The Multi-Channel Measurements for pH-Sensitivity and Drift Coefficient of Thin Hafnium Oxide with CF_4 Plasma Treatment

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1. Introduction

Ion sensitive field effect-transistor (ISFET) was invented by P. Bergveld in 1970. [1] Compare with conventional ion-selective electrode, ISFET has many advantages, such as small size, fast response, low output impedance, small sample requirement, high durability and low cost. [2] The first pH-sensitive membrane for ISFET application was silicon dioxide (SiO_2) layer. [3] Then many kinds of insulators such as Si_3N_4 [4], Al_2O_3 [5] and Ta_2O_5 [6] were verified as the superior sensitive membrane for ISFET commercial products. Recently, hafnium oxide (HfO_2) directly deposited on silicon substrate without buffering SiO_2 layer was studied as a new pH-sensitive material, which had high sensitivity and low drift coefficient. [7] However, the applicable pH range of HfO_2 layer was decreased to from pH 2-12 to pH 4-12 when the thickness of HfO_2 layer was decreased from 30 nm to 8 nm. In addition, the serious drift effect will degrade the measurement accuracy of ISFET. To improve the pH-sensing performance of 8 nm thick HfO_2 layer, a CF_4 plasma treatment was performed. To efficiently check the drift coefficient of all samples, a program based on LabVIEW was developed for multi-channel automatically long term drift measurement.

2. Experimental

<u>2.1 Processes flow of HfO_2-EIS structure</u>

To investigate pH-sensitive properties of HfO_2 layer, the EIS structures were fabricated. After standard initial RCA cleaning, the HfO_2 thin film was deposited on silicon substrate by reactive radio frequency (RF) sputtering. The hafnium target with purity of 99.9% was used. The RF power was controlled at 150 watt. The flow rate ratio of O_2/Ar gas mixture was 5/20 sccm. Afterwards, the CF_4 plasma treatments on HfO_2 surface were performed with the RF power at 30 watt and the process pressure of 0.5 torr. The process time period for plasma treatment was controlled at 1, 5, and 10 min.

<u>2.2 Multi-channel automatically controlling program</u>

The connection of measurement system including E5250A, HP4284A and LabVIEW is shown in Fig. 1. To perform series capacitance-voltage (C-V) measurements for three samples, a program based on LabVIEW was used to control HPE5250 low leakage switch mainframe and HP4284A high precision LCR meter. The control panel of this program is presented in Fig. 2. To obtain the long term response of EIS structures from C-V curves, the measurement parameters such as signal frequency, sweep voltage, time period and channel number can be adjusted.

<u>2.3 pH-sensing measurements</u>

For the extraction of pH sensitivity, C-V curves were measured in standard buffer solutions from pH 2 to 12. Sensitivity and linearity can be calculated with the corresponding pH of buffer solution by this program after finished all measurements. In the drift measurement, response voltages were extracted from the measured C-V curves every five minutes in pH 7 buffer solution. The drift coefficient was calculated by linearly fitting with the response voltages (V_{REF}) in the range of 5 to 12 hours immersion.

3. Results and discussions

Figure 3 shows the C-V curves of three HfO_2-EIS structures collected by this controlling program. For the extraction of pH sensitivity, C-V curves were measured in various buffer solutions as shown in Fig. 4 (a). V_{REF} for all samples were automatically calculated with 0.6 C_{max}. [8] Then pH sensitivity and linearity can be obtained by the linear fitting of V_{REF} and the corresponding pH of buffer solution as shown in Fig. 4 (b). The sensitivity distribution of 8 nm thick HfO_2-EIS structure with CF_4 plasma for various time periods was shown in Fig. 5. Sensitivity can be increased with CF_4 plasma time.

A typical time dependent distribution of response voltages in pH 7 buffer solution for 8 nm thick HfO_2-EIS structure with CF_4 plasma surface treatment for 10 min was shown in the Fig. 6. The distribution of drift coefficient for HfO_2-EIS structures with CF_4 plasma treatment for various time periods was shown in Fig. 7. The drift coefficient increased with CF_4 plasma time. The comparison of all performances of 8 nm thick HfO_2-EIS structure with various CF_4 plasma time was shown in Table I.

4. Conclusion

A high efficient automatically multi-channel measurement system was built for the long term stability monitoring of EIS structures. For high sensitivity and low drift coefficient, an optimized process time of CF_4 plasma treatment is 5 min.

References

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Table I The performance comparison of 8 nm thick HfO_2-EIS structures with CF_4.plasma treatment for various time periods.

Plasma time	Sensitivity (mV/pH)	Drift (mV/h)
w/o	46.27	1.40
1 min	48.69	1.51
5 min	49.52	1.98
10 min	49.57	6.55

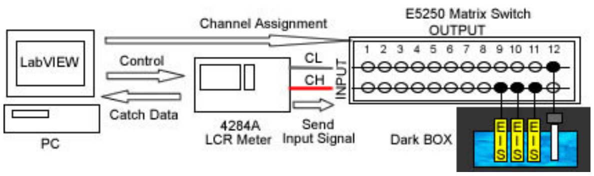

Fig. 1 The connection diagram for measurement system including E5250A, HP4284A and LabVIEW.

