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HfO_xF_y Based ISFETs with Reactive Fluorine Doping for K^+ ion Detection

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Electrolyte-insulator-semiconductor (EIS)- and ion-Sensitive field-effect transistors (ISFET)-based sensors with a fluorinated hafnium oxide (HfO_2) thin film treated by thermal carbon tetrafluoride (CF_4) plasma was investigated for potassium (K^+) ion detection. The HfO_2 thin film was deposited using radio frequency (RF) sputtering and then CF_4 plasma treated on HfO_2 surface with substrate heating at 300°C during processing in the plasma system. The developed fluorinated-HfO_2 (HfO_xF_y) ISFETs have an average sensitivity of 59.5 mV/pK in the concentration range between 0.01 and 100 mM. To explain the increases of pK sensitivity by thermal CF_4 plasma treatment, the polar dipole formation in HfO_2 thin-film was proposed based on surface analysis by using XPS. The drift rate considered as the long-term stability is 1 mV/h, which is in the acceptable range. The fluorinated-HfO_2 film treated by thermal CF_4 plasma, which is compatible with advanced CMOS technology, could be a potential candidate for preparation of K^+ ion sensitive layers.

Keywords: EIS, hafnium oxide, ISFET, potassium ion, thermal CF_4 plasma

1. INTRODUCTION

The detection of potassium (K^+) ion concentration is important for biomedical, industrial, and environmental applications. For example, the K^+ ion concentration of serum is considered as an important indicator for diseases prediction of human health like acute cardiac arrhythmia and kidney failure [1,2]. Moreover, the concentration of K^+ ions is a meaningful parameter for quality control in food industry and water pollution to avoid the unwanted contamination [3,4]. Therefore, the development of sensors for continuous monitoring in real-time and on-line measurement is required for these applications.

With advantages of small size and robustness, field-effect silicon-based sensors, such as ion sensitive field-effect transistor (ISFET) [5,6] and electrolyte-insulator-semiconductor (EIS) [7,8] are two of the best approaches to acquire the data on (bio)chemical composition of electrolytes [9,10]. ISFET is a potentiometric sensor which can be used to detect the changes of threshold voltages and Drain-to-source current v.s. gate-to-source voltage (I_{DS}-V_{GS}) curves from variations of ion concentration in an electrolyte. [11] In EIS-type sensor, the concentration variations can be measured as shifts of capacitance-voltage (C-V) curves [12]. Comparing with a conventional glass electrode, ISFET and EIS structures exhibit a number of advantages including small size, rapid response, low cost, rugged solid construction, and compatible process with complementary metal-oxide semiconductor (CMOS) technology [13].

To obtain a high sensitivity to hydrogen ions, good reliability and long lifetime, many inorganic materials have been widely tested based on ISFET and EIS structures [14-17]. Recently, metal oxides with high dielectric constant (high-k), such as titanium oxide (TiO_2) [18], ruthenium oxide (RuO_2) [19], tin oxide (SnO_2) [20], zirconium oxide (ZrO_2) [21], and others were extensively investigated as pH-sensitive membranes. The major advantage of high-k metal oxides as pH-sensitive membranes is the compatibility of their deposition with advanced CMOS technology. Among numerous high-k metal oxides, hafnium oxide (HfO_2) was considered as the promising material due to its high dielectric constant (~25), relatively large band gap (~5.8 eV) and good thermal stability (>900 ^oC) [22-25]. In our previous works, a single HfO_2 layer with high pH-sensitivity, low drift rate, and small body effect was proposed as a promising sensing membrane for pH detection [26-29]. However, the low sensitivity of K^+ ions is observed in the HfO_2 sensing membrane. For K^+ ions detection, many approaches have been proposed including deposition of polymeric ion selective membrane [30-33], ion-implantation of potassium and aluminum into the silica insulators [34], and ion-partitioning membrane [35]. However, some instability problems may occur in membranes prepared by the above-mentioned methods, including the poor adhesion when deposit an extra polymeric ion-sensitive membrane on an insulator surface, some damages and defects in membranes due to the high energy of ion implantation and a limited lifetime. To obtain a multi-ion sensing array, selectivity to other interference ions and sensor lifetime are still the criteria need to be meet for the development of surface modification on sensing membrane. Therefore inorganic treatment of thermal CF_4 plasma on HfO_2 layer is investigated in this study. In the past few years, many papers about using plasma technique to improve the electrical properties of metal-oxide-semiconductor (MOS) based devices [36-38], pH-sensing characteristics of silicon-based sensors [39,40] and selectivity of protein absorption

for bioanalytical sensors [41] have been presented. The advantages of the plasma technique are low power fabrication process for making sensing membrane with fewer defects, high ability of functionalization of sensing membrane, and compatibility with a standard CMOS technology.

