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Thin titanium oxide films deposited by e-beam evaporation with additional rapid thermal oxidation and annealing for ISFET applications

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A B S T R A C T

Titanium oxide (TiO_2) has been extensively applied in the medical area due to its proved biocompatibility with human cells [1]. This work presents the characterization of titanium oxide thin films as a potential dielectric to be applied in ion sensitive field-effect transistors. The films were obtained by rapid thermal oxidation and annealing (at 300, 600, 960 and 1200 °C) of thin titanium films of different thicknesses (5 nm, 10 nm and 20 nm) deposited by e-beam evaporation on silicon wafers. These films were analyzed as-deposited and after annealing in forming gas for 25 min by Ellipsometry, Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy (RAMAN), Atomic Force Microscopy (AFM), Rutherford Backscattering Spectroscopy (RBS) and Ti–K edge X-ray Absorption Near Edge Structure (XANES). Thin film thickness, roughness, surface grain sizes, refractive indexes and oxygen concentration depend on the oxidation and annealing temperature. Structural characterization showed mainly presence of the crystalline rutile phase, however, other oxides such Ti_2O_3, an interfacial SiO_2 layer between the dielectric and the substrate and the anatase crystalline phase of TiO_2 films were also identified. Electrical characteristics were obtained by means of *I–V* and *C–V* measured curves of Al/Si/TiO_x/Al capacitors. These curves showed that the films had high dielectric constants between 12 and 33, interface charge density of about 10^{10}/cm^2 and leakage current density between 1 and 10^{-4} A/cm^2. Field-effect transistors were fabricated in order to analyze I_D x V_{DS} and log $I_D \times$ Bias curves. Early voltage value of -1629 V, R_{OUT} value of 215 MΩ and slope of 100 mV/dec were determined for the 20 nm TiO_x film thermally treated at 960 °C.

1. Introduction

Health-care industry, food quality appraisal and food monitoring are responsible for the ever increasing research and development in the field of biosensors. Especially in the medical area, biosensors represent an astonishing expanding field [1], and particularly an increasing interest is found in applications related to cell monitoring biosensors. In this field, ion sensitive field-effect transistors (ISFETs) have been explored since they have advantages such as very small size, rapid response and low output impedance, in addition to be compatible with CMOS process and have a low cost [2]. The concept of ISFET device is based on the metal–oxide–semiconductor field-effect transistor operating theory, where metal gate is replaced by a reference electrode, buffer solution and an ion sensitive membrane. As an ISFET is basically a type of MOSFET without the metal gate, the study of the insulator material is an important part of the process, because it is directly exposed to the buffer solution. Therefore, the insulator material will be responsible for the detection of the specimens since a change in the electrolyte pH concentration induces a change in the electrolyte and insulate surface potential that results in alterations in the insulator–semiconductor electric field interface, channel conductance and current modulation. Due to the interest in measuring biological specimens, a biocompatible gate dielectric is a requirement. As titanium oxide (TiO_2) has been extensively applied in the medical area due to its proved biocompatibility with human cells [1] it becomes a potential gate dielectric material. It also has the advantage to be a material with high dielectric constant (k) which is a mandatory requirement for the sub-32 nm CMOS technology development. High-k insulators can present dielectric constant values between 4 and 80, which are higher than the 3.9 of silicon oxide. This characteristic allows reduction of tunneling current effect presented by ultra-thin silicon oxide gate insulators. Because of this interesting characteristic, deposition of TiO_2 films have been investigated by different techniques such as electron beam evaporation, ion sputtering, chemical vapor deposition, atomic layer deposition and sol–gel method [3–6]. This paper

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deals with TiO_x thin films obtained by rapid thermal oxidation (RTO) and annealing (RTA) of titanium thin films deposited on Si substrates by e-beam evaporation for future application as gate dielectrics in ISFETs device fabrication.

2. Experimental procedure

Enhanced nMOSFETs were fabricated on n-type single-crystal Si (1 0 0) wafers with resistivity ranging from 1 to 10 Ω cm. These devices with areas from 10 μm × 100 μm to 200 μm × 200 μm and MOS capacitors with area of 200 μm × 200 μm were defined with five lithography steps. The substrates were cleaned by the RCA method between each process step and were oxidized (1000 °C for 280 min in $O_2 + H_2O(v)$) to grow a 1 μm field silicon oxide. Phosphorus ion implantation (80 keV P^+ ions and dose of 7×10^{15} ions/cm^2) and dopant activation annealing (1000 °C for 30 min in N_2) were used to form source and drain junctions.

