ISSN 0002-306X. Proc. of the RA NAS and NPUA Ser. of tech. sc. 2019. V. LXXII, N1.

UDC 537.226:66.02 MICROELECTRONICS

A.A. DAVTYAN

I/V CHARTERISTICS OF A FERROELECTRIC NANOFILM TOWARDS THE HYDROGEN PEROXIDE STEAM

The I/V characteristics of ferroelectric (barium-strontium titanate, BST) nano-film - based Pt-BST-Pt structure in the environment of the hydrogen peroxide (H_2O_2) steam in the temperature range of t=36...42° C and densities of H_2O_2(0% (distilled water), 0,5%, 1%, 1,5% and 3%) is experimentally studied. It is justified that the BST membrane shows good sensitivity that can be used for the rapid and early invasive diagnosis of respiratory diseases. Sensitivity mechanisms are also proposed and discussed.

Keywords: ferroelectric BST thin film, diagnosis of respiratory diseases, I/V dependencies, H_2O_2 concentration high sensitivity.

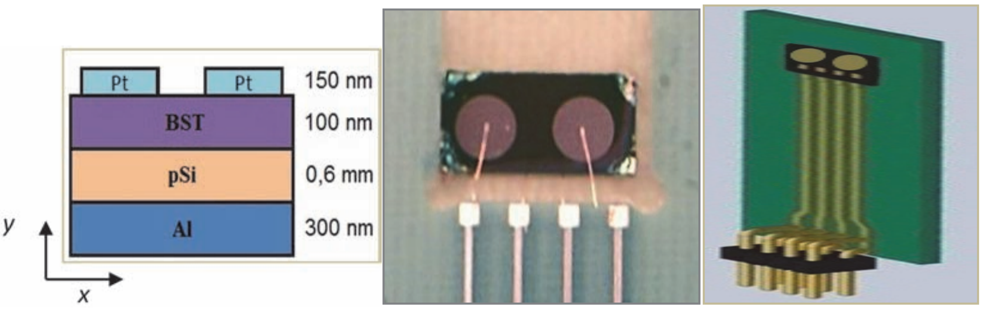
Introduction. As we have already mentioned in our previous study [1], the concentration of non-vaporizing substances that are excreted in healthy individuals is quite low, but it is significantly increasing in patients with pulmonary-asthmatic diseases [2-4]. When a person has lung inflammation, white blood cells release hydrogen peroxide and other chemical elements to kill the harmful bacteria in the body. In addition to pulmonary diseases, smoking also causes inflammatory reactions in the respiratory tract, in other words, the H_2O_2 concentration also increases. Thus, the H_2O_2 concentration in the exposed air can be a very important indicator for the diagnosis of the lung condition and respiratory diseases of different types for the first time.

On the other hand, due to their specific dielectric, piezoelectric, pyroelectric, electrooptical properties, ferroelectric, ceramics and thin film structures have long been used as passive elements of microelectronic schemes, microwave voltage-controlled capacitors (varactors), Film Bulk Acoustic Wave Resonators (FBARs), microelectromechanical systems (MEMS), electro-optic modulators, etc. [5, 6]. At present, various constructions based on these materials are tested as high density DRAMs (dynamic random access memories), non-volatile FeRAMs (ferroelectric random access memories), ferroelectric FETs (field-effect transistor) [7, 8].

Numerous theoretical and experimental studies have shown that in the crystal structure of ferroelectrics, as a result of the inevitable presence of oxygen vacancies, their thin films exhibit chemical catalytic great activity with respect to hydrocarbons [9, 10], hydrogen [11], ethanol [12], acetone [13], moisture [14], ammonium [15], pH of bio(chemical) medium [16, 17], conductivity of electrolytic solutions [18, 19], hydrogen peroxide vapor [20-22], and has perspectives in biological and chemical sensors in terms of application.

Taking into account the fact that barium-strontium titanium in the family of ferroelectric materials is the most researched and applicable, the goal of this paper is to present the sensitivity properties of BST nano-film of a Pt-BST-Pt structure with respect to hydrogen peroxide vapor (0% density (distilled water), 0.5%, 1%, 1.5% and 3% of H_2O_2 in the temperature range (36…42°C)) for the first time.

