Extended Abstracts of the 2005 International Conference on Solid State Devices and Materials, Kobe, 2005, pp.80-81

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Thickness Effects on pH Response of HfO_2 Sensing Dielectric Improved by Rapid Thermal Annealing

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1. Introduction

We firstly proposed HfO_2 and HfON as sensing membranes for Ion-Sensitive Field-Effect Transistors (ISFETs) application for the advantages, such as high dielectric constant, large band gap and thermal stability in contact with silicon [1]. ISFET could be fabricated by VLSI technology with the advantages of small size, low cost, high input impedance, low output impedance and rapid response over conventional ion selective electrode [2-3]. Some high *k* materials such as Si_3N_4, Al_2O_3, Ta_2O_5 had been under intense investigation for hydrogen ion sensing material more than 15 years [4-6]. In this work, HfO_2 was directly deposited on silicon as sensing dielectric was first proposed to replace HfO_2/SiO_2 stacked structure [1]. Thickness effects on pH response of HfO_2 sensing dielectric were improved by rapid thermal annealing (RTA), including better sensitivity and lower drift.

2. Experiment

The pH sensing properties of HfO_2 dielectrics were all extracted by capacitance-voltage (C-V) curves of Electrolyte-Insulator- Semiconductor (EIS) structures. All EIS samples were separated into three parts for systematic study. P-type (100) Si wafers were used to grow silicon dioxide to the thickness of 500Å by thermal oxidation at 950°C after standard RCA cleaning. Then, a HfO_2 layer was deposited on SiO_2 by sputtering. Second group was HfO_2 layer deposited directly on silicon as sensing dielectric. The third one was HfO_2 sensing dielectrics deposition followed a RTA annealing treatment at 500, 700, 900°C, respectively. The thickness of HfO_2 layers were modified by deposition time in reactive r.f. sputtering with power, 150W. The Ar/O_2 mixture ratio was 20/5 and process pressure was controlled at 2mTorr. The process flows of all groups were summarized as shown in Fig. 1. A photosensitive epoxy, SU8, was used to define sensing area. The EIS structure was schematic in Fig. 2.

C-V curves for various pH buffer solutions of *Merck Inc.* were measured through Ag/AgCl reference electrode by HP4284A. All setups were shielded in black box. The a.c. signal frequency was 100Hz. In order to stabilize the surface reaction, all EIS samples were immersed in the reversed osmosis (R.O.) water for 12 hours. The flatband voltage drifts between two hours immersion in pH4 buffer were used to estimate the pH sensing stability of HfO_2.

3. Results and Discussions

Single HfO_2 sensing dielectric for pH response

The typical C-V curves of HfO_2/SiO_2 stacked EIS were shown in Fig. 3. The C-V curves were shifted to positive bias as increasing hydrogen ion concentration. Flatband voltages (V_{FB}) in each pH solution were extracted and shown in Fig. 4 (a) and (b). The sensitivity was defined as equation (1):

$$Sensitivity = \Delta V_{FB} / \Delta pH \qquad (1)$$

The calculated sensitivity of HfO_2/SiO_2 stacked EIS and HfO_2 EIS was 50.48mV/pH and 49.18mV/pH, respectively. HfO_2/SiO_2 stacked layer can be fully replaced by HfO_2 single layer in EIS structure. This performance of HfO_2 EIS is also comparable to other applied ion sensing material, such as Ta_2O_5 and Al_2O_3 [7].

The thickness limitation in HfO_2 EIS

The 10nm thick HfO_2 layer was verified by TEM as shown in Fig. 5. Figure 6 shows the extracted sensitivity and voltage drift of HfO_2 layer with thickness from 4 to 30nm. The highest sensitivity 50.48mV/pH appeared in 30nm thick, which is supposed due to its minimum drift [8]. However sensitivity was decreased to 45.23mV/pH when thickness of HfO_2 was down to 4nm.

