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TiO_2 thin and thick films grown on Si/glass by sputtering of titanium targets in an RF inductively coupled plasma

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Abstract. TiO_2 thin and thick films were deposited on silicon/glass substrates using RF inductive plasma in continuous wave. The films thickness, as well as phases control, is achieved with a gradual increase in temperature substrates varying supplied RF power or working gas pressure besides deposition time as well. The deposition conditions were: argon 80%/oxygen 20% carefully calibrated mixture of 2 to 7×10^{-2} mbar as working gas pressure range. Deposition time 0.5 to 5 hours, 500 or 600 W RF power at 13.56 MHz frequency and 242-345 ºC substrates temperature range. The titanium dioxide deposited on the substrates is grown by sputtering of a titanium target negatively polarized at 3-5 kV DC situated 14 mm in front of such substrates. The plasma reactor is a simple Pyrex-like glass cylindrical vessel of 50 cm long and 20 cm in diameter. Using the before describe plasma parameters we obtained films only anatase and both anatase/rutile phases with stoichiometric different. The films were characterized by X-ray photoelectron spectroscopy (XPS), stylus profilometer, X-ray diffraction (XRD), scanning electron microscopy (SEM) and Raman spectroscopy.

1. Introduction

The titanium dioxide (TiO_2) has been reported as one material for applications in different areas as agent antibacterial, antimicrobial on prostheses and catheters [1-4], as a photocatalytic vehicle in the water purification and in the atmospheric pollutants such as (NO_x) and volatile organic compounds (VOC_s) [5-6]. In such analysis, Blake [7] identified about 600 patents and found about 500 additional references were found in the form of journal and conferences papers. Now today, has been reported applications in the visible light as photocatalytic agent and optoelectronic employment [8].

There are several reports to obtain TiO2 thin films that have been mainly prepared by various methods such as plasma enhanced chemical vapor deposition [9], sputtering [10]. In comparison with other methods, sputtering deposition is one of the widest techniques employed for obtaining large area coatings and strong adhesion. The reactive sputtering technique, for coating nanocrystalline TiO2 thin films, are mainly employed radio frequency (RF) and direct current (DC). In other hand, the reactive DC+RF sputtering technique provide a wide range for to vary the sputtering parameters such as total

pressure, partial pressure ratio, DC or RF power, substrate temperature according to the plasma parameters. In these experiments, we observed that the crystal structure and chemical composition of deposited films varied with the employed plasma parameters, as well as the rate of the sputtering from the target.

The objective of this work is to obtain TiO_2 thin or thick films in anatase or rutile phases by controlling the temperature of substrates. This temperature depends on the density of the plasma, which is a function of the RF power and the working gas pressure keeping the rate for Ar and O_2 constant.

2. Experimental details

TiO^2 thin and thick films were deposited on glass slides and silicon wafer, the temperature was kept between 242-345 °C by the action of the plasma alone, that is to say, the temperature substrates depend only plasma density, the gas working pressure and the RF power supply plasma reactor, the deposited films on glass and silicon by the sputtering action were situated 14 mm from titanium target. For this experiment, the target consisted in titanium commercially pure (CpTi) piece cylindrical of 9 mm in diameter and 5 mm long, the dimensions of the substrates were 20×20 mm with glass and 10×10 mm for the silicon. Deposited films were obtained in a home Pyrex-like glass cylindrical vessel of 50 cm long and 20 cm in diameter by sputtering process. The plasma density was controlled by the working gas pressure and RF power supply. In this experiment we employed a calibrated mixture of 4:1 argon/oxygen gas mixture from 2×10^{-2} to 7×10^{-2} mbar preview the vessel was to $<5\times10^{-6}$ mbar pressure base, one RF power supply between 500 and 600 W connected to copper pipe antenna wounded helicoidal cylindrical vessel through an automatic coupling network and one power supply between -3 and -5 kV DC that polarize the target. Figure 1 shows a diagram of the sputtering system preview reported [11].