Experimental results. The study is carried out in terms of I/U dependencies in the interval of the applied DC voltages between –19*V*...+19*V*, in cases of different concentrations and temperatures of steam H_2O_2. Studies are carried out towards heterojunction structures shown in Fig.1, on horizontal x-direction of Pt-BST-Pt, the sensitive upper layer of which is the ferroelectric $Ba_xSr_{1-x}TiO_3$ nano-film, formed by the pulsed laser deposition method.



a) b) c)

Fig.1. a- The cut of the BST/Si hetero-samples, b- the look above, c- the final appearance of the sample

The investigations were carried out at National Polytechnic laboratory of Armenia “ANEL” (Armenian National Engineering laboratory-ANEL). The NI PXI2-SLOT6 measuring device was used to measure the current. To measure the temperature the NI78-4353 measuring device was used to which the J-type thermocouple was connected. It works at a temperature of 0...760°C, accuracy +/- 2.2°C or 0.75%, and the limit of permissible error is +/- 1.1°C or 0.4%. The J-type thermocouple is well attached to an oxidizing environment.

The experiments were carried out for the following concentrations of H_2O_2: 0% (distilled water), 0.5%, 1%, 1.5% and 3%. In the case of all densities, the same temperature limit was applied (36…42° C). The measurement results were saved both in tabular and in graphical form. The H_2O_2 solution was heated to those temperatures so that on the friction surface with the membrane the temperature of the vapor H_2O_2 was in the mentioned interval. The table below shows the change in the current between Pt-contacts in the range of the applied DC voltages of –19*V*…+19*V*, and the results of individual modes are shown in Fig's.2-4.

Table

T,°C / H_2O_2, %	36°C, I (*mA*)	40°C, I (*mA*)	42 °C, I (*mA*)
0 (H2O)	-15…14	-18…18	-18…22
0,5	-9…13	-11…18	-15…24
1	-11…13	-16…18	-30…23
1,5	-8…10	-12…17	-30…22
3	-6…10	-10…14	-30…17

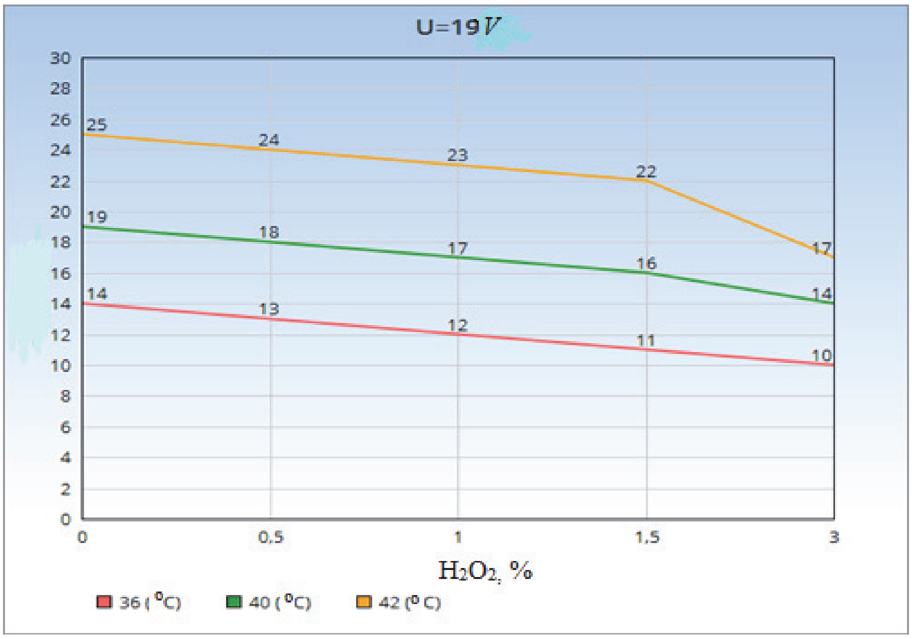


Fig. 2. Dependence of current on the H_2O_2 vapor concentration for different temperatures