Annealing time and temperature effect on sensitivity

Annealing time effects at 500°C on the sensitivity improvement for all samples were shown in Fig. 7. The delta sensitivity (ΔS) was defined as equation (2):

$$\Delta S = Sensitivity_{(annealing\ temp.)} - Sensitivity_{(without\ annealing)} \qquad (1)$$

ΔS were saturated to 8~10.5mV/pH in all annealing time. The thermal energy transfers to HfO_2 thin film was saturated around 1 min at 500°C. For the samples with thickness of 6nm annealing at 500°C, annealing time effects on sensitivity and drift were shown in Fig. 8. RTA annealing for 1 minute at 500°C is enough to improve sensitivity and voltage drift. Moreover, RTA annealing temperature effect for sensitivity was shown in Fig. 9. The sensitivity of thick HfO_2 layer would be increased to the near ideal case (59.2mV) by annealing at 500°C and higher temperature. For thinner HfO_2 layer, annealing at higher temperature improved sensitivity to near ideal case. ΔS of thicker HfO_2 would be easily saturated than thinner HfO_2. In Fig. 10, all sensitivities of 6nm HfO_2 EIS at 500, 700 and 900°C annealing was increased toward ideal case and the corresponding drift decreased to 10mV. HfO_2 of 6nm thick annealed at 900°C could obtain the better sensitivity and lower drift.

4. Conclusions

A systematic study on HfO_2 sensing dielectric directly deposited on silicon was firstly proposed. The sensitivity of HfO_2 EIS with 30nm thick was 50.48mV/pH. The ion sensing performance of HfO_2 EIS, such as sensitivity and flatband voltage drift were both improved by RTA treatment. The verified minimum thickness for HfO_2 sensing dielectric was 4nm.

Acknowledgement

This work was supported by the National Science Council under the contract of NSC 93-2215-E-182-002.

References

[1] C.S. Lai, et al., IEEE ICSE Proc. (2004) 569
[2] T. Mastsuo, et al., Sens. & Actu. 1 (1981) 77
[3] J.C. Chou, et al., Jpn. J. Appl. Phys. 41 (2002) 5941
[4] B.D. Liu, et. al., Int. J. Electron. 67 (1) (1989) 59
[5] L. Bousse, et al., Sens. and Actu. B2 (1990) 103
[6] A.S. Poghossian, Sens. and Actu. B7 (1992) 367
[7] J.C. Chou, et al., Sens and Actu. B66 (2000) 367
[8] C.S. Lai, et al., INFOS Proc. (2005)

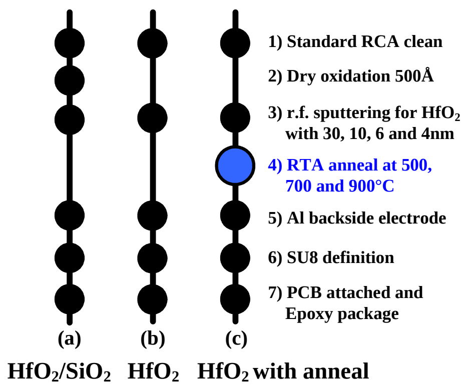

Fig. 1 The process flow of (a) HfO_2/SiO_2 EIS, (b) HfO_2 EIS, (c) HfO2 EIS with annealing.

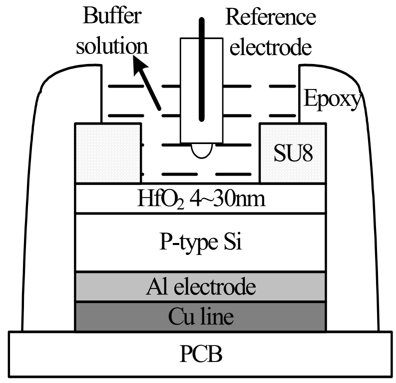

Fig. 2 The schematic cross section structure of HfO_2 EIS including reference electrode.

