J. Sens. Sens. Syst., 4, 17–23, 2015
www.j-sens-sens-syst.net/4/17/2015/
doi:10.5194/jsss-4-17-2015

JSSS Journal of Sensors and Sensor Systems Open Access

Development of a capacitive chemical sensor based on Co(II)-phthalocyanine acrylate-polymer/HfO_2/SiO_2/Si for detection of perchlorate

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Received: 30 July 2014 – Revised: 20 October 2014 – Accepted: 11 December 2014 – Published: 16 January 2015

Abstract. We report the development of a chemical sensor based on a Co(II) phthalocyanine acrylate polymer (Co(II)Pc-AP) for perchlorate anion detection. We have used two types of transducers, silicon nitride (Si_3N_4) and hafnium oxide (HfO_2). The adhesion of the Co(II)Pc-AP on different transducers and their surface qualities have been studied by contact angle measurements. We have studied the pH effect on Al/Si/SiO_2/HfO_2/electrolyte capacitance values for different phosphate buffer solutions (PBS). This optimization step has allowed a sensitivity value of about 44 mV decade^{-1} towards H^+ ions. The fabricated sensors based on Si_3N_4 and HfO_2 transducers functionalized with a Co(II)Pc-AP membrane have been characterized by C(V) measurements for different perchlorate concentrations (from 10^{-7} to 10^{-2} M). The sensor developed with the HfO_2 transducer shows better performances compared to that based on Si_3N_4: a larger detection range (10^{-7} to 10^{-2} and 10^{-3} to 10^{-2} M, respectively) and lower detection limits (10^{-7} and 10^{-3} M). The specificities of our perchlorate sensor have been tested for some interfering ions (nitrate, sulfate and carbonate).

1 Introduction

Sensors are widely used in various technological applications and have become basic enabling technologies in many fields, including safety-related areas, diagnostic and drug discovery, environmental monitoring and the food industry. However, it is a frequent task of many analytical laboratories to develop chemical sensors to detect many toxic ions that present an environmental health risk to humans. Perchlorate can present a danger to the thyroid gland, as it interferes with its iodine uptake and is associated with the disruption of its function. The perchlorate can be taken up in place of the iodide ion through the mammalian thyroid gland, and affects the hormone production. In this way, perchlorate causes abnormalities in child development and the thyroid development of cancer. Chemical sensors are based on two important parameters, namely transducers and membranes. Cobalt phthalocyanines are well known, with good chemical and thermal stabilities. Relatively important attention has been paid to the potential utility of these compounds as active sensing materials, molecular recognition species or a promising class of ionophores (Kumar et al., 2012). Another important component in the chemical sensor is the transducer. In the literature, many chemical sensors are based on an insulator substrate in which the latter plays an important role as a chemical barrier. Silicon dioxide or silica was the most widely used in

sensor devices (Wang, 2006; Castellarnau et al., 2007; Gustavsson et al., 2008). However, some inherent disadvantages reduce its effectiveness for passivation, and its high permeability toward water and other impurities (Chu et al., 1967). To overcome these problems, the use of other insulators has a larger permittivity and is more thermodynamically stable in contact with a silicon like aluminum oxide (Al_2O_3), tantalum pentoxide (Ta_2O_5), titanium dioxide (TiO_2), or zirconium dioxide (ZrO_2), and hafnium dioxide (HfO_2) is necessary to obtain a stable sensor (Campabadal et al., 2011; Park et al., 2010). These important properties can favor the development of bio/chemical sensors; for example, improved thermal stability creates a good interface for electrical performance.

In this work, we have developed two perchlorate sensors based on two types of transducers, silicon nitride (Si_3N_4) and hafnium dioxide (HfO_2) and Co(II)Pc-AP as a sensing molecule. The sensor responses were studied by capacitance voltage (C(V)) measurements in a phosphate buffer solution (10 mM, pH = 7). The sensor developed with a HfO_2 transducer shows better performances compared to that based on Si_3N_4. HfO_2/Co(II)Pc-AP shows a detection range between 10^{-7} and 10^{-2} M, larger than that of Si_3N_4/Co(II)Pc-AP from 10^{-4} to 10^{-2} M and with a lower detection limit of 10^{-7} M. The specificities of the developed sensors to perchlorate have been studied for some interfering ions: nitrate (NO_3^-), sulfate (SO_4^{2-}) and carbonate (CO_3^-).

