High pH sensitivity and low concentration detection of urea/H_2O_2 by using IrO_x/HfO_x membrane in electrolyte-insulator-semiconductor structure

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Abstract

Iridium-oxide (IrO_x) on hafnium oxide (HfO_x) membrane in electrolyte-insulator-semiconductor (EIS) structure with high pH sensitivity of 72 mV/pH, low concentration of 1 nM urea and 0.5 pM H_2O_2 has been reported for the first time. Due to porous IrO_x and catalytic activity of both IrO_x and HfO_x membranes, a high pH sensitivity is obtained. In contact of H_2O_2, the Ir^0 changes to Ir^{4+} and Hf^{2+} changes to Hf^{4+} states, which are confirmed by X-ray photo-electron spectroscopy.

1. Introduction

First ion-sensitive field effect transistor (ISFET) with SiO_2 insulator for bio-chemical application was proposed by Bergveld in 1970 [1]. In present, the detection of ions and molecules in a bio-chemical environment plays an important role in chemical science and biotechnological application. In this article, we propose the EIS structure due to its some advantages like simple structure, label-free detection, fast pH response time, easy fabrication process and low cost [2]. Among various types of reported high-κ oxide materials [3-5], IrO_x on HfO_x is one of the most reliable metal-oxide materials to perform good sensing characteristics. The sensor performs high sensitivity as well as low concentration (0.5 pM) detection of H_2O_2 and 1 nM urea to identify some disease in analogy with acidity, kidney malfunction, indigestion and ulcers of human body in future.

2. Device fabrication

A 4" p-type Si (100) wafer was cleaned by standard Radio Corporation of America (RCA) process to remove the native oxide from the surface. Then 40 nm-thick SiO_2 layer was grown on Si wafer by dry oxidation process. Then 2 nm-thick HfO_x film was deposited on SiO_2 layer by using RF. sputtering process. Then 300 nm-thick Al was deposited as a backside contact of Si wafer by thermal evaporation. A sensing area of 3.24 mm² was defined by negative photo-resist (PR) SU8 using the photolithography process and fabricated on copper (Cu) printed circuit board (PCB) using Ag.

3. Results and discussions

Fig. 1 shows X-ray photo-electron spectroscopy (XPS) characteristics of Hf$4f_{7/2}$ ($4f_{5/2}$) at 16.8 eV (18.4 eV), which represents the hafnium in the HfO_x film formed a mixed valence of Hf^{2+} and Hf^{4+} The peak binding energy (BE) at 17.6 eV (19.3 eV) and 16.2 eV (17.9 eV) corresponds to Hf^{4+} from HfO_2 and Hf^{2+} from HfO [6]. In Fig. 2, the O*1s* spectrum has the peak energy at 530.6, 532.2 and 533.6 eV. [7]. Fig.3 shows the BE peak line of Ir$4f_{7/2}$ ($4f_{5/2}$) at 61.1 eV (64.1 eV) and 62.1 eV (65.1 eV) corresponds to metal Ir and IrO_2 (Ir^{4+}) respectively [8]. The C-V characteristics of HfO_x (Fig. 4) and IrO_x (Fig. 5) sensor is investigated from pH 2-10 at an optimized frequency 100 Hz. Fig. 6 shows the sensitivity and linearity comparison in between SiO_2, HfO_x and IrO_x membranes. The HfO_x sensor shows improved sensitivity (51 mV/pH) as well as good linearity (99.8%) than bare SiO_2 (35mV/pH and 94.1 %), whereas IrO_x membranes show the super-Nernstian response (72 mV/pH) and good linearity (99.9%) because of its porosity nature. The HfO_x sensor shows acceptable drift of 3.37 mV/hr (Fig. 7) as well as lower hysteresis of approximately 8 mV (Fig. 8). Fig. 9 indicates the reference voltage (V_{fb}) shift with different concentration of urea. During this measurement, we use 5 U urease enzyme to hydrolyze urea into ammonium (NH_4^+), CO_2 and OH^- ions. These OH^- ions increase the pH value of the electrolyte solutions; as a result the V_{fb} increases [9]. The limit of detection is 1 nM in a linear range of 10-500 nM. Fig. 10 shows the C-V characteristics of HfO_x sensor with and without H_2O_2. Time response behavior [Fig. 11] represents the reversible properties of the device. Fig. 12 shows the calibration curve HfO_x and IrO_x/HfO_x membranes with different concentration of H_2O_2. The V_{fb} gradually increases with increasing the H_2O_2 concentration due to increase of the oxidation state from Hf^0 to Hf^{4+} as well as the work function increases from 3.9 to 4.3 eV also electron affinity increases from 0.114 to 2 eV [10-11]. The limit of detection is 10 pM of HfO_x and 500 fM of IrO_x membrane. The reason to sense H_2O_2 is due to Ir^0 changing to Ir^{4+} and Hf^{2+} changing to Hf^{4+} oxidation states. On the other hand, pure SiO_2 membrane does not sense H_2O_2. Therefore, the catalytic activity of porous Ir on HfO_x membrane plays a role to sense H_2O_2. This sensor can be reused because of reversible properties.