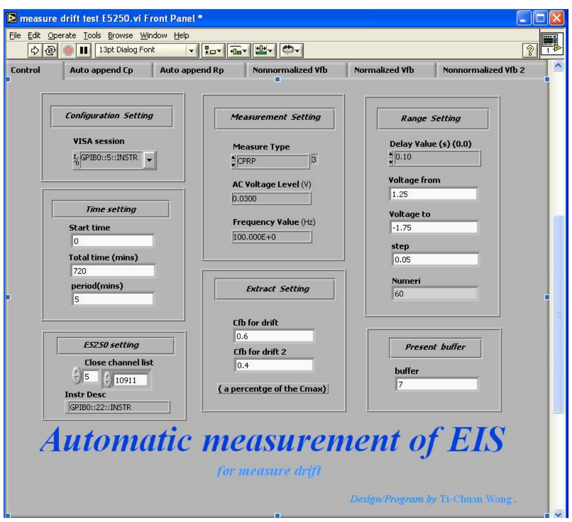

Fig. 2 The control panel based on LabVIEW program was designed to measure drift curves of EIS structure.

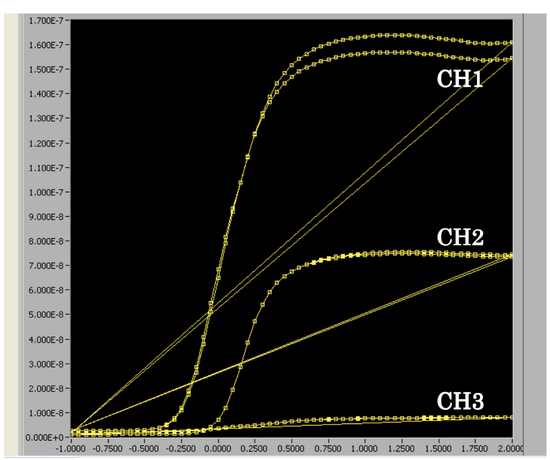

Fig. 3 C-V curves measured by the designed program.

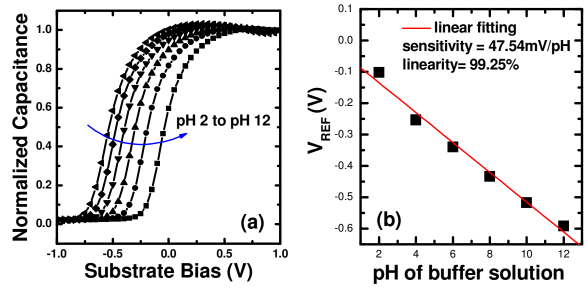

Fig. 4 (a) The C-V curves of 8 nm thick HfO_2-EIS structure measured from pH 2 to pH 12; (b) linear fitting results of V_{REF} and pH of buffer solution.

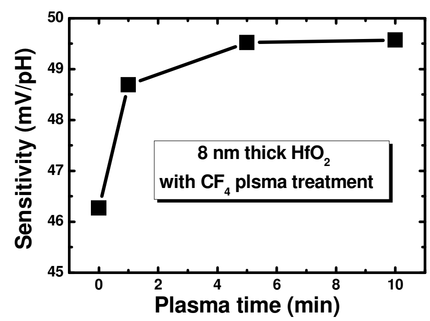

Fig. 5 Sensitivity distributions with CF_4 plasma treatment for various time periods.

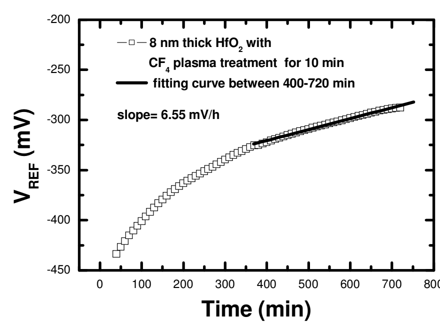

Fig. 6 A typical time-dependent reference voltage distribution of 8 nm thick HfO_2 structure with CF_4 plasma treatment for 10 min.

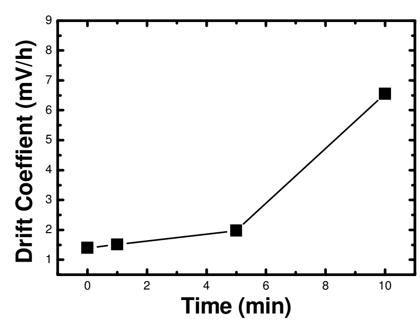

Fig. 7 The distribution of drift coefficients for HfO_2-EIS structures with CF_4 plasma treatment for various time periods.