EIS capacitor sensor, with TiO_2 dielectric, applied in the evaluation of phosphate in wastewater.

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***Abstract*—This work presents the development of an Electrolyte-Insulator-Semiconductor (EIS) device with a built-in reference electrode to detect phosphate in wastewater. The idea of developing this device comes from the need to improve the use of water processed by the effluent treatment plant. After treatment process, a fraction of the water can be used as wastewater, this water cannot be consumed, however it can be used for other purposes including cleaning public spaces, such as streets and squares. In the fabrication process of the EIS device, titanium oxide (TiO_2) deposited on a silicon substrate was used as a sensor element, and titanium nitride (TiN) was used for the reference electrode. Both materials were deposited by the reactive sputtering process. Aluminum (Al) was used for the electrode on the back of the slide deposited by evaporation. Preliminary results of structural and electrical characterizations indicate that the manufactured device has good sensitivity to phosphate ions (66 mV/ppm). This sensitivity is due to the good quality of the film, which is shown using Raman spectroscopy, atomic force microscopy (AFM) and X-ray diffraction (XRD) techniques, in addition to electrical measurements.**

***Index Terms*—TiO_2, TiN, Electrolyte-Insulator-Semiconductor, phosphate, reference electrode.**

I. Introduction

Since the 60s, there has been a concern to minimize the phosphate contamination of aquatic environment, essentially lakes, rivers and coastal estuaries which receive wastewater directly from human activities, mainly with high concentrations of pharmaceutical industries and sewage. The scale of the problem is worrying, and unfortunately some activities are related to the contribution of pumping around of 3 Tg (Tg = million metric ton) of phosphorus into waters every year and such event could undergoes an increasing about 5 Tg until 2050 [1], [2]. The environmental impact of high levels of such nutrients is related to eutrophication. Although rivers and lakes have a low concentration of nutrients in the water, with the increase of phosphate rates, the water became a source of overfeeding the algae ecosystem. As they receive this amount of nutrients, its population becomes larger, and an algae bloom is induced, forming a greenish layer near the surface [3]. This layer is harmful for the living forms in the water because it blocks or reduces the sunlight and consequently causes the extinguishing of certain living forms, such plants and other fauna that cannot swim away, thus reducing fish and aquatic life diversity [4]. In addition to it, the eutrophication particularly of rivers can be accelerated in some regions due to agricultural spraying that uses fertilizers and pesticides with a high concentration of phosphate, adding this to the sewage that is directed to the rivers and with the incorrect treatment of industrial waste, the phosphate levels in the environment will increase [5]. Beside the environmental damage, phosphate can also cause serious problems in humans, despite being a crucial nutrient for life, excessive levels can cause serious complications such as kidney and vascular problems. Phosphate can bond with calcium and form calcium phosphate which is insoluble and can cause blood vessel blockage [6].

Considering this, much research has been conducted towards developing ways to detect contaminants during the capture, treatment, distribution, effluent treatment, and water reuse stages. With technological advances, sensor devices have been gaining ground since detection techniques are currently expensive [7]. To provide the monitoring of high levels of phosphate, it is mandatory to sensing the water, which includes means like colorimetric, fluorescent phosphate detection and electrochemical methods. Among these techniques, electrochemical can be superior in many aspects, but the superior advantage is related to avoiding some sophisticated optical structures to read the data from analysis [8]. Using electrochemical methods can provide some electrical disturbances capable of being checked with parameters analyzers and even portable devices. The electrochemical sensors based on EIS (Electrolyte Insulator Silicon) have been attractive due to their fast response, large variety of ions and similarity with MOSFET integration technology that leads to miniaturization [9]. Such devices generally used oxides like SiO_2, Al_2O_3, ZnO, Ta_2O_5, and ZrO_2 [10], [11]. One drawback that remains is about the degradation of these materials, once in such conditions they are exposure to a very long period of reactive environment and sometimes occurs the formation of thin interfacial compounds that can affect the measurements [12]. In order to explore new materials with similar properties of oxides and to provide further investigation of the previous work [13]-[15] the authors decided to analyze the results of TiN and TiO_2. Some studies related to sensors developed at the School of Electrical and Computer Engineering (FEEC), such as: [13]-[15], provide some models of sensor devices that have been used for many years. Sensors that are studied could be manufactured in a relatively simple way and applied in solutions such as detection of contaminants in water. An example of this is the work of [16], who manufactured ion-sensitive devices for detecting lead in water. Using the techniques and materials studied, to develop a simple and cost-effective sensor device based on EIS capacitors, using TiO_2 as a dielectric and sensor element, to evaluate the concentration of phosphate ions in the water post-processed by the effluent treatment plant.

