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Impedance Characterization of the Capacitive field-Effect pH-Sensor Based on a thin-Layer Hafnium Oxide Formed by Atomic Layer Deposition

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Abstract: As a sensing element, silicon dioxide (SiO_2) has been applied within ion-sensitive field effect transistors (ISFET). However, a requirement of increasing pH-sensitivity and stability has observed an increased number of insulating materials that obtain high-k gate being applied as FETs. The increased high-*k* gate reduces the required metal oxide layer and, thus, the fabrication of thin hafnium oxide (HfO_2) layers by atomic layer deposition (ALD) has grown with interest in recent years. This metal oxide presents advantageous characteristics that can be beneficial for the advancements within miniaturization of complementary metal oxide semiconductor (CMOS) technology. In this article, we describe a process for fabrication of HfO_2 based on ALD by applying water (H_2O) as the oxygen precursor. As a first, electrochemical impedance spectroscopy (EIS) measurements were performed with varying pH (2-10) to demonstrate the sensitivity of HfO_2 as a potential pH sensing material. The Nyquist plot demonstrates a high clear shift of the polarization resistance (*Rp*) between pH 6-10 (R^2 = 0.9986, Y = 3,054X + 12,100). At acidic conditions (between pH 2-10), the *Rp* change was small due to the unmodified oxide gate (R^2 = 0.9655, Y = 2,104X + 4,250). These preliminary results demonstrate the HfO_2 substrate functioned within basic to neutral conditions and establishes a great potential for applying HfO_2 as a dielectric material for future pH measuring FET sensors. *Copyright © 2014 IFSA Publishing, S. L.*

Keywords: Hafnium oxide, Field-effect transistor, Ph, Electrochemical impedance spectroscopy.

1. Introduction

The ion-sensitive field effect transistor (ISFET) has been a prominent cause in research for pH analysis and it was first developed in the 1970s by Bergveld [1]. Based on a semi-conducting material, the ISFET is a pH sensor capable of measuring minute ion concentration changes that creates a potential on the gate surface material [2]. Here, thermally grown silicon dioxide (SiO_2) and silicon nitride (Si_3N_4) based on silicon has been most favored over the past decades [3-7]. This material has provided ISFETs that can be integrated with complementary metal oxide semi-conductor (CMOS) procedures and at reduced costs.

Over the last few decades, alternative high-*k* materials have emerged to replace SiO_2 gate dielectrics due to potential problems and limitations with ~ 5 Å SiO_2 layers [8]. In sub 100 nm technology node, metals have excellent advantages when applied as gate electrodes. Metal gates could eliminate dopant penetration through the dielectric and thus prevent gate depletion. Many materials have been considered as potential alternatives for high-*k* gate materials instead of SiO_2 as they present the required capacitance due to physical thickness and a reduction of the gate leakage current [9]. These include: titanium dioxide (TiO_2), aluminum oxide (Al_2O_3), zirconium dioxide (ZrO_2), tantalum pentoxide (Ta_2O_5) and hafnium oxide (HfO_2) [10-12]. One of these widely researched materials is HfO_2 [13-19]. HfO_2, HfO_xN_y, and its silicates and aluminates have been chosen due to their good thermodynamic stability with Si [20-23]. HfO_2 also has a high-*k* of ~ 16-45, a high formation of heat (-271.6 kcal/mol), a large band gap (5.68 eV), a refractive index of 2.1, and a high bulk density (9.68 g/cm^3) [24]. The thermal expansion of HfO_2 (5.85×10^{-6}/K) is also comparable to that of SiO_2 (7.6×10^{-6}/K). Therefore, HfO_2 can be considered a promising high-*k* gate material. Recently, we have reported on the fabrication of HfO_2 substrates by atomic layer deposition (ALD). Here, HfO_2 was functionalized with an aldehyde-silane ((11-(Triethoxysilyl) undecanal (TESUD)) monolayer, to immobilize the anti-human interleukin-10 (IL-10) monoclonal antibody (mAb) by direct covalent bonding. The bio-recognition of the mAb with the human IL-10 antigen (Ag) was measured by electrochemical impedance spectroscopy (EIS) in phosphate buffered solution (PBS) with detection between 0.1 – 20 pg/mL [25].

