Thin titanium oxide films obtained by RTP and by Sputtering

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***Abstract*— In this paper, two methods to obtain titanium oxide (TiO_2) thin films are compared. In the first method metallic titanium (Ti) is deposited by sputtering and then oxidized by rapid thermal process (RTP) in an oxygen atmosphere to form the TiO2 thin films. The second method consists in TiO2 deposition by reactive sputtering. Structural characterization of the prepared samples shows the rutile crystal structure for both films, but TiO2 thin film deposited by sputtering also presented anatase crystal structure. Capacitors were fabricated and the electrical characterization of TiO2 films realized in order to determine which method forms the best dielectric film, defined by high dielectric constant value (high-k), lower charge density (Q_0/q) and flat-band voltage (V_{FB}) around -0.9V.**

Keywords*— Sputtering; dielectric constant; titanium oxide.

I. Introduction

Titanium dioxide (TiO_2) thin film has been studied extensively due to its exceptional qualities, adequate for wide range of applications that include Electrolyte-insulator-semiconductor (EIS)[1], biosensor[2] and Ion Sensitive Field Effect Transistor (ISFET)[3] devices, due to its chemical stability[2] and a high dielectric constant (high k)[1] along with the ability to form hydrogen bonds[4] which provide a high sensitivity for the device. Solar cells device[5] using TiO_2 thin film shows high efficiency of conversion of light to electrical energy due to its high value of refractive index[6].

There are several ways of obtaining TiO_2 such as sol-gel[7], e-beam[8], sputtering[1] and rapid thermal process (RTP)[3].

In this paper is realized a comparison between two of these methods for obtaining TiO_2. In the first one, Ti is deposited by sputtering and then oxidized using RTP in oxygen ambient to form the TiO_2 thin film. In the second method TiO_2 is deposited by reactive sputtering technique. Structural and electrical characterizations of the obtained samples were carried out to determine which of the method allow obtaining TiO_2 that has the best dielectric constant films.

II. Materials and Methods

A. Capacitor fabrication

The samples used in these studies were manufactured on p-type (100) Si wafers as substrates. First, the substrates were cleaned by the RCA method[9].

Then 300 nm thick aluminum layer was deposited over TiO_2 thin film deposited by both methods, described in sections B and C. The capacitor region was defined by a photolithographic step. After the native oxide removal from the bottom of the wafer, about 300 nm thick aluminum layer was deposited to form the contact. The fabricated samples were characterized without and after annealing, along different annealing steps ranging from 2min to 30min, in a conventional furnace using nitrogen gas.

One sample from each method was chosen to electrical and structural analyses. Both samples presenting similar physical thicknesses were named according to the method they were obtained as RTP_1 and as Sp_1. The electrical characterization of the capacitors, were carried out using the parameter analyzer Keithley 590-SCS and capacimeter Keithley. The capacitance versus voltage curves (CxV) were measured at high frequency (1 MHz) and dedicated software was used to correct the maximum capacitance values of the series resistance (Rs). This curve is called CxV Measured curve, and with these data was obtained the CxV Simulated curves.

From CxV Simulated curves are obtained equivalent oxide thickness (EOT), flat-band voltage (V_{FB}) and effective charge density (Q_0/Q) for this purpose was used Cvc program. This program was developed by professor John R. Hauser of NCSU (North Carolina State University)[10], [11]. The error between CxV Measured values and CxV Simulated values should be less than 10%.

B. TiO_2 thin film by RTP process

In this process to form the TiO_2 thin films, first 30 nm of metallic titanium was deposited by DC sputtering, then the thin titanium film oxidized in a rapid thermal process (RTP) at 960°C, in oxygen ambient using an oxygen flow rate of 1000 sccm for 2 minutes.

Two types of samples were fabricated, one named as RTP_1 for electrical characterizations and another, for structural characterizations named RTP_2. Raman spectroscopy and ellipsometry was used for the structural characterizations of the samples.

C. TiO_2 thin film by sputtering process

This process consists in depositing 60 nm of TiO_2 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. One sample Sp_1 was fabricated for electrical characterization and other one, Sp_2

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for structural characterization of the films, using Raman and ellipsometry.

III. STRUCTURAL CHARACTERIZATION

A. *Ellipsometry and Raman spectroscopy in TiO_2 films by RTP process*

The ellipsometry analysis of RTP_2 sample with TiO_2 thin film prepared by RTP process presented 56.5 nm thick TiO_2 layer and refractive index of 2.40, this refractive index is similar to the 2.44 reported in the literature related to the rutile crystalline structure[12][13].

The Raman analysis performed on these samples with Si/TiO_2 structure before the contacts deposition, as shown the Fig. 1, they exhibited peaks in 430 cm^{-1}, 600 cm^{-1} and 820 cm^{-1}, indicating presence of the rutile crystal structure[3] and also the presence of silicon in the shifts 300 cm^{-1} and 520 cm^{-1}.