4. Conclusions

The IrO_x/HfO_x/SiO_2/p-Si EIS structure has shown high pH sensitivity of 72 mV/pH, 1 nM urea and 0.5 pM H_2O_2 detection. This novel sensor is useful for health care unit in future due to its high potential sensing performance. In future, this can detect prostate/breast cancer biomarker.

Acknowledgements

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References

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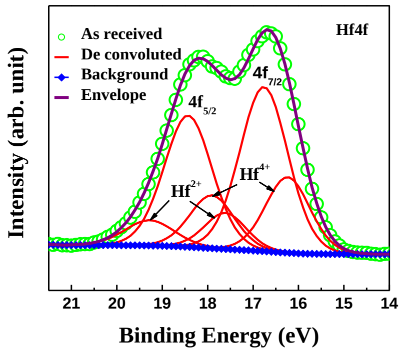

Fig. 1 XPS characteristic peaks of Hf*4f* state from HfO_x membrane on SiO_2/p-Si substrate with Hf^{2+} and Hf^{4+} states.

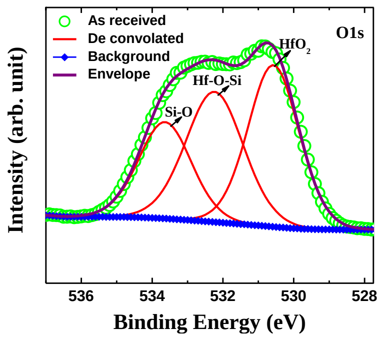

Fig. 2 XPS spectra of O*1s* from HfO_x membrane on SiO_2/p-Si substrate.

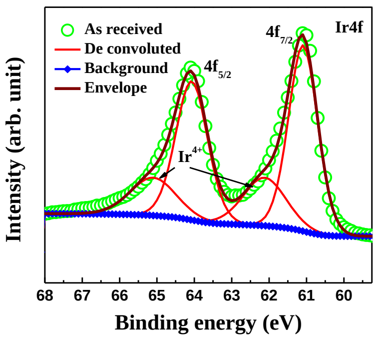

Fig. 3 *Ir4f* spectra from IrO_x membrane on SiO_2/p-Si substrate with Ir^0 and Ir^{4+} oxidation states.

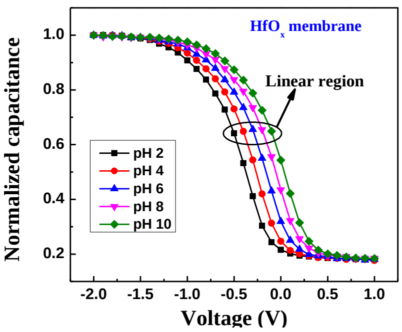

Fig. 5 C-V characteristics of 2 nm-thick HfO_x ($Ar:O_2$=20:5) membrane in EIS structure from pH 2-10.

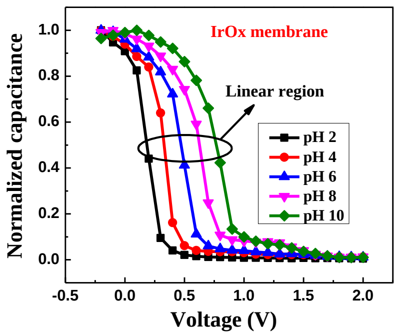

Fig. 4 C-V characteristics of 2 nm-thick IrO_x membranes in EIS structure from pH 2-10.