For pH detection, HfO_2 has a high pH sensitivity, low drift, low hysteresis, and is promising as a pH material. Wang et al [19] used p-type silicon wafers with tetrakis(ethylmethylamino)hafnium as the precursor at 200 °C. The authors applied varying ALD-HfO_2 thicknesses at 3.5, 5, 7.5, and 10 nm. They found that thicknesses under 10 nm, produced a pH sensitivity of around 40-45 mV/ pH when measuring between pH 2 to 12 using capacitance-voltage (*c-v*) measurements. At a thickness of 3.5 nm, the *c-v* curve was unstable at pH 2 and the author's relate this problem to the leakage current of the thin HfO_2 layer.

In this paper, we applied HfO_2 substrates that were fabricated by ALD with a metal oxide thickness of 10.7 nm. The non-functionalized surfaces were analyzed from basic > neutral > acidic conditions in Tris(hydroxymethyl)aminomethane (TRIS, 1 M) adjusted to cover the pH range. Measurements were analyzed by EIS and at present no previous publications have analyzed this FET by this electrochemical technique for a potential pH sensitive material.

2. Experimental

2.1. Process for Substrate Fabrication

The fabrication of HfO_2 has been previously published in [20]. In the ALD technique, very thin monolayers can be developed by sequential self-terminating gas-solid reactions. The cyclic nature of this deposition procedure creates a layer-by-layer deposition, which presents a very important advantage in relation to both thickness and composition control. In general, a deposition cycle consists on the introduction of the first required precursor gas into the reaction chamber (short time pulse) which produces the chemisorption of the precursor onto the surface of the substrate. This is then followed by a purge step using an inert gas to remove the excess precursor and the reaction by-products. Next, the second precursor gas is pulsed and brought into the chamber which then reacts with the first precursor that is already present on the substrate. Finally, another purge step is performed with the same function as the first one. This represents one cycle of the procedure and a monolayer growth by cycle is attained due to the self-limiting nature of the reactions.

The samples structures were made on 100 mm-diameter p-type silicon wafers that were (100) oriented and obtained a resistivity of 4-40 Ω×cm (Fig. 1). After general cleaning, the high-*k* dielectric was deposited by the ALD protocol that was previously described. The Savannah-200 ALD system set up at IMB-CNM consists of a thermal ALD system that is used with controlled temperature and under vacuum. Here, the system applied water (H_2O) as the oxygen precursor, together with Tetrakis(Dimethylamido)-Hafnium for HfO_2 deposition. Nitrogen was used as the carrier/purging gas. The deposition of the HfO_2 layer was implemented at a temperature of 225°C H_2O and at a base pressure of 300 mTorr using 100 ALD cycles. An estimation of the deposited HfO_2 layer thickness was realized by means of ellipsometry. An obtained thickness of 10.7 nm was measured with a fixed refractive index at 2.07. Finally, a 500 nm-thick aluminum layer was deposited on the back of the wafers to electrically contact the silicon substrate.

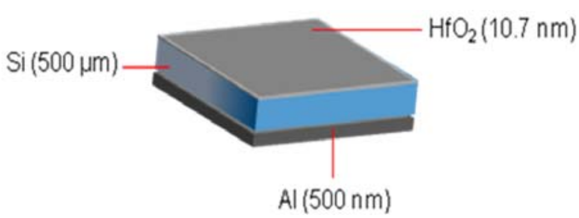
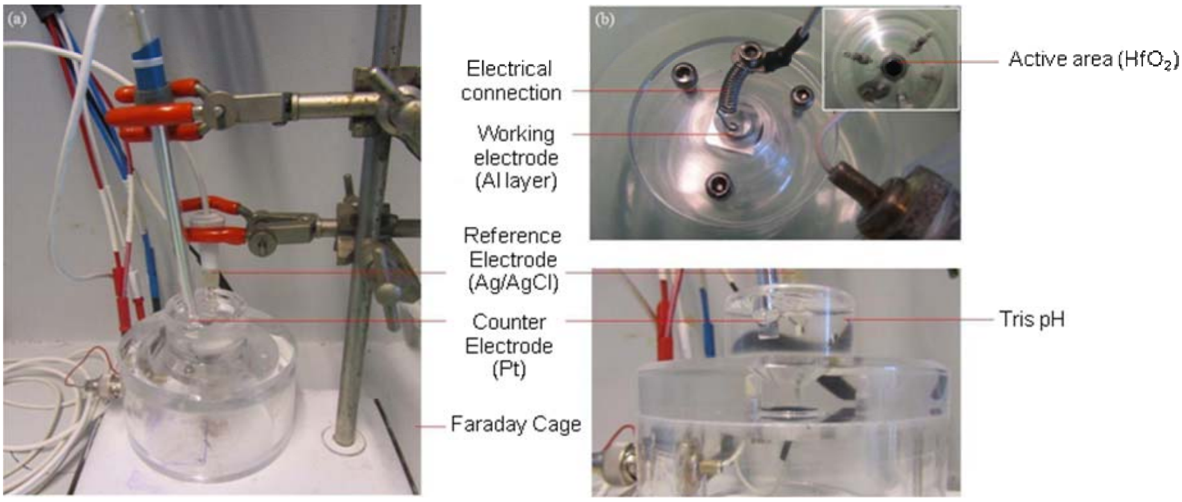