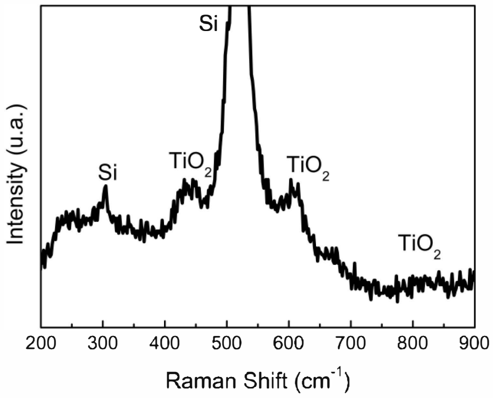

Fig. 1. Raman spectrum of the Si/TiO_2 film obtained by RTP process.

B. *Raman spectroscopy and Ellipsometry in TiO_2 films by Sputtering process*

The Raman analysis was performed on samples with Si/TiO_2 structure. Fig. 2 shows not only the presence of the rutile crystal structure[3] in 430 cm^{-1}, 612 cm^{-1}, and 826 cm^{-1}, but also the anatase[3] structure in 666 cm^{-1} besides the presence of the silicon substrates in shifts 300 cm^{-1} and 500 cm^{-1}.

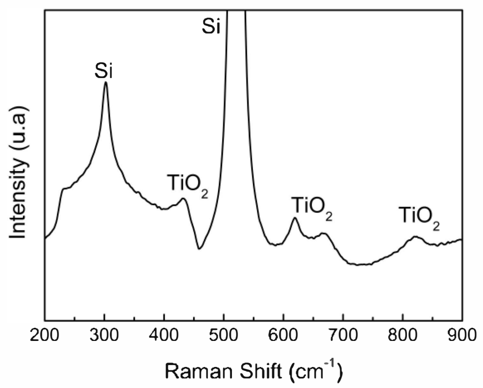

Fig. 2. Raman spectrum of the Si/TiO_2 film obtained by sputtering process.

The ellipsometry analysis of the sample Sp_2 showed that TiO_2 thin film obtained by sputtering process was 61 nm thick and refractive index of 2.43. This refractive index is similar to the one obtained for RTP_1 sample.

IV. ELECTRICAL CHARACTERIZATION

A. *Capacitor with TiO_2 films by RTP process*

It can be noted from Fig. 3 that the CxV Measured and CxV Simulated curves substantially overlap. In fact, the error of the Simulated curve was less than 3%, indicating that the Measured curve shows a near ideal behavior.

Table 1 shows the values of the physical thickness (Tox), calculated from ellipsometry measurements and the equivalent oxide thickness (EOT) obtained using the analysis of the CxV Simulated curves. With these values it was possible to calculate the dielectric constant (k). The best chosen annealing time is 10 minutes, because it has the lowest charge density value (1.16 e^{11}/cm^2), V_{FB} of -1.0V, C_{FB} of 40.7pF and the highest dielectric constant of 20.1 calculated using thickness (57 nm) and EOT (11 nm).

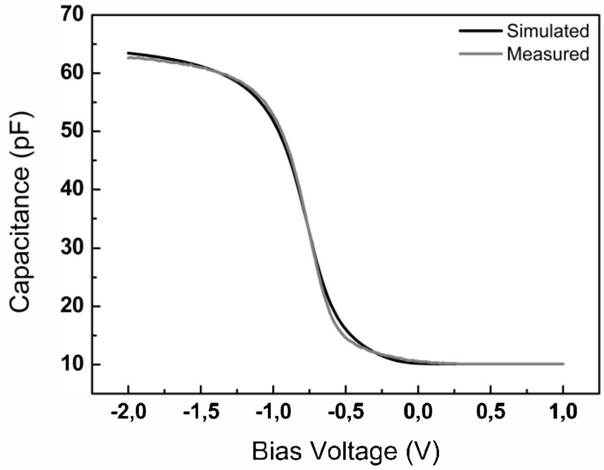

Fig. 3. In gray the CxV Measured curve and in black CxV Simulated curve of RTP_1 sample.

TABLE I. CXV SI/TIO2 BY RTP PROCESS

Annealing time (min)	Capacitor - Si/TiO_2 by RTP process					
	Tox (nm)	*EOT (nm)*	*K*	*V_{FB} (V)*	*C_{FB} (pF)*	*Q_0/q (/cm^{-2})*
0	57	9.8	22.4	-1.2	52.3	3.9E+11
2		14.7	15.0	-2.9	41.9	2.9E+12
5		12.8	17.3	-1.1	38.7	2.4E+11
10		**11.0**	**20.1**	**-1.0**	**40.7**	**1.1E+11**
15		14.3	15.4	-1.0	35.2	7.5E+10
20		12.9	17.0	-1.4	39.1	1.7E+11
25		18.3	12.0	-1.0	42.2	1.1E+11
30		14.3	15.4	-1.0	35.0	4.6E+10

According to the literature[14][15] the reason for low dielectric constant in RTP_1 sample may be due to the formation of a SiO_2 layer between the TiO_2 film and the silicon substrate (this silicon oxide layer decreases the dielectric constant value).