2 Experimental details

2.1 Materials

All the chemicals used were of an analytical reagent grade. Deionized distilled water was used throughout. Tetrahydrofuran (THF), lithium perchlorate ($LiClO_4$) and piranha (1/3 hydrogen peroxyde (H_2O_2) + 2/3 sulfuric acid (H_2SO_4)) have been purchased from Aldrich. The new cobalt phthalocyanine-C-monoamido-butyl acrylate carboxyl acid (Co(II)Pc-AP) molecules (Fig. 1a) used in this work have been synthesized and purified according to the method described in the reference (Abbas et al., 2011). The phosphate buffer saline (PBS) solution ischaracterized by a concentration of 0.01 M and pH = 7.

2.2 Sensor development

The studied sensors are based on the EIS (electrolyte/insulator/semi-conductor) structure functionalized with Co(II)Pc-AP.

2.2.1 Substrate fabrication

Silicon nitride: the studied Al/Si/SiO_2/Si_3N_4 (made at the Institute of Microtechnology of the University of Neuchatel (Switzerland)) structures were based on a p-type silicon substrate, 400 µm thickness, with a resistivity of 10 Ω cm, covered with a 50 nm layer of thermally grown silicon dioxide and a 100 nm layer of silicon nitride prepared using the low-pressure chemical vapor deposition (LPCVD) technique at 750 °C. The ohmic contact was obtained using deposition of an indium/gallium alloy on the silicon unpolished face.

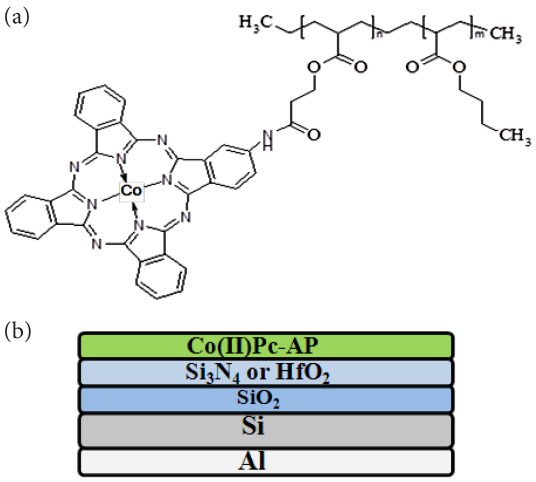

Figure 1. **(a)** Cobalt phthalocyanine-C-mono amido-butyl acrylate carboxyl acid. **(b)** Scheme of the developed perchlorate sensors: Al/Si/SiO_2/Si_3N_4 or HfO_2/Co(II)Pc-AP.

Hafnium dioxide (HfO_2) substrate was fabricated by the atomic layer deposition (ALD) technique. This technique allows the deposition of very thin layers by sequential self-terminating gas–solid reactions (Campabadal et al., 2011; Hausmann and Gordon, 2003). The sample structures were made on 100 mm diameter oriented p-type silicon wafers (1 0 0), with a resistivity of 4–40 Ω cm. We have used the Savannah-200 ALD system set up at IMB-CNM (Campabadal et al., 2011), which consists of a thermal ALD system at a controlled temperature and under vacuum. The system uses deionized H_2O as the oxygen precursor, together with tetrakis(dimethylamido)-hafnium for HfO_2 deposition and N_2 as the carrier/purging gas. Deposition of the HfO_2 layer was carried out at a temperature of 225 °C and at a base pressure of 300 mTorr using 100 ALD cycles. A first estimation of the deposited HfO_2 layer thickness was carried out by means of ellipsometry, obtaining a thickness of 10.7 nm having fixed the refractive index to 2.07. Finally, a 500 nm thick aluminum layer was deposited on the back of the wafers for electrically contacting the silicon substrate.