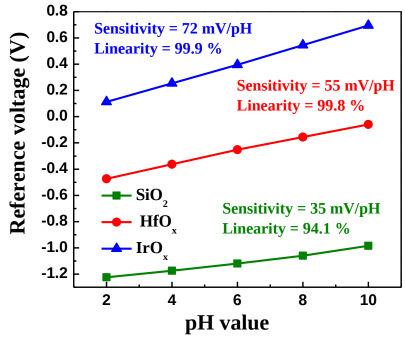

Fig. 6 Comparison of sensitivity and linearity behaviors in between SiO_2, IrO_x, and HfO_x membranes.

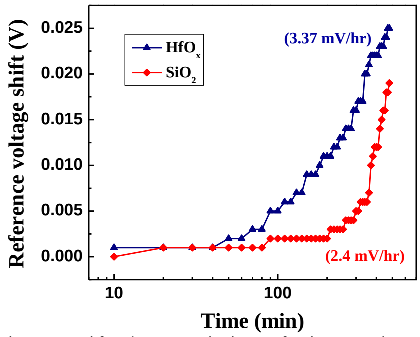

Fig. 7 Drift characteristics of SiO_2 and HfO_x stacked EIS sensor in pH 7 for 8 hours. Drift of IrO_x membrane is less than 5 mV.

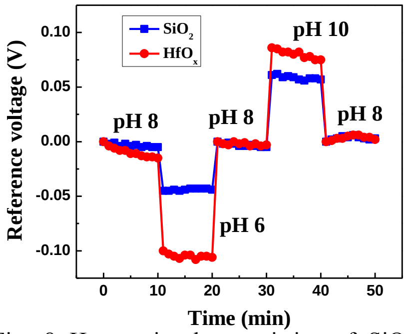

Fig. 8 Hysteresis characteristics of SiO_2 and HfO_x based EIS sensor of 10 cycles through pH 8-6-8-10-8 loop.

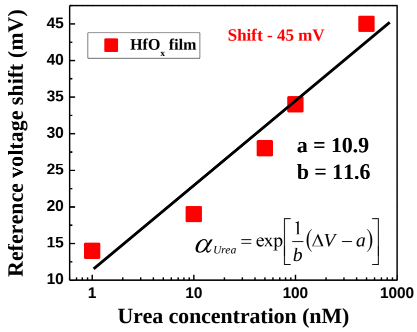

Fig. 9 Urea sensing with low concentration of 1 nM by using HfO_x membrane with different concentration of urea at 5 mL Tris buffer (pH7.4) solution.

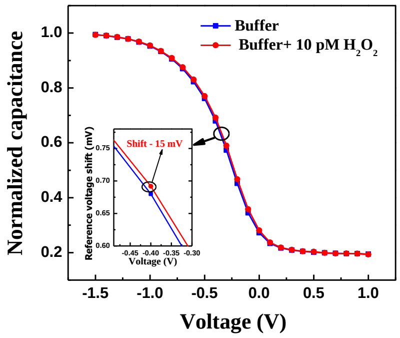

Fig. 10 C-V characteristic with PBS buffer and 10 pM H_2O_2 concentration at 5 mL PBS (pH 7) solution. Inset fig. shows the shift of H_2O_2 with respect to buffer solution.

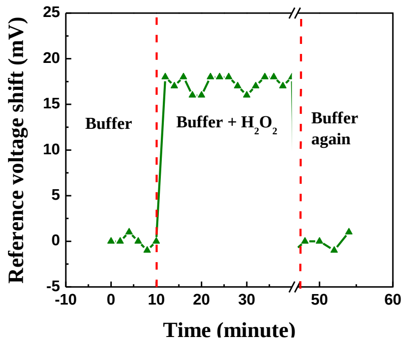

Fig. 11 Time response behavior of HfO_x based sensor in 10 pM H_2O_2 concentration at 5 mL PBS (pH 7) solution.

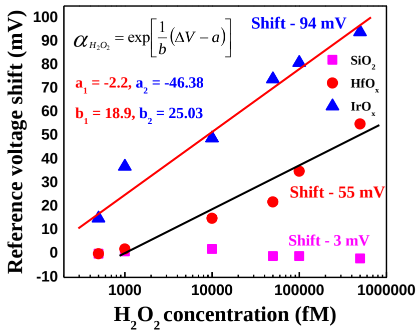

Fig. 12 V_{fb} shift with different H_2O_2 concentration of SiO_2, HfO_x and IrO_x membrane at 5 mL PBS (pH 7) solution (a = intercept, b = slope value).