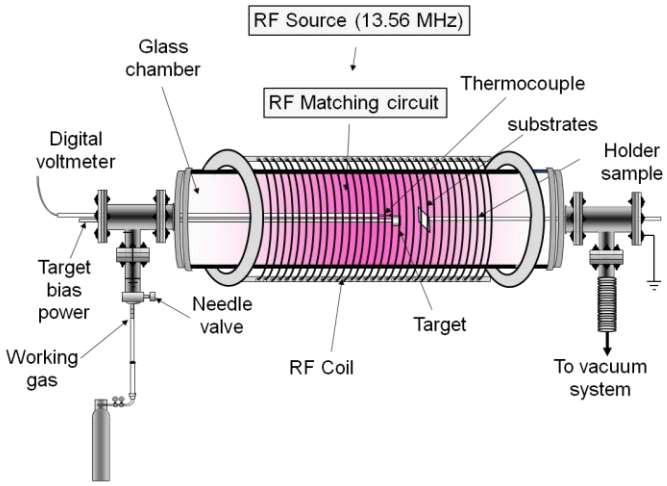
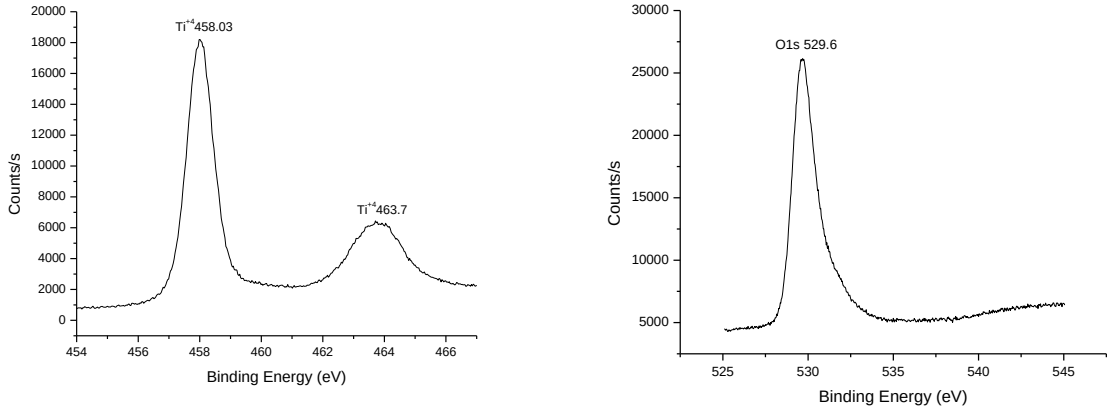


Figure1. Schematic diagram of the experimental sputtering system.

The crystalline structure of the films deposited on silicon wafers were characterized by X-ray photoelectron spectroscopy (XPS) using monochromatized AlKα X-ray source (hν=1486.6 eV), the recorded spectra of all films were referenced to the C1s line of the residual carbon set at 284.6 eV, the thickness of the films were determined by a stylus profilometer, the crystallinity of the films were carried out with an X-ray powder diffractometer (XRD) using CuKα radiation lambda= 1.54056 angstroms from 20º to 90º scan range set applied voltage 35 kV/25 mA and Raman spectroscopy, the surface morphologies, the stoichiometry (titanium:oxygen ratio) and the atomic percentage in the sputtered films analyzed using a scanning electron microscopy (SEM).

3. Results

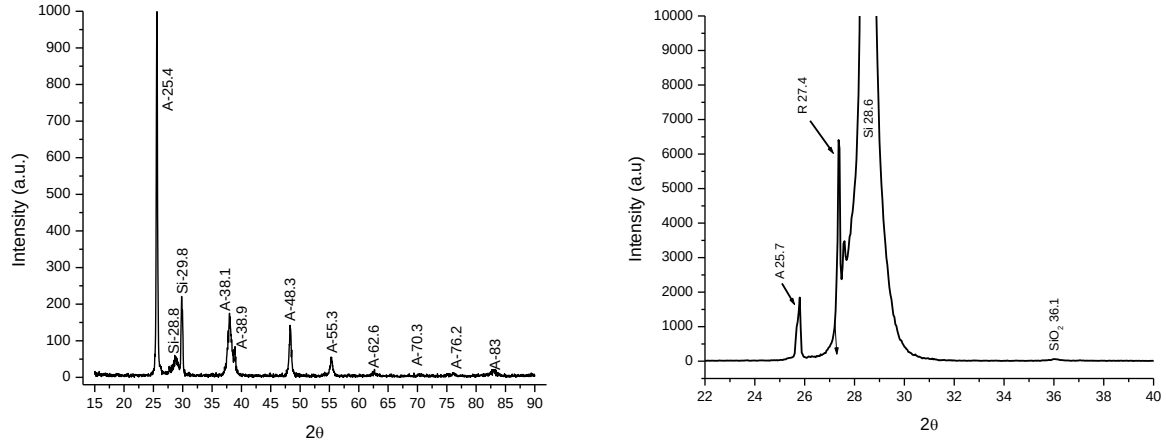
Figure 2 shows the XPS spectra of the TiO_2 film grown on the silicon substrate. Figure 2(a) shows the peaks of the doublet of Ti2p with energies of 458.03 eV link for $Ti2p_{3/2}$ and 463.6 eV for $Ti2p_{1/2}$ on the surface respectively, the binding energy difference (splitting) between $Ti2p_{1/2}$ and $Ti2p_{3/2}$ is 5.57 eV which indicated that addition of a Ti^{+4} oxidation state titanium. On the other hand, the figure 2(b) shows O1s peak with a binding energy at 529.6 eV of the as-deposited TiO_2 film that is related to oxygen chemically bounded to Ti.