To distinguish gate titanium oxide formation methods, the samples were named Ti_5 nm, Ti_10 nm and Ti_20 nm, the titanium oxide formed by rapid thermal oxidation and annealing for 40s at temperatures of 300, 600, 960 and 1200 °C of 5 nm, 10 nm and 20 nm of Ti deposited by e-beam evaporation. For the process control, bare Si substrates were oxidized and annealed in the same conditions by rapid thermal (RT) processes (omitting the Ti e-beam evaporation step) and were named Control (SiO_2).

To complete MOS capacitor and nMOSFET device fabrication, the source, drain, gate and body electrodes were formed by sputtering of a 300 nm thick aluminum film, sintered by conventional furnace in forming gas at 430 °C for 2, 5, 10, 15, 20 and 25 min.

FTIR spectra, used to reveal the titanium oxide film chemical bonds, were obtained using a Digilab Scimitar FTS 2000 Series FTIR Spectrometer and Raman spectroscopy by NTEGRA Spectra PNL. The thickness and refractive index were obtained using a Rudolph/AutoEL Technologies Inc., Ellipsometer.

Ti–K edge XANES measurements were conducted at the Brazilian Synchrotron Light Laboratory (LNLS, Campinas, Brazil), performed at room temperature and were recorded in the 4900–5200 eV range.

Electrical properties of the Al/TiO_x/Si/Al capacitors were investigated using high-frequency capacitance–voltage (C–V) and leakage current–voltage (I–V) measurements. The capacitance was measured at a frequency of 1 MHz at room temperature. A relative dielectric constant of 3.9 was adopted to extract the equivalent oxide thickness (EOT) of films from C–V curves under strong accumulation condition. nMOSFET electrical characteristics, such as flat-band voltages, threshold voltages and sub-threshold slopes were obtained.

3. Results and discussion

Structural characterization of Ti_5 nm, Ti_10 nm and Ti_20 nm titanium oxide films formed by rapid thermal oxidation and annealing at temperatures of 300, 600, 960 and 1200 °C, show that independently of the initial e-beam evaporated titanium thickness, all evaluated samples present the same structural characteristics. Figs. 1–5 show the results of the characterizations of Ti_20 nm titanium oxide film thermally treated at the temperatures already described and Ti_20 nm titanium oxide film thermally treated at 960 °C with additional annealing in forming gas for 25 min.

According to Fig. 1, FTIR analyses, every obtained spectra exhibit the presence of a low intensity absorbance peak at 513 cm^{-1}. This peak is attributed to the Ti–O anatase crystal structure stretching vibrational mode [7]. With the increase of the process temperature this peak decreases significantly, and the peaks at ~485 and ~615 cm^{-1} become more pronounced, which are usually

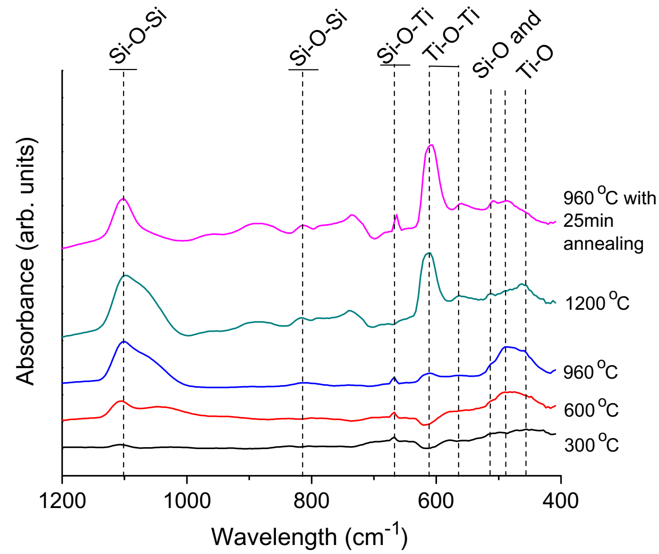

Fig. 1. FTIR spectra of Ti_20 nm titanium oxide films thermally treated at 300, 600, 960, 1200 °C and titanium oxide films thermally treated at 960 °C with 25 min annealing at 430 °C in forming gas.