The idea presented in this work is the development and application of carbon tetrafluoride (CF_4) plasma treatment with substrate heating on hafnium oxide (HfO_2) thin film for ISFET and EIS structures to become sensitive to K^+ ions. The low-power CF_4 plasma produced by plasma-system on wafer with substrate heating during processing is proposed to investigate the pK sensitivity of HfO_xF_y thin film. To analyze surface composition on HfO_2 thin film with different plasma treatment, the surface chemical states of HfO_xF_y membranes were studied by the X-ray photoelectron spectroscopy (XPS) technique. The possible mechanism based on the polar bonding formation and charge attraction was proposed with the evidences from F 1*s*, O 1*s* and Hf 4*f* spectra. In addition, the characteristic of time dependent drift as a long-term stability was examined for practical applications.

2. EXPERIMENTAL

2.1. Fabrication of devices

To investigate the sensing properties of fluorinated-HfO_2 thin films to K^+ ions, both EIS structures and ISFETs were fabricated. For EIS structure, a 15-nm-thick HfO_2 film was directly deposited on a *p*-type Si wafer by reactive radio frequency (rf) sputtering from a pure Hf target (99.99%) in an Ar/O_2 ambient after a standard RCA cleaning. The rf power was set at 150 watts and the processing pressure is 20 mtorr. After sputtering of HfO_2, a carbon tetrafluoride (CF_4) plasma treatment for 1 and 5 min were processed in a plasma-system with substrate heating at 300°C. The plasma power was 30 watts and the process pressure was 500 mtorr. Then, a contact layer of 300-nm-thick aluminum (Al) film was evaporated on the backside of *p*-Si wafer after removing native oxide by HF dip. To define the sensing area, a negative-photoresist, SU8-2005 (Micro Chem. Inc.), was used. The radius of the sensing area exposed to an electrolyte was 1 mm. Finally, an epoxy was used for hand-made encapsulation of the EIS devices assembled with a silver gel on copper line of printed circuit board (PCB). The ISFETs were fabricated at the Institute of Electron Technology (IET), Poland. Details of the HfO_2-gate ISFET fabrication is presented in our previous publication [29]. The process settings of plasma treatment used in ISFETs fabrication were 500 mtorr of process pressure, 30 watts of plasma power, and substrate temperature at 300°C, which is the same process as using for EIS structures.

2.2. Measurements

For the investigation of pK-sensing characteristic, a 5 mM tris(hydroxymethyl)-aminomethane (Tris) buffer solution of pH 8.0 fixed with 1 N HCl was prepared. The concentration of K^+ ions in a range between 10^{-5} and 10^{-1} M was controlled by a standard method of adding different volume of 150 mM and 3 M KCl/Tris-HCl standards, respectively.

2.3. Physical and electrical characterization

To study the composition and chemical state of the HfO_2 films with and without CF_4 plasma treatment, XPS measurements were carried out with XPS (Microlab-350 Thermo VG Scientific Co.) using a standard Mg Kα (1253.6 eV) X-ray source. XPS spectra were collected with a passing energy of 30 eV and 0.05 eV in each sweeping step.