(a) (b)

Figure 2 XPS spectra of (a) Ti2p and (b) O1s on the surface silicon film.

Figure 3 shows XRD spectra of the TiO_2 film deposited at two different working gas pressures. Figure 3(a) shows the crystallinity of the TiO_2 film in the anatase phase deposited at 242 ºC on the substrate of silicon in the working gas pressure of 5×10^{-2} mbar at diffractive angles 2θ of 25.4º , 38.1º, 38.9º, 48.3º, 55.3º, 62.6º, 70.3º, 76.2º, and 83.0º. And the other hand, the figure 3(b) shows TiO_2 film when the gas working pressure was 2×10^{-2} mbar with this pressure the substrate reached a temperature of 345 ºC, at this temperature, clearly shows the transition from the phase of anatase to rutile phase, in the spectrum are observed both phases at diffractive angles 2θ of 25.3º and 27.4º.



(a) (b)

Figure 3. (a) X-ray diffraction pattern of anatase on silicon and (b) show the transition to rutile phase

Figure 4 shows the different thickness measured by a surface profiler meter of the film deposited on glass substrate, it was variable, in the center of the pattern of deposit thickness was 2500 nm (this graph shows that 0.1 mm is the second ring of deposit which has a thickness of around 1000 nm), at the midpoint of the pattern was 1150 nm and on the periphery of the pattern was around 70 nm, this

variation is because the deposited films has a circular patters caused for the magnetic field generated by solenoidal antenna.

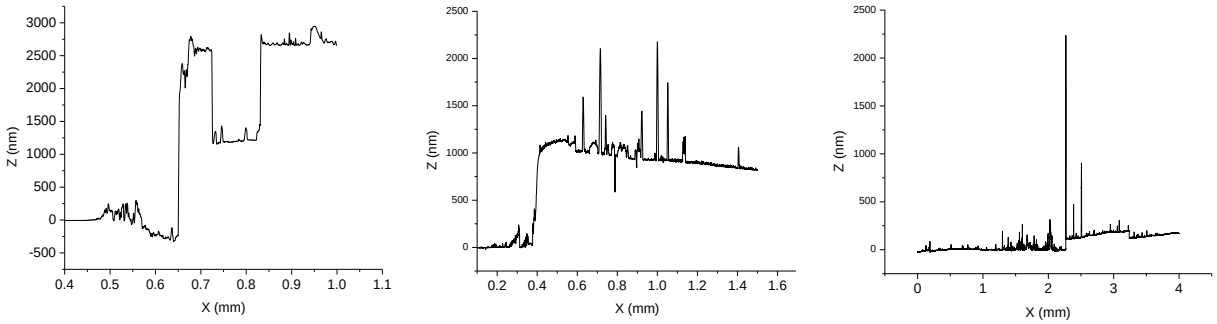
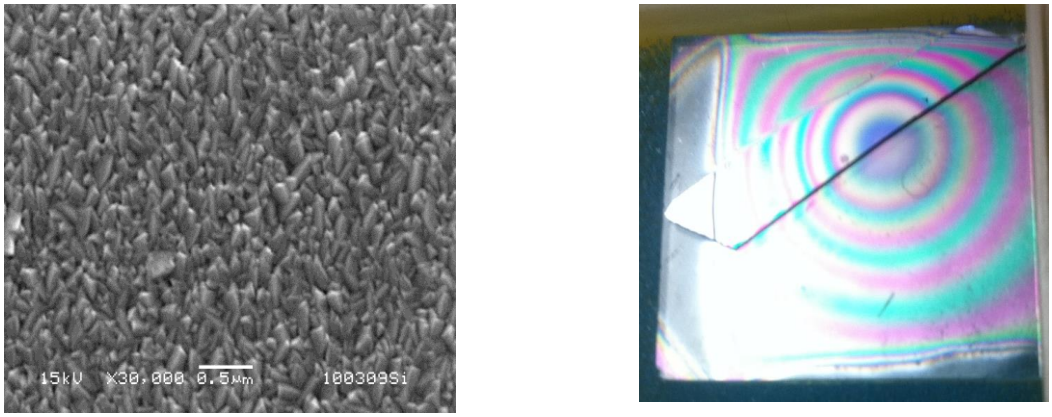