Fig. 1. Schematic for the fabrication of HfO_2 based on the topside of p-type silicon wafers with an aluminum conducting layer based on the backside.



(a) (b)

Fig. 2: Set-up for EIS measurements with (a) plastic cell with external reference and auxiliary electrodes inside a Faraday cage, and (b) backside of the plastic cell for connection of the working electrode (HfO_2) through the aluminum conducting layer. Inset: top view of the measurement window.

2.2. Electrochemical Impedance Measurements by Varying pH Solutions

The HfO_2 substrate was cleaned by sonication in ethanol (96 % vol, VWR International, France) for ten minutes. The substrate was then rinsed with ethanol followed by Milli-Q water and dried with nitrogen. The substrate was connected to a conventional plastic cell, where, the measurement window for the HfO_2 working electrode was calculated with an effective surface of ~ 0.80 cm^2 (Fig. 2). Measurements were made with an external platinum plate counter electrode (Radiometer Analytical, France), and a silver/silver chloride (Ag/AgCl) reference electrode (BVT Technologies, Czech Republic). All measurements were made from freshly prepared Tris(hydroxymethyl)aminomethane (TRIS 99+ %, pH 9 at 1 M, Sigma Aldrich France) with pH varied accordingly by hydrochloric acid (HCl (1 M), Sigma Aldrich France) or potassium hydroxide (KOH (1 M), LauryLab France). Here, the pH range was measured from pH 2, 4, 6, 7, 8, 9 and 10. The analysis was performed inside a Faraday cage. First, the basic pH solutions were measured at a fixed potential that formulated a classical Nyquist curve using a VMP3 Bio-Logic Science Instrument, France. The preliminary plot established the required potential on the HfO_2 substrate. The frequency range was made from 600 kHz to 15 MHz, and an amplitude of 200 mV with a polarization potential of -1.0 V. EC-Lab V10.18 modeling software (Bio-Logic Science Instrument, France) was applied to analyze the impedance data. For the Z-fit, the Nyquist plots were observed with Randomize + Simplex method, with randomize stopped on 100,000 iterations and the fit stopped on 5000 iterations.

3. Results and Discussion

The electrical behavior of the HfO_2 was observed after each analysis by the various pH solutions. The results show a decrease of the polarization resistance (*Rp*) when measurements were made from basic to acidic conditions (Fig. 3). The Nyquist plot shows that bare HfO_2 is highly sensitive as significant variations (*Rp*) within the impedance curves were observed when measuring each pH solution.

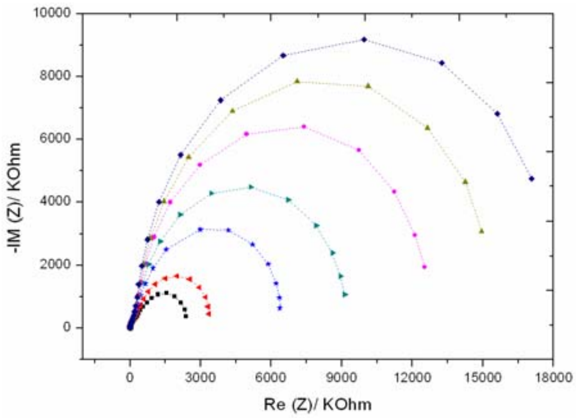


Fig. 3. Nyquist plot of the Rp variation from pH 2 – 10 on HfO_2. The frequency range from 600 kHz to 15 MHz, sinus amplitude of 200 mV and a polarization potential of -1.0 V was applied. pH 10, ♦; pH 9, ▲; pH 8, ●; pH 7, ►; pH 6, *; pH 4, ◄; and pH 2, ■.

