Program Digest, 2019 IEEE International Ultrasonics Symposium (IUS)
Glasgow, Scotland, October 6-9, 2019

Gas Sensor Based on the Piezoelectric Resonator with Lateral Electric Field and Films of Chitosan Salts

Boris Zaitsev
Laboratory of Physical Acoustics
Kotel'nikov Institute of Radio Engineering and Electronics of RAS, Saratov Branch
Saratov, Russian Federation
zai-boris@yandex.ru

Fedor Fedorov
Laboratory of Nanomaterials
Skolkovo Institute of Science and Technology
Moscow, Russian Federation
f.fedorov@skoltech.ru

Alexander Semyonov
Laboratory of Physical Acoustics
Kotel'nikov Institute of Radio Engineering and Electronics of RAS, Saratov Branch
Saratov, Russian Federation
alex-sheih@yandex.ru

Andrey Teplykh
Laboratory of Physical Acoustics
Kotel'nikov Institute of Radio Engineering and Electronics of RAS, Saratov Branch
Saratov, Russian Federation
teplykhaa@mail.ru

Irina Borodina
Laboratory of Physical Acoustics
Kotel'nikov Institute of Radio Engineering and Electronics of RAS, Saratov Branch
Saratov, Russian Federation
borodinaia@yandex.ru

Albert Nasibulin
Laboratory of Nanomaterials
Skolkovo Institute of Science and Technology
Moscow, Russian Federation
A.Nasibulin@ skoltech.ru

***Abstract*—The possibility of developing a gas sensor based on a piezoelectric resonator with a lateral electric field combined with a chitosan film is discussed. It has been shown that in the presence of saturated vapors of water, ammonia 10%, and ethanol the conductance of the chitosan film increases by several orders of magnitude. If the film is located near the resonator, such a change in conductivity also causes a significant change in the frequency of parallel resonance and the resistance value on this frequency. The physical reason of such changes is discussed.**

Keywords—piezoelectric resonator with lateral electric field, resonant frequency, electrical impedance, chitosan glycolate and chitosan lactate films, response and relaxation times

I. INTRODUCTION

Advances in development of liquid and biological sensors are primarily concerned with the wide employment of the lateral electric field excited piezoelectric resonators [1-6]. Recently, it has been demonstrated that a change in conductivity of a thin layer located near such a resonator yields a change in frequency of the parallel resonance and real part of the electrical impedance [7-9]. Consequently, this fact allows to anticipate further progress to be in the field of development of gas sensors when using a layer located near the resonator whose conductivity is affected by the change in environment.

One of the promising candidates to serve as a gas sensitive layer is biopolymer chitosan which is biocompatible, biodegradable and suggested to possess good adsorption properties [10]. Chitosan is amino polysaccharide which represents N-deacetylated derivative of chitin; it is a linear polymer consisting of ß-1,4 linked GlCN and GlcNAc units, i.e. with hydroxyl group, amino group and some number of N-acetyl groups. Nucleophilic primary amino groups make it extremely reactive [11]. Such high reactivity has facilitated its application for room-temperature chemiresistive sensors to detect acetone, 0.1–100 ppm. [12], hydrogen in case of polyaniline-chitosan nanocomposite. Bouvree et al. [13] have designed polar vapor sensors (water, methanol, toluene) based on chitosan-carbon nanoparticle materials. Chitosan has been also tried as an active material for mass sensors like quartz crystal microbalance (QCM), i.e., for methylamine detection [14], and for CO detection when using ferrocene branched chitosan derivatives.

In this paper, for the first time we show the possibility of realizing a gas sensor based on a resonator with a lateral electric field and gas sensitive films based on rather new chitosan derivative, chitosan lactate.