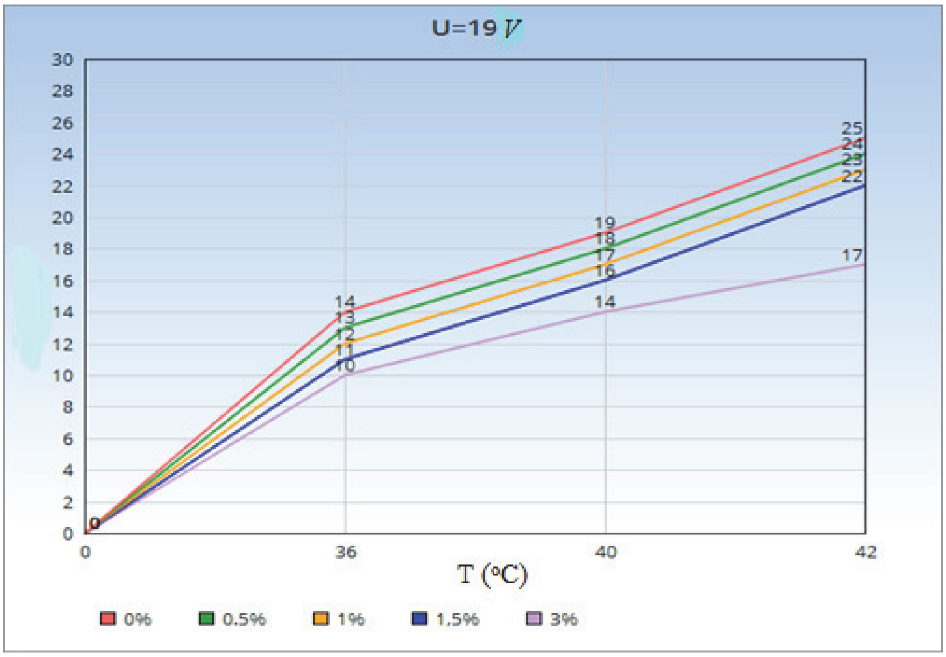


Fig.3. Dependence of current on temperature for different densities of the H_2O_2 vapor

Discussion of the results and the model description. From the obtained results, it is obvious that in parallel with the increase in the concentration of hydrogen peroxide, the sensor current decreases, and the reduction function is close to linear. The other result is as follows: in the case of a constant concentration of hydrogen peroxide, with the increase in the vapor temperature, the current also increases. First of all, a decrease in current is equivalent to an increase in the sensor resistance. Such a recall of the sensor parameters can be explained by a change in the density of oxygen vacancies which inevitably exist in ferroelectric membranes, as well as by new phenomena cases to change the electrical "activity" of trapping energetic levels in the forbidden bands of ferroelectrics which arise due to the presence of these oxygen vacancies [23-25]. First, it has long been approved by experimental and theoretical studies that all complex metal-oxide materials inevitably contain various defects in the crystal network, including the oxygen vacancies, which have the greatest density and affect the material's electro-physical parameters [23, 24].

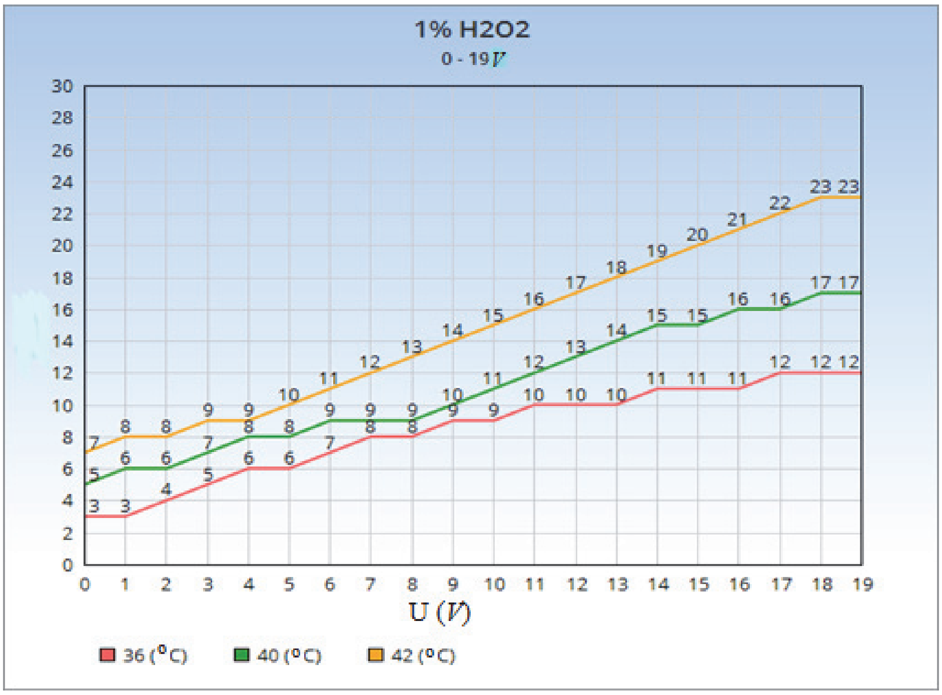


Fig.4. The I/V characteristics of the sensor for different temperatures (1% H_2O_2 vapor)

