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ELECTROLYTE-FERROELECTRIC-INSULATOR-SEMICONDUCTOR (EFIS) PH-SENSOR PARAMETERS

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Based on site-binding model of the oxide/aqueous electrolyte interface and experimental data, parameters of membrane pH-capacitive field effect-based sensors (Ba,Sr)TiO₃ were evaluated and calculated. Particularly, when the flat-band voltage shifts to 0.6 *V* with pH sensitivity of 54-59mV/pH, pH_{pzc} changes in the range of 3.3-3.5, the calculated intrinsic buffer capacity is $\beta_{int} \approx 0.5 \cdot 10^{15}$, and the total number of available active surface sites N_s per unit area is $N_s \cong 0.78 \, 10^{14} \, group/\, cm^2$.

Figs. 1, references 13.

Introduction

As it was indicated in our previous works [1-5] due to the presence of oxygen vacancies and ionic conductance, perovskite oxides had a high catalytic activity towards oxygen reduction and oxidation, and thus were 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), capacitively coupled electrolyte-conductivity contactless sensors. They were also used as sensing material in oxygen, carbon monoxide, hydrocarbon, nitrite oxide, humidity, ethanol, hydrogen peroxide, etc. Barium strontium titanate (BST) belongs to the most popular ferroelectric materials exhibiting unique ferroelectric, pyroelectric, piezoelectric, microwave and electro-optic properties. Recently, BST films of various compositions have been used as pH-sensitive material in semiconductor field-effect-based pH sensors [1-2]. During last decade many pH-sensitive materials, such as, SiO₂, Si₃N₄, Al₂O₃, Ta₂O₅, WO₃, SnO₂, PbTiO₃, Li_{2x}Ca_{0.5-x}TaO₃, GdTixOy, AlN, etc. [6-9] have been investigated.

In spite of numerous studies on SiO_2 , Ta_2O_5 , Si_3N_4 , Al_2O_3 insulators, as well as on physico-chemical and material sensing parameters and characteristics of EIS systems based thereon, there are no data on the BSTelectrolyte-based EIS sensors so far.

In this work, based on site-binding model [10] and Gouy-Chapman-Stern theory[11] describing the sensitivity in terms of the intrinsic buffer capacity and the differential capacitance, as well as using the experimental data obtained in [1-5], parameters of (Ba,Sr)TiO₃ sensing pH-capacitive membrane based on field effect were evaluated and calculated. Particularly, the pH_{pzc} and intrinsic buffer capacity, as well as available surface site concentration for the (Ba_{0.25}Sr_{0.75}TiO₃) – insulator (SiO₂)-pSi field effect based capacitive pH- sensors were calculated for the first time.

Calculation procedure

As it was indicated in [1-3], for the electrolyte-ferroelectric ($Ba_{0.25}Sr_{0.75}TiO_3$)insulator (SiO₂)-pSi field effect-based capacitive pH-sensors experimentally proved that BST exhibited high sensitivity (48-59mV/pH, and even more, Fig.1) with hysteresis less than 2 *mV*(or 0.035 pH) in the pH range from 3 to 11. That is comparable with values reported for Si₃N₄ (54 *mV*/pH), Al₂O₃ (49–57 *mV*/pH) and Ta₂O₅ (55–59 *mV*/pH[3,6]) films, which have often been utilized as pH-sensitive transducer material in ion-sensitive field-effect transistors or capacitive field-effect sensors. According to site-binding theory [10], the presence of ion-specific binding sites at the surface of the insulator exposed to the electrolyte is responsible for the ion-dependent charge distribution on the insulator layer which in turn leads to change of surface potential and shift of flat-band voltage in insulator-semiconductor system.

On the other hand, based on experimental measurement data obtained for MIS and E(BST)IS structures, it was established that in comparison with bare p-Si-SiO₂ structure, the C-V curves and flat-band voltage of p-Si-SiO₂-BST structure shifted $\Delta V_{FB} \sim 0.6V$ to more negative gate voltage. This is the first indication of the presence of additional positive charges (conditioned not only by Ba²⁺, Si²⁺ or Ti⁴⁺, but oxygen vacancies too) in the BST/SiO₂ and electrolyte-BST interfaces. Using the method for determination of pH_{pze} developed in [12] and results obtained in [1-3] for the BST-based E(BST)IS structure with sensitivity of (54-59) mV/pH one can estimate the pH_{pzc} according to this procedure. We used the equation $\Delta V_{FB}(pH) = B-\psi(pH)$, where $B = \varphi_r - \phi^M / q + \chi_s$, $\varphi_r = (\varphi_{r/H} + E_H)$ is reference electrode potential relative to the normalized hydrogen electrode, $\psi(pH)$ is the potential at the insulator-electrolyte interface, ϕ^M / q is the metal work function, χ_s is the surface dipole potential on the solvent, ΔV_{FB} is the difference of flat-band voltages of E(BST)IS and MIS structures.



