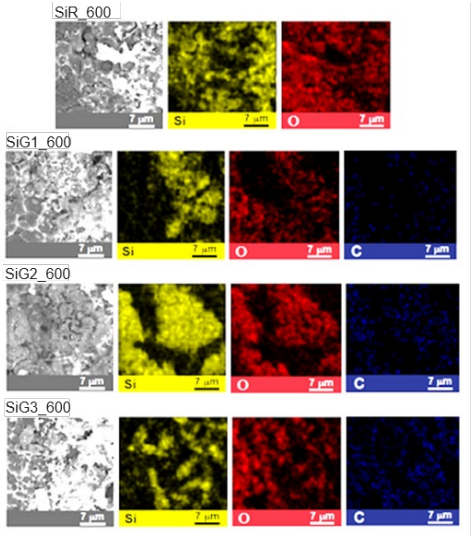

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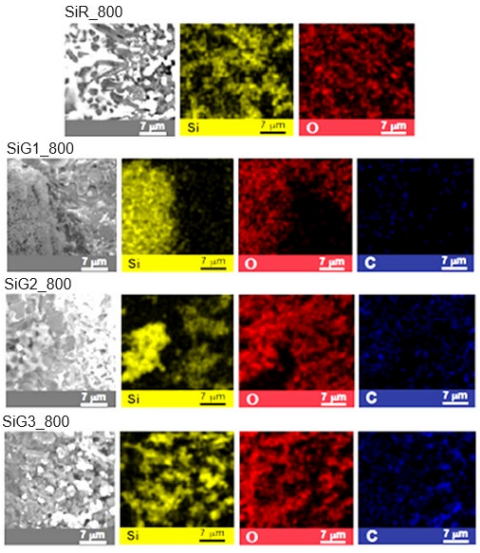
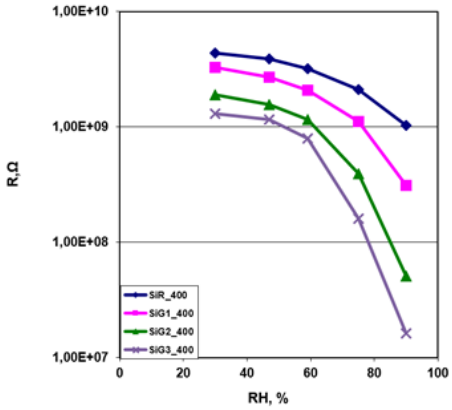


c)

Fig. 2. SEM and EDX images of the surface layers of samples SiR, SiG1, SiG2, and SiG3 sintered at temperatures: a) 400 °C, b) 600 °C, and c) 800 °C.



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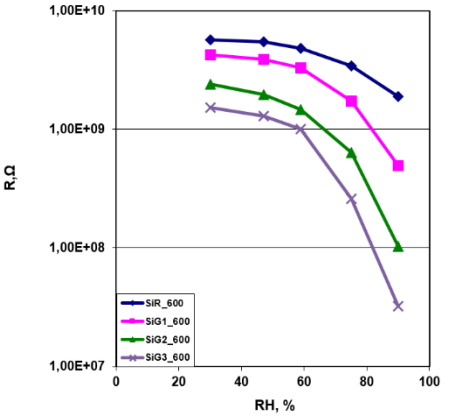

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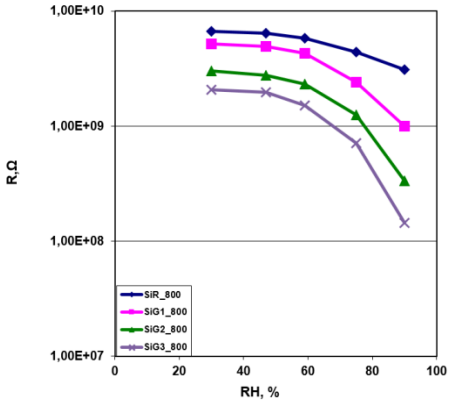

c)

Fig. 3. Characteristics R = f(RH) for samples SiR, SiG1, SiG2, and SiG3 at sintering temperatures: a) 400 °C; b) 600 °C, and c) 800 °C, investigated at a frequency of 20 Hz and a temperature of 25 °C.

In all three groups of samples, an increase in sensitivity is observed with the addition of graphene compared to the reference samples containing only SiO_2, expanding the range of resistance R variation with changes in relative humidity RH from 30% to 90%. This sensitivity increases with the increasing graphene amount at the respective sintering temperatures. In the case of sample SiG3 sintered at 400°C, a range of R variation of about two orders of magnitude is achieved. Furthermore, the increase in the amount of graphene leads to a reduction in their active resistance.

It should also be noted that with the addition of 15 ml of the graphene-containing solution, the mentioned changes become less pronounced compared to the previous amounts of graphene solution additives, indicating a slowing down of the graphene's effect.

Regarding the sintering temperature, the obtained results show that for the same amounts of graphene dopant, an increase in the sintering temperature leads to an increase in the resistance R and a decrease in its range of variation. The samples sintered at a temperature of 400 °C show the best sensitivity to change in relative humidity, and in the case of the SiG3 sample it reaches 28MΩ/%RH in the range from 55% to 90% RH.

B. Modeling of sensor characteristics

Since the source data represents only a limited number of reference points, in order to present the characteristics of the developed samples, it is necessary to make an interpolation based on the measured reference points. Interpolation of the characteristics of the sensing elements was carried out on the basis of cubic splines, and the obtained results are presented graphically in Figure 4. The obtained curves are for a temperature of 400 °C of samples sintering.