On the other hand, it was justified that oxygen vacancies in ferroelectric materials exhibit a behavior that is inherent in donor impurities known from the physics of semiconducting materials, give an n-type conductivity to the ferroelectrics. At high temperatures, the oxygen vacancies are double ionized, each supplying two electrons to the conduction band. This process at a low oxygen partial pressure can be described as: $O_0 \leftrightarrow \frac{1}{2}O_2(gas) + V_0^{''} + 2e^-$. An interstitial oxygen atom can form different types of defects $x = O^0,\ O^-,\ O^{2-}$ which means, that the triplet states of oxygen corresponds to three different energies of the ferroelectric film. Since the interface with electrodes is poor in O^{2-}, these interfacial layers have n – type conductivity.

In this sense, oxygen vacancies are positively charged centers, which can attract electrons and be replaced with a conduction band. The energy levels corresponding to these "donor" centers, from conduction band edges have an energy distance $E_c - E_t = 0.06 \dots 0.4 eV$, and the density of the oxygen vacancies, depending on the characteristics of different technologies, vary from 10^{14} to $10^{18} cm^{-3}$ [25] (Fig. 5).

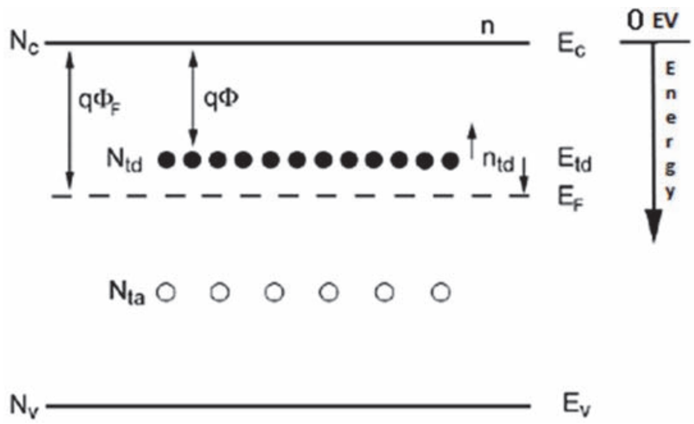


Fig. 5. Schematics of trap levels for electrons

From the point of view of electrical charge, an oxygen vacancy can be in different states, like donors in classical materials. A donor atom is neutral when it attracts an electron, it is positively charged when the corresponding electron is in the conduction band in a free state. Since oxygen is bivalent, its absence is equivalent to a double positively charged center. An oxygen vacancy is said to be neutral if two electrons, the corresponding ones, are occupied in the energy trap levels or in the conduction band, and this will be considered a positively charged unit, if it corresponds to one electron in the conduction band and trap. An oxygen vacancy will be considered a double positively charged center, if in the conduction band or at the trap levels there are no two necessary electrons that retain electro-neutrality.That is, an oxygen vacancy can act as a neutral center, causing the corresponding energy levels in the forbidden band to attract and replace electrons.

Now, based on the abovementioned, we propose two electrophysical versions (model/mechanism) for explanation the change in the resistance (current) of a sample, experimented under the influence of hydrogen peroxide, according to the aforementioned energy structure. However, it is worthwhile to notice that in terms of defect properties of BST, the experimental results are mainly explained by a model in which oxygen vacancies are the key defects responsible for the conductivity behavior of this material [6, 7, 22, 23]. The essence of the first physical model is as follows. At a temperature above room temperature, as it is known, hydrogen peroxide decomposes into water vapor and oxygen atoms $2H_2O_2=2H_2O+2\ O^-$.

On the other hand, atomic oxygen, at almost all temperatures, is a strong oxidizing agent. Before the contact with the exhaled steam, that is, in a relaxed state, the double positive charge is replaced (neutralized) by the existing free electrons at the "trap" E_t levels (Fig.5).

At temperatures above room temperature, in the exhale of a sick person, oxygen O^-, atoms, approaching the BST surface, as atoms endowed with high oxidative qualities, are removed from the shell of the existing oxygen atom, and joining them, disappear in the form of molecular oxygen. As a result, new vacancies of oxygen appear in the BST layer, for neutralization of which the elementary BST cell from the conduction band draws electrons and keeps them "at the trap levels" as a binding state. Thus, the BST cell retains its electrical neutrality.