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II. EIS SENSOR AND THE TiO_2

With the aim of improving the quality of life, a range of sensors are used, each with its specificity dedicated to a predefined purpose or not. A widely used solution is the Ion Sensitive Field-Effect Transistor - ISFET, which is a transistor that detects a variation in the current x voltage (IxV) curve, according to the change in its gate, however, the ISFET demands many steps during the manufacturing process, taking time and increasing costs of the final device.

Figure 1, show the structure of an ISFET(a) and EIS(b).

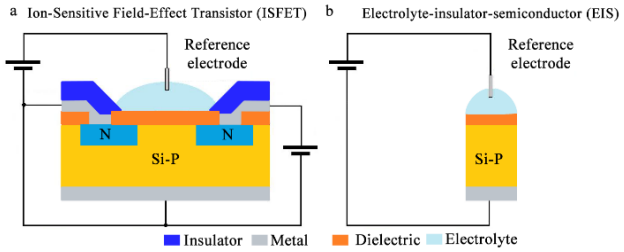

Figure 1- Comparison between the structures of the ISFET and EIS devices

Analyzing the ISFET device and its operation, it is noted that the region most affected by the electrolyte is the gate, and checking its operation, it is noted that it is close to a capacitor, with that, there was the idea of using only the gate region and developing a device that would be able to detect variations in the electrolyte at a significantly lower cost. The device created was the EIS capacitor, such a device is quite simple when compared to the ISFET, quick to manufacture and equivalent in terms of sensitivity, with the difference that the capacitance voltage curve (CxV) is used to check the device.

Figure 2 shows two models of capacitive EIS sensors, both are fabricated on a semiconductor substrate (p-type Si) with a back side metal contact layer and dielectric thin film deposited on the bottom of the p-Si wafer. The analyte under study will be dripped onto the device, the metallic oxide will function as a selective membrane and sensor element, and the metal as a reference electrode. In Figure 2a is showed a traditional model of EIS sensor, where the reference electrode is extern while in figure b, the sensor presents here, the reference electrode was fabricated on the TiO_2 layers. The integrated reference electrode improves the measurements because the place where the manipulator electrode will be positioned is fixed, preventing the researcher from having to align the external electrode to perform the measurements, with this the researcher gains time and reliability in measurements, in addition to the reference electrode helps to delimit the area of the electrolyte position.

In figure 2c we can see the device that was manufactured in this work. The arrows indicate the TiO_2 selective membrane and the TiN reference electrode, both deposited by sputtering. Such structural characteristics of the films will be discussed later in the structural characterization section.

Figure 2d shows the curve that exemplifies the generic variables you would like to obtain with the proposal. In the behavior of the readings, we must note that the curves are displaced in relation to the previous curve, the behavior obtained with this work was the displacement to the right as the phosphate concentration was increased will be shown in the electrical characterization section.

