A glucose biosensor based on pH-sensitive Sm$_2$TiO$_5$

electrolyte-insulator-semiconductor

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1. Introduction

High-k materials, including ZrO$_2$, HfO$_2$, Y$_2$O$_3$, Pr$_2$O$_3$, and Gd$_2$O$_3$ [1-5], have recently been proposed as pH-sensitive membranes due to their good sensing performance in electrolyte-insulator-semiconductor (EIS) devices. In recent years, the Sm$_2$O$_5$ films have been considered as potential gate insulators because of their reasonably high relative permittivity (15-30), good thermal stability, and large conduction band offset (> 2 eV) [6]. In addition, the incorporation of TiO$_2$ or Ti into the lanthanide oxide dielectrics has attracted a considerable amount of attention as a method to achieve a high-k gate oxide material with excellent electrical properties for CMOS applications [7-8]. Jeon et al. showed that a PrTiO$_3$ film deposited on the Si substrate exhibited a lower reactivity to water, thinner interfacial layer, higher capacitance value and lower leakage current [9].

2. Experiments

A ~40 nm Sm$_2$TiO$_5$ film was deposited on the Si substrate through reactive co-sputtering from a samarium target and a titanium target in diluted O$_2$. The samples were annealed in O$_2$ ambient by rapid thermal annealing (RTA) at various temperatures to form Sm$_2$TiO$_5$. The sensing membrane size was defined through photolithographic processing under a photosensitive epoxy that behaved as an anti-acid polymer. A handmade epoxy package was employed to encapsulate the EIS structure and the Cu line. A thin glucose oxidase-containing alginate gel was employed to encapsulate the EIS structure and the Cu line.

3. Result and Discussions

In the as-deposited sample (without, W/O), only small Sm$_2$TiO$_5$ (216) peak was observed in the XRD pattern (Fig. 1), suggesting a crystal Nature for this sample. The film annealed at 700 °C exhibited one weak (112) peak, while the one annealed at 800 °C displayed one strong (216) peak, and two weak (020) and (123) peaks. This finding suggests that the Ti atom cannot obtain enough kinetic energy reaction with Sm$_2$O$_5$ to form a better stoichiometry Sm$_2$TiO$_5$ structure during PDA temperature less than 800 °C. In addition, a strong (302) peak and two weak (123) and (216) peaks appeared in the 2θ plot for the 900 °C annealed sample, indicative of a polycrystalline structure.

Fig. 2 shows the AES depth profiles of Sm$_2$TiO$_5$ film annealed at 900 °C. The composition of the film annealed at 900 °C showed a Sm$_2$TiO$_5$ compound with a Sm:Ti:O ratio of approximation 2:1:5.

Fig. 3 shows the pH-dependence of the reference voltage of a Sm$_2$TiO$_5$ EIS device annealed at 900 °C. During a cycle from pH 2 to 12, the reference voltage for the Sm$_2$TiO$_5$ sensing film annealed at 900 °C shifted by ~605 mV; i.e., the average pH response of this Sm$_2$TiO$_5$ film was about 60.5 mV/pH. The inset to Fig. 3 shows the pH-dependence of one group of C-V curves for the EIS structure incorporating a Sm$_2$TiO$_5$ sensing film annealed at 900 °C.

Fig. 4 reveals that the hysteresis voltage of the EIS device with a Sm$_2$TiO$_5$ sensing film performed at the PDA of 900 °C had hysteresis voltages of 2.72 mV in the pH loop 7→4→7→10→7. Fig. 5 shows the drift characteristics of EIS devices with Sm$_2$TiO$_5$ sensing membranes annealed at various RTA temperatures, measured in solutions of pH 7. The degradation slope of the gate voltage variation reflects the EIS stability. The Sm$_2$TiO$_5$ EIS capacitor performed at 900 °C exhibited the best long-term stability (slope=1.15 mV/h); in contrast, the EIS diode without PDA treatment featured a serious drift of 6.52 mV/h. The lower drift effect after annealing at 900 °C resulted from the low density of crystal defects.

The biosensor measured the glucose concentration by detecting the variation in pH caused by the generation of hydrogen ions by the dissociation of glucose acid. Glucose oxidase typically hydrolyzes glucose according to the equations shown as follows:

\[ \beta \rightarrow 2 (\text{glucose} + H_2O \rightarrow \text{gluconic acid} + \text{H}^+ + \text{H}_2O) \]

Fig. 6 presents the shift in the reference voltage of the enzymatic EIS-based glucose biosensor incorporating a Sm$_2$TiO$_5$ sensing film (RTA at 900 °C) as a function of the glucose concentration. The sensitivity of this biosensor device, in terms of its response to glucose concentrations between 2 and 8 mM, was 7.71 mV/mM.

4. Conclusion

The electrolyte-insulator-semiconductor (EIS) device incorporating a high-k Sm$_2$TiO$_5$ sensing film annealed at 900 °C exhibited good sensing characteristics, including a high sensitivity (60.5 mV/pH in solutions from pH 2 to 12), a small hysteresis voltage (2.72 mV in the pH loop 7→4→7→10→7), and a low drift rate (1.15 mV/h in the buffer solution at pH 7). In addition, the enzymatic EIS-based glucose biosensor incorporating a high-k Sm$_2$TiO$_5$ sensing membrane annealed at 900 °C allowed the potentiometric analysis of glucose with a sensitivity of 7.71 mV/mM.

References

Fig. 1. XRD analysis of Sm$_2$TiO$_5$ film for as-deposited and annealed samples.

Fig. 2. AES depth profiles of Sm$_2$TiO$_5$ film annealed at 900 °C.

Fig. 3. C–V curves response of Sm$_2$TiO$_5$ dielectrics after PDA at 900 °C when inserted into solutions with pH values from 2 to 12. The inset shows reference voltage of an Sm$_2$TiO$_5$ sensing membrane annealed at 900 °C as a function of pH.

Fig. 4. Hysteresis voltages of EIS devices with Sm$_2$TiO$_5$ sensing membranes annealed at various temperatures during the pH loops of 7→4→7→10→7.

Fig. 5. Drift rates of EIS capacitors with Sm$_2$TiO$_5$ sensing membranes after RTA at different temperatures.

Fig. 6. Reference voltage of the enzymatic EIS-based glucose biosensor with a Sm$_2$TiO$_5$ sensing film (RTA at 900 °C) plotted as a function of the glucose concentration.