Influence of steps temperature on microstructure and hardness of TiO₂ thin films deposited by co-sputtering

L García González¹, J B Santaella González¹, F López Huerta²,*, E. Díaz Trueba², L Zamora Peredo¹, C Zuñiga Islas³ and C Guaneros Aguilar⁴
¹ Centro de Investigación en Micro y Nanotecnología, Universidad Veracruzana, Veracruz, 94294, Boca del Río, Veracruz, México.
² Facultad de Ingeniería Eléctrica y Electrónica, Universidad Veracruzana, Veracruz, Boca del Río, Veracruz, México.
³ Departamento de Electrónica, Instituto Nacional de Astrofísica, Óptica y Electrónica (INAOE), C.P. 72840 Tonantzintla, Puebla, México.
⁴ CONACYT, Instituto Politécnico Nacional, CICATA, 89600, Altamira, Tamaulipas, México.
*e-mail: frlopez@uv.mx

Abstract. TiO₂ thin films were synthetized by magnetron co-sputtering on silicon (100) substrates. Two targets were used: Ti and TiO inside an inert atmosphere of Argon gas at room temperature. Post-deposition thermal annealing treatments were performed with different numbers of step temperature segments to reach 500 °C for 3 hours. The effect of the variation of the number of step temperature segments in the micro hardness and microstructure of the films was studied, using XRD, Raman spectroscopy, SEM, AFM, photoluminescence (PL) and Vickers hardness. Vickers hardness evinced values between 14.7 and 19.8 GPa. Raman spectroscopy showed that the film without thermal annealing does not present any active bands, while films with post deposit annealing treatments had rutile and anatase phases with higher intensity as the number of step temperature segments increased, this behavior was corroborated by XRD. SEM and AFM showed a change in the morphology as the number of step temperature segments increased. Moreover, PL showed that oxygen defects decrease as the annealing time increases; which could be related to the change in hardness and morphology.

1. Introduction
Titanium dioxide (TiO₂) has three crystalline phases, anatase, rutile and brookite [1], which give it great versatility in applications such as gas sensors, photocatalysis and protective material [2]. Recent investigations mention various ways of synthesizing TiO₂ thin films, wherein they can be deposited by diverse processes, such as sol-gel, electrodeposition, pulse laser deposition (PLD) or Sputtering, among others. Magnetron Sputtering is used due to its advantages of reproducibility, film composition which is relatively easy to control, good adhesion to the substrates, a controllable thickness, and the possibility to scale the fabrication of the films at industrial levels [3-4]. The formation of TiO₂ films has varying certain parameters during the sputtering process such as, bias voltage [1,3], source power supplies [5], or substrate temperature to favor the presence of a crystalline phase [6] and with the atmosphere of argon + oxygen [7]; which has been reported in several studies.
However, only a few studies allude to post-deposit annealing treatments that form a crystalline phase, such as the anatase and rutile phases [8-9], or mention the application of step temperature segments (dwell segments), and study the effect it has on its hardness. Therefore, we carried out studies to analyze the way in which the heating conditions, like step temperature segments, in post-deposit annealing treatments can improve the formation of the TiO$_2$ crystalline phases, as well as the consequences these changes have on their hardness, microstructure and crystalline defects.

2. **Methodology**

2.1. **Substrate preparation and coating synthesis**

TiO$_2$ thin films were deposited onto 4-inch Silicon (100) wafers using a sputtering system, Intercovame V3, where two targets were used: Ti (99.995%) in the DC source with a power of 120 W and TiO (99.99%) in the RF source with a power of 40 W. Formerly, the silicon wafers were cleaned using the RCA method [10]. In the co- sputtering deposition process, co-sputtering consists of starting the two targets simultaneously to carry out the deposition process of TiO$_2$ thin films for 20 minutes and was performed at ambient temperature using an inert atmosphere of ultra-high purity Argon gas (99.999%) at a flow rate of 15 standard cubic centimeters per minute (sccm), the pre-deposit vacuum was $2.0 \times 10^{-6}$ Torr.