As it is well known, the charge current located at the "trap levels" do not participate in electrical conductivity, and as a result, the resistance of the film increases, and the current decreases other conditions being equal. Consequently, the higher is the density of hydrogen peroxide, the more often oxygen vacancies will occur and the resistance will increase, and as a result, the current drops significantly (Fig.2).

Another version of this I/V dependence is as follows. Adsorption of O^- ions at the BST surface will cause a net surface charge. As a consequence of this surface charge, a space charge region is induced in the interface region of the BST that balances the charge at the surface [28]. In our case, the adsorbed negative charge of O^- will lead to the creation of a positively charged space charge in the BST interfacial region that leads to a change in the charge carrier chemical potential (i.e. a shift in the Fermi level) and thus a decrease in the charge carrier's concentration, and a decrease of conductivity occurs which, in turn, is observed experimentally.

The second experimental result is as follows. For the constant density of hydrogen peroxide in vapor and fixed applied voltages, the current of BST film increases with the increase of temperature. This dependence can also be explained within the framework of the aforementioned model, if we take into account another phenomenon, very well known in solid state physics, studied and approved: the Pool-Frenkelionization from the "trap" levels [26, 27] (Fig. 6) and Schottky barrier thermo ionization mechanisms.

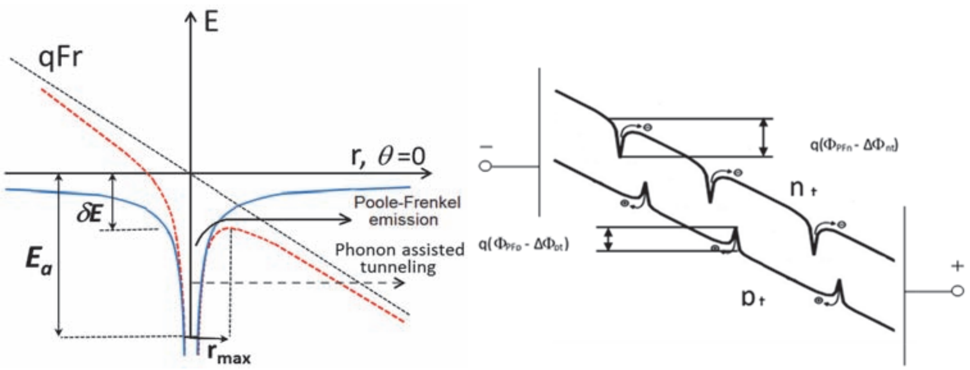


Fig.6. One-dimensional representation of the Coulomb attractive potential (solid line) at the defect state E_a and its changes in the presence of a uniform electric field E (dashed line)

The modification of the carrier emission process by the Poole-Frenkel effect (barrier lowering by d*E*) and by phonon-assisted tunnelling is shown (a), and lowering of the barriers by $\Delta\Phi_n$ for electrons and $\Delta\Phi_p$ for the holes under the applied field (b) [26, 27].

The physical essence of this phenomenon is as follows. The electrons which are "trapped" in the forbidden bands energy levels under the influence of different external electric, thermal, optical and other fields acquire the necessary energy to overcome the potential barrier of a "trap" center, then they can go from these "binding" condition to the conducting band, become free electrons and participate in conduction. In the case under discussion, an increase in temperature may lead to an increase in the possibility of such ionization processes, and as a result, the current will increase, which is noticeable from our experiments.

Conclusion. According to the results of the experiments, the ferroelectric BST thin film exhibits sufficient sensitivity with respect to vapor of hydrogen peroxide, and this can be used for the rapid and early invasive diagnosis of respiratory diseases due to its high sensitivity and emphasized sensorial qualities.

REFERENCES

1. **Buniatyan V.V., Davtyan A.A., Begoyan L.K.** The sensitivity of ferroelectric nanomembrane towards the vapor of hydrogen peroxide // Proceed. of Engineering Academy of Armenia (PEAA). –2017. –V.14. –P. 460-465.
2. **Knobloch H., Becher G., Decker M., Reinhold P.** Evaluation of H_2O_2 and pH in exhaled breath condensate samples: methodical and physiological aspects // Biomarkers. –2008. –13 –P. 319-341.
3. Reasons for Delay in Seeking Care for Tuberculosis / **D. Schneider, S.J.N. McNabb, M. Safaryan, et al** // Republic of Armenia, 2006–2007, Interdisciplinary Perspectives on Infectious Diseases, Article ID 412624, 2010.