The V_{FB} value equal to -1.0V is near to the ideal which considers that V_{FB} is -0.9V for MOS structures that use aluminum as the electrode [14].

The voltage-current curve (IxV) with the 10 minute time of annealing shows that the current through the dielectric is approximately $1x10^{-6}$A, which means that this device presents low leakage current through the dielectric.

B. Capacitor with TiO_2 films by sputtering process

In this electrical measurement was used Sp_1 sample. First was done de CxV Measured curve and then was made the CxV Simulated curve.

Fig. 4 shows the CxV Measured and CxV Simulated curves overlap. This indicates that the error of the Simulated curve continues less than 3%, near to ideal behavior.

In the Table 2 it is highlighted the best annealing time that presents the lowest charge density value equal to $-4.30e^{12}/cm^2$, V_{FB} of -0.6V, C_{FB} of 87.9pF and the highest dielectric constant equals 133.3 obtained through the calculation of the thickness (61 nm) and EOT (1.8 nm).

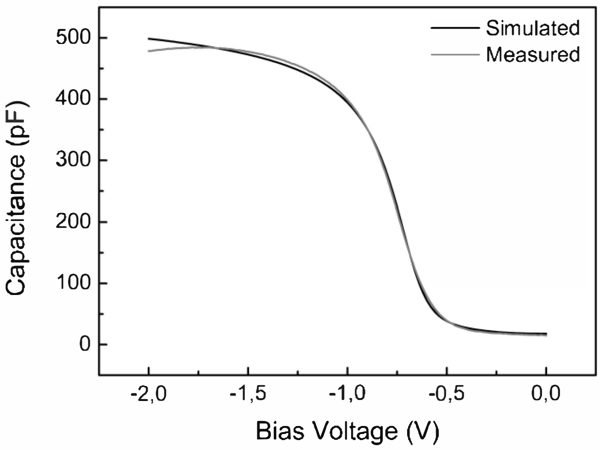

Fig. 4. In gray the CxV Measured curve and in black CxV Simulated curve of Sp_1 sample.

TABLE II. CXV Si/TiO_2 BY SPUTTERING PROCESS

Annealing Time (min)	*Capacitor - Si/TiO_2 by sputtering process*					
	Tox (nm)	***Eot (nm)***	***K***	***V_{FB} (V)***	***Cfb (pF)***	***Qo/q ($/cm^{-2}$)***
0	61	7.8	30.4	0.1	55.9	-2.90E+12
2		1.8	135.5	-1.6	210.5	7.80E+12
5		1.6	149.6	-1.1	185.5	1.70E+12
10		5.1	46.8	-0.6	54.9	-1.73E+12
15		**1.8**	**133.3**	**-0.6**	**87.9**	**-4.30E+12**
20		5.6	42.6	-0.6	70.2	-1.30E+12
25		1.9	125.2	-0.6	79.2	-4.80E+12
30		1.8	133.7	-0.6	86.6	-4.80E+12

The main advantage of sputtering process is that it is carried out at ambient temperature avoiding oxidation between the TiO_2 film and the silicon substrate. The value of the dielectric constant of TiO_2 can be varied from 120 to150 according to the literature[14].

The voltage-current curve (IxV) shows the current through the dielectric is approximately $1x10^{-6}$A, for capacitors with 15 minute annealing, showing that the device also has a low leakage current through the dielectric.

V. CONCLUSIONS

The structural characterization of TiO_2 thin films fabricated by RTP process shows a rutile crystal structure, 57 nm thickness and refractive index of 2.4, and the electrical characterization of capacitors shows that 10 minutes annealing is the best annealing time, exhibiting 20.1 of dielectric constant and Q_0/q in the order of $10^{+11}/cm^2$.

On the other hand, the structural characterization of TiO_2 thin films fabricated by sputtering process shows rutile and anatase crystal structure, 61 nm thickness and refractive index of 2.43. The electrical characterization of capacitors shows that 15 minutes annealing is the best annealing time, exhibiting 133 of dielectric constant and Q_0/q in the order of $10^{+12}/cm^2$.

These features can be because the RTP process is carried out in high temperature and creates a layer of SiO_2 between Si/TiO_2 interfaces, decreasing the value of the dielectric constant. Deposition by sputtering process is done at ambient temperature avoiding the oxidation of the silicon in the Si/TiO_2 interface, thus the value of the dielectric constant was 133.

The method that presents the best values of dielectric constant, refractive index and charge density for EIS, ISFET and solar cells device is by sputtering process with 15 minutes of annealing.

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