DOI 10.5162/IMCS2012/3.5.2

Fluorinated-HfO_2 ISFET as pK sensor with highly sensitivity

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Abstract

Ion Sensitive Field-Effect Transistor (ISFET)-based sensors with fluorinated-hafnium oxide (HfO_2) thin film fabricated by atomic layer deposition (ALD) and thermal carbon tetrafluoride (CF_4) plasma post-treatment was investigated for pK detection. The developed fluorinated-HfO_2 ISFET is highly sensitive to K^+ ions (59.5 mV/pK) in the concentration range between 0.01 and 100 mM. When compared to the same structure without plasma treatment, the sensitivity was improved by fourteenfold.

Key words: ISFET, ALD, HfO_2, CF_4 plasma, and pK sensor

Introduction

The measurement of pK is significant for biomedical, industrial, and environmental applications. Therefore, the development of sensors for continuous monitoring in real-time and on-line measurement is required for these applications. For K^+ ion detection, many approaches have been proposed *e.g.* deposition of polymeric ion selective membrane [1], ion-implantation of potassium and aluminum into the silica insulators [2], and ion-partitioning membrane [3]. However, some instability problems may occur in membranes deposited by the above-mentioned methods, including the poor adhesion when deposit an extra polymeric ion-sensitive membrane on an insulator surface, some damages of membranes due to the high energy of ion implantation and a limited lifetime. In this study, a plasma technique for treatment of hafnium oxide layer as a potassium sensitive membrane is proposed. The advantages of the plasma technique are low power fabrication process for making sensing membrane with less defects, high ability of functionalization of sensing membrane, and compatibility with a standard CMOS technology.

Experimental

For the investigation of pK-sensing characteristics, a 5 mM tris(hydroxymethyl)-aminomethane (Tris) buffer solution of pH 8.0 fixed with 1 N HCl was prepared. The concentration of K^+ ion in a range between 10^{-5} and 10^{-1} M was varied by a standard addition method using 150 mM and 3 M KCl/Tris-HCl standards. The selectivity coefficients were evaluated by the fixed interference ion (FIM) method. The primary ion is K^+ while the interfering ions are as follows: Li^+, Na^+, NH_4^+ and Ca^{2+}. The activity of interfering ions is kept constant at 10 mM and the activity of K^+ is varying.

Results and Discussion

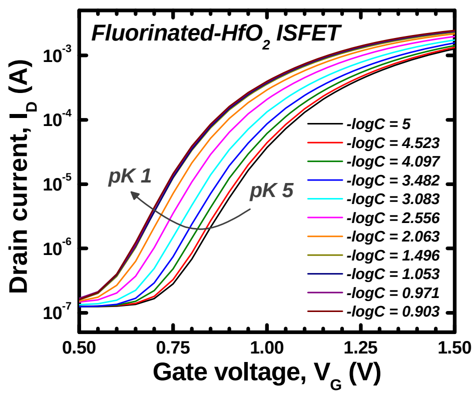

Fig. 1. I-V curves of fluorinated-HfO_2 ISFET in different pK values (pK 1~ pK 5).

DOI 10.5162/IMCS2012/3.5.2

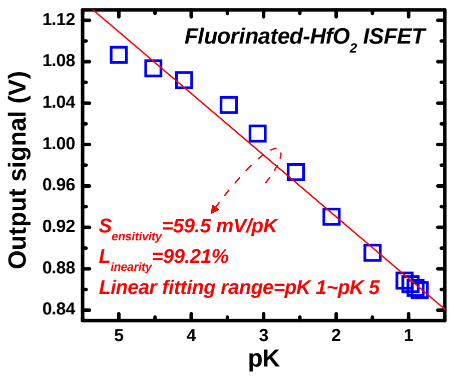

Fig. 2. pK-sensitivity and linearity of fluorinated-HfO_2 ISFET.

