Technical Physics Letters, 2024, Vol. 50, No. 5

13.1

Organic quasi-two-dimensional structure based sensor for assessing volatile organic compounds

© A.N. Lachinov[1], D.D. Karamov[1], A.F. Galiev[1], A.A. Lachinov[1], E.V. Kuzina[2], T.Yu. Korshunova[2]

[1] Institute of Molecule and Crystal Physics, Ufa Federal Research Centre, Russian Academy of Sciences, Ufa, Russia
[2] Institute of Biology, Ufa Federal Research Centre, Russian Academy of Sciences, Ufa, Russia
E-mail: azat-red@ya.ru

Received November 29, 2023
Revised November 29, 2023
Accepted February 14, 2024

The paper presents the study of the influence of volatile organic compounds on the resistance of a quasi-two-dimensional region of the polymer/polymer interface in alternating electric field. It is shown that the studied structure can be promising for manufacturing resistive-type biological sensors. The sensor distinctive feature is large absolute and relative changes in the resistance, which may be used for *in situ* monitoring of the processes of emission of volatile organic compounds.

Keywords: sensor, organic materials, dielectrics, volatile organic compounds.

DOI: 10.61011/TPL.2024.05.58428.19820

Advances in Internet technology (IoT) have driven the development of flexible/wearable gas sensors. In this regard, resistive gas sensors have attracted much attention due to their high sensitivity, stability, low power consumption, low operating costs, and easy integration into wearable electronics. Electrically conductive polymer materials are increasingly used as electronic materials in resistive gas sensors [1–3].

In this connection, there is observed a significant increase in interest to low-cost and user-friendly sensors [4,5]. The main problems of resistive sensors are low sensitivity, selectivity and narrow variation range of the measured parameter. This stems from low charge-carrier mobility of organic semiconductors [3].

One of the ways to increase the charge-carrier mobility may be to use the interface conductivity along the regions separating two polymer films [6]. Earlier, in study [7], there was obtained a concentration dependence of conductivity of the polymer film interface in the atmosphere of various volatile organic compounds (VOCs).

The goal of this work was to study the possibility of using a quasi-two-dimensional structure formed at the interface of two submicron films of organic dielectric polydiphenylene phthalide [7–9] as a basis for a biological gas sensor.

Experimental samples consisted of two polymer films with electrodes between them (Fig. 1). The bottom film was formed on a glass slide by centrifuging a polymer solution in cyclohexanone at 2000 rpm for 1 min. After applying the film, the sample was subjected to two-stage drying: first for 60 min under normal conditions, then for 60 min at 150°C in vacuum. After that, gold electrodes 50 nm thick and 2 mm long were formed by thermodiffusion sputtering; the inter-electrode distance was $\sim 30\,\mu$m. The top polymer layer was fabricated according to the above-described procedure; the polymer layer thicknesses were 800 nm for the bottom layer and 200 nm for the top one; they were governed by the polymer weight concentration in the solution. The surface morphology and functional layer thicknesses were controlled at all the stages of sample preparation by using atomic force microscope NTEGRA II (NT-MDT Spectrum Instruments, Zelenograd, Russia).

As the biological object, a strain of microscopic fungus *Alternaria alternata* VKM F-3047 (*A. alternata*) was chosen; this is one of the main pathogens causing post-harvest rot of vegetables and fruits [10,11]. It is known that metabolism of carbohydrates by micromycetes gives rise to various organic acids; carboxylic acids get accumulated in the medium during the so-called „rejected“ metabolism; in general case, carbohydrates can be catabolized by micromycetes to carbon dioxide and water. Depending on the fungus cultivation conditions and growth phases, VOCs such as acetaldehyde, acetone, methanol, isopropanol, ethanol, isobutanol, etc. are also detected in the environment during its development. [12].

The sensor was connected to an AC power supply with the effective root-mean-square voltage of 1 V and frequency of 530 Hz. These parameters were selected so as to ensure high response of the sensor [5]. Frequency dependences of the sensor resistance are presented in Fig. 2.

In the experiment, three 350 ml flasks were used: 1) a flask with atmospheric air; 2) a flask with a layer of sterile potato-glucose agar (PGA) about 10 mm high; 3) a flask with PGA inoculated with the VKM F-3047 strain. Inoculation was made by injection into the agar plate center. The first two flasks were necessary for comparative analysis. After installing the sensors, the flasks were sealed and placed in a noise-proof and light-proof cell. The resistance was measured automatically every 30 min during eight days.

