Electrolyte-Insulator-Semiconductor device with integrated titanium nitride reference electrode for pH detecting.

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1. Abstract

In this work Electrolyte-Insulator-Semiconductor (EIS) device has been developed for pH measurements. This device operates as a Metal-Oxide-Semiconductor capacitor but instead of having the metal contact electrode, an electrolyte solution and a reference electrode are used to apply voltage. Titanium nitrite (TiN) was used deposited by sputtering as reference electrode integrated with EIS device. As dielectric material and sensitive membrane was chosen titanium dioxide (TiO_2). This film was obtained by sputtering, and was structurally characterized by Atomic Force Microscopy, Raman and Ellipsometry. For electrical measurement of EIS was used Normalized Capacitance x Voltage curve (CxV curve) using different pH (4, 7 and 10) solutions. From the flat band voltage (V_{FB}) of the Normalized CxV curves was possible to test the TiN reference electrode and to determine the sensitivity of 20mV/pH for pH.

2. Introduction

The structure of the Electrolyte-Insulator-Semiconductor (EIS) and their operation are similar to the Metal Oxide Semiconductor (MOS) capacitor [1]. As advantages over other types of devices, the EIS have small size, fast response time, low cost and because of their size it can be used as a micro portable analysis system [1]. It makes it possible to test different sensitive membranes for chemical, biological or medical applications without the necessity of a complex processing, as the amount of lithographic steps.

Titanium dioxide (TiO_2) thin film, in particular, is material extremely studied and of great interest for many researches due to its attractive qualities, which includes chemical stability, high dielectric constant (high k) and ability to form hydrogen bonds [2]. These qualities permit the application of TiO_2 thin film as sensitive membrane into EIS devices resulting in a high sensitivity [2].

TiN is widely used as metal gate in MOSFET [3]. In this work TiN will be used as reference electrode and will be integrated into the EIS device. In most of the works the EIS does not have internal reference electrode, integrated to the device [2].

Therefore, this work presents the development of the EIS with TiO_2 being the sensitive membrane and having the TiN reference electrode integrated into the device.

A. Fabrications of EIS

The samples were manufactured in this work using p-type Si wafers with 100 crystal orientation as substrates. First, the substrates are cleaned by the RCA method. Then was made dry oxidation, to form the insulation oxide. This oxide has a thickness of 0.7 µm. For the next step was used photolithographic process. The silicon dioxide thermally grown was corroded, to form the small wells were the solutions should be confined. Then was used the same photolithographic process for titanium dioxide deposition. About 50 nm of titanium dioxide was deposited by reactive DC sputtering. The best near-stoichiometric TiO_2 was obtained using 65% of Ar and 40% of O_2 as reactive gases and 1000W power applied to the cathode. In this step the control samples were separated for structural analyses of TiO_2 thin film. The TiO_2 film was deposited on the bottom of the well in contact with the silicon substrate. After the native oxide was removed from the bottom of the wafer and 300 nm of aluminum was deposited by sputtering to form the back contact. Then the annealing process was carried out. This process occurred in a conventional oven in green gas (H_2 and N_2) for 10 min. This is the time that TiO_2 has the best electrical performance [1]. To form the reference electrode was used a photolithographic process and 200 nm of titanium nitride was deposited by sputtering DC. Fig. 1 shows de EIS device with TiN as a reference electrode and the TiO_2 with sensitive membrane.

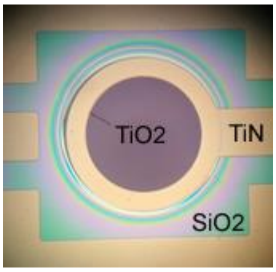

Fig.1. *Electrolyte-Insulator-Semiconductor with TiN as reference electrode.*

B. Structural characterization of TiO_2 thin film

In this analysis were used Ellipsometry, Raman spectroscopy and Atomic Force Microscopy from TiO_2

control samples.

From Ellipsometry analysis was possible to extract the physical thickness (Tox) and refractive index (η). The Tox was equal to 50nm and the refractive index was 2.44, which is similar to the 2.41 reported in the literature [2] related to rutile crystalline structure.

Fig. 2 shows the raman analysis, and reveals the presence of the rutile crystal structure [2] due to the raman shifts in 430 cm^{-1} and 600 cm^{-1} (in red) and the presence of the anatase [2] structure in 666 cm^{-1} (in blue), as well as the presence of the silicon Raman shifts in 300 cm^{-1} and 500 cm^{-1} (in black) [2].

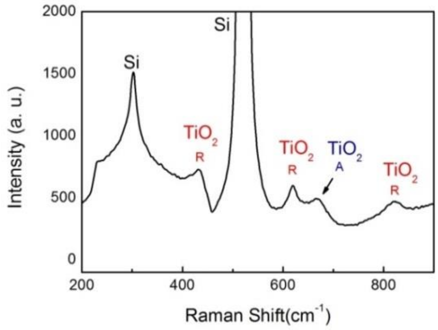

Fig.2. *Raman spectrum of the TiO_2 film.*

Is very common the presence of the two crystalline forms in the same film, because the sputtering process occurs at room temperature [2].

From Atomic force microscopy (AFM) was possible to note the presence of a smooth surface, with Root Means Square (RMS) value equal to 0.4 nm. According to literature [5] films used in EIS device shows RMS equal 0.8 to 2nm.

C. Measurement of EIS for pH detection.

For this measurement the EIS sensor was placed in a probe station. For front contact was used TiN reference electrode and for back contact the probe station holder. The solution was applied in contact area (inside the well) in EIS. The measurements have been performed in dark and at room temperature. In order to measure the EIS, we used reference calibration solutions for commercial pHmeters (Labsynth Inc.). Fig. 3 shows the Normalized CxV curves for pH 4, 7 and 10.

The TiN reference electrode showed to be a very resistant material. Since it resisted the electrical measurements with the pH solutions. Without suffering any corrosion.

From Fig. 3 was possible to extracted a V_{FB} values for each pH solution tested, making it possible to obtain the V_{FB} x pH curve (the inset curve of Fig. 3) and to calculate the sensitivity of the device. For the studied sample we determined the sensitivity of 20mV/pH. This result is very low than those found in the literature [5]. High sensitivity values are expected for a device using TiO_2 as the sensitive membrane [1, 2]. Further testing should be performed.

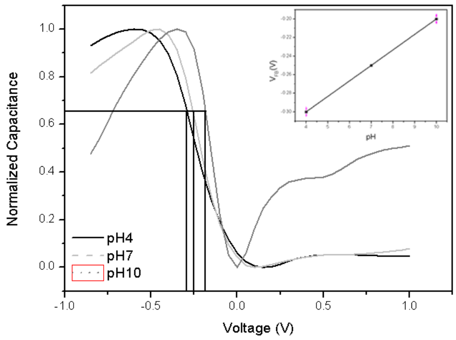

Fig 3. *Normalized CxV curve for each pH value. The inset shows V_{FB}xpH curve.*

4. Conclusions

The structural characterization of TiO_2 thin film shows the presence of rutile and anatase crystal structure, physical thickness of 50 nm and refractive index of 2.44. The presence of both crystal structures does not degrade the film. Atomic force microscopy shows roughness of 0.4 nm, which result are in the range of those found in the literature (0.8~2 nm) [5].

Measurements of Normalized CxV curves of the EIS structures using pH 4, 7 and 10 showed that the sensitivity of this device is 20mV/pH, which is lower than reported in the literature [1]. The TiN reference electrode showed to be a very resistant material, but further testing should be performed.

Acknowledgments

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