High pH sensitivity and low concentration detection of urea/H$_2$O$_2$ 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$_2$O$_2$ has been reported for the first time. Due to porous IrO$_x$ and catalytic activity of both IrO$_x$ and HfO$_x$, high pH sensitivity and low concentration detection of urea/H$_2$O$_2$. In this article, we propose the EIS structure due to its some 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. Among various types of reported high-$\kappa$ 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$_2$O$_2$ and 1 nM urea to identify some disease in analogy with acidity, kidney malfunction, indigestion and ulcers of human body in future.

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-$\kappa$ 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$_2$O$_2$ 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$_2$ film was deposited on SiO$_2$ layer 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 mm$^2$ 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 HfIr$_{5.2}$/H$_2$O$_2$$(4f_{5/2})$ at 16.8 eV (18.4 eV), which represents the hafnium in the HfO$_2$ film formed a mixed valence of Hf$^{4+}$ and Hf$^{5+}$. The peak binding energy (BE) at 17.6 eV (19.3 eV) and 16.2 eV (17.9 eV) corresponds to Hf$^{4+}$ from HfO$_2$ and Hf$^{5+}$ from HfO$_x$ [6]. In Fig. 2, the O1s spectrum has the peak energy at 530.6, 532.2 and 533.6 eV. [7]. Fig. 3 shows the BE peak line of IrIr$_{4.2}$/H$_2$O$_2$$(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$_0$) 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$_2$O$_2$. 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$_2$O$_2$. The V$_{fb}$ gradually increases with increasing the H$_2$O$_2$ concentration due to increase of the oxidation state from Hf$^{4+}$ to Hf$^{5+}$ 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 H$_2$O$_2$ and 500 pM of IrO$_x$ membrane. The reason to sense H$_2$O$_2$ is due to Ir$^{4+}$ changing to Ir$^{3+}$ and Hf$^{5+}$ changing to Hf$^{4+}$ oxidation states. On the other hand, pure SiO$_2$ membrane does not sense H$_2$O$_2$. Therefore, the catalytic activity of porous Ir on HfO$_x$ membrane plays a role to sense H$_2$O$_2$. 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$_2$O$_2$ 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.

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References

Fig. 1 XPS characteristic peaks of Hf4f state from HfOx membrane on SiO2/p-Si substrate with Hf6+ and Hf4+ states.

Fig. 2 XPS spectra of O1s from HfOx membrane on SiO2/p-Si substrate.

Fig. 3 Ir4f spectra from IrOx membrane on SiO2/p-Si substrate with Ir5+ and Ir4+ oxidation states.

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

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

Fig. 6 Comparison of sensitivity and linearity behaviors in between SiO2, IrOx, and HfOx membranes.

Fig. 7 Drift characteristics of SiO2 and HfOx stacked EIS sensor in pH 7 for 8 hours. Drift of IrOx membrane is less than 5 mV.

Fig. 8 Hysteresis characteristics of SiO2 and HfOx 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 HfOx membrane with different concentration of urea at 5 mL Tris buffer (pH 7.4) solution.

Fig. 10 C-V characteristic with PBS buffer and 10 pM H2O2 concentration at 5 mL PBS (pH 7) solution. Inset fig. shows the shift of H2O2 with respect to buffer solution.

Fig. 11 Time response behavior of H2O2 based sensor in 10 pM H2O2 concentration at 5 mL PBS (pH 7) solution.

Fig. 12 Vb shift with different H2O2 concentration of SiO2, HfOx, and IrOx membrane at 5 mL PBS (pH 7) solution (a = intercept, b = slope value).