The *A. alternata* life activity was recorded by measuring the radius of the micromycete colony (Fig. 3). Under the

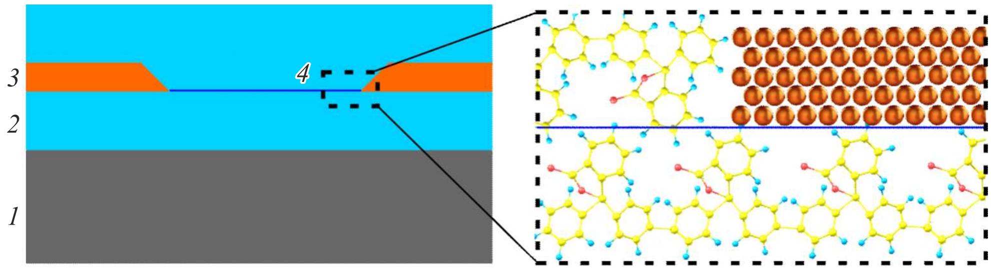

Figure 1. Schematic structure of the sensor and functional layers. *1* — substrate, *2* — polymer film, *3* — electrodes, *4* — quasi-two-dimensional region and its zoomed view (right panel).

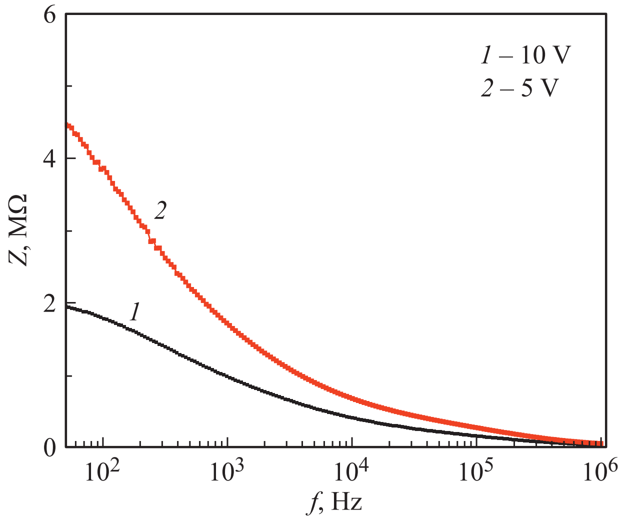

Figure 2. The sensor impedance versus frequency at two effective root-mean-square voltages.

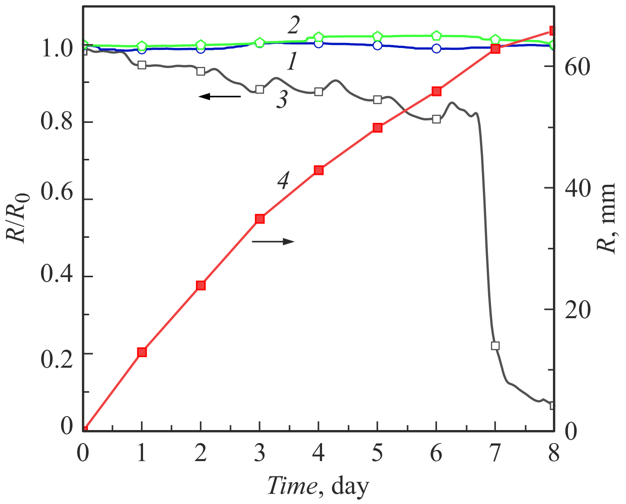

Figure 3. Time dependences of the sensor relative resistance in the flask with air (*1*), with PGA (*2*), and with the micromycete strain (*3* /). *4* — micromycete radius versus time.

given experimental conditions, this radius depended on time nonlinearly and reached saturation at a certain time.

The sensor initial resistance was $\sim 2.0\,\mathrm{M\Omega}$. In the reference flasks, the relative resistance varied within the measurement error (Fig. 3). The sensor resistance in the flask containing the micromycete strain decreased with time. Relative variation in the sensor resistance during the first six days is well describable by a straight line. Over this time, the absolute resistance change appeared to be $\sim 0.4\,\mathrm{M\Omega}$. By the end of the experiment, the resistance decreased to $\sim 0.1\,\mathrm{M\Omega}$.