Fig. Typical set of C–V curves (a) and calibration curve (b) calculated from the linear region of the C-V curves at ~60% of the maximum capacitance of an EFIS sensor with a 100 nm thick $Ba_{0.25}Sr_{0.75}Ti O_3$ layer measured in Titrisol buffer solutions with different pH values from pH 11 to pH 3[1-2].

According to experimental studies of the pH response of E(BST)IS structure, the dependence of surface potential on the BST membrane is sufficiently linear. The linear relationship between φ and pH_{pzc} can be expressed as [12],

$$\psi = \Delta p H \times S$$
,

where $\Delta pH=pH-pH_{pzc}$ and *S* is the pH sensitivity.

Using the values $E_{H}=4.715\pm0.015V$, $\phi_{r/H}=0.2\pm0.003V$ for Ag/AgCl reference electrode at 25°C, $\chi_s=0.03V$, and $\Phi^{M}/q=4.15V$ (for Al), we obtain B= 0.796±0.018V[12]. Based on these data for the sensitivity of $S \approx (55\div59 \text{ mv/pH})$ we obtain pH_{pzc(BST)} $\approx 3.5\div3.3$.

Assuming that pH_{pzc} for BST is about 3.3, we can calculate the surface potential via

$$\psi(pH) = S(pH_{pzc} - pH).$$

A change in the pH will change the oxide surface potential. At pH >pH_{pzc} the oxide surface is charged negatively and at pH < pH_{pzc} positively. The resulting pH-dependent electrical surface charge of the gate insulator will lead to a modulation of the capacitance of the E(BST)IS structure. For calculation of the intrinsic buffer capacity β_{int} , $a_{H_s^+}$ and the total number of available surface sites N_s , as the key parameters determining the pH-sensitivity, let's assume that pH_{pzc(BST)} ≈ 3.3 and take for k_b and k_a values for the BST as in Ta₂O₅, that is p k_a =4, p k_b =2, where k_b and k_a are respectively, the intrinsic dissociation constants, for the surface reactions[10,11,13].

$$MOH \leftrightarrow MO^{-} + H_{s}^{+}, \ k_{a} = \frac{V_{MO^{-}}a_{H_{s}^{+}}}{V_{MOH}},$$
$$MOH_{2}^{+} \leftrightarrow MOH + H_{s}^{+}, \ k_{b} = \frac{V_{MOH}a_{H_{s}^{+}}}{V_{MOH_{2}^{+}}}$$

where $a_{H_s^+}$ is surface activity of H^+ and $a_{H_s^+} = a_{H_B^+} \exp\left(-\frac{q\psi}{kT}\right)$, $a_{H_B^+}$ is the

activity of H^+ in bulk solution, v_i is the surface activity of species i (the number of sites per unit area).

Taking into account that based on site-dissociation model and the Gouy-Chapman-Stern theory, the general expression for the pH sensitivity S of the EIS system, derived in [10,11,13] is:

$$S = \frac{\delta \psi_0}{\delta_p H_B} = -2.3 \frac{kT}{q} \alpha \text{ with } \alpha = \frac{1}{\left(\frac{2.3kT C_{dif}}{q^2 \beta_{\text{int}}}\right) + 1}, \qquad (1)$$

where β_{int} is the intrinsic buffer capacity which characterizes the ability of the oxide surface to deliver or take up protons,

$$\beta_{\text{int}} = \frac{N_s a_{H_s^+}^2 + 4 k_a a_{H_s^+} + k_a k_b^2}{\left(k_a k_b + k_b a_{H_s^+} + a_{H_s^+}^2\right)^2} 2.3 a_{H_s^+}, \qquad (2)$$

$$a_{H_{s}^{+}} = \frac{k_{b}C_{dif}\psi + \sqrt{(k_{b}C_{dif}\psi)^{2} + 4k_{a}k_{b}(q^{2}N_{s}^{2} - C_{dif}^{2}\psi^{2})}{2(qN_{s}k_{b} - C_{dif}\psi)}.$$
(3)

 C_{dif} is the differential double-layer capacitance, which is mainly determined by the ion concentration of the bulk solution via the corresponding Debye length, kis the Boltzmann constant and T is the absolute temperature,

$$\frac{1}{C_{dif}} = \frac{x}{\varepsilon \varepsilon_0} + \frac{1}{\left(\frac{2\varepsilon \varepsilon_0 z^2 q^2 n^0}{kT}\right)^{1/2} \cosh\left(\frac{zq\varphi_2}{2kT}\right)}$$

where \mathcal{E}_0 is the permittivity of the free space, \mathcal{E} is the relative permittivity, n^0 is concentration of each ion in the bulk, \mathcal{X} is the diffusion layer distance from the surface. \mathcal{P}_2 is the potential at \mathcal{X} , \mathcal{Z} is the valency of ions, \mathcal{Q} is the elementary charge.