II. PREPARATION OF FILMS

For the synthesis we used chitosan with deacetylation degree 90% and molecular weight 150-200 kDa by "Natural'nyye ingridienty" (141010), lactic acid 80 %, Acros (Ac 41296), ethanol "Basic". Heterogeneous synthesis of chitosan salt has been performed in 1 L flat bottom flask at 50 C. The samples were prepared by drop casting from 1.5% aqueous solution of chitosan lactate onto glass plate with subsequent drying for 24 hours in air at room temperature. The topology of the obtained films was studied using Bruker Multimode V8 Atomic Force Microscope (AFM) in Peak-Force TM mode.

The work is supported by grant of Russian Foundation of Basic Research # 19-07-00300.

III. Measurements of Chitosan Films Conductivity

A. Description of Setup and Method of Measurement

We experimentally examined effect of the vapors of water, 10% ammonia aqueous solution and ethanol on the electrical conductivity of chitosan glucolate and chitosan lactate films. To carry out the experiments a glass plate (2) with a deposited film was located in a special sealed camera (1) (Fig. 1). Thin aluminum films were applied on the plate to create the contact electrodes, at that these electrodes partially covered the edges of the investigated chitosan film. The special clamps (3) were attached to the contact electrodes in order to create a reliable electrical contact between the electrodes and wires (5). The wires were connected to a universal ohmmeter GDM 78251A (GW-Instek) (6) for measuring the electrical resistance/conductivity of the film under study.

First, the electrical resistance of the structure was fixed at the absence of the vapors of volatile liquids. Then a 2 ml container (4) with a volatile liquid was placed in the camera and the cover of the camera was tightly closed. After this, at the different time points the electrical conductance/resistance of the film was recorded in the presence of a specific gas. When the saturation of the change in the electric conductance/resistance was reached, the camera was opened and a container with a volatile liquid was removed. After this, at the different time points the value of the conductance/resistance of the film was recorded until the initial parameter was completely restored. For comparison, the effect of the gas vapors used on the surface conductivity/resistance of exactly the same glass plate with the contact electrodes without a film was also investigated. Prior to experiments we established that the surface conductivity of the glass between the electrodes, i.e., without chitosan film, did not depend on the presence of the gas vapors (water, 10% ammonia, ethanol).

B. The Influence of Tested Analytes on Conductivity

The chitosan glucolate and chitosan lactate films are characterized by conductivity about 0.0067μS. This should be due to great ionic component present in these films, which are

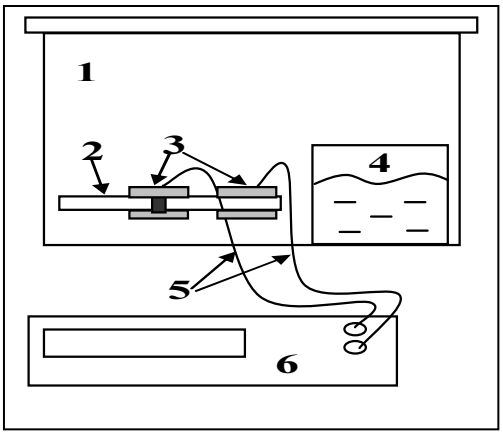

Fig. 1. Draft of the setup for measuring the fim conductivity: 1-camera, 2-glass plate with the test film, 3-contact clamps, 4-container for volatile liquid, 5-wires, 6-ohmmeter.