attributed to the stretching vibrational mode of a rutile crystal structure [8]. A peak at ~430 cm^{-1} is related to Si–O rocking vibrational mode [9], however, as the absorbance peaks between 430 and 513 cm^{-1} form a broad band, they cannot define the film crystal structure. Furthermore, according to Verma et al [7], there is also existence of a Ti_2O_3 peak at ~480 cm^{-1}, which means that anatase crystalline structure and Ti_2O_3 may be present in the studied films. It is easy to note however, that increasing the process temperature, the absorbance peak at 615 cm^{-1} becomes pronounced, confirming the existence of the rutile crystalline structure, especially after 25 min annealing at 430 °C in forming gas. Moreover, the samples exhibit peaks at ~810 and ~1100 cm^{-1} assigned to bending and stretching vibrational modes of SiO_2, respectively [9], indicating that all films showed formation of a SiO_2 layer between the TiO_x film and the substrate. Finally, the peak found at ~664 cm^{-1} is attributed to the presence of Ti–Si–O [9].

Fig. 2 shows the Raman spectra taken on these samples. In all spectra the presence of Raman shifts at 430, 612 and 826 cm^{-1} are clearly identified, and they correspond to the rutile crystal structure [10]. However, similarly to the FTIR analyses, our samples also exhibited a Raman shift at 650 cm^{-1} related to the anatase crystal structure [11,12]. Fig. 3, shows that Raman shift peak intensity of the Ti_20 nm sample thermally treated in 960 °C increases when the samples are subjected to 25 min annealing at 430 °C in forming gas. The observed result indicates that even varying the process temperature it was not able to isolate a single-crystal structure of TiO_2.

Furthermore, in regard to the microelectronics applications, it is not interesting to have a TiO_2 layer with crystalline structure, since this may leads to cause an increase in the leakage current of the devices [13]. Finally, the Raman analysis support the results of the Infrared Spectroscopy, since it also revealed the existence of anatase and rutile phases in the obtained films, but in both techniques rutile is the predominant crystalline structure.

Ti–K XANES analyses realized on the fabricated samples, Fig. 4, shows that the spectra of the films are similar to the spectra of the TiO_2 rutile type control, in all the used thermal treatment temperatures, which is in agreement with the results obtained by RAMAN and FTIR analyses.

The results obtained from Raman and FTIR measurements were also confirmed by RBS simulations, which considered Si/SiO_2/

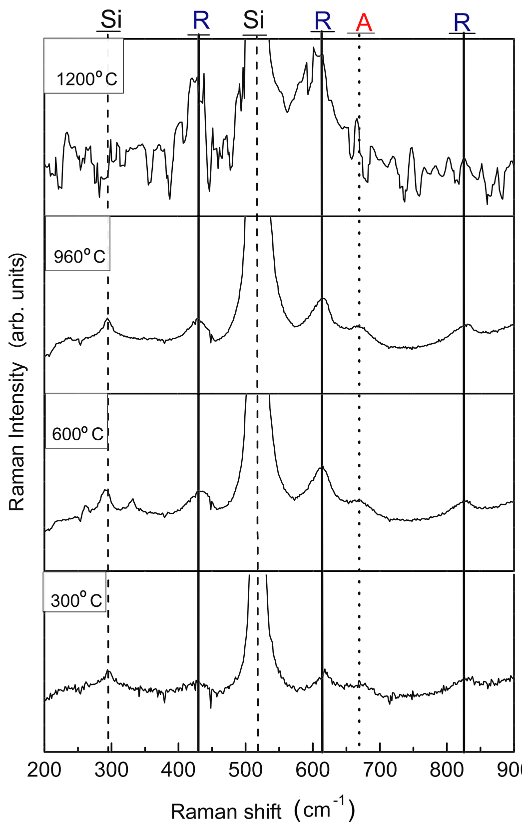

Fig. 2. Raman spectra of Ti_20 nm titanium oxide films thermally treated at 300, 600, 960 and 1200 °C.