In Table 1, the fitting parameters of the Nyquist plot semi-circles were calculated through the equivalent circuit shown in Fig. 4 (inset). The equivalent circuit: $R_1 + C_2/R_2 + C_3/R_3 + C_4/R_4$ provided the best fit for the data. The equivalent circuit consisted of capacitive and resistive components. The electrolyte solution (R_S) is given as R_1. The other capacitance and resistive components are in parallel to one another and signify the three curves observed for each pH within the impedance spectral curves (C_2/R_2; C_3/R_3; and C_4/R_4) (note: C_2/R_2 curves occur at a high frequency and are not observable in Fig. 3). The final part of the equivalent circuit consists of C_4 in parallel with R_4, with the latter being the R_p value corresponding to the electrical resistance of the HfO_2 as a variation to the pH solution. The analysis of the different pH solutions caused a systemic decrease in the polarization where a change in either the dielectric or the conductive properties on the metal oxide surface caused this response. The R_p variation between each of the pH values (pH 10 - 4) were ~ 3000 KΩ apart (Table 1). This suggests the high sensitivity of HfO_2 as a response to the measurement of different pH values. Between pH 4 and pH 2, the R_p was reduced to a difference of 1054 KΩ.

Table 1. Fitting parameters from the applied equivalent circuit.

pH	R_1 (Ω)	C_2 (nF)	R_2 (KΩ)	C_3 (nF)	R_3 (KΩ)	C_4 (nF)	R_4 (KΩ)	χ2
10	678.3 ± 0.8	80.50 ± 0.89 x10^{-3}	227.8 ± 0.9 x10^{-3}	0.16 ± 15.06 x10^{-6}	6.9 ± 0.7 x10^{-3}	99.01 ± 20.03 x10^{-6}	18,240 ± 0.3 x10^{-3}	0.1532
9	797.5 ± 0.8	75.89 ± 0.78 x10^{-3}	248.6 ± 1.1 x10^{-3}	0.15 ± 18.34 x10^{-6}	7.3 ± 0.8 x10^{-3}	95.84 ± 25.17 x10^{-6}	15,540 ± 0.8 x10^{-3}	0.1328
8	888.4 ± 1.1	70.46 ± 0.68 x10^{-3}	269.6 ± 1.2 x10^{-3}	0.13 ± 41.20 x10^{-6}	6.7 ± 1.0 x10^{-3}	92.46 ± 33.32 x10^{-6}	12,650 ± 1.1 x10^{-3}	0.0909
7	705.5 ± 2.0	66.86 ± 0.65 x10^{-3}	270.6 ± 1.5 x10^{-3}	0.12 ± 180.10 x10^{-6}	3.8 ± 1.9 x10^{-3}	91.27 ± 53.23 x10^{-6}	8,964 ± 1.4 x10^{-3}	0.0463
6	619.7 ± 1.7	62.07 ± 0.53 x10^{-3}	291.4 ± 1.5 x10^{-3}	0.13 ± 161.90 x10^{-6}	3.9 ± 1.7 x10^{-3}	90.75 ± 84.42 x10^{-6}	6,259 ± 1.0 x10^{-3}	0.0607
4	453.9 ± 2.2	51.93 ± 0.46 x10^{-3}	297.9 ± 2.3 x10^{-3}	0.14 ± 446.00 x10^{-6}	2.3 ± 2.1 x10^{-3}	104.40 ± 216.50 x10^{-6}	3,224 ± 2.4 x10^{-3}	0.0679
2	432.3 ± 6.3	41.81 ± 0.36 x10^{-3}	305.1 ± 2.0 x10^{-3}	0.11 ± 165.50x 10^{-6}	1.3 ± 6.5 x10^{-3}	162.3 ± 429.20 x10^{-6}	2,171 ± 2.0 x10^{-3}	0.1187