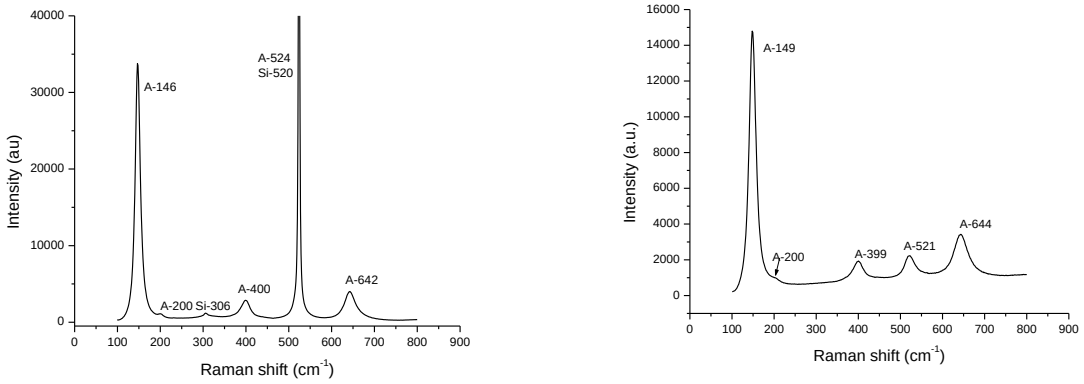
Figure 4 pattern of thickness of the film of the Centre to the Board

Figure 5 shows the micrograph and a photograph of the film in the anatase phase obtained by SEM with an amplification of 30000 on silicon substrate, the grain size was calculated by Sherrer´s formula, whose size was around 80 nm, which is congruent with the sizes observed in the micrograph. The pattern of colors of the photograph of Fig. 5(b) represents the different thicknesses deposited on silicon substrate



(a) (b)

Figure 5. (a) SEM micrograph and (b) normal photograph film on silicon substrate



(a) (b)

Figure 6 Raman spectra of the TiO_2 film in: (a) silicon and (b) glass.

Figure 6 shows the graphics acquired by Raman of TiO_2 film in the anatase phase. The Fig. 6(a) and 6(b) Spectra confirm the presence of anatase phase grown on silicon and glass substrates at temperatures below 300 ^oC. Difference in shift (cm^{-1}) recorded in the graphics is due to a light contrast to the growth of the anatase since silicon and glass substrates differ in their material structure.

4. Conclusions

In this research, we use a plasma reactor inductively coupled to RF generator with which was obtained TiO_2 thin and thick films in anatase and rutile phases by means sputtering of a target of titanium, in this sputtering process, titanium atoms sputtered target and oxygen atoms generated by plasma were deposited on silicon and glass substrates. Atomic concentrations of 60 at.% atoms of titanium and 30 at.% atoms of oxygen obtained by SEM leads to a stoichiometry 2 only in target. In contrast, the atomic concentrations obtained by SEM for the TiO_2 films on silicon and glass substrates were of the order of 75 at.% of oxygen and 25 at.% titanium respectively, it is considered that this rate stoichiometry of 3:1 is due to two reasons: 1) substrates have a percentage of oxygen bigger than target and 2) the applied voltage in the SEM was 20 kV, this rate low to 2 when 15 kV is applied in SEM. Color changes of the films during and the end the oxidation process, the concentric circular patterns suggest the evolution of the composition structure thickness and is related to the deposited film depth. The deposited anatase and rutile phases did not require any additional annealing after the oxidation.

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