The electrochemical characterization of EIS sensors has been performed by means of low-frequency capacitance-voltage (LF-CV) measurements at a frequency of 100 Hz using a HP4284A high precision LCR meter. For all EIS devices, the output signal is defined as a voltage for 60% of maximum capacitance ($0.6\times C_{max}$), which is in the depletion operating mode of the measured C-V curves. The electrochemical characterization of ISFET sensors have been performed by means of Agilent 4156C semiconductor parameter analyzer. I_{DS}-V_{GS} curves were measured with drain-to-source voltage at 0.5 V and a reference electrode connected for gate bias. Output voltage of I_{DS}-V_{GS} curves measured in different solutions is defined as the voltage with I_{DS} of 100 μA. pH value of buffer solution was monitored by using a commercial combined pH electrode S120C (Sensorex) and pH-meter HTC-201U (HOTEC). An Ag/AgCl electrode in part of the aforementioned combined pH electrode was used for reference electrode. All measurements were performed in a dark Faraday cage at room temperature. To obtain a stable K^+ ion sensing response, all EIS structures and ISFETs were immersed in the 5 mM Tris/HCl buffer solution for 12 h before measuring. The drift coefficient was calculated by linear fitting of the output voltage in the time period from 5 to 12 h [42].

3. RESULTS AND DISCUSSION

3.1. X-ray photoelectron spectroscopy analysis

To identify the composition and chemical state of an HfO_2 film with or without thermal CF_4 plasma treatment, the XPS analyses were performed. The obtained results of F 1*s*, O 1*s*, Hf 4*f* peak are shown in Fig. 1, Fig. 2, and Fig. 3, respectively. To eliminate charge-up effect, all XPS spectra were calibrated by setting C 1*s* peak at 284.5 eV. The background line was defined using a tougaard-type shape and the peaks were fitted with a Lorentzian-Gaussian function. Fig. 1 (a) and (b) illustrates the F 1*s* peaks for the HfO_2 film treated with CF_4 plasma at 300°C for 5 min and the HfO_2 film without plasma treatment, respectively. In Fig. 1, F 1*s* peaks intensity is clearly increased by plasma treatment and further increased by thermal plasma treatment, which results from the increases of Hf-F bonds formed in HfO_2 films [43]. However, a small peak exists in the case of untreated HfO_2 film as shown in Fig. 1(b). It is possibly due to the residual content of F atoms at the interface Si/HfO_2 film resulting from the HF dip before HfO_2 film deposition. The higher Hf-F peak related to the concentration of fluorine incorporation is for the sample with thermal plasma treatment at 300°C. This peak of sample with thermal CF_4 plasma treatment is also higher the peak of sample with CF_4 plasma without substrate heating after normalized the control sample without CF_4 plasma treatment. [44] It suggests

that the thermal energy provided by substrate heating at 300°C is beneficial for fluorine incorporation into HfO_2 film during plasma processing.

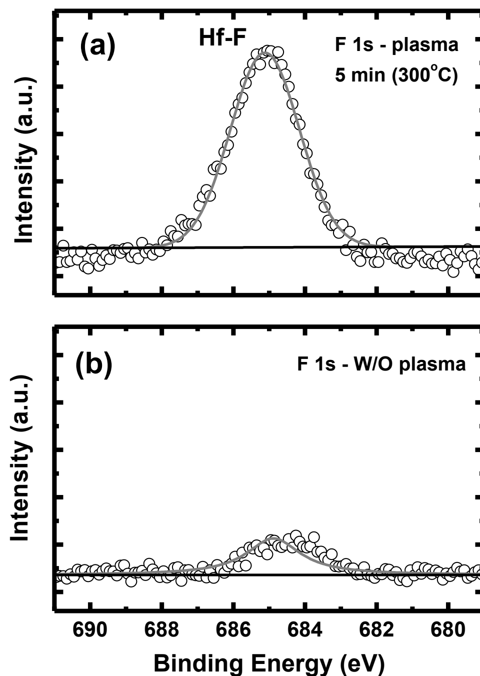

Figure 1. F 1*s* peak of HfO_2 thin film with (a) CF_4 plasma treatment for 5 min at 300°C, (b) CF_4 plasma treatment for 5 min at 25°C and (c) as-deposited and no CF_4 plasma treatment.

