ՀԱՅԱՍՏԱՆԻ ՀԱՆՐԱՊԵՏՈԻԹՅԱՆ ԳԻՏՈԻԹՅՈԻՆՆԵՐԻ ԱՁԳԱՅԻՆ ԱԿԱԴԵՄԻԱ НАЦИОНАЛЬНАЯ АКАДЕМИЯ НАУК РЕСПУБЛИКИ АРМЕНИЯ NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF ARMENIA

՝Հայասփանի քիմիական հանդես

Химический журнал Армении 69, №1-2, 2016 Chemical Journal of Armenia

UDC 541.124.2

ON SENSITIVITY OF ELECTROLYTE-FERROELECTRIC-INSULATOR (EFIS) PH-SENSORS

V. V. BUNIATYAN, A. L. MANUKYAN, A. M. KHALILI and L. A. SUKIASYAN

National Polytechnic University of Armenia 105, Teryan Str., Yerevan, 0009, Armenia Fax: +374 10 545 843 E-mail: 19aram91@gmail.com

The possible adsorption mechanisms of H^+ (OH⁻) in (Ba, Sr)TiO₃-based field effect capacitive EIS sensors are discussed. To explain pH-sensing mechanisms in these structures, it is suggested to regard some new factors, namely: I) the fact of the presence of oxygen vacancies; II) the crystallographic orientation of sensing plane; III) the initial polarization of BST film.

Figs. 4, references 28.

Introduction

Measurement of analytes in aqueous solution is very important for environmental and industrial monitoring, bio-agricultural and medical processes, military applications, etc. One of the most informative parameter of the electrolyte solutions is the pH. Exploring new materials with high sensitivity and efficiency for the immobilization and detection of biosignals and conversion of biochemical signal into quantifiable electronic signal is of importance in biosensor research. Among the variety of proposed concepts and different types of biochemical sensors for measuring pH of electrolyte solutions, the integration of chemically or biologically active materials with semiconductor field-effect devices based on an EIS (electrolyte-insulator-semiconductor) system is one of the most attractive approaches [1,2]. The concept of EIS device is based on the theory of metalinsulator-semiconductor field-effect capacitance where metal gate is substituted by the electrolyte and a reference electrode. Change of pH in electrolyte leads to corresponding change of surface potential and thus leads to change of flat-band voltage (i.e. insulator-semiconductor interface depletion layer capacitance) of EIS device. On the other hand, it is well known that due to the presence of oxygen vacancies and ionic conductance, perovskite oxides have a high catalytic activity towards oxygen reduction and oxidation, and thus suitable for a large variety of sensor applications: magnetic sensors, pyroelectric detectors, optical memories and electro-optic modulators, microwave capacitors, solid-oxide fuel cells (SOFC), as a sensing material in oxygen, carbon monoxide, hydrocarbon, nitrite oxide, humidity, ethanol, hydrogen peroxide, and other sensors [1,2].

In recent years, various high-k dielectric materials (e.g. HfO_2 , ZrO_2 , Ta_2O_5 , AlN, Al_2O_3 , Si_3N_4 , PZT)[1,2] have been used as pH sensitive membranes in EIS devices because of their good sensing performance. Particularly in [3-5], the barium-strontium titanate ($Ba_xSr_{1-x}TiO_3$) is used as pH sensitive membrane for the first time, showing very high sensitivity 48...59mV/pH (even 60mV/pH for certain samples), from which it can be concluded that BST films are promising alternative gate material for capacitive field-effect pH sensor system.

While the BST ferroelectric, pyroelectric, piezoelectric, microwave and electrooptic properties have been well studied [6-8], to our knowledge, very little is known so far about the interaction of electrolyte solutions with ferroelectric oxide surfaces and therefore about pH-sensing mechanisms of BST thin films.

In this context the aim of the present paper is to study the sensing mechanisms and physico-chemical processes which take place in electrolyte-BST interface.

Theoretical model

There are two general approaches in colloid chemistry to describe the titration data of oxides. The one is the porous gel model [9], according to which H^+ , OH^- and counter ions can penetrate into porous layers on the surface of the oxide. In this way quite large amounts of charge could be developed, but there is no independent evidence for porous layers on most oxide surfaces, except for silica.