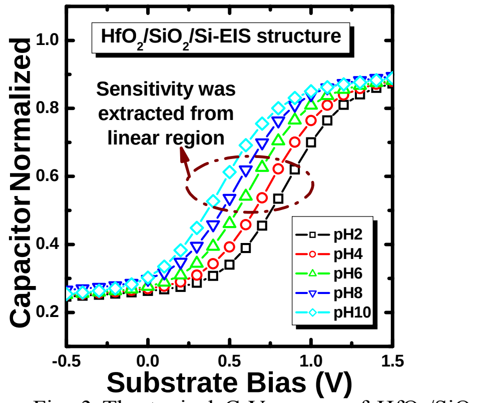

Fig. 3 The typical C-V curves of HfO2/SiO2 EIS structure in different pH buffer solution.

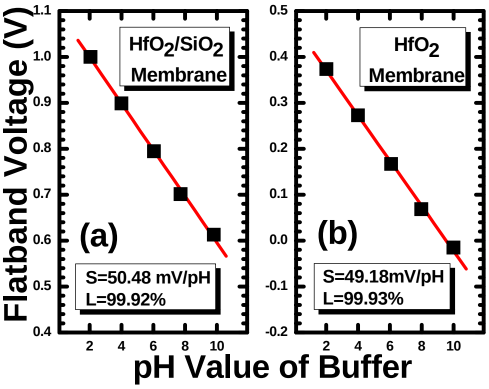

Fig. 4 Sensitivity and fitting linearity extracted from V_{FB} in different pH buffer solution of (a) HfO_2/SiO_2 EIS, (b) HfO_2 EIS. Both of them were with the sensitivity about 50mV/pH.

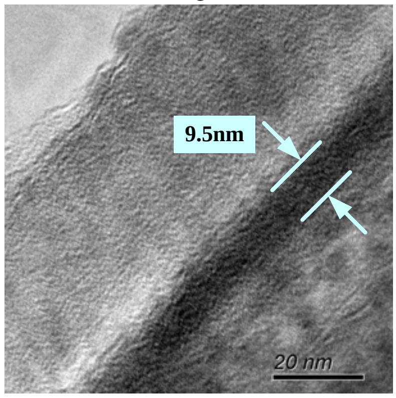

Fig. 5 The thickness of HfO2 layer deposited on Si was 9.5nm verified by TEM picture. The uniformity of HfO2 layer was good.

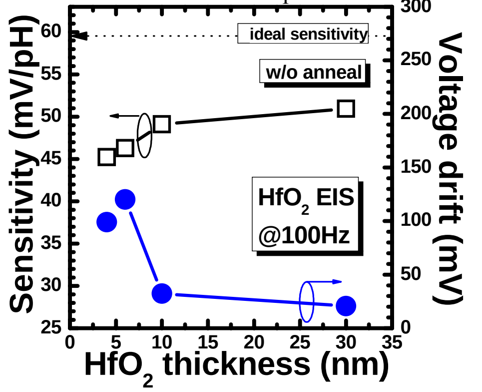

Fig. 6 The Sensitivity and flatband voltage drift distribution with thickness of HfO2 EIS. The highest sensitivity is 50.94mV/pH in HfO2 with 30nm thick.

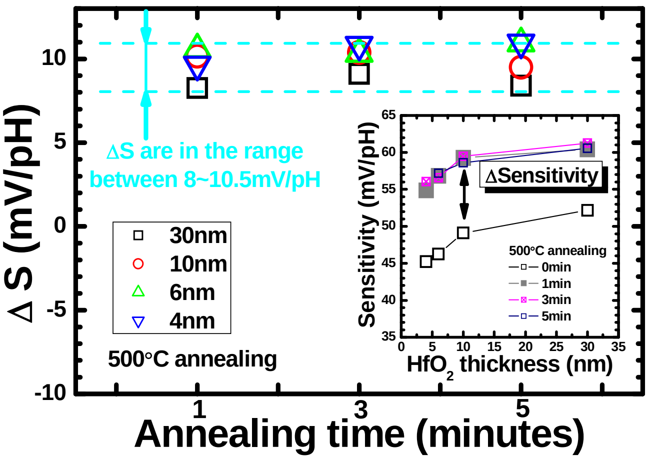

Fig. 7 The sensitivity variations of HfO_2 EIS with 500ºC RTA annealing for 1, 3 and 5 minutes. There is no obvious improvement on annealing interval.