2.2.2 Sensors fabrication

Silicon nitride and hafnium dioxide transducers were cleaned for 15 min with acetone in ultrasonic, and then rinsed with ultra-pure water and dried under nitrogen flow. Afterwards, we spent time activating these surfaces:

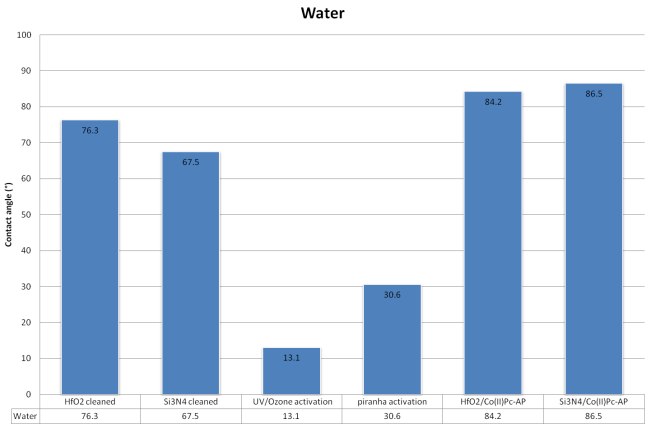

Figure 2. Contact angle histogram for $Al/Si/SiO_2/HfO_2$ and $Al/Si/SiO_2/Si_3N_4$ electrodes.

– the electrode based on hafnium was put in a UV-ozone cleaner for 30 min;

– the nitride electrode has been activated by piranha solution for 3 min and then rinsed with UPW and dried with N2.

Using the spin coating technique, we have deposited 50 µL of a Co(II)Pc-AP solution with a concentration of 4 mg into 1 mL of THF on the surface transducers. Finally, the thin films were dried at room temperature for 24 h to evaporate the solvent. The developed sensors are shown in Fig. 1b.

2.3 Instrumentation

Contact angle measurements were performed with a model contact instrument (Digidrop) form GBX (Romans, France) in order to verify the presence of the deposited thin film. First, we applied 5 µL of deionized water to the thin film surface. Afterward, the water droplet behavior obtained on the surface was acquired with a digital camera and analyzed.

All electrochemical experiments were conducted at 25 ± 3 °C inside a Faraday cage. The measurement window of the working electrode was calculated with an effective surface of 0.3 cm^2. Measurements were made with a platinum plate counter electrode, and an Ag/AgCl reference electrode (Radiometer Analytical, France). All measurements were made with a 5 mL freshly prepared PBS solution (10 mM and pH = 7) in order to fill the electrochemical cell, while the analysis was performed using a VMP3 Bio-Logic Science Instrument, France. Capacitance-voltage C(V) measurements were carried out at a DC voltage that was swept from −1 to 1.5 V, and an AC voltage was superposed with a fixed frequency of 10 kHz.

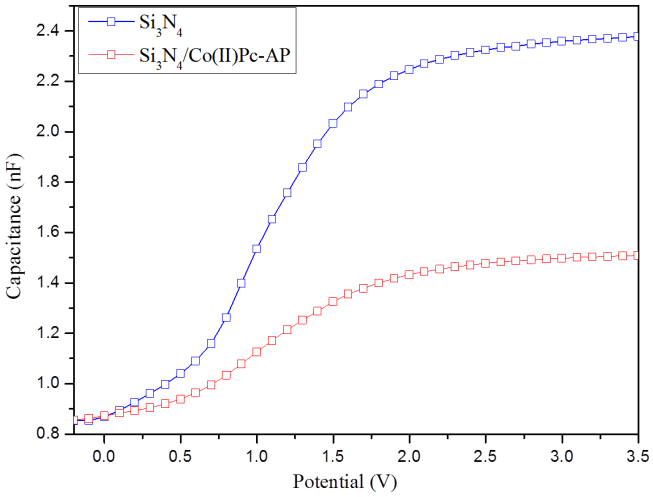

Figure 3. C(V) characteristics of $Al/Si/SiO_2/Si_3N_4$ before and after functionalization with Co(II)Pc-AP.