The second approach describes the charging mechanism of oxides by surface reactions which are based on the so-called site-binding (site-dissociation) model together with the double-layer theory [10-13], which is widely used up to now. The principal features of these theories are:

- Interactions take place at specific sites;
- Interactions can be described via mass law equations;
- Surface charge results from these interactions;
- The effect of surface charge on the interaction can be taken into account by applying the double layer theory.

The theory, which describes the interaction between an inorganic insulator and an adjacent electrolyte, is based on the assumption that the surface contains a discrete number of surface sites which can dissociate. The surfaces of these oxides contain hydroxyl groups, which act as discrete sites for chemical reactions of the surface when it is brought into contact with an electrolyte solution. According to the site-binding model, the surface of any metal oxide always contains only one type of neutral amphoteric hydroxyl groups, MOH, where M represents metal ion. The surface charging mechanism for oxides is the adsorption of proton or hydroxyl ions by surface hydroxyl groups to form positive or negative sites respectively. Depending on the pH value of the solution, the neutral surface hydroxyl sites of oxides are either able to bind (MOH_2^+) or release (MO^-) a proton according to the following reactions [10-13]: in acidic medium

$$MOH \leftrightarrow MO^{-} + H_{B}^{+}, \ k_{a} = \frac{V_{MO^{-}}a_{H_{s}^{+}}}{V_{MOH}},$$

and in alkaline medium

$$MOH_{2}^{+} \leftrightarrow MOH + H_{B}^{+}, \ k_{b} = \frac{V_{MOH}a_{H_{s}^{+}}}{V_{MOH_{2}^{+}}}, \tag{1}$$

where v_i is the surface activity of species i, $k_{a,} k_b$ are chemical equilibrium constants and H_B^+ represents the protons in the bulk of the solution.

Returning to $Ba_xSr_{1-x}TiO_3$, we think that for understanding and explanation of its pH-sensing mechanisms, a few features that BST films possess should be taken into account. First, the chemistry of the transition metal oxides (TMO) can strongly influence the adsorption mechanism. On the other hand, it is well known that the properties of BST and its surface directly depend on the fabrication process and the methods of surface treatment, which can change the total number sites of surface and the ratio of positively/negatively charged sites. Based on the results obtained in [14-15] where diluted NaCl is used as a typical univalent supporting electrolyte, it is found that both types of surface sites (MOH₂⁺ and MO⁻) are more sensitive towards H⁺ than to such ions as Na⁺, K⁺, Cl⁻, etc. Thus, the effect of ion-containing solutions on the process of H⁺ ion dissociation/association on the BST surface may be neglected to a first approximation.

In the present paper, using the above mentioned and well-established sitebinding theory and results as a basic concept [10-13], we suggest that the following factors can also affect sensing processes of BST. Particularly, for the BST to account for the fact that both signs of charge were experimentally observed [3-5], the site considered should be also amphoteric, which means it can act as a proton donor or acceptor. This means that each surface site can be neutral, act as a proton donor (acid reactions) or as a proton acceptor (alkaline reactions). We therefore assume that the oxide surface contains sites in three possible forms: negative (MO⁻), neutral (MOH), and positive (MOH²⁺). This surface property is schematically represented in Fig.1[1].



Second, as BST has a cubic structure [6-8], these sites amount should also depend on crystallographic (h, k, l) directions and surfaces (Fig.2).



Fig. 2. Atomic arrangements for the <100>, <110> and <111> axial directions in SrTiO₃.

The unit cells of cubic SrTiO₃ lattice sectioned by three different planes, (100), (110) and (111), are shown in Fig. 3a-c. For example, for any given planar direction (*h*, *k*, *l*) of a perovskite structure, there are always two distinct types of alternating equally spaced atomic planes having different areal densities of three constituent elements; in this case, Sr(Ba), Ti and O. For instance, the (100) SrTiO₃ surface can exhibit two different types of atomic alternating planes. One is formed by a TiO₂ plane and the other by a SrO plane (Fig.3.) [16]. The SrTiO₃ primitive unit cell contains five atoms which is also the case for other ABO₃ perovskites. Oxygen ions in a cubic unit cell of SrTiO₃ form a perfect octahedron, thus internal titanium ion in its center is closer to O atoms ($RTi-O=a_0/2$) than strontium ions outside oxygen octahedron ($RSr-O = a_0/\sqrt{2}$). Therefore, chemical bonding along Ti–O bonds could be stronger than for Sr–O bonds.