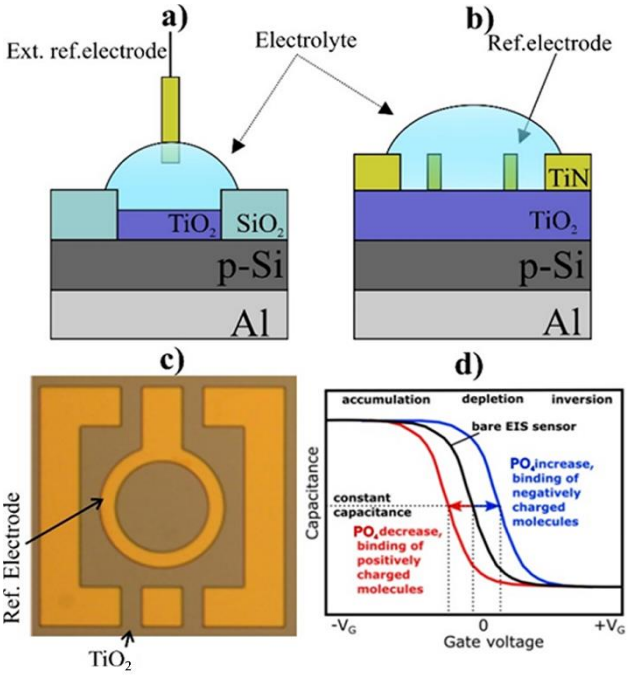

Figure 2: *a) EIS capacitor without reference electrode; b) proposed EIS capacitor; c) manufactured EIS capacitor and d) generic curves of the behavior of electrical measurements. adapted from [8]*

Once an analyte (electrolyte) in the sensor, it is applied a tension between reference electrode and the back side to modulate the capacitance. The equivalent can be approached in two capacitances in series, the gate-insulate capacitance (C_G) and the variable semiconductor space charge capacitance (C_S) which is a function of gate voltage (V_G) and the electrolyte insulator interfacial potential (φ) - $C_S(V_G, \varphi)$. The Total Capacitance (C) is evaluated by Equation 1 [17]:

$$C = \frac{C_G C_s(V_G,\varphi)}{C_G + C_s(V_G,\varphi)} = \frac{C_G}{1 + C_G/C_s(V_G,\varphi)} \quad (1)$$

When the V_G is fixed, the interfacial potential is the only variable component, and works as applied voltage on the gate. The change of the interfacial potential will occur when the surface of the metal oxide interacts with the analyte components by chemical reaction, furthermore, TiO_2 is characterized by chemical stability-durability, non-toxic, environmentally friendly, and low cost [18].

TiO_2 is adequate dielectric thin to this device due its affinity with phosphate. Moreover, the surface of TiO_2 deposited by sputtering is rich in hydroxyl [19] groups which allow the binding with PO_4. In addition, in a recent work, TiO_2 was applied to removal phosphate from aqueous environmental. These properties have improved the attention to TiO_2 [20].

III. METHODS

In this section, the manufacturing means and characterization techniques will be presented. The preparation was carried out with a photo aligner (Karl Suss MJB3) with photoresists 1518 and 5214, MIF 300 developer and quartz masks. The metallic films were deposited via sputtering (Sputtering Orion 8 phase III), with TiO_2 99.99% and Ti for TiN targets. And Al was deposited by evaporator in ultra-high vacuum. TiO_2 was characterized by Raman (Remishal InVia), XRD

(Philips X'Pert-MPD X-ray Diffraction System), AFM (Park NX10 Park Atomic Force Microscope), ellipsometry (Rudolph Auto EL III, SS292 Ellipsometer). Electrical measurements on the semiconductor parameter analyzer (Keithley 4200-SCS).

A. EIS Device Fabrication Process

The fabrication of ion-sensitive devices requires, in principle, basic studies about microdevice fabrication methods and physical characterization of thin films [21]. The device proposed in this research is simple, and has reduced costs and production time, when compared to current methods of phosphate detection [22]. Despite the simplicity, it has a new feature which combine integration of a reference electrode with the structure, which adds more practicality and reliability to electrical measurements.