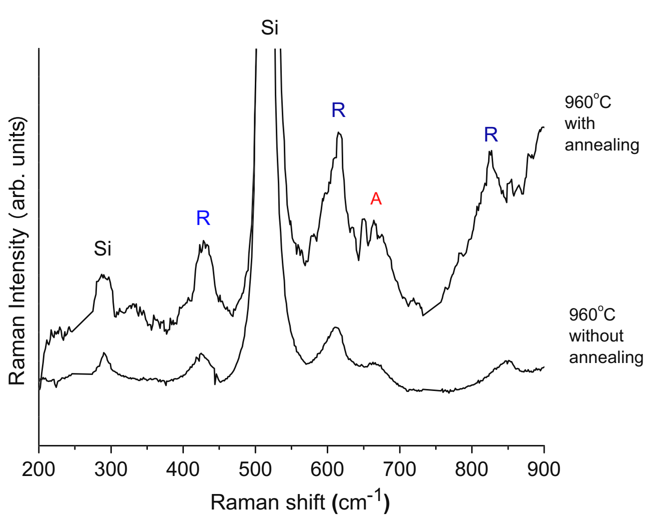

Fig. 3. Raman spectra of Ti_20 nm titanium oxide films thermally treated at 960 °C and thermally treated at 960 °C with 25 min annealing at 430 °C in forming gas.

Ti_2O_3/TiO_2 layers to fit the simulation curve with the obtained data. The most optimized [O]/[Ti] ratio of 1.9 was obtained for the films annealed at 600 °C. Films annealed at 300 °C showed a smaller ratio, indicating that Ti film was not completely oxidized, and films thermally treated above 600 °C showed a higher ratio.

From AFM characterizations, the RMS data obtained for the samples thermally treated at temperatures from 300 to 960 °C showed formation of very smooth and uniform films with surface roughness <2 nm, which is an interesting attribute in regard to the electronic device construction.

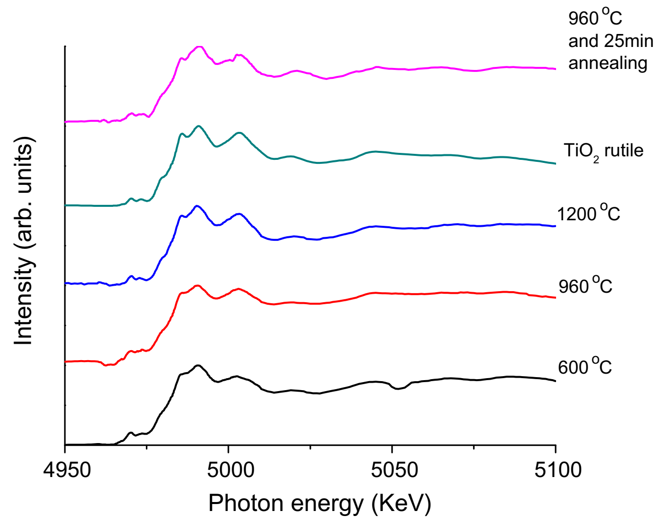

Fig. 4. Ti–K XANES analyses of TiO_2 rutile crystalline phase sample, Ti_20 nm titanium oxide films thermally treated at 600, 960 and 1200 °C and Ti_20 nm titanium oxide films thermally treated at 960 °C with 25 min annealing at 430 °C in forming gas.

Electrical characterization of MOS capacitors fabricated using obtained titanium oxide films, showed the best results for the films oxidized and annealed at 960 °C. The dielectric constant determined from C–V characteristics of Al/Ti_20 nm/Si/Al capacitors showed value equal to 22, considering the physical thickness obtained by ellipsometry of 47 nm using refractive index equal to 2.35. The flat-band voltages (V_{FB}) were found to be −0.95 V for the Ti_20 nm sample sintered during 10 min, whereas the control sample (Al/control oxide – SiO_2/Si/Al) presented V_{FB} of −1.03 V. With these values of V_{FB}, effective charge densities in the films of about $10^{10}/cm^2$ were obtained. This indicates that the Ti_20 nm/Si interface presents similar behavior when compared to the control/Si interface. These results are better than those obtained by thermally oxidized Ti gate MOS devices [14]. The leakage current densities (Jg) through the insulator were determined by the ratio between leakage current extracted from the I–V characteristics for the bias voltage Vg=−1 V (accumulation region for p-type substrate) and the capacitor area (4×10^{-4} cm^2). The value obtained for the Ti_20 nm sample was 0.6 mA/cm^2, while the control sample value was 60 mA/cm^2. These results confirm the high quality of the obtained films. The threshold voltages (V_T) were extracted from the x-axis intercept from the $I_D \times V_{GS}$ curves. It was observed that for a V_{DS} value of 0.1 V and V_{BS} equal to 0 V, the extracted values of V_T were −0.22 and −0.02 for Ti_20 nm sample and control sample, respectively.