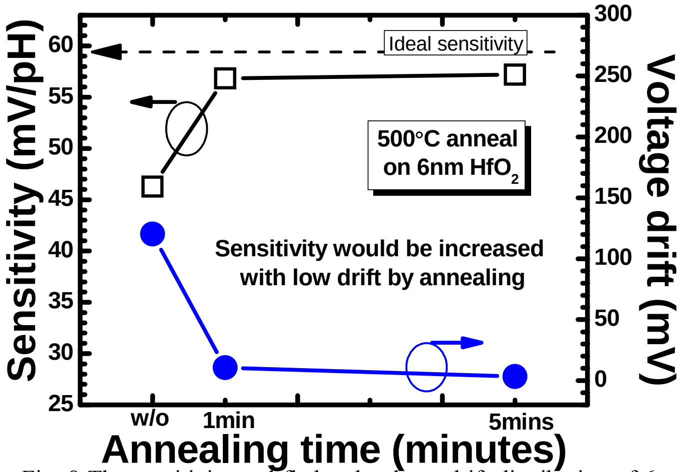

Fig. 8 The sensitivity and flatband voltage drift distribution of 6nm HfO_2 EIS in different the annealing time of RTA at 500ºC.

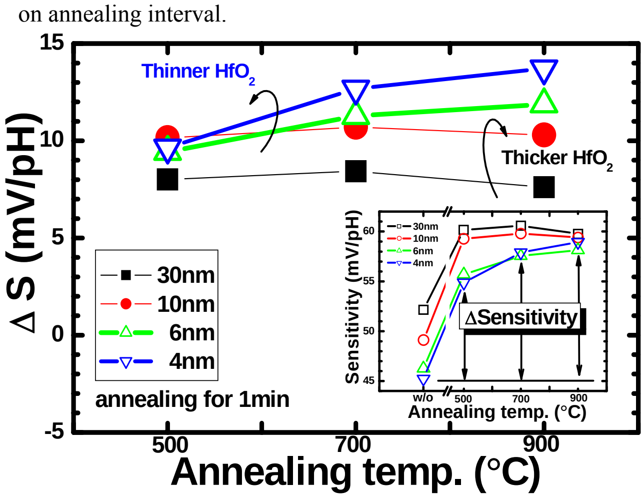

Fig. 9 The sensitivity distribution of HfO_2 EIS annealed for 1 minute at different temperature. Sensitivity would be increased with annealing temperature.

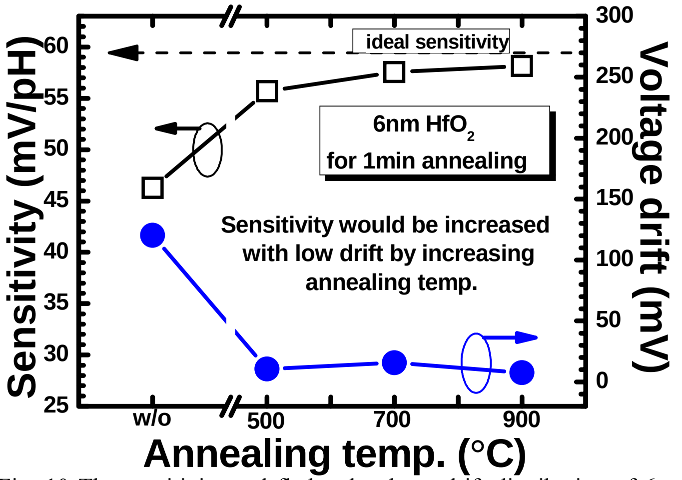

Fig. 10 The sensitivity and flatband voltage drift distribution of 6nm HfO2 EIS in different annealing temperature of RTA for 1minutes. Sensitivity and drift would be improved at annealing temperature higher than 500 ºC.