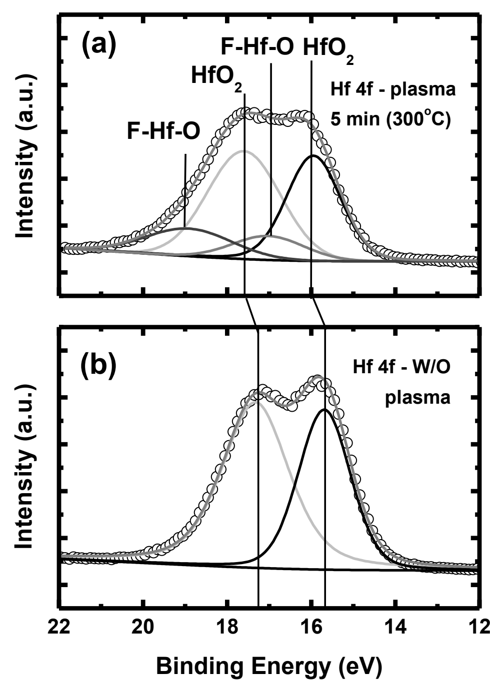

Figure 2. Hf 4*f* peak of HfO_2 thin film with (a) CF_4 plasma treatment for 5 min at 300°C, (b) CF_4 plasma treatment for 5 min at 25°C and (c) as-deposited and no CF_4 plasma treatment.

This explanation is further confirmed with the Hf 4*f* XPS spectra. Fig. 2 (a) and (b) present the de-convoluted Hf 4*f* peaks for the HfO_2 film treated with CF_4 plasma at 300°C for 5 min and for the HfO_2 film without plasma treatment. In Fig. 2(b), the spectrum showed two major peaks at the binding position of 15.7 eV and 17.35 eV related to the oxidized Hf $4f_{7/2}$ and Hf $4f_{5/2}$ bindings for untreated-HfO_2 film. As shown in Fig. 2(a), the binding energies of 15.95 eV and 17.6 eV of the oxidized Hf $4f_{7/2}$ and Hf $4f_{5/2}$ were obtained both for the samples with plasma post-treatment at 300°C. Compare to un-treated sample, the peaks are shifted positively by 0.25 eV due to the incorporation of fluorine atom into HfO_2 film. In Fig. 2(a), two additional peaks with smaller intensity at binding energies of 17.05 eV and 19 eV relative to the F-Hf-O bindings were applied to well fit the Hf 4*f* spectrum for the sample with CF_4 plasma treatment at 300°C [45]. It could be explained by the enhancement of the reaction between HfO_2 thin film and fluorine atoms from additional energy by the high substrate temperature during plasma processing.

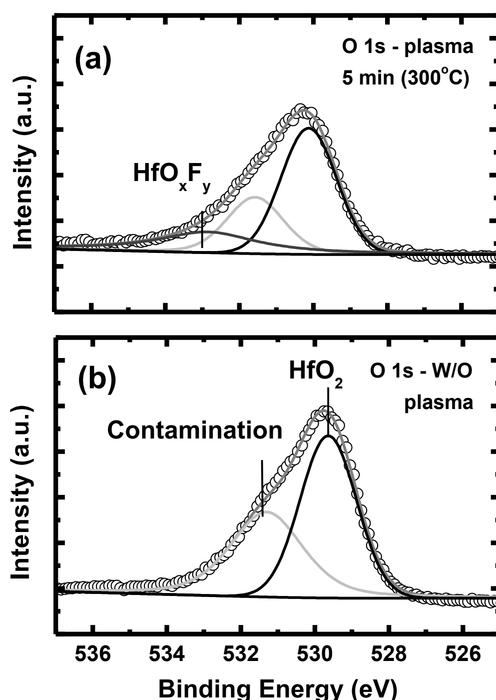

Figure 3. O 1*s* peak of HfO_2 thin film with (a) CF_4 plasma treatment for 5 min at 300°C, (b) CF_4 plasma treatment for 5 min at 25°C and (c) as-deposited and no CF_4 plasma treatment.