4. An efficient and reproducible method for measuring hydrogen peroxide in exhaled breath condensate / **W.J.C. van Beurden, G.A. Harff, P.N.R. Dekhuijzen, et al** // Respir. Medicine. –2002. –96. –P. 197-203.
5. **Gevorgian S.Sh., Tagantsev A.K., Vorobiev A.K.** Tunable Film Bulk Acoustic Wave Resonators. –Springer-Verlag, London, 2013. – 243p.
6. **Dawber M., Raba J.F., Scott J.F**. Physics of thin-film ferroelectric oxides // Rev. of Modern Phys. –2005. – V.77. –P. 1083-1130.
7. **Waser R.** Nanoelectronics and information technology: advanced electronic materials and novel devices. – Wiley, Berlin, 2005.– 995p.
8. **Ishiwara H.** Current Status and Prospects of FET-type Ferroelectric Memories // Journal of Semiconductor Technology and Science. –2001. –Vol.1, №1. –P. 1-14.
9. **Logothetis E.M.** CO/HC sensors based on thin films of $LaCoO_3$ and $La_{0.8}Sr_{0.2}CoO_3$ metal oxides // Sens. Actuators B. –2000. –69. –P. 171-182.
10. **Sahner K., Moos R.** Modeling of hydrocarbon sensors based on p-type semiconducting perovskites // Physical Chemistry Chemical Physics. –2007. – 9. –P. 635-642.
11. Microstructure and hydrogen gas sensitivity of amorphous (Ba, Sr) TiO_3thinfilm sensors / **W. Zhu, O.K. Tan, Q. Yan, et al** // Sensors and Actuators B: Chemical. – 2000. – 65, №1-3. –P. 366-370.
12. A high performance ethanol sensor based on field-effect transistor using a $LaFeO_3$nano-crystalline thin-film as a gate electrode / **S. Zhao, J.K.O. Sin, B. Xu, et al** // Sens. Actuators B. –2000. – 44. – P. 83-88.
13. Acetone gas sensing properties of $SmFe_{1-x}Mg_xO_3$ perovskite oxides / **X. Liu, J. Hu, B. Cheng, et al** // Sens. Actuators B. – 2008. – 134. – P. 483–487.
14. **Agarwal S., Sharma G.L.** Humidity sensing properties (Ba, Sr) TiO_3 thin films grown by hydrothermal-electrochemical method // Sensors and Actuators B: Chemical. – 2002. – 85. –P. 205-211.
15. Novel ammonia-sensing phenomena in sol-gel derived $Ba_{0,5}Sr_{0,5}TiO_3$ thin films / **S.C. Roy, G.L. Sharma, M.C. Bhatnagar, et al** // Sensors and Actuators B: Chemical. –2005. – 110, №2. –P. 299-302.
16. A new perovskite phase Li2x Ca0.5-xTaO3: Li+ ion conductivity and use as pH sensor / **Q.N. Phan, C.B. Bohnke, J. Emery, et al** // Solid State Ionics. –2005. – V.176. – P. 495-504.
17. pH-sensitive properties of barium strontium titanate (BST) thin films prepared by pulsed laser deposition technique / **V.V. Buniatyan, M.H. Abouzar, N.W. Martirosyan, et al** // Physica Status Solidi A. –2010. – 207. – P. 824-830.
18. Multi-parameter sensing using high-*k* oxide of barium strontium titanate / **C. Huck, A. Poghossian, M. Bäcker, et al** // Phys. Status Solidi A. –2015. – 212, №6. – P. 1254-1250.
19. Capacitively coupled electrolyte-conductivity sensor based on high-k material of barium strontium titanate / **C. Huck, A. Poghossian, M. Schoening, et al** // Sensors and Actuators B: Chemical. – 2014. –31. – P. 102–109.