3 Results and discussion

3.1 Surfaces study

To investigate the hafnium and nitride surface quality, a wettability study was performed. Before and after thin film deposition, the surfaces were analyzed with water as the liquid probe. Figure 2 shows the evolution of the contact angle as a function of the treatments performed on the transducer surfaces. A contact angle of 76.3° was measured, showing the slightly hydrophilic nature of the HfO_2 surface. Upon surface activation with UV/ozone, HfO_2 became highly hydrophilic, with a contact angle value of about 13.1°. The k value of HfO_2 is 25 (Wilk et al., 2001) and thus highly polar. As shown in accordance with the k value of HfO_2, upon activation, this surface increased in polarity. For Si_3N_4 we notice an increase in the hydrophilic character of the surface from 67.5 to 30.6° after piranha activation. This is attributed to the presence of silanol (Si–OH) and silylamine (Si–NH) groups (Hajji et al., 2000) on the silicon nitride surface, which leads to a good adhesion of the membrane. The contact angle of the Co(II)Pc-AP surface was measured and given a value of about 87.6°. This clearly demonstrates that the Co(II)Pc-AP molecule has been deposited on the transducer surfaces, and it indicates that the surface has decreased in its hydrophilic properties.

3.2 Sensor performance study

3.2.1 $Si/SiO_2/Si_3N_4$/Co(II)Pc-AP sensor structure

Figure 3 shows the measured C(V) characteristics before and after functionalization of the transducer with the sensing molecule. A typical set of C(V) curves was obtained and a decrease in the capacitance in the accumulation regime was observed. This is due to the membrane deposited onto the

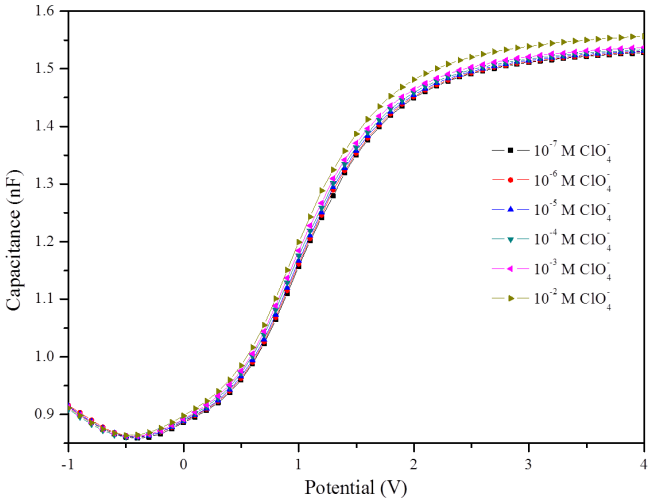

Figure 4. Variation of capacitance versus potential for the Al/Si/SiO_2/Si3N4/Co(II)Pc-AP structure for various perchlorate ion concentrations. Test solution PBS 10 mM and pH = 7.

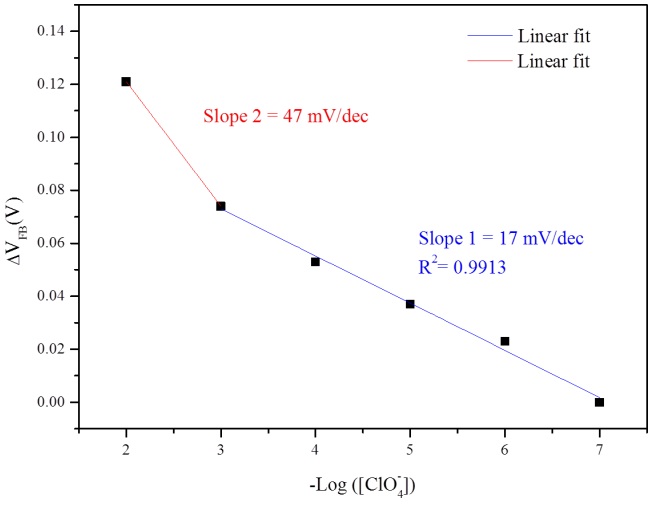

Figure 5. Variation of the flat band potential of the Al/Si/SiO_2/Si_3N_4/Co(II)Pc-AP structure versus perchlorate anion concentrations.

Si_3N_4 surface. Indeed, the insulator thickness increases in the EIS structure induce a decrease in the capacitance, which is given by

$$C = \frac{\varepsilon s}{e},$$

where C is the capacitance, ε is the insulator dielectric permittivity, S the surface area of the work electrode, and e is the insulator thickness.