The corresponding O 1*s* spectra for the HfO_2 film treated with CF_4 plasma at 300°C for 5 min and for the HfO_2 film without plasma treatment were presented in Fig. 3. In Fig. 3(b), two major peaks can be found for the untreated-HfO_2 film. One peak is at the binding energy of 529.65 eV related to the chemical bond of HfO_2 and the other peak is at the larger binding energy of 531.3 eV related to some contamination. As shown in Fig. 3(a), to fit the O 1*s* spectra well, the additional peak is applied for samples with plasma treatment at 300°C. The corresponding O 1*s* spectrum of the sample with plasma treatment at 300°C showed three peaks at binding energies of 530.15, 531.6, and 532.9 eV. The peak with lowest binding energy in Fig. 3(a) that is positively shifted from the 529.61 eV in the case of the

untreated-HfO_2 film is attributed to the peak of HfO_2. The second peak with the binding energy of 531.6 eV in Fig. 3(a), which is near the binding energy of 531.3 eV of the untreated-HfO_2 film, is the contamination peak. The peak with highest binding energy of 532.9 eV in Fig. 3(a) is considered as a peak of HfO_xF_y. [46] This is probably attributed by the presence of the bond between O and F in the HfO_2 film after plasma treatment. A similar formation of $Al(OF)_x$ and $Si(OF)_x$ layers after plasma treatment were described in previous literatures [47,48]. Similar results were reported by Huang et al. [46], who suggested formation of HfO_xF_y film during CF_4 plasma treatment. Based on the analysis of XPS, fluorine incorporation in the HfO_xF_y film after CF_4 plasma treatment is evidenced, and the higher concentration of fluorine incorporation is observed in the HfO_xF_y film with CF_4 plasma treated at 300°C.

3.2. pK sensitivity of the EIS and ISFET sensors functionalized with CF_4 plasma

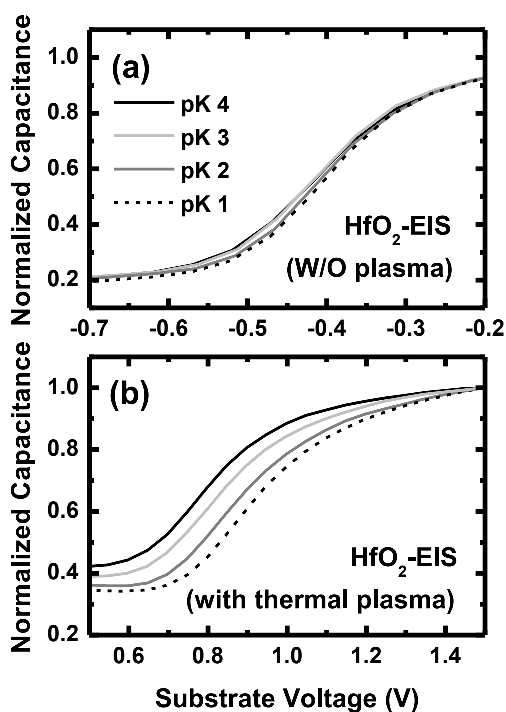

Figure 4. Normalized C-V curves in different pK values for EIS structures with (a) as-deposited HfO_2 and (b) CF_4 plasma treated-HfO_2 for 5 min at 300°C .

Figure 4 shows the normalized C-V curves for HfO_2-EIS structures without plasma treatment and HfO_2-EIS structure with thermal CF_4 plasma for 5 min, measured in K^+ ion concentration range from pK 1 to 4. It was found that the normalized C-V curves shift gradually along the X-axis in positive direction with decrease of the pK value. For more background information, sodium ion detection was investigated on light addressable potentiometric sensor (LAPS) with CF_4 plasma treatment in ref. [49]. Comparing Fig. 4(a) and (b), the magnitude of C-V shift for the sample with thermal CF_4 plasma treatment is greater than for the sample without plasma treatment. It means the

increase of sensitivity to potassium ions of samples after thermal plasma treatment, which may be explained by the fluorinated bonds (F-O bond) formation in HfO_xF_y film surface evidenced by the XPS analysis. Calculated pK sensitivity is 49 mV/pK and the linearity of fitting curve is 99%. The achieved sensitivity of samples with thermal CF_4 plasma treatment was around 6 times greater than the sensitivity of samples without plasma treatment. It means that the thermal CF_4 plasma treatment could be applied to increase the sensitivity for K^+ ions. In order to clarify the phenomena, the fluorinated HfO_2-EIS structures with different time of CF_4 plasma treatment were also investigated.