The sub-threshold slopes (S) were extracted by gradient of the $\log I_D \times V_{GS}$ curves for V_{DS} = 0.1 V and V_{GS} bias ranging from −1 V to 2 V, as shown in Fig. 5. S of about 60 mV/dec is an ideal value for MOS devices, indicating low leakage gate current and semiconductor surface states. It was observed that for V_{DS} of 0.1 V, the extracted values of S were 61 mV/dec and 100 mV/dec for the Ti_5 nm and Ti_20 nm samples thermally treated at 960 °C and annealed in forming gas for 10 min, respectively. For the control silicon oxides, S value was 123 mV/dec. All samples presented subthreshold slopes lower than 100 mV/dec, indicating very low semiconductor surface states, especially the Ti_5 nm samples. This agrees with C–V results. Based on presented results, the obtained titanium oxide films may be considered as the promising materials for gate insulator in ISFETs, as well as for other MOSFETs applications.

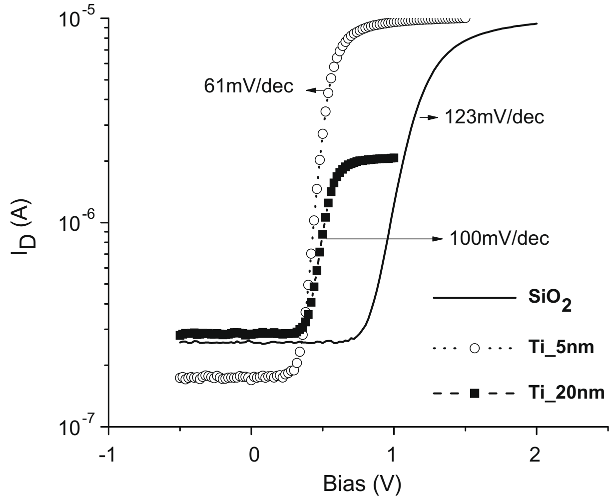

Fig. 5. Control silicon oxide, Ti_5 nm and Ti_20 nm titanium oxide gate transistor, thermally treated at 960 °C, log $I_D \times V_{GS}$ curves for V_{GS} bias ranging from −0.1 to 2.0 V and V_{DS} of 0.1 V.

4. Conclusions

Structural and electrical properties of titanium oxide thin film obtained by rapid thermal oxidation and annealing of titanium film e-beam evaporated on a silicon substrate were studied using different characterization techniques, in order to evaluate its applicability as the alternative gate insulator material for ion sensitive field effect transistors (ISFET) device. According to FTIR analyses the obtained TiO_x films showed mainly the presence of rutile crystal structure, but the presence of the anatase crystal structure and SiO_2 were also identified. Raman analysis of the same samples, indicated TiO_2 Raman shifts related to the rutile and anatase crystal structure, similarly to the FTIR results. XANES analyses also revealed formation of TiO_2 rutile type crystal structure. These structural characteristics are quite similar to those observed for the films obtained by other techniques such as sputtering, chemical vapor deposition and atomic layer deposition. Besides, the observed results indicate that even varying the process temperature it is hard to isolate a single-crystal structure of TiO_2, but according to the physical characterization results, rutile is the predominant crystalline structure formed in our TiO_x films. RBS measurements and its data simulations confirm the results observed by Raman and FTIR. The optimized [O]/[Ti] ratio determined for the films annealed at 600 °C was 1.9. AFM images of the samples showed formation of very uniform and smooth films with surface roughness <2 nm, which is an interesting attribute for the electronic device construction.

Electrical characterization of the obtained samples showed the best results for the films oxidized and annealed at 960 °C. From *C–V* characteristics of Al/Ti_20 nm/Si/Al capacitors, dielectric constant of the films equal to 22, V_{FB} of −0.95 V and effective charge densities of $10^{10}/cm^2$ were determined. The Jg through the insulator was 0.6 mA/cm^2. The V_T of −0.22 was obtained for Ti_20 nm sample. The S of 100 mV/dec for Ti_20 nm indicated very low semiconductor surface states. Therefore, the observed results indicate formation of high quality titanium oxide films using this method, with physical and electrical properties desirable as the gate dielectric film for the ISFET devices applications.

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