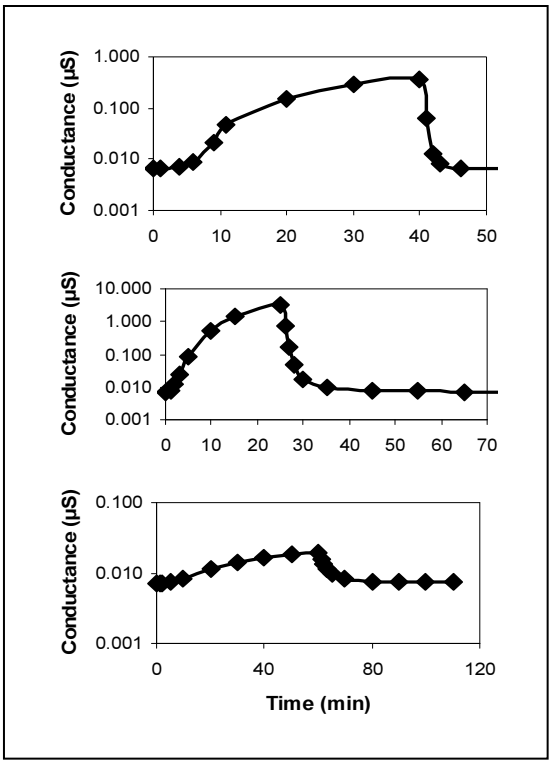

Fig. 2. Conductance change of chitosan lactate film exposed to water (upper graph), ammonia 10% (middle graph) and ethanol (lower graph).

salts of chitosan and contain some water (as shown in experimental part), being similar to gels. The observed effect of the vapors has been accompanied by an increase in their conductance by several orders of magnitude. Based on the results of the measurements, we have constructed the dependencies of the surface conductivity on time for chitosan lactate film which is presented in Fig. 2. In all cases in the presence of the vapors of a volatile liquid the conductance of the investigated film increases and after a certain time reaches saturation value of G. For these cases, the response time $T1$ has been estimated; it is defined as the time required for reaching the conductance value of $0.95G$. After removing the container with the volatile liquid, the conductance of the films has decreased and has reached the initial value in the time $T2$. The values of time interval $T1$ are equal to 34, 22, and 50 min for water, 10% ammonia, and ethanol vapors, respectively. The corresponding values of time $T2$ turned out to be 3, 3, and 10 min. One can see that the rise time of the conductance in a gas vapors is substantially greater than the relaxation time to the initial value in air. This could be explained by the fact that, in addition to the gas adsorption, the biopolymer film undergoes swelling, which, accordingly, could affect the diffusion of gas molecules in the film.

IV. Influence of Gas Mixtures on Parameters of Sensor

A. Description of Setup and Method of Measurement

The piezoelectric resonator with a lateral electric field represented a plate of ceramics PZT 2.5 mm thick with the shear dimensions of 20×18 mm. The polar axis was oriented

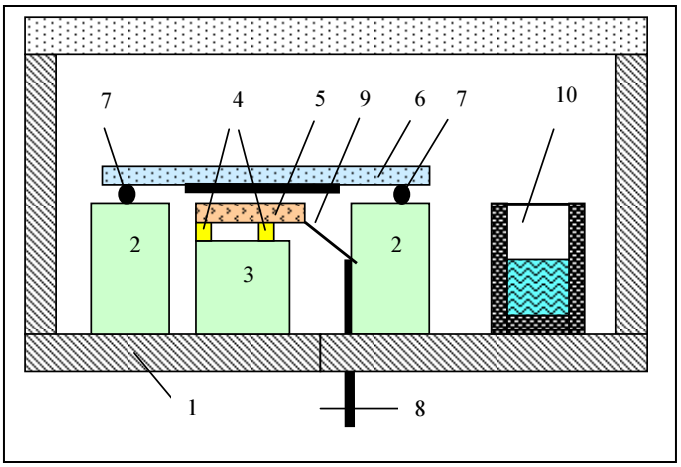

Fig. 3. The sheme of a gas camera with a sensor: 1-camera, 2-holder for a glass plate with a film, 3-holder for a resonator, 4-sealant supports, 5-resonator, 6-glass plate with a film under study, 7-copper wires with diameter of 0.18 mm, 8-contact strips for connection with LCR meter, 9-gold wires, 10-container with volatile liquid.