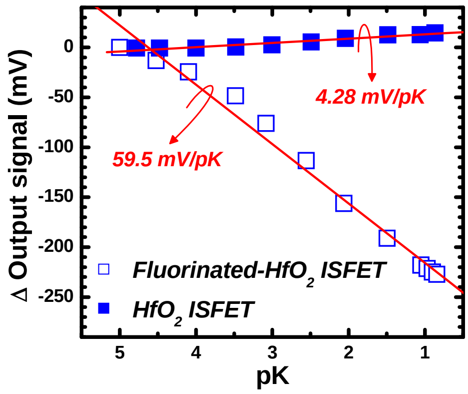

Fig. 3. pK-sensitivity of fluorinated-HfO_2 ISFET and HfO_2-ISFET

Figure 1 shows the I-V curves for fluorinated-HfO_2 ISFET by thermal CF_4 plasma for 5 min, measured in pK range from 0.9 to 5. As can be seen, the I-V curves shift gradually along the X-axis in negative direction with decrease of the pK value, which is due to the potassium ion (K^+) with the positive univalent. The pK-sensitivity evaluated from Fig. 1 was close to the Nernstian response, namely 59.5 mV/pK, with the linearity of 99.21% as shown in Fig. 2. The achieved sensitivity was around 14 times greater than the sensitivity of samples without plasma treatment. The comparison of pK-sensitivity between fluorinated-HfO_2 ISFET and HfO_2-ISFET was plotted in Fig. 3. It means that the thermal CF_4 plasma treatment could be applied to increase the sensitivity for K^+ ion. To check the interference from other metal ions, the selectivity coefficient, $K_{X,Y}$, was measured using fixed interference method (FIM), there the symbol X is a primary ion and symbol Y is an interferening ion. The primary ion is K^+ while the interfering ions are as follows: Li^+, Na^+, NH_4^+, and Ca^{2+}. The activity of interfering ions is kept constant at 10^{-2} M and the activity of K^+ is varying. The illustration of FIM measurement was presented in Fig. 4 and the selectivity coefficients were calculated using the following equation:

$$K_{X,Y} = a_X / (a_Y)^{Z_X / Z_Y} \quad (1)$$

The calculated selectivity coefficients of $K_{K,Li}$, $K_{K,Na}$, $K_{K,NH4}$, and $K_{K,Ca}$, were -1.311, -1.264, -0.674, and -2.119, respectively. Compared to the proposed pK-sensing membranes as listed in Table I, the fluorinated-HfO_2 ISFET exhibits highly pK-sensitivity and wide detecting range. These results indicate that the fluorinated-HfO_2 thin film fabricated by thermal CF_4 plasma treatment which is compatible with advanced CMOS technology is a promising material for development of K^+ ion sensor.

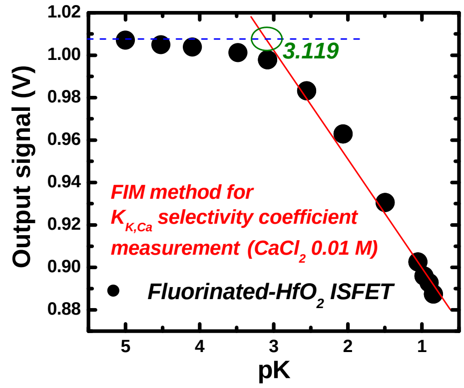

Fig. 4. The illustration of FIM measurement for $K_{K,Ca}$ selectivity coefficient extraction.

Conclusion

In this work, an ISFET-based sensor with fluorinated-HfO_2 thin film as a sensing membrane fabricated by thermal CF_4 plasma for K^+ ion detection was successfully developed. The proposed sensor is highly sensitive to the wide concentration range of K^+ ion with good linearity (> 99%). When compared to the same structure without plasma treatment, the sensitivity was improved by fourteenfold.

Acknowlwdge

This work is supported by the National Science Council of the Republic of China under the contract numbers of NSC99-2221-E-182-056-MY3.

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Tab. 1:Comparison of pK-sensitivity, linear range, and selectivity coefficient of various sensing membranes.

Methods	Sensitivity (mV/pK)	Linear range (mM)	$log(K_{K,Li})$	$log(K_{K,Na})$	$log(K_{K,NH4})$	$log(K_{K,Ca})$	*Ref.*
Fluorinated-HfO_2 by thermal CF_4 plasma	~59.5	0.01-100	-1.311	-1.264	-0.674	-2.119	this work
PVC matrix	40~50	0.1-1000	-3.2	-2.6	-1.6	-3.9	[1]
Ion-implantation of K^+ and Al^+ into silica	36~44	1-100	-	-	-	-	[2]
Ion-partitioning membrane	~58.5	0.001-10	-	-	-	-	[3]