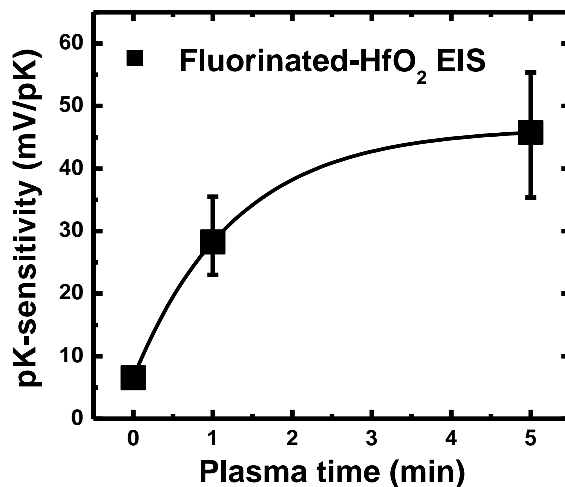

Figure 5. Plasma processing time dependent pK-sensitivity of the thermal CF_4 plasma treated-HfO_2 based EIS structures.

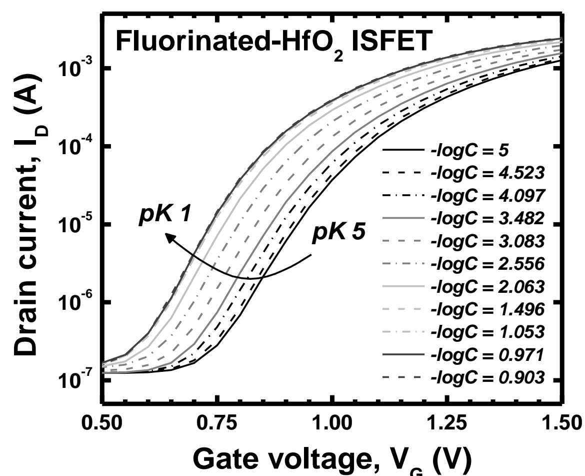

Figure 6. I_{DS}-V_{GS} curves measured in buffer solution of different pK value for a HfO_2-ISFET with thermal CF_4 plasma treatment for 5 min.

Figure 5 shows pK sensitivity of samples with CF_4 plasma treatment time of 0, 1, and 5 min, respectively. Five samples were measured for each condition. It exhibits that K^+ ion sensing response was improved after surface modification by thermal CF_4 plasma treatment and a highly correlated

relationship between the pK sensitivity and the processing time of thermal CF_4 plasma on the HfO_2 film surface is observed. As shown in Fig. 5, process time-dependent pK sensitivity curve increased quickly and nearly saturated for process time longer than 1 min. It was attributed by the formation of more of fluorinated bonds (F-O bonds) on HfO_2 film surface by the substrate heating during plasma processing. To confirm this sensing behavior, ISFETs with fluorinated HfO_2 film treated with thermal CF_4 plasma for 5 min were fabricated. Figure 6 shows I_{DS}-V_{GS} curves for fluorinated HfO_2-ISFET measured in buffer solution with pK value ranging from 0.9 to 5. I-V curves shift to negative bias gradually along the X-axis with decrease of the pK value. It implies that more K^+ ions were absorbed on fluorinated-HfO_2 surface with increasing K^+ ion concentration. The comparison of pK responses of HfO_2-ISFET structures without plasma treatment and HfO_2-ISFET structure with thermal CF_4 plasma treatment for 5 min was presented in Fig. 7.

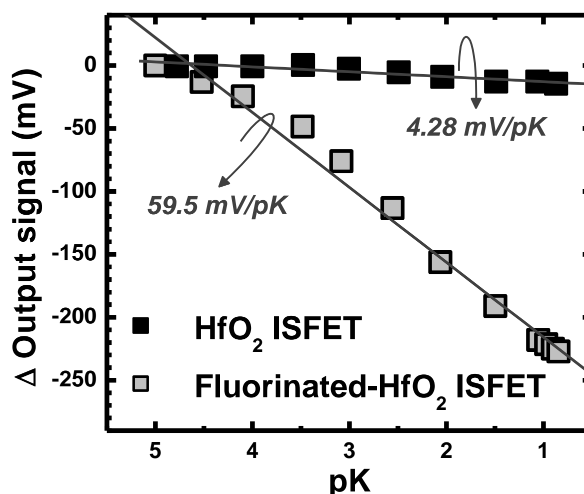

Figure 7. pK responses of ISFETs with as-deposited HfO_2 and thermal CF_4 plasma treated for 5 min.