Figure 2.a and 2.b shows the schematic representation of cross section profile of the EIS capacitor. Figure 2.c is an optical microscope image of the surface of the EIS, where is possible to observe the TiN and TiO_2 structures.

Figure 3 presents a flowchart of the fabrication steps of the EIS capacitor. The device was fabricated on Si-p+ wafer which was followed by RCA cleaning to remove Na+ and Cl- ion contaminates. Next, the 40 nm TiO_2 was deposited by sputtering DC over all the wafers. In sequence, the electrode structures were defined by photolithography and 100 nm TiN were deposited by sputtering DC. Then, the sample went through the Lith-off process to eliminate the excess TiN deposited. The next step was to protect the surface structure by photolithography. In fact, a thin film of photoresist was deposited via spin coating over the sample. Next, a chemical etching as applied behind the sample, removing the native SiO_2 of the Si wafer. And finally, 150 nm Al was deposited by evaporation and the photoresist was removed by organic cleaning.

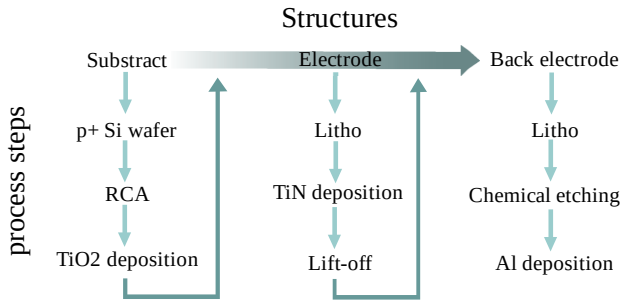

Figure 3-Flowchart of EIS process fabrication

IV. Results and Discussions

A. Structural Characterization

At the end of the device fabrication process, physical characterization of TiO_2 active region was carried out. Hence, the techniques of Raman spectroscopy, X-Ray Diffraction (XRD), and Atomic Force Microscopy (AFM) was applied to obtain information about the crystalline structure and surface characteristic of the TiO_2 deposited.

Figure 4 presents the results of the characterization methods. Figure 4.a) present the Raman analyses of the TiO_2/Si. One can observed peaks of silicon (Si), due to the thin thickness of the oxide, and peaks of crystalline forms of TiO_2, rutile (R) and anatase (A). Details about Raman spectroscopy and oxide characteristics can be better studied through research developed by [23]-[25].