Comparative analysis of the obtained data allows asserting that there is a good correlation between changes in the sensor resistance and micromycete vital activity. Apparently, in the first days of development of the micromycete colonies, a gradual accumulation of VOCs takes place in the flask air space. Thus, the sensor used in this study exhibits a response to changes in the composition of air above the micromycete colony.

Previously it was reported that sensors in a similar configuration are highly sensitive to changes in humidity and acidity of the environment and on concentration of ethyl alcohol vapor [7]. The presumable mechanism for variation in sensor resistance with VOC concentration is the adsorption-field mechanism. This model implies that polar molecules adsorbed on the sensor surface create an electric field that can affect the mobility of charge carriers in a thin quasi-two-dimensional layer [8,9].

Thus, the possibility of using an organic sensor containing a quasi-two-dimensional electroactive layer for qualitative assessment of VOCs variations during the microorganisms life activity has been demonstrated.

Acknowledgements

The study was performed by using the equipment of Distributed Common Use Center „Agidel“.

Conflict of interests

The authors declare that they have no conflict of interests.

References

[1] C.M. Cova, E. Rincón, E. Espinosa, L. Serrano, A. Zuliani, Biosensors, **12** (2), 51 (2022). DOI: 10.3390/bios12020051

[2] S. MacDougall, F. Bayansal, A. Ahmadi, Biosensors, **12** (4), 239 (2022). DOI: 10.3390/bios12040239

[3] P. Velusamy, C.-H. Su, P. Ramasamy, V. Arun, N. Rajnish, P. Raman, V. Baskaralingam, S.M.S. Kumar, S.C.B. Gopinath, Crit. Rev. Anal. Chem., **53** (8), 1828 (2022). DOI: 10.1080/10408347.2022.2043145

[4] R. Capuano, E. Paba, A. Mansi, A.M. Marcelloni, A. Chiominto, A.R. Proietto, E. Zampetti, A. Macagnano, L. Lvova, A. Catini, R. Paolesse, G. Tranfo, C. Di Natale, Sensors, **20** (14), 4004 (2020). DOI: 10.3390/s20144004

[5] T. Lu, A. Al-Hamry, J.M. Rosolen, Z. Hu, J. Hao, Y. Wang, A. Adiraju, T. Yu, E.Y. Matsubara, O. Kanoun, Chemosensors, **9** (12), 360 (2021). DOI: 10.3390/chemosensors9120360

[6] T. Zhang, H. Qi, Z. Liao, Y.D. Horev, L.A. Panes-Ruiz, P.S. Petkov, Z. Zhang, R. Shivhare, P. Zhang, K. Liu, V. Bezugly, S. Liu, Z. Zheng, S. Mannsfeld, T. Heine, G. Cuniberti, H. Haick, E. Zschech, U. Kaiser, R. Dong, X. Feng, Nat. Commun., **10** (1), 4225 (2019). DOI: 10.1038/s41467-019-11921-3

[7] R.B. Salikhov, A.N. Lachinov, R.G. Rakhmeev, R.M. Gadiev, A.R. Yusupov, S.N. Salazkin, Meas. Tech., **52** (4), 427 (2009). DOI: 10.1007/s11018-009-9277-4

[8] D.D. Karamov, A.F. Galiev, A.A. Lachinov, K.I. Davlyatgareev, S.N. Salazkin, A.R. Yakhin, A.N. Lachinov, Polymers, **15** (16), 3366 (2023). DOI: 10.3390/polym15163366

[9] A.R. Yusupov, R.M. Gadiev, A.N. Lachinov, V.M Kornilov, L.R. Kalimullina, A.F. Galiev, M. Kian, S.N. Salazkin, Synth. Met., **274**, 116733 (2021). DOI: 10.1016/j.synthmet.2021.116733

[10] C. Shu, H. Zhao, W. Jiao, B. Liu, J. Cao, W. Jiang, Scientia Horticulturae, **256**, 108636 (2019). DOI: 10.1016/j.scienta.2019.108636

[11] W. Li, Y. Long, F. Mo, R. Shu, X. Yin, X. Wu, R. Zhang, Z. Zhang, L. He, T. Chen, J. Chen, J. Fungi, **7** (11), 937 (2021). DOI: 10.3390/jof7110937

[12] F. Weikl, A. Ghirardo, J.P. Schnitzler, K. Pritsch, Sci. Rep., **6**, 22152 (2016). DOI: 10.1038/srep22152

Translated by EgoTranslating