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A glucose biosensor based on pH-sensitive Sm_2TiO_5 electrolyte-insulator-semiconductor

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1. Introduction

High-k materials, including ZrO_2, HfO_2, Y_2O_3, Pr_2O_3, and Gd_2O_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_2O_3 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 $PrTi_xO_y$ 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_2TiO_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_2TiO_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 subsequently shaped according to the zone of the Sm_2TiO_5 sensing membrane using a borer; it was then attached to the surface of the sensing membrane.

3. Result and Discussions

In the as-deposited sample (without, W/O), only small Sm_2TiO_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_2O_3 to form a better stoichiometry Sm_2TiO_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_2TiO_5 film annealed at 900 °C. The composition of the film annealed at 900 °C showed a Sm_2TiO_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_2TiO_5 EIS device annealed at 900 °C. During a cycle from pH 2 to 12, the reference voltage for the Sm_2TiO_5 sensing film annealed at 900 °C shifted by ~605 mV; i.e., the average pH response of this Sm_2TiO_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_2TiO_5 sensing film annealed at 900 °C.

Fig. 4 reveals that the hysteresis voltage of the EIS device with a Sm_2TiO_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_2TiO_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_2TiO_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:

$$\beta-D-\text{glucose}+O_2+H_2O\xrightarrow{\text{glucose oxidase}}D-\text{glucono}-\delta-\text{lactone}+H_2O_2$$

$$D-\text{glucono}-\delta-\text{lactone}\longrightarrow D-\text{gluconoate}+H^+$$

Fig. 6 presents the shift in the reference voltage of the enzymatic EIS-based glucose biosensor incorporating a Sm_2TiO_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_2TiO_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_2TiO_5 sensing membrane annealed at 900 °C allowed the potentiometric analysis of glucose with a sensitivity of 7.71 mV/mM.

References

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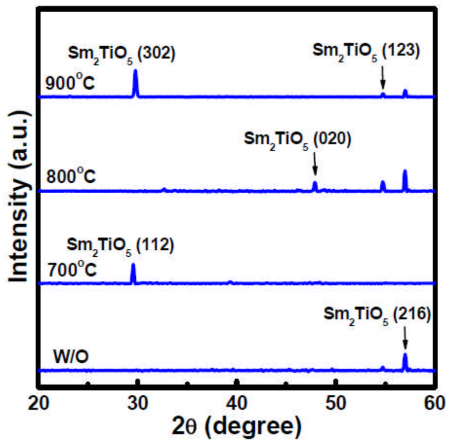

Fig. 1. XRD analysis of Sm_2TiO_5 film for as-deposited and annealed samples.

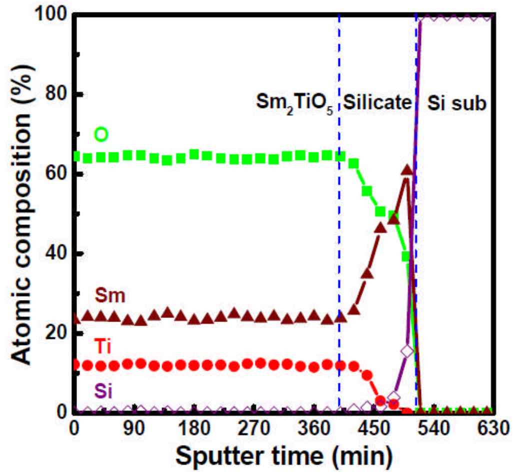

Fig. 2. AES depth profiles of Sm_2TiO_5 film annealed at 900 °C.

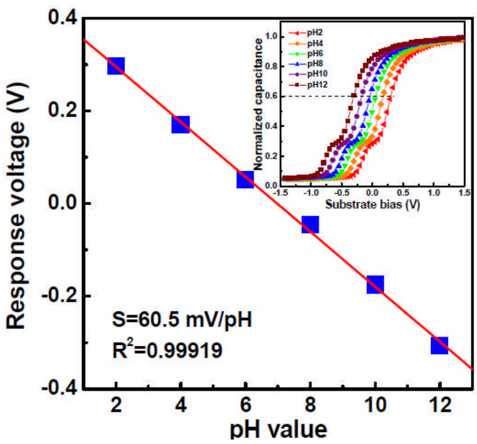

Fig. 3. C–V curves response of Sm_2TiO_5 dielectrics after PDA at 900 °C when inserted into solutions with pH values from 2 to 12. The inset shows reference voltage of an Sm_2TiO_5 sensing membrane annealed at 900 °C as a function of pH.

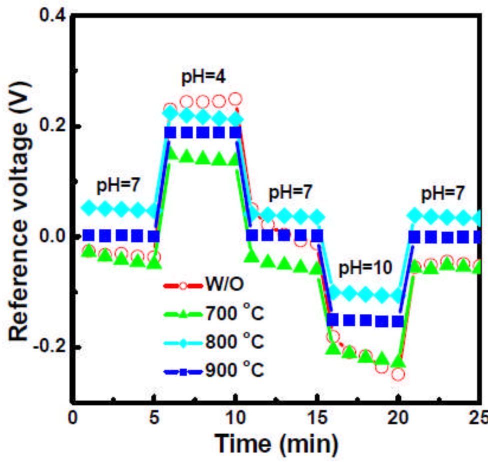

Fig. 4. Hysteresis voltages of EIS devices with Sm_2TiO_5 sensing membranes annealed at various temperatures during the pH loops of 7→4→7→10→7.

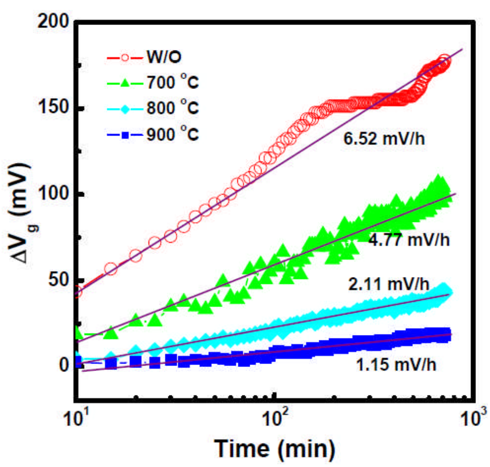

Fig. 5. Drift rates of EIS capacitors with Sm_2TiO_5 sensing membranes after RTA at different temperatures.

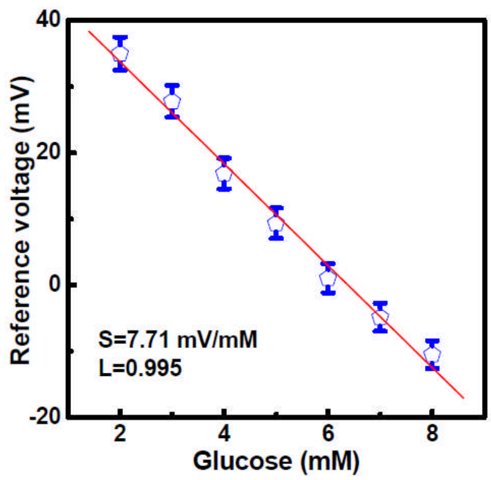

Fig. 6. Reference voltage of the enzymatic EIS-based glucose biosensor with a Sm_2TiO_5 sensing film (RTA at 900 °C) plotted as a function of the glucose concentration.