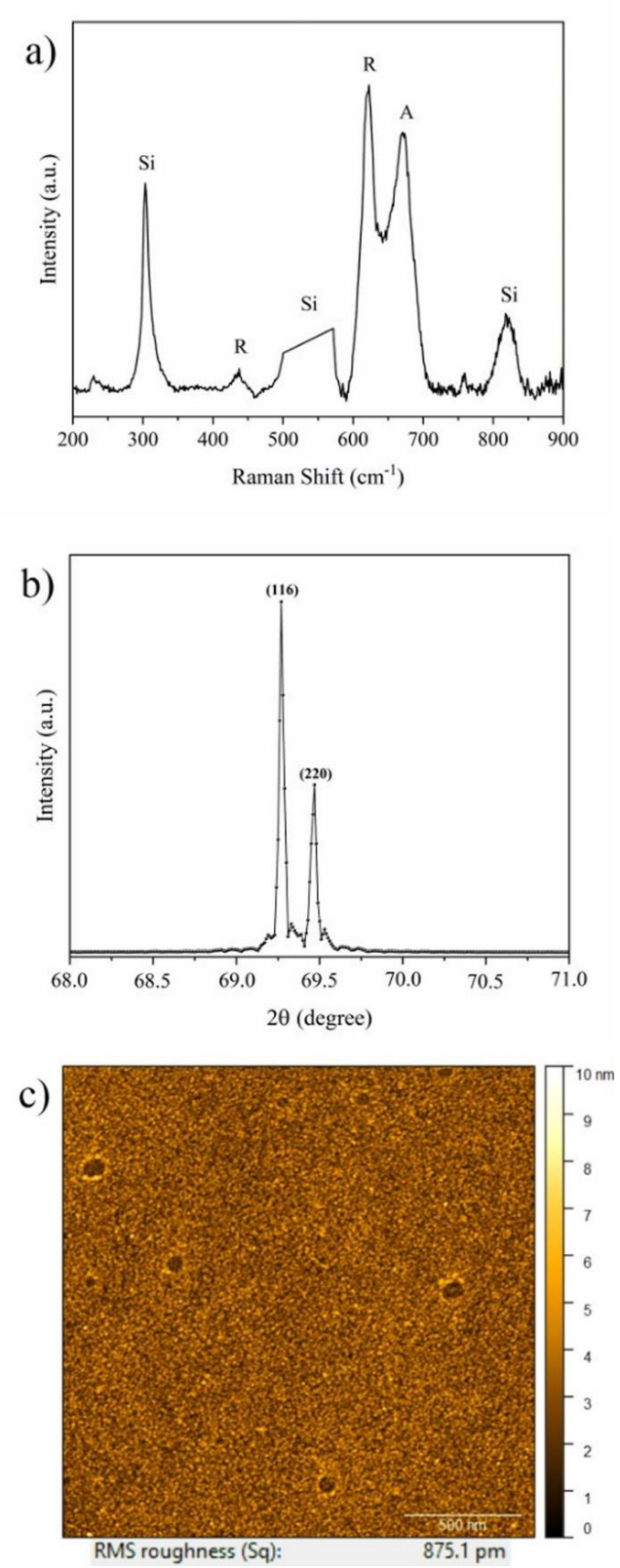

Figure 4- Structure characterization. a) Raman, b) xrd and c) AFM.

Figure 4.b) presents the XRD analyses of TiO_2/Si where the peaks that represent the anatase and rutile forms, in the (116) and (220) orientations stand out (JCPDS 21-1272 and JCPDS 21-1276) [26], rutile is the most sought-after form

when it comes to biochemical sensors using titanium dioxide as a sensing element [27].

Figure 4.c) presents the acquisition of AFM images, the INTEGRA Spectra equipment operating in non-contact mode was used. Images with an area of 2 μm^2 were acquired from samples of TiO_2 films with a thickness of 40 nm obtained by reactive sputtering. Thin film thickness was measured using an ellipsometry technique. With the aid of the image processing software MIPAR and Image Analysis, it was possible to obtain the three-dimensional images and the RMS (Root Mean Square) roughness values, as shown in Figure 4.c). In this analysis, the grain size was measured, which had around 12 nm and an average roughness of 875.1 pm. The values of grain size and roughness are important because we can obtain a larger contact area, increasing the sensitivity of the device, due to the possibility of carrying out a larger volume of chemical bonds between TiO_2 and the PO_4 solution.

B. Electrical Characterization

For the electrical characterization of the EIS device, voltage capacitance measurements (C-V) were performed as a function of the phosphate ion concentration in deionized water. All measurements were performed using a Keithley 4200-SCS semiconductor parameter analyzer available on Centro de Componentes Semicondutores e Nanotecnologia (CCSNano).

For phosphate concentration measurements, voltage capacitance measurements were performed using an AC signal with a frequency of 10 kHz. Different concentrations of phosphate salt dissolved in deionized water were tested. The solutions were dripped in amounts between 0.2~0.8 µL, using a 2.0 ±0.2 µL micropipette. Before dripping the solution onto the device, measurements were carried out to equip both the device and the electrical signal handling equipment. The measurements were then carried out by the solution containing 0.1 ppm and the C-V measurement was made, then, without washing the device, the second solution with 1 ppm of phosphate was dripped and the C-V measurement was performed again, repeated with the solutions of 10 ppm, 100 ppm and 1000 ppm. The measurements were made in this way to minimize the chances of contamination and voltage drift effects caused by residual potentials in the materials and equipment used. The results are shown in Figure 6, where the reader can see the sensor response for each concentration, it is noted that the flat band voltage Vfb, shifts to the right whereas the phosphate concentration in the solution increases, because of the bonds made between the phosphate ions and the titanium oxide of the dielectric, causing the device capacitance to change according to the concentration value. In Figure 5, the graph shows that the higher the phosphate concentration, the higher the flat band voltage (Vfb), as the curves shift to the right, as the substrate is p-type.
With measurements of voltage capacitance as a function of phosphate concentration, it is possible to extract the Vfb values for each of the phosphate concentration values, thus obtaining the Vfb curves as a function of phosphate concentration, as shown Figure 5, and thus, obtain the sensitivity value for phosphate which is shown in Figure 6.