This expression shows that the differential capacitance is made up of two components. The former part of this expression describes the contribution of the Stern layer the letter part describes the diffuse layer contribution. A high buffer capacity can be achieved when the amount of surface sites is high, as follows directly from expression of β_{int} A lower number of surface sites or a higher value

for the Stern layer capacitance will reduce the sensitivity. Thus, it can be concluded that the intrinsic buffer capacity is the major parameter influencing the sensitivity. Maximum Nernstian sensitivity (59.2 mv/pH at 25°C) can be obtained only in the case that $\alpha =>1$. Condition $\alpha=1$ is reached for oxides with a large value of the surface-buffer capacity, β_{int} (high density of surface-active sizes) and a low value of the C_{dif} (low electrolyte concentration).

Based on our previous experimental results obtained for E(BST)IS sensors with the sensitivity of S \approx 56mV/pH[1-3] and assuming that $C_{dif} \approx 0.8$ F/m² [10-11,13], from the Eq.(1-2) we can evaluate α and β_{int} .

$$S \approx 55 \cdot 10^{-3} \text{ V/pH} = -59.3 \cdot 10^{-3} \alpha$$
, $\alpha \approx 0.944$ and $\beta_{\text{int}} \approx 0.5 \cdot 10^{15}$.

Then, having the value of the β_{int} , using the above obtained and assumed parameters, for the case of $\psi \approx 0.18V$ (which corresponds to $pH_B = 1$ (0.1M solution), from Eq.(2-3) for N_s one can obtain:

$$N_s \simeq 0.7810^{15} \, group/cm^2 = 0.7810^{14} \, group/cm^2$$

The higher the total number N_s of available surface sites per unit area, the higher pH-sensitivity can be obtained.

Conclusions

Using the measured values of the flat band voltages of MIS and EIS structures, measured value of sensitivity as well as calculated material parameters B, based on analytical expressions describing the sensitivity of field effect capacitive EIS pH-sensors (based on the combination of the Gouy-Chapman-Stern theory with the site-dissociation model) in terms of the intrinsic buffer capacity of the surface and the differential capacitance, it is possible to determine and calculate the main important parameters of E(BST)IS pH-sensors.

ПАРАМЕТРЫ ЭЛЕКТРОЛИТ-СЕГНЕТОЭЛЕКТРИК-ДИЭЛЕКТРИК-ПОЛУПРОВОДНИКОВОГО (EFIS) РН-ДАТЧИКА

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Параметры мембранных pH-емкостных датчиков (Ba,Sr)TiO₃, основанные на эффекте поля, оцениваются и рассчитываются на основе модели местной связи в приповерхностном слое оксид/электролит и экпериментальных данных. В частности, при смещении напряжения плоских зон около 0.6 V и pH чувствительности 54-59mV/pH получено, что pH_{pzc} изменяется в диапазоне 3.3-3.5, расчетная внутренняя буферная емкость $\beta_{int} \approx 0.5 \cdot 10^{15}$, а общее число возможных активных поверхностных состояний N_s на единицу площади составляет $N_s \simeq 0.78 \cdot 10^{14}$ group/ cm².

ԷԼԵԿՏՐՈԼԻՏ-ՍԵԳՆԵՏՈԷԼԵԿՏՐԻԿ-ԴԻԷԼԵԿՏՐԻԿ-ԿԻՍԱ৲ԱԽՈՐԴԻՉ (EFIS) PH-ՍԵՆՍՈՐԻ ՊԱՐԱՄԵՏՐԵՐԸ

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

Հիմնվելով օջսիդ/էլեկտրոլիտ ենԹամակերևուԹային չերտում տեղային կապերի մոդելի և փորձնական տվյալների վրա, գնաՀատվում և Հաչվարկվում են (Ba, Sr)TiO₃ մեմբրանով դաչտային երևույԹի վրա Հիմնված pH-ունակային սենսորի պարամետրերը: Ընդունելով ՀարԹ գոտիների չեղման լարումը մոտավորապես 0.6V, pH-զգայնուԹյունը 54-59 mV/pH, ստացվում է, որ pH_{pzc},-ը փոփոխվում է 3.3-3.5-ի սաՀմաններում, Հաչվարկային ներջին բուֆերային ունակուԹյունը՝ $\beta_{int} \approx 0.5 \cdot 10^{15}$, իսկ Հնարավոր մակերևուԹային ակտիվ վիճակների ջանակը` $N_s \cong 0.78 \cdot 10^{14} group/cm^2$:

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