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Novel Reference Electrode-Insulator-Nitride-Oxide-Semiconductor (RINOS) Structure with Sm_2O_3 Sensing Membrane for pH-sensor Application

Hui-Yu Shih, Jer-Chyi Wang*, Tseng-Fu Lu, Chao-Sung Lai, Chyuan-Haur Kao and Tung-Ming Pan
Department of Electronic Engineering, Chang Gung University,
259 Wen-Hwa 1st Road, Kwei-Shan Tao-Yuan, Taiwan, 333, R.O.C.
Phone: +886-3-2118800 ext.5784 E-mail: jcwang@mail.cgu.edu.tw

Introduction

Concentration of hydrogen ion (H^+) is a very important indicator for human diseases prediction. To this end of H^+ detection, the ion sensitive field-effect transistors (ISFETs) proposed by Bergveld in 1970 have been attracted recently because of their great potential for label-free, real-time, and in vivo sensors [1]. In past years, for higher pH-sensitivity and better stability, most of metal oxide films as the ion-sensitive insulators were proposed to detect the hydrogen ion concentration, such as Si_3N_4, Al_2O_3, Ta_2O_5, HfO_2, and other kinds of the high-k materials. However, the small hydrogen ion fluctuation caused by the hydrolysis reaction of bio-molecules is difficult to be measured because the theoretical maximum sensitivity based on Nernstian equation is only 59 mV/pH. For precise detection on small pH variation of micro-fluids of human body, higher output sensing signal of sensors is important and necessary. Therefore, many structures to obtain higher sensing pH-responses were proposed, such as suspended-gate field-effect transistor (SGFET) [2], charge coupled device (CCD) [3], metal-insulator-gap-insulator-semiconductor [4], and nanocrystals embedded device [5].

In this article, a novel RINOS device with ONO (oxide- nitride-oxide) structure was proposed with the Sm_2O_3 as the sensing membrane. Through voltage stress, the great improvement on the pH-sensitivity compared with the fresh sample is obtained. To study the trapping effect, the electrical characteristics were presented based on the metal-insulator-nitride-oxide-semiconductor (MINOS) structure. For retention enhancement, we added another SiO_2 as the blocking layer on Sm_2O_3.

Experimental

In this work, the RINOS device with $Sm_2O_3/Si_3N_4/SiO_2$/Si/Al structure was fabricated and the processes were shown in Fig. 1(a). Before 3 nm SiO_2 was thermally grown in dry oxidation, the p-Si wafer was cleaned with the standard RCA process. Then, the 10 nm Si_3N_4 as the charge trapping layer was deposited by PECVD. After that, the 10 nm Sm_2O_3 sensing film was deposited by rf sputtering. Finally, 300 nm Al film was evaporated for backside contact electrode. To define the sensing area of RINOS for pH detection, a negative-photoresist (SU8-2005, MicroChem) was used. After assembling the RINOS device on the Cu line of the printed circuit board (PCB) by silver gel, a hand-made epoxy package was used to encapsulate. The cross-section view of the RINOS structure was shown in Fig. 1(b). For charge trapping phenomenon investigation and retention study, the MINOS structure as shown in Fig. 1(c) and extra SiO_2 blocking layer on the Sm_2O_3 film were also both fabricated. To extract the H^+ sensing properties, the C-V curves of RINOS structures were measured in standard pH buffer solutions through the Ag/AgCl reference electrode by using HP4284A high precision LCR meter. The ac signal frequency was chosen at 100 Hz for RINOS structure and 100 kHz for MINOS structure. For getting the steady pH responses, all samples were immersed in the reversed osmosis (RO) water for 12 h before measurement.

Results and Discussion

Figure 2 exhibits the C-V curves by hysteresis sweeping of MINOS structure at different sweeping ranges. The memory window increases with increasing the sweeping voltage. Follow the results of hysteresis measurement, it indicated that the dominated behavior is substrate injection. Figure 3 shows the program speed of the MINOS structure. It shows obviously that the higher program speed could be achieved for device with large program voltage. To calculate the pH-sensitivity, the C-V curves of RINOS devices were measured in buffer solutions (Merck Inc.) from pH 2 to pH 12 as shown in Fig. 4. The shift of C-V curves with the change of pH value was observed, which is due to the ionization of the surface hydroxyl groups by hydrogen ions or hydroxyl ions. The pH-sensitivity was obtained by linear fitting of the voltages at $0.5C_{max}$ of C-V curves as illustrated insert Fig. 4. The actual pH values of buffer solutions were measured by pH meter before and after measurement for pH-sensitivity calculation. The sensitivity of the RINOS structure in this work is 45.58 mV/pH. The C–V curves in pH 7 at different stress voltages were shown in Fig. 5. We can find that the more stress voltage we gave and the more flat-band voltage shift was obtained as shown in Fig. 6. Figure 7 represents the normalized C-V curves measured in pH 4 to pH 10 buffer solutions of the $Sm_2O_3/Si_3N_4/SiO_2$/Si/Al RINOS device with and without voltage stress. Comparing with the device without stress, the device with large voltage stress (15 V) exhibits obvious C-V shift with pH changing from pH 4 to pH 10 and the flat-band voltages were shifted to higher voltage. Figure 8 shows the effective pH-sensitivity improvement with different stress voltages and times. The total stress time is from 1μs to 10s and the stress voltage is from 5 V to 13 V. The pH-sensitivity was obtained by linear fitting of the voltages at $0.5C_{max}$ of C-V curves in buffer solutions at pH 4, 7 and 10. The delta sensitivity (ΔS) was calculated according to the Eq. (1) as shown below:

$$\Delta S = S_{(stress)} - S_{(fresh)} \quad (1)$$

The $S_{(stress)}$ is the pH-sensitivity of device after stressing and the $S_{(fresh)}$ is the pH-sensitivity of device without stressing. As the results shown in the Fig. 8, with larger voltage stress, the higher delta sensitivity could be obtained. The maximum enhancement of pH-sensitivity is about 40 mV/pH at 15 V after 10s stress. In pH-sensitivity retention test, the sensitivity decreases very fast which means that the data retention is very poor. To enhance the retention property, the extra 30 nm SiO_2 film as the blocking layer was added on the Sm_2O_3. The higher band offset of SiO_2 than Sm_2O_3 could be benefit to keep the sensitivity after stress. Fig. 9 shows the pH-sensitivity variation of the RINOS structure with and without the SiO_2 blocking layer, respectively. After 10s stress, it clearly shows that the device with the SiO_2 blocking layer has less pH-sensitivity decrease than the control one. In our opinion on this phenomenon, the charge storage in the charge trapping layer and the surface of the sensing membrane both could happen and influence the surface site binding as illustrated in Fig. 10.

Conclusions

In this paper, we proposed a novel programmable RINOS structure for pH sensing. With voltage stress, the sensitivity of this RINOS device will get the effective improvement in the H^+ detection. The maximum pH-sensitivity enhancement of 40 mV/pH is achieved under 15 V stress for 10s. The higher pH-sensitivity of this device structure provides the possibility for the small pH fluctuation detection in bio-sensor applications.

References

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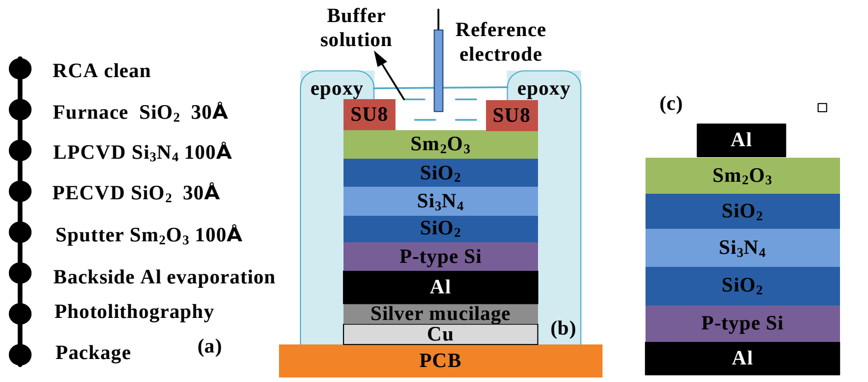

Fig. 1 (a) The process flow of the $Sm_2O_3/Si_3N_4/SiO_2$/Si/Al RINOS structure and the schematic of the cross-section of the (b) RINOS and (c) MINOS structures.

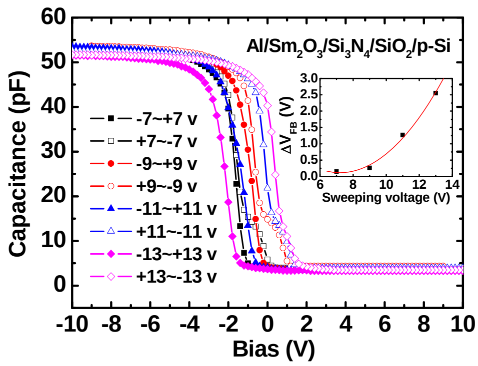

Fig. 2 The hysteresis memory window of $Al/Sm_2O_3/Si_3N_4/SiO_2$/p-Si MINOS structure. The inset shows ΔV_{FB} on sweeping voltage.

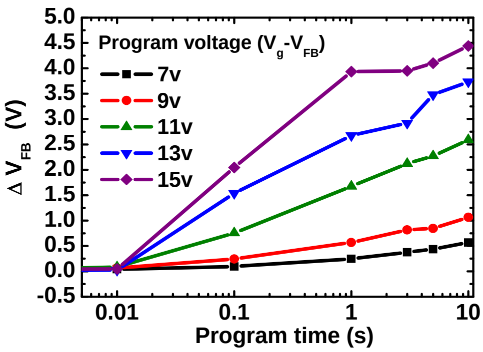

Fig. 3 The program speed of $Al/Sm_2O_3/Si_3N_4/SiO_2$/p-Si MINOS structure.

