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Anions Sensing and Interfering Behaviors of Electrolyte-Insulator-Semiconductor Sensors with Nitrogen Plasma Treated Samarium Oxide

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Abstract

In this paper, we demonstrate a samarium oxide (Sm_2O_3) electrolyte-insulator-semiconductor (EIS) sensor with nitrogen plasma immersion ion implantation (PIII) treatment for anions sensing and interfering characterization. The chloride (Cl^-), nitrite (NO_2^-), and nitrate (NO_3^-) ions were detected and the sensitivity was about 49.75 mV/pCl, 53.8 mV/pNO_2, and 56.19 mV/pNO_3, respectively. The ion sensitivity was enhanced with the increase of ionic radius of the target ion. The titration measurement was performed to analyze the interference of anions. The Sm_2O_3 EIS sensor with nitrogen PIII treatment exhibits superior anion sensitivity, selectivity and stability, which is suitable for future biosensing applications.

1. Introduction

The first ion sensitive field-effect transistor (ISFET) with silicon dioxide sensing membrane for bio-chemical applications was invented by P. Bergveld in 1970 [1]. Compared with ISFET, electrolyte-insulator-semiconductor (EIS) sensor presents great potential as a sensing device because of the simple structure, few processing steps, low cost, and convenient detection system. Over the past years, many high-dielectric constant (high-k) materials such as Ta_2O_5 and HfO_2 [2-3] have been proposed to obtain a superior pH sensing performance. However, for the high-k sensing materials, it is difficult to sense anions in serum and water. Traditionally, for anions sensing, the organic ion selective membrane is adopted but suffered from the short lifetime [4]. Recently, a samarium oxide membrane with nitrogen plasma immersion ion implantation (PIII) treatment has been proposed to sense chloride ions [5]. In this study, some common anions such as chloride, nitrite and nitrate ions were detected by using the nitrogen PIII treated Sm_2O_3 sensing membrane. The interference of these ions was characterized by using the fixed interference method (FIM). The Sm_2O_3 EIS sensor with nitrogen PIII treatment demonstrates superior anions sensing characteristics.

2. Experimental

The EIS sensors with Sm_2O_3 sensing membrane were fabricated on 4-inch p-type (100) silicon wafers. First, all wafers were cleaned by a standard RCA method. A 50-nm-thick SiO_2 film was thermally grown on Si wafers. Then, a 10-nm-thick Sm_2O_3 sensing membrane was deposited by RF sputtering with a 99.9% pure samarium target in Ar and O_2 mixed ambience. After that, the nitrogen was incorporated into Sm_2O_3 film by using the PIII system at 5 kV for 3 min for anions sensing [5]. Subsequently, all samples were rapid thermal annealed at 700 ^oC for 30 s in N_2 ambient. Finally, a 300-nm-thick Al film was deposited by thermal evaporator for backside contact. The negative-photoresist SU8-2005 was used to define the sensing area as the electrolyte contact using the photolithography process. The schematic structure of the device and the detail process flows were shown in Fig. 1. All samples were immersed in 5-mM Tris/HCl buffer solution for 12 hours to get a steady response. The concentration of KCl, KNO_2, and KNO_3 solutions in a range between 10^{-4} and 100 M was varied. The *C–V* curves were measured at different ion concentrations through Ag/AgCl reference electrode by HP4284A precise LCR meter at a frequency of 1 kHz. The output voltage at different concentrations was extracted from the voltage at 60% of maximum capacitance in *C–V* curves. Further, the drift was calculated by the linear fitting of the output signal in time range from 4 to 12 h.