20. Combined amperometric/field-effect sensor for the detection of dissolved hydrogen / **C. Huck, A. Poghossian, P. Wagner, M.J. Sch¨oning** // Sensors and Actuators B: Chemical. – 2010. – doi:10.1016/j.snb. – 2012.10.050.
21. Multi-sensor chip for the investigation of different types of metal oxides for the detection of H2O2 in the ppm range / **S. Reisert, B. Schneider, H. Geissler, et al** // Phys. Status Solidi A. – 1–7 (2013) / DOI 10.1002/pssa. –201200930.
22. Towards a multi-sensor system for the evaluation of aseptic processes employing hydrogen peroxide vapor (H2O2) / **S. Reisert, H. Geissler, et al** // Phys. Status Solidi A 208. – 2011. – №6. – 1351–1356. – / DOI 10.1002/pssa. – 201001138.
23. **Wang R.-V. and Mclntyre Paul C.** Point defect distributions and their electrical effects on (Ba,Sr) TiO/Pt thin films // J Appl.Phys. –2003. – V. 94, №3. – P. 1926-1932.
24. **Robertson J.** Energy levels of point defects in $SrTiO_3$ and related oxides // J.Appl. Phys. – 2003. – V. 93, №2. – P. 1054-1059.
25. **Buniatyan V.V., Martirosyan N.W., Vorobiev A., Gevorgian S.** Dielectric model of point charge defects in insulating paraelectric perovskites // Journal of Applied Physics. – 2011. – 110. – P. 094110-1-11.
26. **Mitrofanov O. and Manfa M.** Pool-Frenkel electron emission from the traps in AlGaN/GaN transistors // J. Appl. Phys. –2004. – V.95. – P. 6414-6419.
27. **Antula J.** Hot-electron concept for Poole-Frenkel conduction in amorphous dielectric solids // J. Appl. Phys. – 1972. – V.94, №11. – P. 4663-4668.
28. **Modou M.J., Morrision S.R.** Chemical Sensing with Solid State Devices. – Acad. Press., Boston, 1989. –468p.

National Polytechnic University of Armenia. The material is received on 11.02.2019.

Ա.Ա. ԴԱՎԹՅԱՆ

ՖԵՐՈԷԼԵԿՏՐԱԿԱՆ ՆԱՆՈԹԱՂԱՆԹԻ I/V ԲՆՈՒԹԱԳՐԵՐԸ ՋՐԱԾՆԻ ՊԵՐՕՔՍԻԴԻ ԳՈԼՈՐՇՈՒ ՄԻՋԱՎԱՅՐՈՒՄ

Փորձնականորեն ուսումնասիրվել են ֆերոէլեկտրական նանոթաղանթի (բարիում-ստրոնցիում-տիտանատ՝ BST) վրա հիմնված Pt-BST-Pt կառուցվածքի I/V բնութագրերը t=36...42°C ջերմաստիճանային միջակայքում՝ տարբեր խտությամբ ջրածնի պերօքսիդի (0% (թորած ջուր), 0,5%, 1%, 1,5% եւ 3% H_2O_2) գոլորշիների առկայությամբ: Պարզվել է, որ BST թաղանթը դրսևորում է բարձր զգայնություն: Նանոթաղանթի այդ հատկությունը կարող է օգտագործվել շնչառական հիվանդությունների արագ և վաղ ախտորոշման համար: Առաջարկվել և քննարկվել են նաև զգայնության մեխանիզմները:

Առանցքային բառեր. ֆերոէլեկտրական BST նանոթաղանթ, շնչառական հիվանդությունների ախտորոշում, I/V բնութագրեր, ջրածնի պերօքսիդի խտություն, բարձր զգայնություն:

А.А. ДАВТЯН

I/V ХАРАКТЕРИСТИКИ ФЕРРОЭЛЕКТРИЧЕСКОЙ НАНОПЛЕНКИ В СРЕДЕ ПАРОВ ПЕРОКСИДА ВОДОРОДА

Экспериментально исследованы I/V характеристики ферроэлектрической (титанат бария-стронция, BST) нанопленки на основе структуры Pt-BST-Pt в среде паров пероксида водорода (H_2O_2) в интервале температур t=36...42^{o}C и плотности H_2O_2 (0% (дистиллированная вода), 0,5%, 1%, 1,5% и 3%). Выявлено, что мембрана BST демонстрирует хорошую чувствительность. Это свойство может быть использовано для быстрой и ранней инвазивной диагностики респираторных заболеваний. Предложены и обсуждены механизмы чувствительности.

Ключевые слова: ферроэлектрические BST нанопленки, диагностика респираторных заболеваний, I/V характеристики, плотность H_2O_2, хорошая чувствительность.