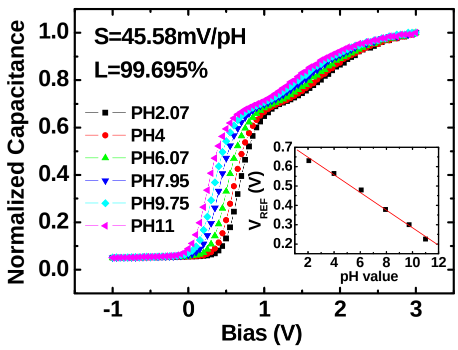

Fig. 4 The sensitivity of $Sm_2O_3/Si_3N_4/SiO_2$/Si/Al RINOS structure. The inset shows the linearly of 99.695%.

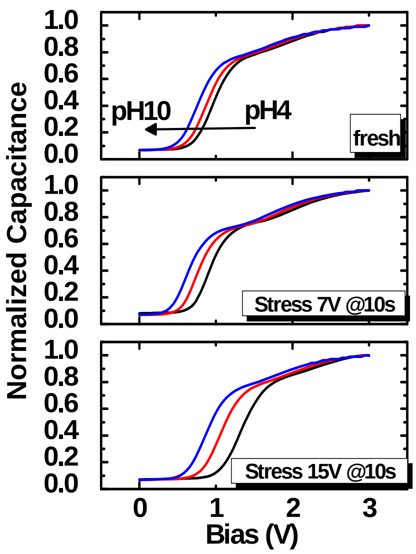

Fig. 7 Normalized C-V curves of the $Sm_2O_3/Si_3N_4/SiO_2$/Si/Al RINOS structures measured from pH 4 to pH 10 buffer solutions (a) without stress, (b) with 7 V stress for 10s, and (c) with 15 V stress for 10s.

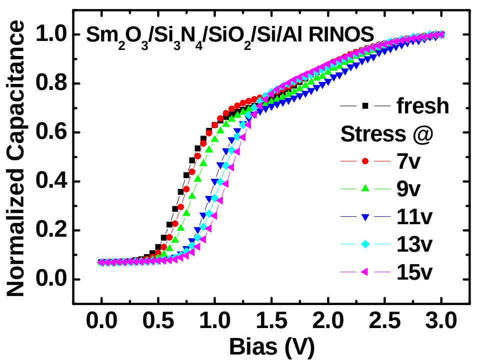

Fig. 5 The C-V curves shift after different voltage stress for 10s of $Sm_2O_3/Si_3N_4/SiO_2$/Si/Al RINOS structure.

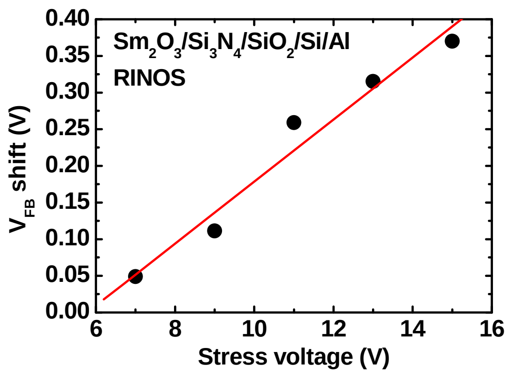

Fig. 6 The flat band voltage shift under different voltage stress extracted from the C-V curves in Fig. 5.

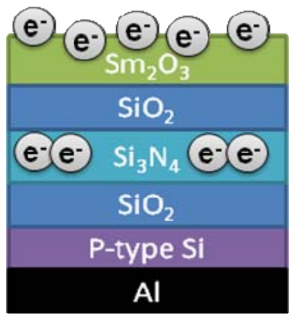

Fig. 10 The sensitivity improvement mechanism of the RINOS structure with electron programming into the storage nitride layer and the surface of Sm_2O_3 sensing membrane.

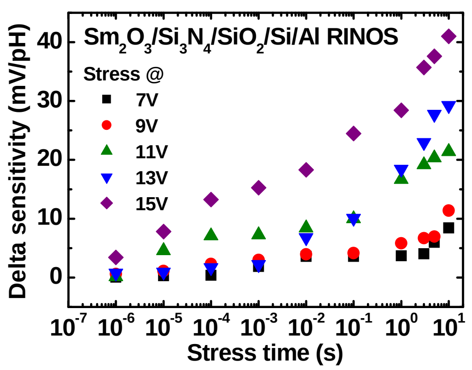

Fig. 8 The pH-sensitivity enhancement of $Sm_2O_3/Si_3N_4/SiO_2$/Si/Al RINOS structure stressed at 7 to 15 V for 1μs to 10s.

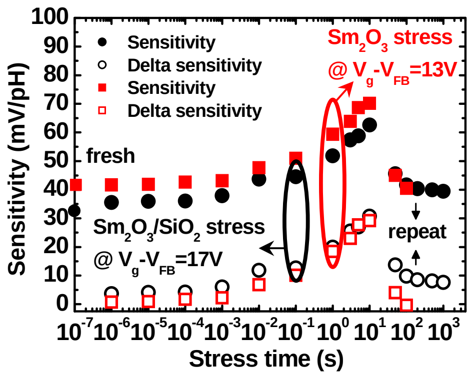

Fig. 9 The retention enhancement of the RINOS structures with and without SiO_2 blocking layer.