3. Results and Discussion

Fig. 2(a)-(c) show the output voltages versus pKCl, pKNO_2 and pKNO_3 respectively extracted from typical *C-V* curves of the nitrogen-incorporated Sm_2O_3 EIS sensor. The output voltages were shifted toward the negative direction, indicating the sense of anions. The anions sensing for the Sm_2O_3 film with nitrogen PIII treatment can be attributed to the introduction of positive charges, NO^+ and N_2O^+, in Sm_2O_3 film to attract anions [5]. The pCl, pNO_2 and pNO_3 sensitivity was extracted in Fig. 2(d) and found to be 49.75 mV/pCl, 53.8mV/pNO_2 and 56.19 mV/pNO_3 respectively. It can be observed that the higher molar mass and ionic radius of target anion can exhibit higher ion sensitivity. This is due to the large ionic radius of target anion can easily react with the surface sites of OH_2^+ and prevent the potassium ions from binding with the surface sites of O^-, as illustrated in Fig. 3. Fig. 4(a) presents the real time detection of the chloride, nitrite and nitrate ions by titration. The output voltages were collected per minute and monitored continuously for 10 min during each titration step. The calibrated curve corresponding to the dynamic response is displayed in Fig. 4(b). The sensitivity of NO_2^- and NO_3^- ions in 10^{-4} M KCl inference solution was about 52.11 mV/pNO_2 and 48.51mV/pNO_3 respectively and the sensitivity of NO_3^- ions in 10^{-4} M KNO_2 inference solution was 53.5 mV/pNO_3. To understand the effect of measured potential by interfering ions within the solution, interfering analysis between these anions should be performed. Regarding the methods for determining the coefficient, fixed

interference method (FIM) is used to monitor the potential of a cell comprising an ion-selective electrode and a reference electrode with solutions of constant level of interfering ion, a_B, and varying activity of the primary ion, a_A. The potentiometric selectivity coefficient $\left(\log\left(K_{A,B}^{pot}\right)\right)$ can be calculated from the following equation [6]:

$$\log\left(K_{A,B}^{pot}\right) = \log\left(a_A\right) - \left(z_A / z_B\right)\log\left(a_B\right) \qquad (1)$$

where z_A and z_B are the charges of the primary and interfering ions respectively and should have the same signs. Table I lists the selectivity coefficient $\left(\log\left(K_{A,B}^{pot}\right)\right)$ of A=NO_2^- and B=Cl^- for -1, A=NO_3^- and B=Cl^- for -1.717, and A=NO_2^- and B=NO_3^- for -1.083, meaning that the interference can be ignored. Fig. 5 displays the drift characteristics of the EIS device with nitrogen PIII treated Sm_2O_3 sensing membrane in 10^{-4} M KCl, KNO_2 and KNO_3 solutions. From this figure, the sample exhibits a long-term stability for significantly low ion drift of chloride, nitrite and nitrate ions for 0.143, -5.78, and 1.95 mV/hr, respectively.

4. Conclusions

In this work, the anions of chloride (Cl^-), nitrite (NO_2^-), and nitrate (NO_3^-) ions were detected and interferingly analyzed by using the Sm_2O_3 sensing membrane with nitrogen PIII treatment. The nitrate ions with the largest ionic radius show the highest sensitivity of 56.19 mV/pNO_3. The superior anions sensitivity, selectivity and stability of the nitrogen incorporated Sm_2O_3 EIS sensor make the future biosensing application possible.

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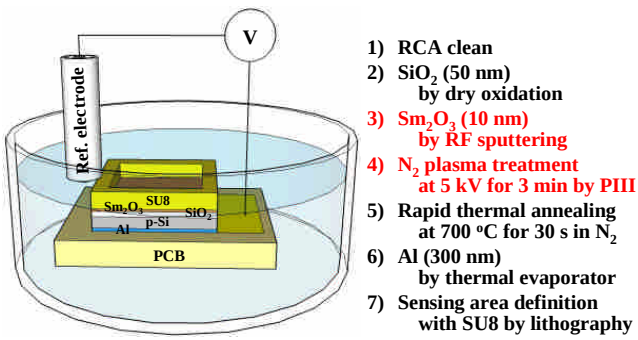

Fig. 1 The schematic structure and detail process flows of EIS sensor with nitrogen PIII treated Sm_2O_3 sensing membrane.