along a size of 18 mm. One side of the plate was covered with an aluminum film with a gap in the center 4 mm wide, which was oriented perpendicular to the polar axis. Both parts of the coating formed the resonator electrodes. The resonator and plate with the film under study were placed in a sealed camera (1) presented in Fig. 3. Two holders (2) for the glass plate (6) with the film under study were set on the bottom of the camera. A resonator holder (3) was also placed on the bottom of the camera, on which the resonator (5) was fixed with the help of supports of the sealant (4). The electrodes (not indicated in the figure) were located on the lower side of the resonator. The electrodes of the resonator were connected by means of wires to the metal strips with the help of conductive glue. The height of the supports of the sealant was chosen in a way that the free side of the resonator and the upper faces of the supports were located in the same plane. The low acoustic impedance of the sealant allowed to ensure the condition of the mechanically free side of the resonator. The glass with the chitosan film was located above the resonator with a gap of 0.18 mm. This gap was provided by pieces of copper wire (7) with a diameter of 0.18 mm. The camera was connected to the LCR meter 4285A (Agilent) by using the metal strips. Then a container (10) with a test analyte of volume ~2 ml was placed on the bottom of the camera and the camera was tightly closed with a cover. Using the LCR meter, the frequency dependencies of the real and imaginary parts of the electrical impedance of the resonator were measured at the different points of time in the presence of the gas under study. Then the cover was opened, the container was removed from the camera and the measurements continued in the air. The measurement time in the range 75-150 kHz was ~3.5 min.

B. Effect of Gas Mixture on Resonance Properties of Sensor

As already noted, the sensor has been studied in the presence of vapors of water, 10% ammonia and ethanol. The obtained dependencies of the frequency of the parallel resonance (f) and the maximum value of the real part of the electrical impedance (r) of the sensor with the films of

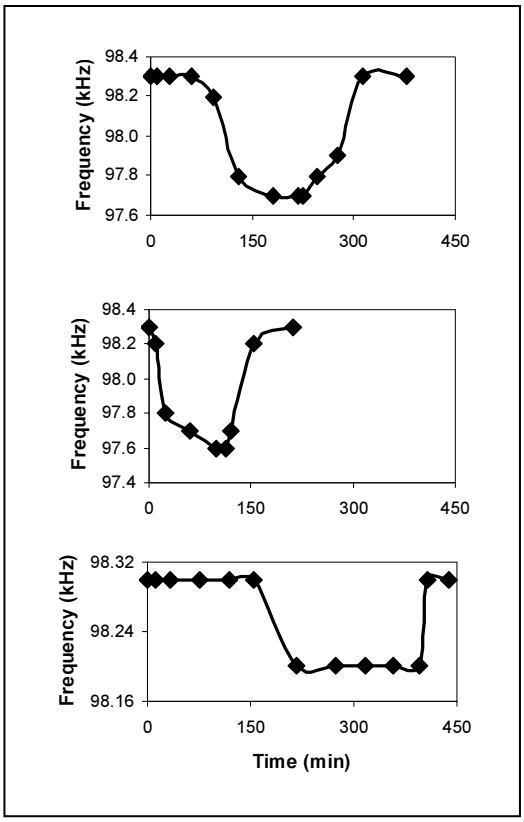

Fig. 4. Time dependencies of the frequency of parallel resonance of the sensor with the film of chitosan lactate exposed to water (upper graph), ammonia 10% (middle graph) and ethanol (lower graph).

chitosan lactate on the time of exposure in the investigated gas vapors and in air are shown in Figs. 4 and 5. We have found that in all cases the values of f and r after placing in any gas vapors have decreased monotonically and after some time have reached the saturation values F and R. For these cases, the response times $t1$ and $\tau1$ have been determined as the values of the time required for reaching the values of $0.95F$ and $0.95R$, respectively. The exposure to air during the time intervals $t2$ and $\tau2$ leads to a complete restoration of the initial parameters of the sensor. The values of the response time of the resonant frequency ($t1$) for the chitosan lactate film are equal 180, 100, and 220 min for water, 10% ammonia, and ethanol vapors, respectively. The values of the corresponding relaxation time of the resonant frequency ($\tau1$) for the chitosan lactate film turned out to be 80, 90, and 5 min. The values of the response time of the maximum value of the real part of the electrical impedance ($t2$) for the chitosan lactate film are equal 130, 20, and 400 min for water, 10% ammonia, and ethanol vapors, respectively. The values of the corresponding relaxation time of the resonant frequency ($\tau2$) for the chitosan lactate film turned out to be 140, 90, and 40 min.