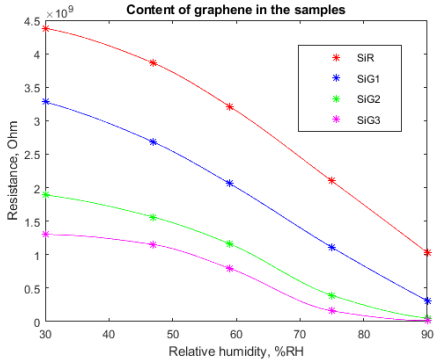

Fig. 4. Characteristics at different amount of graphene

The set of curves and the large number of points that can be obtained based on them are used to generate a 3D interpolated surface of the resistance, which depends on the variation of the relative humidity at different values of the graphene content. Three-dimensional interpolation can be implemented in different ways, in this case generating a set of spline curves at different values of relative humidity and varying the graphene content from 0 to 15 ml with a step of 0.01 ml.

Figure 5 presents a plot of the interpolated 3D surface.

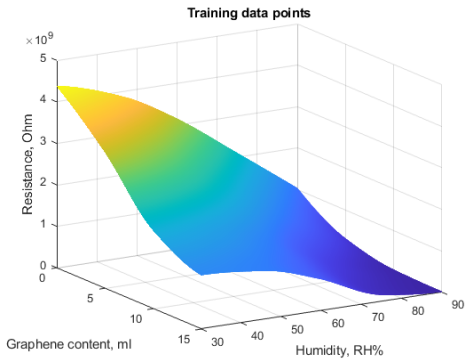

Fig. 5. 3D interpolation

The interpolated three-dimensional data can be used to generate training vectors for training an artificial neural network which can be used as a simulation model to determine the resistance value of a sensing element synthesized at 400 °C while the relative humidity changes, taking into account the amount of graphene used in the preparation of the sensing element.

The training input vector contains an array of [2x902101] elements, and the output vector of expected values contains 902101 elements. Ten percent of the training samples are set aside to be used to test the performance of the neural network after training.

To create the virtual model of the sensor element, a feedforward neural network was used. The network has one hidden layer having 15 neurons in it and one output layer containing one neuron respectively. The neurons in the hidden layer have a sigmoidal transfer function, while in the output layer the transfer function is linear.

The two inputs of the neural network receive data on the relative humidity and the content of graphene, and the output receive results on the value of the resistance of the sensor element at these values.

Since the value of the output resistance varies within very large limits, normalization of the training sample is applied during the training of the neural network. The purpose of normalization is to scale the training data and shrink its range.

Neural network training was performed using the Levenberg-Marquardt training algorithm in the Matlab environment. The training itself was performed for 1000 iterations. As a result, an extremely small error was achieved when validating the operation of the network - 2.86×10^{-6} (Table 1).

After the training of the neural network, its performance was tested using the test samples, and the errors after denormalization of the generated resistance value were determined.

TABLE 1 TRAINING PROGRESS

Unit	Initial value	Stopped value	Target value
Epoch	0	1000	1000
Elapsed time	-	00:29:40	-
Performance	14.1	2.86e-06	0
Gradient	17.9	9.83e-07	1e-07
Mu	0.001	1e-08	1e+10
Validation Checks	0	0	6

After the training of the neural network, its performance was tested using the test samples, and the errors after denormalization of the generated resistance value were determined.

The average value of the testing errors is 4.99×10^{-4}% for the relative humidity RH variation range from 30% to 90% and the amount of graphene in the solutions from 0 to 15 ml, respectively.

From the testing of the neural network, it is found that it can successfully generate at its output data that corresponds to the change in the resistance of the sensor element due to the change in relative humidity at different amounts of graphene dopant.

IV. CONCLUSIONS

Humidity sensing elements based on SiO_2 and graphene prepared via a sol-gel method have been developed. The possibility of improving the parameters of the SiO_2-based sensing elements by using different amounts of graphene dopant and sintering the samples at different temperatures was investigated.

Three groups of samples (SiG1, SiG2 and SiG3) were prepared at different amounts of graphene dopant in the starting solution and reference samples (SiR) based only on SiO_2 precursor.

The influence of sintering temperature was investigated at 400 °C, 600 °C and 800 °C for each of the sample groups.

The obtained characteristics R = f(RH) of the change in the active resistance of the developed sensing elements with a change in the relative humidity RH show that the increase in the amount of graphene as a dopant leads to both a decrease in the resistance of the prepared samples and an improvement in their sensitivity, extending the range of change of resistance with change of relative humidity. Regarding the sintering temperature, the highest sensitivity was obtained for all sample groups at the lower sintering temperature of 400°C. EDX analysis confirmed the presence of Si, O, and C in each of the graphene-doped samples. These samples at the corresponding sintering temperatures have better properties as humidity sensing elements compared to the reference samples based only on SiO_2. For the SiG3 sample sintered at 400 °C, the variation of the active resistance R reaches almost two orders of magnitude when the RH changes in the range from 30% to 90%, and this sample has the lowest resistance compared to the others. This confirms the possibility of improving the performance of SiO_2-based humidity sensing elements with graphene dopant in their preparation by the sol-gel method.

Using an artificial neural network, a model representing the characteristics of the sensing elements was created. The test results show that the model can successfully generate output data corresponding to the resistance change of the sensing elements when the relative humidity changes at different amounts of graphene in the starting solutions.

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