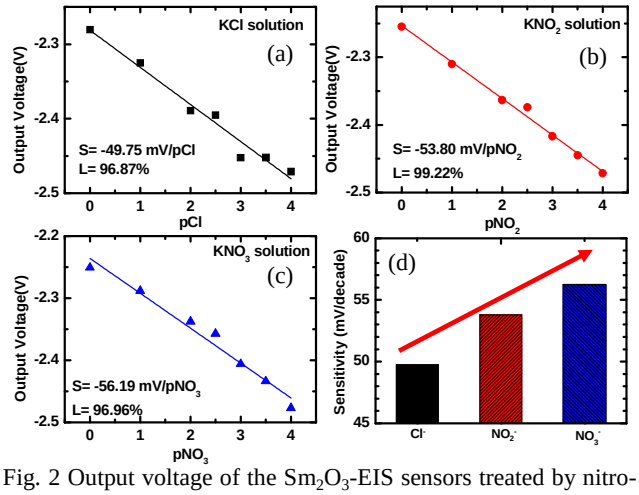

Fig. 2 Output voltage of the Sm_2O_3-EIS sensors treated by nitrogen PIII as a function of (a) pKCl, (b) pKNO_2 and (c) pKNO_3. (d) Summarized sensitivity of chloride, nitrite and nitrate ions.

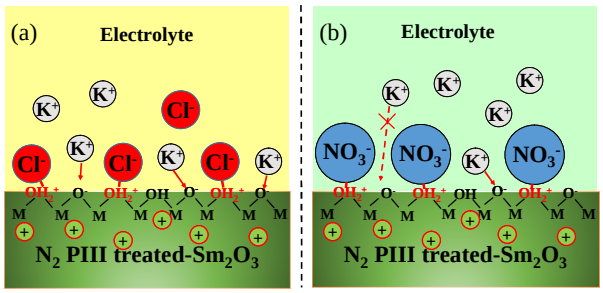

Fig. 3 Sensing mechanism of (a) chloride and (b) nitrate ions with Sm_2O_3-EIS sensors treated by nitrogen PIII.

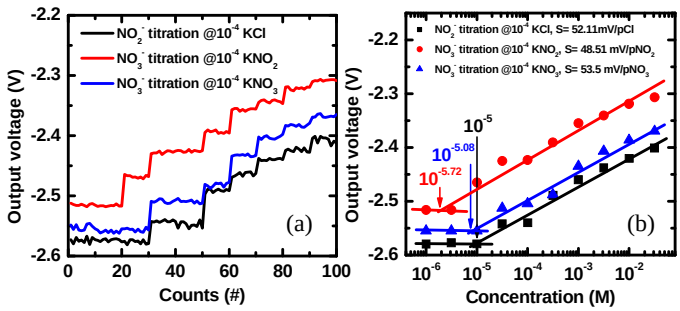

Fig. 4 (a) Responses of chloride, nitrite and nitrate ions in titration sequence and (b) output voltage versus chloride, nitrite and nitrate ions concentrations of Sm_2O_3-EIS sensors with nitrogen PIII treatment.

Table I Sensitivity coefficients of Sm_2O_3-EIS sensors treated by nitrogen PIII for chloride, nitrite and nitrate ions

Activity of primary ion, a_A	Level of interfering ion, a_B	Log($K_{A,B}$)
NO_2^- (10^{-5} M)	Cl^- (10^{-4} M)	-1
NO_3^- ($10^{-5.72}$ M)	Cl^- (10^{-4} M)	-1.717
NO_2^- ($10^{-5.08}$ M)	NO_3^- (10^{-4} M)	-1.083

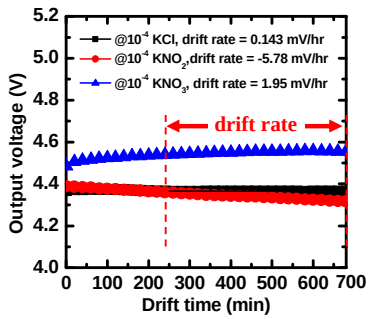

Fig. 5 Drift rate of Sm_2O_3-EIS sensors with nitrogen PIII treatment in 10^{-4} M KCl, KNO_2 and KNO_3 solutions.