Figure 4 shows the response of the Al/Si/SiO_2/Si_3N_4/Co(II)Pc-AP structure versus different perchlorate concentrations from 10^{-7} to 10^{-2} M. We note a low evolution in the C(V) curves as a function of perchlorate concentrations. When charges are adsorbed

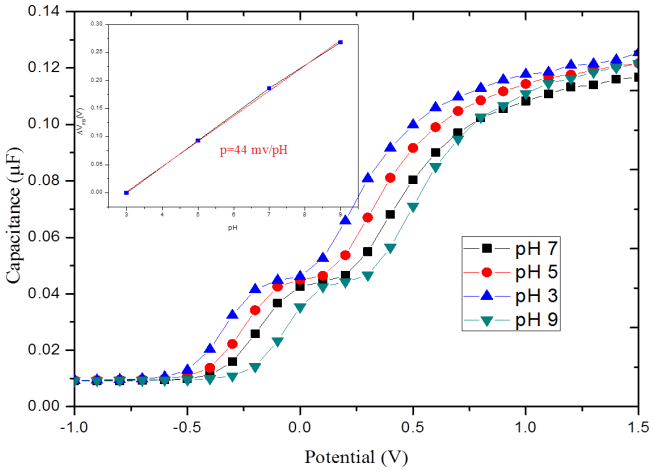

Figure 6. Evolution of the C(V) characteristics of Al/Si/SiO_2/HfO_2 as function pH; inset: flat band potential variation versus pH.

at a pH-sensitive insulator–semiconductor (IS) transducer surface, the C(V) curves shift along the potential axis. The flat-band potential varies with perchlorate concentrations in a bulk solution. The sensor sensitivity is determined by the slope of the curve, giving ΔV_{FB} as a function of the perchlorate concentrations. We note in Fig. 5 the presence of two slopes: slope (1) of about 17 mV decade^{-1} indicates a very low detection of perchlorate in low concentrations and slope (2) of about 47 mV decade^{-1} indicates sub-Nernstian sensitivity in high concentrations. Also, we notice a very low decrease in the capacitance in the accumulation regime. Viewing the poor performances of the sensor based on a nitride transducer, we have thought to change the nitride with the hafnium, which is characterized by a high dielectric constant.

3.2.2 Si/SiO_2/HfO_2/Co(II)Pc-AP sensor structure

To study the pH sensitivity of the Al/Si/SiO_2/HfO_2 structure, the capacitance voltage of the EIS structure was measured in various standard pH buffer solutions ranging from pH = 3 to pH = 11. As shown in Fig. 6, we notice that the C(V) characteristics exhibit a hysteresis behavior significant charge trapping in the SiO_2/Si interface (Fan et al., 2012). We note a variation in the flat band voltage (ΔV_{FB}) as a function of pH values. The pH sensitivity was calculated from the slope of flat band voltage, which is obtained from the C(V) curves. The dependences of the calculated pH sensitivity and linearity of the Al/Si/SiO_2/HfO_2 structures are exhibited in the inset of Fig. 6. The pH sensitivity obtained is about 44 mV/pH; this value is close to the values reported in the literature for HfO_2 deposited by the ALD technique (Lu et al., 2011; Wang et al., 2012).

The functionalization of the hafnium transducers has been followed by C(V) measurements, as indicated in Fig. 7. To characterize the response of the developed

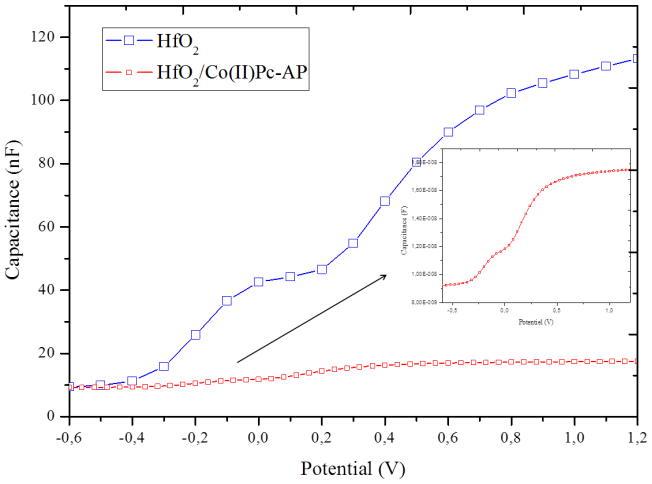

Figure 7. C(V) characteristics of Al/Si/SiO_2/HfO_2 before and after functionalization with Co(II)Pc-AP. Test solution PBS 10 mM and pH = 7.