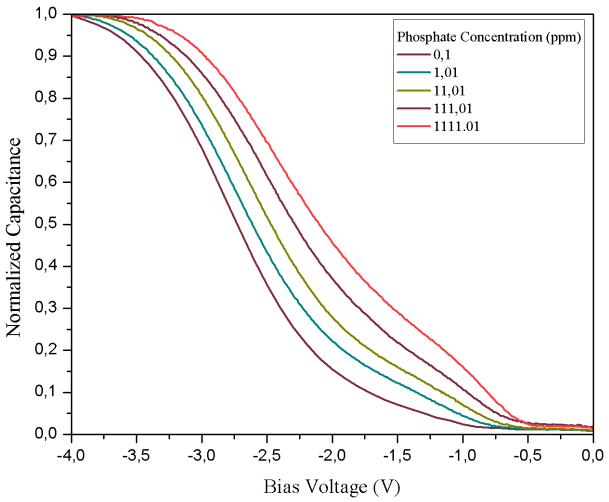

Figure 5-Normalized capacitance x voltage curves as a function of the phosphate concentration in water of the measurements performed on the EIS devices.

In the literature we did not find sensors equal to what was proposed in this work, so for comparison purposes, we used studies that use sensors with the same principle to evaluate pH solution, in these works the sensitivity values vary between 51.32 mV/pH [28], 58.3_mV/pH [29] and 61 mV/pH [30], values close to the Nernst number ~59.2 mV/pH.

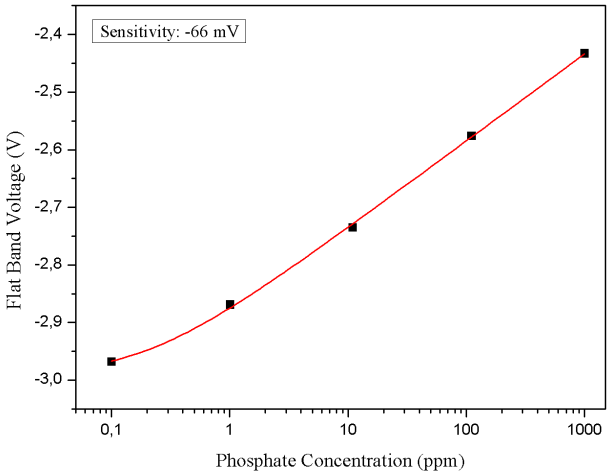

Figure 6-Vfb flat band voltage curve as a function of phosphate concentration used to calculate the sensitivity of the EIS device for measurements of phosphate concentration in deionized water.

V. Conclusions

The work showed the results in obtaining MOS devices, such as EIS devices. The result obtained from the sensitivity extracted from the V_{fb} curve as a function of the phosphate concentration (66 mV) showed the device's good sensitivity in detecting phosphate ion in aqueous environment. This can be attributed to the higher adsorption capacity of the surface area of TiO_2 obtained by reactive sputtering. Therefore, the use of the EIS device for measurements of phosphate (PO_4) concentration in the final total dialysate proved to be feasible. In this work, the EIS device fabricated evidenced to be efficient in view of the proposed measurements, being a good alternative to replace the analyzes performed in the laboratory.

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