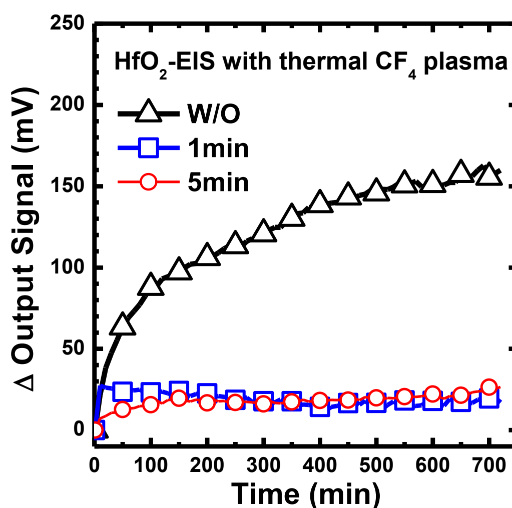

Figure 8. Long-term output voltage variation measured in a 10 mM KCl/Tris-HCl solution for EIS structures with thermal CF_4 plasma treated-HfO_2 for different time.

The output signal is considered as the V_{GS} for I_{DS} of 100 uA and the delta output signal is the difference of the output signals between buffer solution of pK 5 and that of different pK value. As shown in Fig. 7, calculated pK sensitivity of samples of thermal CF_4 plasma treatment is 59.5 mV/pK close to Nernstian response and the corresponding linearity is 99%. This achieved sensitivity was around 14 times greater than the sensitivity of samples without plasma treatment.

To study the long-term stability, the fluorinated HfO_2-EIS structures were tested in a 10 mM KCl/Tris-HCl solution for its response as a function of time. The measurements were lasted for 12 h and the output signals also were calculated based on 60% of C_{max} of C-V curves collected every 10 min. As shown in Fig. 8, the increment of output voltage (ΔV) was defined as the following voltage shift from first measured point. The fluorinated-HfO_2 films have much stable surface potentials than the HfO_2 film without plasma treatment, which could be used to demonstrate rare additional damages on membrane by this low power plasma process. The definition of the drift coefficient of EIS structures is expressed as a change of the output signal per hour calculated for period of measurement time between 5 and 12 h. The calculated drift coefficients were 4.9, 0.24, and 1.09 mV/h for samples with thermal CF_4 plasma processing time of 0, 1, and 5 min, respectively. An improved long-term stability of fluorinated HfO_2-EIS structures could result from the repair of defects in the HfO_2 film by fluorine incorporation. [50]

To check the interference from other metal ions, the selectivity coefficient, $K_{X,Y}$, is an important factor that needed to be examined, there the symbol X is a primary ion and symbol Y is an interfering ion. In this study, the selectivity coefficients were evaluated by the fixed interference ion (FIM) method described in [51] and [52]. The primary ion is K^+ while the interfering ions are as follows: Li^+, Na^+, and Ca^{2+}. For the fluorinated HfO_2-ISFET with thermal CF_4 plasma treatment for 5 min, the activity of interfering ions is kept constant at 10^{-2} M and the activity of K^+ is varying. The obtained selective coefficients for $K_{K,Li}$, $K_{K,Na}$, and $K_{K,Ca}$ are -1.311, -1.264, and -2.119, respectively. The selectivity coefficients obtained in the fluorinated HfO_2-ISFET with thermal CF_4 plasma treatment for 5 min is not good enough and still needs to be improved by other methods before real applications for K^+ ions detection.