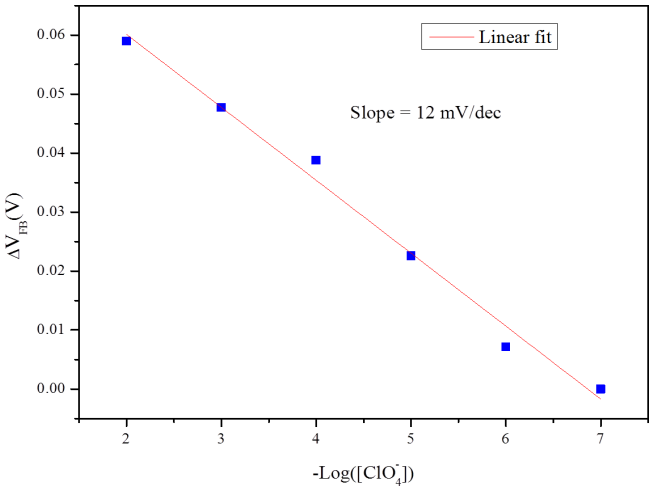

Figure 9. Variation of the flat band potential of the Al/Si/SiO_2/HfO_2/Co(II)Pc-AP structure versus perchlorate concentrations.

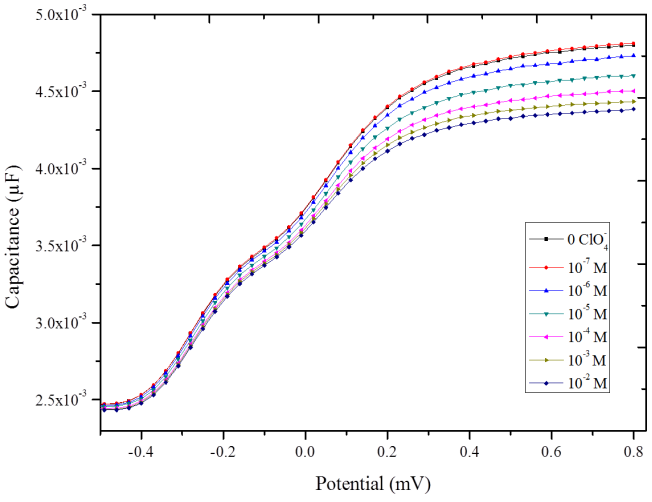

Figure 8. Variation of capacitance various potential for the Al/Si/SiO_2/HfO_2/Co(II)Pc-AP structure for different perchlorate anion concentrations. Test solution PBS 10 mM and pH = 7.

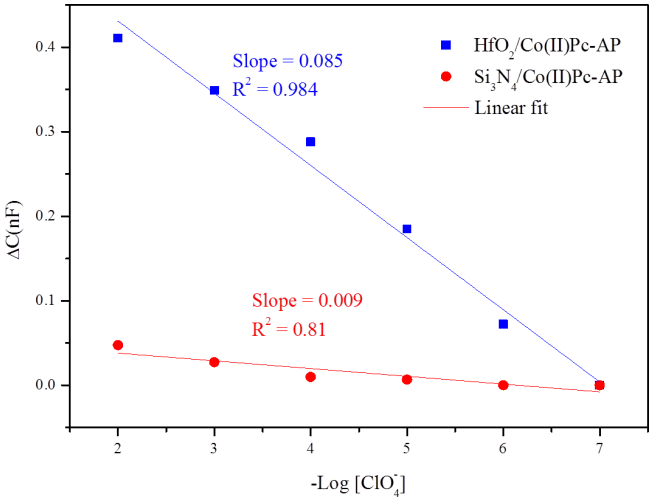

Figure 10. Evolution of the accumulation capacitance for Al/Si/SiO_2/Si_3N_4 Co(II)Pc-AP and Al/Si/SiO_2/HfO_2/Co(II)Pc-AP structures versus perchlorate anion concentrations. Test solution PBS 10 mM and pH = 7.