Analysis of the data in Fig. 4 and Fig. 5 allows us to formulate the following conclusions. The time of the change in the resonant frequency and maximum value of the real part of the electrical impedance when the camera is filled with the test gas vapors is substantially longer than the rise time of the electrical conductance of the investigated films. This may be

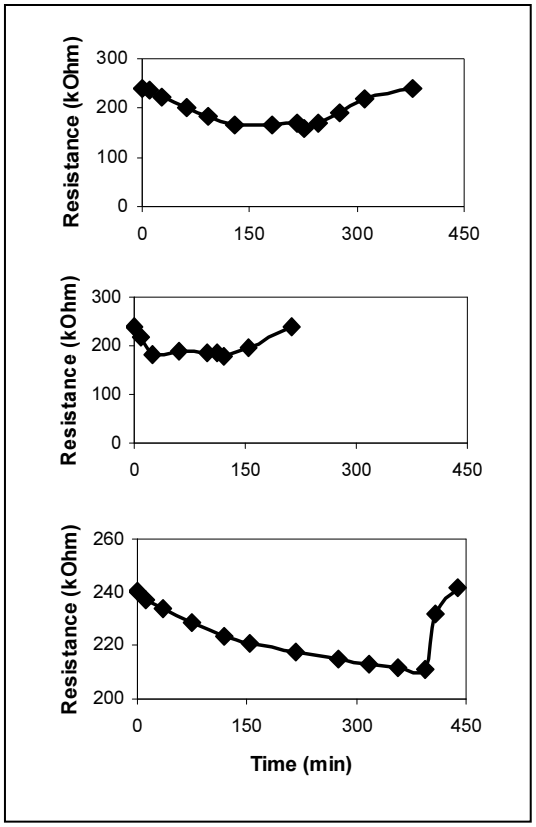

Fig. 5. Time dependencies of the resistance on the frequency of parallel resonance of the sensor with the film of chitosan lactate exposed to water (upper graph), ammonia 10% (middle graph) and ethanol (lower graph).xample of a figure caption. (*figure caption*)

explained by the fact that in addition to the change in the conductance of the films during the gas adsorption a change in their thickness is also observed due to the swelling of the biopolymer. This is confirmed by the fact that in pre-experiments with a gap between the film and resonator of 0.08 mm an acoustic contact of the film with the resonator has been observed, at which the parameters of the resonator changed abruptly. Thus, a change in the thickness of the film has led to a decrease in the gap between the film and the resonator and to an additional change of the parameters of the resonator [7-9]. It can be concluded that the process of film swelling in the presence of gas and the process of relaxation of this thickness are more inertial, when compared with the time of change in the conductivity of the film which should stem primarily from at-surface processes.

The change in films' thickness explains also the recovery time of the resonator characteristics after setting in the air to be substantially greater than the time of restoration of the film's conductivity caused by the desorption of tested gas vapors.

Thus, the gas vapors lead to two effects: first, to a change in the conductivity of the films and, secondly, to a change in their thickness due to the adsorption of the gas under investigation. But, nevertheless, the "resonator – air gap – gas-sensitive film" system fully restores its properties in the air. The difference in the signal types and values, as well as the time of delay between the conductivity signals and the resonant properties open the possibility to create devices such as an electronic nose on the one hand, and also as dosimeters on the other.

ACKNOWLEDGMENT

Authors thank A.K. Grebenko (Skoltech, Moscow, Russia), A.V. Trofimenko and G.I. Filkov *(Moscow Institute of Physics and Technology, Moscow Region, Russia*) for their help with preparation of chitosan salts.