Fig. 3.The structural units of cubic $SrTiO_3$ crystal cross-sectioned by three different planes: a)the (100) surface containing O_2 - and Sr^{2+} ions, b)the (110) surface containing Ti^{4+} , O^2 - and Sr^{2+} , c) the (001) surface containing Ti^{4+} and O_2 - ions. a_0 is the lattice constant.

Moreover, it is found that the SrO(BaO)-terminated perovskite oxide $SrTiO_3$ favors dissociative adsorption, whereas on the TiO_2 -terminated surface molecular adsorption is more stable [17].

Third, we assume that oxygen vacancies, which are inevitably presented in perovskite oxides, can play two important roles in the pH sensing processes of examined sensors. As it is well established [18] by the experimental studies on the SrTiO₃ (100) surface that no evidence for water dissociation on clear surfaces is found, there is strong suggestion that water molecules dissociate at defect sites. The water generally preferentially dissociates on defect sites of oxide surfaces i.e. point defects are the active sites for water dissociation [19-20]. In a wet atmosphere (especially in electrolyte solutions) oxygen ion vacancies V_0^{++} will be readily filled with an oxygen ion and interstitial protons, H_i^* being introduced into the crystal. It is expected to be as:

$$H_2O+V_o^{++}=O_o^x+2H_i^*,$$

where O_0^x is the oxygen ion at the oxygen site [21]. The initial physisorption of molecular water is enhanced by a high oxygen vacancy surface concentration, creating a more positively charged surface. The reaction of proton exchange depends on the diffusion of hydrogen ions and hydroxyl groups through the insulator (BST). At the same time the water can dissociate at an oxygen vacancy into two hydroxyl species, which are about 0.4 to 0.5 eV lower in energy [22,23], that is,

$$H_2O/BTO + V_0^{++} = 2OH^{-}/BTO + 0.5 \text{ eV}.$$

Since H_2O prefers to dissociate at oxygen vacancy site, more vacancies result in more OH and H⁺ on the (STO) BTO surface.

It is also reasonable to assume that there are OH^- species already present both on the surface and in the film before water adsorption. Therefore, the film shows evidence of hydroxyl uptake before the adsorption experiment. This agrees with the observations of [22,23], where the difficulty in obtaining, for example, a pristine TiO₂ surface without OH^- species, even under very clean UHV has been pointed out.

The alkaline character of a hydroxyl group depends strongly on the covalence of the O-H bonds and then on the oxygen coordination. Therefore, the hydroxyl groups present on the oxide surface may be more or less alkaline depending on the oxygen coordination. When water first adsorbs and thereafter decomposes on the surface, OH-groups, produced from the water decomposition, will link to metal cations of the surface (M= Ti, Ba, Sr) and oxygen vacancies (V_o^{++}) present on the surface and the remaining H groups can link to O atoms, adjacent to the M cations of the surface. In the bulk of BST each oxygen atom is coordinated to several ions: two titanium ions and maximum 4 Ba(Sr) ions (may be less, when Ba⁺, Sr⁺ ions or a vacancy is present). The oxygen atoms present on the surface are less coordinated than the ones present in the bulk but it can be assumed that they have more than one link to the cations. Therefore, they have an alkaline nature. H groups can then link to these atoms. Thus, depending on the coordination of the oxygen atoms, different hydroxyl groups can be formed on the oxide surface with different alkaline character. For instance, the oxygen atoms of the hydroxyl groups linked to metal cations (Ti, Ba, Sr) are di-coordinated (can show more alkaline character) and the O atoms of the hydroxyl groups belonging to BST lattice are multi-coordinated (can show less alkaline character).

So, we assume that the oxygen vacancies V_0^{++} "showing" positively charged donor properties [24] and having higher concentration on the surface than in the interior, can act as binding sites for OH hydroxyl ions (Fig. 4). Moreover, as it has been shown experimentally [25], the proton exists in the neighborhood of the oxygen ion and appears preferentially in the site near the oxygen ion with a relatively large trapping energy. It is found that water molecules are attracted more strongly to the surfaces, where oxygen vacancies exist near the surfaces because the energy for the proton on the surface is lower than that for the proton in the interior [26], which means that proton prefers to remain on the surface rather than penetrate into the inside near the clean surface. These results indicate that the presence of surface vacancies is important for the proton absorption.