Al/Si/SiO_2/HfO_2/Co(II)Pc-AP structure to perchlorate anions, we have measured the C(V) as a function of perchlorate concentration. We notice an important decrease in the capacity in the accumulation regime and a low shift of the flat-band potential (V_{FB}), as shown in Fig. 8. The calculated sensitivity from Fig. 9 is about 12 mV decade^{-1}, which is close to the slope obtained for Si_3N_4 (17 mV decade^{-1}). Furthermore, an important variation in the capacitance in the accumulation regime was observed as a function of perchlorate concentration. This means that we have a change in the thickness of the recognition membrane, which can be attributed to the perchlorate detection by Co(II)Pc-AP. The response of the HfO_2/Co(II)Pc-AP sensor for some anions is believed to be due to coordination of the perchlorate anion as an axial ligand to the metal center of the carrier molecule (Said et al., 1999; Eman et al., 2009).

Figure 10 shows a linear capacitance variation as a function of perchlorate concentration in the accumulation regime. We can notice that the capacitance variation for the HfO_2-based structure is larger than that of the Si_3N_4-based one. This behavior can be assigned to better thermal stability on silicon (by using the ALD technique), and a higher dielectric constant of the HfO_2 transducer when compared with Si_3N_4 (Wilk et al., 2001). We have also determined the metrological parameters of the HfO_2-based sensor characterized by an important linear detection range from 10^{-7} to 10^{-2} M and a low detection limit of about 10^{-7} M.

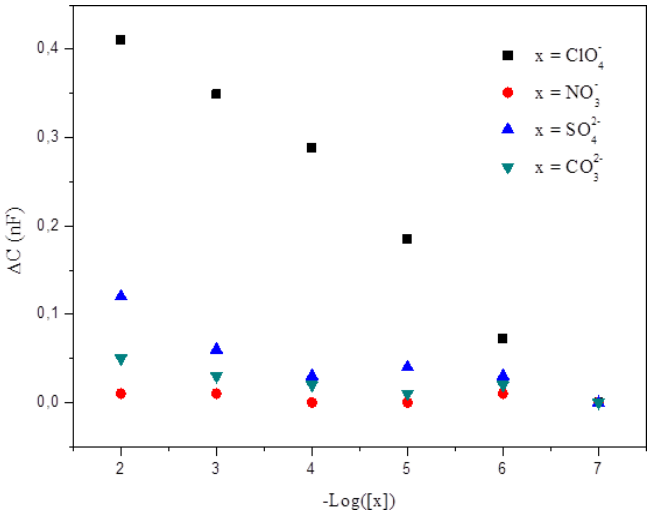

Figure 11. Evolution of the accumulation capacitance as a function of ClO_4^-, NO_3^-, SO_4^{2-}, and CO_3^{2-} anions. Test solution PBS 10 mM and pH = 7.

Table 1. Metrological parameters of the studied sensors based on Si_3N_4 and HfO_2.

Sensor	Detection limit (M)	Detection range (M)
Al/Si/SiO2/Si3N4/Co(II)Pc-AP	10^{-3}	10^{-2} to 10^{-3}
Al/Si/SiO2/HfO2/Co(II)Pc-AP	10^{-7}	10^{-2} to 10^{-7}

The specificity of the Al/Si/SiO_2/HfO_2/Co(II)Pc-AP sensor has been studied towards some interfering anions NO_3^-, SO_4^{2-}, and CO_3^{2-}. Figure 11 shows the accumulation capacitance variation as a function of the interfering anion concentrations. We note an important variation in the capacitance for perchlorate concentration compared with that of the other anions.

4 Conclusions

In this work, we have developed two capacitance sensors based on Al/Si/SiO_2/Si_3N_4 and Al/Si/SiO_2/HfO_2 transducers for detection of perchlorate anions. The latter shows a better sensing performance, with a detection range (10^{-7} to 10^{-2} M) and a low detection limit of 10^{-7} M. These improved performances have been explained by the physical properties (thermal stability and high dielectric constant) of the HfO_2 transducer. The specificity of the Al/Si/SiO_2/HfO_2/Co(II)Pc-AP sensor has been studied towards some interfering anions (NO_3^-, SO_4^{2-}, and CO_3^{2-}).

Acknowledgements. This work was partially supported by FP7-PEOPLE-2012-IRSES no. 318053: SMARTCANCERSENS and NATO Science for Peace (CBP.NUKR.SFP 984173) FP7-PEOPLE-2012-IRSES no. 318053: SMARTCANCERSENS.

Edited by: M. Penza
Reviewed by: two anonymous referees

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