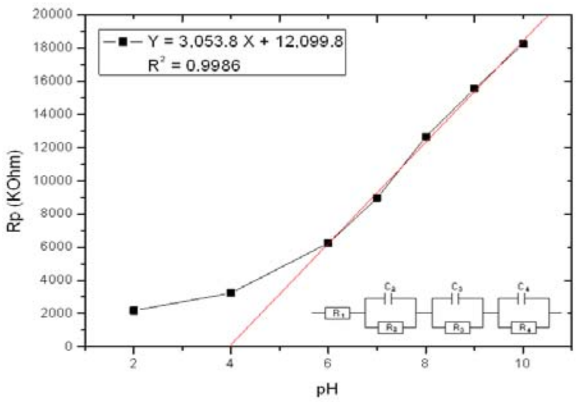


Fig. 4. Normalization after fitting for linear regression and linear fit on non-functionalized HfO_2. Inset: Applied equivalent circuit for normalization of the impedance data.

Normalization of the data obtained the best linear fit between pH 6-10 (R^2 = 0.9986, Y = 3,054X + 12,100) (Fig. 4). The linear regression decreases as the pH analyses increased in acidic conditions, where: between pH 4-10 (R^2 = 0.9885, Y = 2,609X + 8,325), and between pH 2-10 (R^2 = 0.9655, Y = 2,104X + 4,250). This signifies that the preliminary experiments applying the HfO_2 substrate functioned within basic to neutral conditions. At pH 4 the substrate due to the transition states of the HfO_2 surface, may be incapable of complete protonation (i.e. > H^+).

Applying a monolayer of 3-(aminopropyl)-triethoxysilane (APTES), the surface can possibly undergo protonation and deprotonation due to changes of the surface charge based on the amino functionality and the oxide groups based on HfO_2. For instance, Cui et al [26] applied p-type silicon nanowires (SiNWs) and pH dependent conductance measurements showed a non-linear response as conductance change was low at pH 2 to 6. A larger conductance change was observed at a higher pH range of pH 6 to 9. However, with APTES-modified SiNWs, the conductance change in pH solutions within a PDMS microfluidic channel showed step-wise changes from pH 2 to 9. The surface contained surface terminating groups of both $–NH_2$ and –SiOH groups, that at low pH, the $–NH_2$ were protonated to $–NH_3^+$ producing a positive gate which depleted the hole carriers in the p-type SiNW thus decreasing the conductance. However, at a high pH, the –SiOH was deprotonated to $–SiO^-$ and this increased the conductance. Thus, the linear response was attributable to the total surface charge density of the combined acidic and basic properties of both surfaces when versus pH variations [26].

Future experiments will be conducted to validate this preliminary result and if accurate the functionalization of the HfO_2 substrate can be prepared with APTES in order to investigate the full pH range. Measurements will also be made to study the pH shift by *c-v* curves as the change in surface potential will be measured by the capacitive sensing insulator sensor. Here, the pH response will be calculated to provide the Nernstian pH sensitivity for the FET-based high-*k* gate material at a thickness of 10.7 nm.

4. Conclusions

Silicon wafers (p-type) (100) oriented were applied for high-*k* dielectric deposition of HfO_2 by ALD. The system used H_2O as the oxygen precursor with Tetrakis(Dimethylamido)-Hafnium for the deposition of HfO_2 at a temperature of 225°C H_2O using 100 ALD cycles. The HfO_2 layer thickness was 10.7 nm with a 500 nm-thick aluminum layer deposited on the back of the wafers for electrically contacting the silicon substrate. The Nyquist plot demonstrates a high clear shift of the R_p between pH 6-10 (R^2 = 0.9986, Y = 3,054X + +12,100). At acidic conditions (between pH 2-10), the R_p change was small due to the unmodified oxide gate (R^2 = 0.9655, Y = 2,104X + 4,250). These preliminary results demonstrate the HfO_2 substrate functioned best within basic to neutral conditions and future experiments will observe the functionalization of HfO_2 with APTES for possible improvement of the pH sensing behavior.

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