REFERENCES

[1] J.F. Vetelino, "A lateral field excited acoustic wave sensor platform," Proc. IEEE Int. Ultrason. Symp., pp. 2269–2272, 2010.

[2] D.F. McCann, J.M. McCann, J.M. Parks, D.J. Frankel, M. Pereira da Cunha, and J.F. Vetelino, "A lateral-field-excited $LiTaO_3$ high frequency bulk acoustic wave sensor," IEEE Trans. Ultrason Ferroelectr. Freq. Control, vol. 56, pp. 779–787, April 2009.

[3] Z. Zhang, W.Wang, T. Ma, C.Zhang, and G.Feng, "Pseudo-LFE sensors with different electrode configurations on X-cut LiNbO3," Proc. IEEE Int. Ultrason. Symp., pp. 655–658, 2009.

[4] T.G. Leblois and C.R. Tellier, "Design of new lateral field excitation langasite resonant sensors," Proc. IEEE Int. Ultrason. Symp., pp. 2672–2675, 2009.

[5] T. Ma, J. Wang, J. Du, L.Yuan, Z. Qian, Z. Zhang, and C. Zhang, "Lateral-field-excited bulk acoustic wave sensors on langasite working on different operation modes," IEEE Trans. Ultrason. Ferroelectr. Freq. Control, vol. 60, pp. 864–867, April 2013.

[6] T. Ma, J. Wang, J. Du, and J. Yang, "Resonances and energy trapping in AT-cut quartz resonators operating with fast shear modes driven by lateral electric fields produced by surface electrodes," Ultrasonics, vol. 50, pp. 14–20, 2015.

[7] B.D. Zaitsev, A. M. Shikhabudinov, A.A. Teplykh, and I.A. Borodina, "The influence of the metal film, placed close to the free side of the piezoelectric lateral electric field excited resonator on its characteristics," Ultrasonics, vol. 84, pp. 107–111, 2018.

[8] B.D. Zaitsev, A.A. Teplykh, A.M. Shikhabudinov, I.A. Borodina, V.V. Kisin, and I.V. Sinev, "The influence of the conducting film on the characteristics of the lateral electric field excited piezoelectric resonator," Ultrasonics, vol. 84, pp. 96–100, 2018.

[9] B.D. Zaitsev, A.P. Semyonov, A.A. Teplykh, and I.A. Borodina, "The effect of the conductivity of a film located near a piezoelectric resonator with a lateral electric field based on PZT ceramics on its characteristics," Ultrasonics, vol. 94, pp. 169–173, 2019.

[10] W. Suginta, P. Khunkaewla, A. Schulte, "Electrochemical biosensor applications of polysaccharides chitin and chitosan," Chem. Rev., vol. 113, pp. 5458–5479, 2013.

[11] L.Q. Wu, R. Ghodssi, Y.A. Elabd, G.F. Payne, "Biomimetic pattern transfer," Adv. Funct. Mater., vol. 15, pp. 189–195, 2005.

[12] T.I. Nasution, I. Nainggolan, S.D. Hutagalung, K.R. Ahmad, Z.A. Ahmad, "The sensing mechanism and detection of low concentration acetone using chitosan-based sensors," Sensors Actuators B Chem., vol. 177, pp. 522–528, 2013.

[13] A. Bouvree, J.-F. Feller, M. Castro, Y. Grohens, M. Rinaudo, "Conductive polymer nano-biocomposites (CPC): Chitosan-carbon nanoparticle a good candidate to design polar vapour sensors," Sensors Actuators B Chem., vol. 138, pp. 138–147, 2009.

[14] M.M. Ayad, I.M. Minisy, "Detection and kinetics of methylamine on chitosan film coated quartz crystal microbalance electrode," Prog. Org. Coatings., vol. 100, pp. 76–80, 2016.