Thus, we prove that there are two dissociative adsorption sites, oxygen vacancies and on-top surface Ti. The Ti on top site is the dominant site for OH^- chemisorptions.



Fig. 4. Schematic diagram of two adsorpton processes leading to chemoserbed OH^- at the surface of TiO_2 – terminated BST (at a vacant lattice oxygen site or on top a surface Ti).

At last, as the BaTiO3 thin films have a P⁺ polarization, the polar nature of water means that it can interact strongly with the ferroelectric polarization changing the electrical boundary conditions, i.e. the initial physisorption of molecular water is enhanced by high oxygen vacancy surface concentration, creating a more positively charged surface. In [26] it is shown that on the (001) surface of BaTiO₃ (BTO) with in-plane polarization, there are competing molecular and dissociative adsorption mechanisms. The static charge on the surface changes the depth of the physisorption well [26,27], which determines the average residence time of the precursor on the surface leading to a greater chance of finding a chemisorption defect site. Typical molecular and dissociative adsorption energies are ~0.1 to 0.2 *eV* and ~1.0 *eV*, respectively [28].

Conclusions

Based on the above described theories and analyses, we can conclude that:

- (i) for the accurate and precise evaluation of pH sensitivity mechanisms of the BST thin films it is necessary to combine the structural, chemical and energetic information;
- (ii) the hydrophilic character of the BST film and the existence of a negatively charged surface can be ascribed to the presence of hydroxyl groups on the oxide surface;
- (iii) depending on crystallographic direction (plane) there can exist different competing sites for dissociative adsorption ($_{V}^{o++}$, on-top Ti and (Ba,Sr) lattice atoms. For example, for (100) of SrTiO₃, the on-top surface Ti is the dominant O^{H-} chemisorption site; and the concentration of $_{V}^{o++}$ favors initial physisorption;
- (iv) the pH sensitivity is dependent on crystallographic and coordination condition of BST surface components, mainly on coordination of oxygen atoms. Sensitivity of some samples, which is higher than that of Nernstian, can be explained by twofold roles of V_0^{++} ;
- (v) the polarization effects of BTO surfaces should be taken into account.

To reveal the role of each of these factors regarding pH-sensitivity of BST films, more additional quantitative and comparative measurements are required.

О ЧУВСТВИТЕЛЬНОСТИ ЭЛЕКТРОЛИТ- СЕГНЕТОЭЛЕКТРИК-ДИЭЛЕКТРИК(EFIS) PH-CEHCOPOB

В. В. БУНИАТЯН, А. Л. МАНУКЯН, А. М. ХАЛИЛИ и Л. А. СУКИАСЯН

Обсуждаются возможные механизмы адсорбции H⁺(OH⁻) в (Ba,Sr)TiO₃ pH-емкостных EIS датчиков, основанные на эффекте поля. Для объяснения механизмов pH-чувствительности в этих структурах предлагается учитывать несколько новых факторов, а именно, наличие кислородных вакансий, кристаллографическую ориентацию чувствительной плоскости, начальную поляризацию BST пленки.

ԷԼԵԿՏՐՈԼԻՏ-ՍԵԳՆԵՏՈԷԼԵԿՏՐԻԿ-ԴԻԷԼԵԿՏՐԻԿ (EFIS) PH-ՍԵՆՍՈՐԻ ՉԳԱՅՆՈԻԹՅԱՆ ՄԱՍԻՆ

Վ. Վ. ԲՈԲՆԻԱԹՅԱՆ, Ա. Լ. ՄԱՆՈԻԿՅԱՆ, Ա. Մ. ԽԱԼԻԼԻ և Լ. Ա. ՍՈԻՔԻԱՍՅԱՆ

Քննարկվում է H⁺(OH-)-ի կլանման Հնարավոր մեխանիզմները (Ba,Sr) TiO₃-ի վրա Հիմնված ունակային EIS տվիչներում: Առաջարկվում է, որ թH-ի զգայուն մեխանիզմների բացատրելու Համար անՀրաժեշտ է Հաչվի առնել մի քանի նոր գործոններ, ավհլի Հստակ՝ ԹԹվածնի վականսիաների առկայուԹյունը, զգայուն ԹաղանԹի բյուրեղագիտական ՀարԹուԹյան կողմնորոչումը, BST ԹիԹեղի նախնական բևեռացումը:

REFERENCES

- Poghossian A., Schöning M.J., Dickey E.C., Pishko M.V. // Encyclopedia of Sensors, American Scientific Publishers, Stevenson Ranch (USA), 2006, v. 9, ISBN 1-58883-065-9, p. 463.
- [2] Her J.L., Wu M.H., Peng Y.B., Pan T.M., Weng W.H., Pang S.T., Chi L. // Int. J. Electrochem. Sci., 2013, v. 8, p.606.
- [3] Buniatyan V.V., Abouzar M.H., Martirosyan N.W., Schubert J., Gevorgian S., Schöning M.J., Poghossian A. // Phys. Status Solidi, 2010, A 207 (4), p. 824.
- [4] Buniatyan V., Martirosyan N., Abouzar M.H., Schubert J., Zander W., Gevorgian S., Schöning M.J., Poghossian. A. // Proc. Sensors, 2009, v II, ISBN 978-3-9810993-Nürnberg (Germany) 26-28 May, p. 317.
- [5] Huck C., Poghossian A., Bäcker M., Reisert S., Kramer F., Begoyan V.K., Buniatyan V.V., Schöning M.J. // Physica Status Solidi, 2015, A 212, p.1254.
- [6] Dawber M., Raba J.F., Scott J.F. // Rev. of Modern Phys., 2005, v.77, p. 1083.
- [7] Gevorgian S.Sh., Tagantsev A.K., Vorobiev A.K.T. // Springer-Verlag, 2013, London, p. 243.
- [8] Damjanovic D., Muralt P., Setter N. // IEEE Sensors Journal, 2001, v.1, №3, p. 191.
- [9] Perram J.W., Hunter R.J., Wright H.J.L. // Aust. J. Chem., 1974, v.27, p. 461.
- [10] Yates D.E., Healy T.W. // J. Colloid Interface Sci., 1975, v. 52, p. 222.
- [11] Yates D.E., Levine S., Healy T.W. // J. Chem. Soc. Faraday Trans, 1974, v.70, p. 1807.
- [12] Van Hal R.E., Eijkel J.C.T., Bergveld P. // Advances in Colloid and Interface Sciencev, 1996, p. 31.
- [13] Anh D.T.V., Olthuis W., Bergveld P. // Sens. Actuators, 2004, p165.
- [14] Fung C.D., Cheung P.W., Ko W.H. // IEEE Transaction on Electron Devices, 1986, v. ED-33, p. 8. [15] Bousse L., de Rooij N.F., Bergveld P. // IEEE Transaction on Electron Devices, 1983, v. ED-30, p.1263.
- [16] Duncan D.A., Allegretti F., Woodruff D.P. // A quantitative structure determination, 2012.
- [17] Evarestov R.A., Bandura A.V., Alexandrov V.E. // Surf. Sci., 2007, v.601, p. 1844.
- [18] Henderson M.A. // Surf. Sci , 2002, p.308.
- [19] Wang J.L., Gaillard F., Pancotti A., Gautier B.G., Vilquin B., Pillard V., Rodrigues G.L.M., Barrett N. // J. Phys. Chem., 2012, C116, p. 21802.
- [20] Wang J.L., Vilquin B., Barrett N. // Appl. Phys. Lett., 2012.
- [21] Yoshino M., Kato K., Mutiara E., Yukawa H., Morinaga M. // Material Transactions, 2005, v.46, p.1131.
- [22] Wendt S., Frerichs M., Wei T., Chen M.S., Kempter V., Goodman D.W. // Surface Science, 2004, v.565, p.107.
- [23] He D.Y., Qiao L.J., Volinsky A.A., Bai Y., Wu M., Chu W.Y. // Appl. Phys. Lett., 2011.
- [24] Robertson J. // Solid-State Electronics, 2005, v.49, p.283.
- [25] Weber G., Kapphan S., Wolecke M. // Phys. Rev., 1986, p. 8406.
- [26] Shimojo F. // Science and Technology of Advanced Materials, 2007, v.8, p.584.
- [27] Geneste G., Dkhil B. // Phys. Rev., 2009, B 79, 235420.
- [28] Zhao M. H., Bonnell D.A., Vohs J.M. // Surf. Sci., 2008, v.602, p. 2849.