3.3. Sensing mechanism

Above-mentioned results indicate that the CF_4 plasma treated-HfO_2 surface is sensitive to K^+ ions. To explain this phenomenon, we proposed the following model based on F-O polarized dipole and charge attraction. The schematic diagram of proposed model is shown in Fig. 9. Based on XPS analysis, the fluorine-oxygen (F-O) bonds in the HfO_2 thin films were observed after CF_4 plasma treatment. In the F-O bond, the electronegativitity of fluorine and oxygen atoms are 4.0 and 3.5, respectively. High electronegativity of fluorine atom results in the pull of electrons off the oxygen and the polarity was achieved due to the dipole (d^+-d^-) property between F-O atoms. The magnitude of electronegativity difference will be relative to the degree of polarity. Therefore, the F-O dipoles existed on the fluorinated-HfO_2 films surface present the negative charges on the fluorine side. Due to an additional attraction between the negative terminal of F-O dipole and the positive ions in

electrolyte, the negative-charged surface could have a higher sensitivity to K^+ ions. Based on the proposed model, the positive-charged surface should be insensitive to K^+ ions. The similar mechanism of positive-charged diamond surface for negative ions detection was already proposed [53,54].

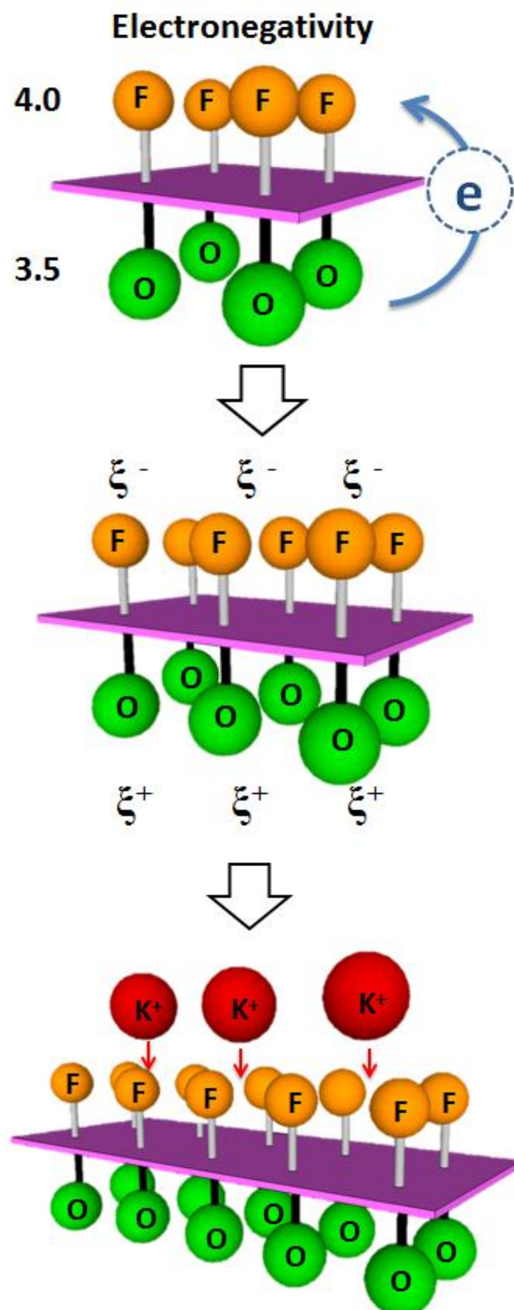

Figure 9. Schematic of the F-O dipole formation and charge attraction for the K^+ ion sensing mechanism of CF_4 plasma treated-HfO_2 thin film.

4. CONCLUSIONS

In this work, an EIS- and ISFET-based sensors with fluorinated-HfO_2 thin film as a sensing membrane fabricated by thermal CF_4 plasma treatment for K^+ ion detection was developed. The

developed sensors are highly sensitive (59.5 mV/pK) in the wide concentration range of K^+ ions (0.01 to 100 mM) with good linearity (> 99%). The possible mechanism of increases of pK sensitivity by F-O dipole and charge attraction was proposed with the evidence of XPS data. For stability testing, this plasma process at low power does not damage the membrane and the drift rate of fluorinated-HfO_2 thin film is relatively lower than for unmodified one due to the repair of defects in HfO_2 film by fluorine incorporation. These results indicate that the fluorinated-HfO_2 thin film fabricated by thermal CF_4 plasma treatment is a potential material for K^+ ion sensor if ion selectivity could be improved by other method.

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