After the films were fabricated, post-deposition thermal annealing treatments (TT) were performed at a maximum temperature of 500 °C for 3 hours in air, varying the number of step temperature segments to decrease the heating rate to reach the maximum temperature. Three different arrangements were used: one-step temperature segment at 250°C (labeled as 1RTT) with a duration of 30 minutes, two-step temperature segments at 167 and 334 °C for 30 minutes for each of the steps (2RTT), and three-step temperature segments at 125, 250 and 375°C for 30 minutes for each of the steps (3RTT). Finally, after completing the temperature steps, the temperature of 500 °C was reached and stabilized, which was maintained for 3 hours, and then it was allowed to cool inside the muffle until it reached room temperature.

2.2. **Characterization techniques**

The vibrational excitations of the TiO$_2$ thin films were obtained by Raman spectroscopy using a DXR Raman Microscope with a 532-nm laser and with a power of 10 mW. The Raman measurements were performed at room temperature. The crystal structures were analyzed with a grazing angle configuration X-ray diffractometer, Bruker D8 Advance, using CuK$_\alpha$ radiation at a scanning speed of 1°/min. The diffractograms were analyzed using the Scherrer method to compute the grain size [11] and additionally, the semi-quantitative analysis of phases was analyzed in the EVA software from BRUKER. To observe the photoluminescence characterization a system is formed by, a 325-nm He-Cd Kimmon laser, a chopper with a frequency of 37 Hz, and a Merlin Radiometry Systems model 70103 were used. The thickness and morphology of the films was measured in a JEOL JSM-7600F field emission scanning electron microscope (FE-SEM) using an acceleration voltage of 3 kV and a working distance of 3.0 mm. Moreover, Atomic Force Microscope (AFM) was used to analyze the topography of the films, using a Nanosurf EasyScan in dynamic mode, with a non-contact tip type and a constant force of 48 N/m. Finally, the hardness measurements were performed with a Mitutoyo Micro Vickers HM-125 hardness testing machine; using load values from 2, 3, 4, 5, 10, 25, 50, 100, 200 and 300 gram-force (gf), was applied load they were repeated five times and then the Korsunsky work of indentation approach [12], whereby despite the contribution of the hardness of the silicon substrate, the adjustment consists of being able to extract the hardness value of the thin film.

3. **Results and discussion**

3.1 **Microstructure**
After the microstructure was studied by X-ray diffraction of the thin films of TiO$_2$ with thermal annealing, where the diffractograms show well defined peaks in addition to the silicon peaks which correspond to the anatase and rutile (TiO$_2$) phases. There, it can be seen that the peaks of the rutile are more intense than the anatase peaks, which could mean that the films are a combination of rutile and anatase, but also, it means that there is a higher percentage of rutile peaks, which corresponds to an EVA analysis that shown in Table 1. This effect is not quite noticeable in Raman, since the bands of the rutile phase are near the anatase phase, and the rutile bands are usually less intense[13-14]. Then Raman spectroscopy was studied, an evolution to a better crystalline quality is seen in Figure 1.b), where the bands at 300 and 530 cm$^{-1}$ correspond to the Silicon substrate (100), There are also well-defined bands that correspond to the anatase phase [15], where the band formation at ~144 cm$^{-1}$ corresponds to the E$_g$ vibrational mode, and the bands at about ~398 cm$^{-1}$ and ~639 cm$^{-1}$ correspond to the B$_{1g}$ and E$_g$ vibrational modes of anatase respectively [13]. Moreover, an increment in the intensity of these anatase bands is seen from the 1RTT to the 2RTT, but the hop in intensity is not visible between 2RTT or 3RTT; apparently a better anatase formation occurs as the number of steps increase. But, according to other Raman analyses of the same material with a mixture of crystalline phases, the peak over the 144 cm$^{-1}$ corresponding to the crystalline phase anatase is always much more intense even if there is presence of rutile in greater proportion [14]. Additional poorly formed bands are seen in Figure 1.b), at about ~238 cm$^{-1}$ (E$_g$), ~448 cm$^{-1}$ (E$_g$) and another at ~615 cm$^{-1}$ (A$_{1g}$) [14], which might be related to the rutile phase, since it is well known that these phases can coexist [13], this is corroborated in Figure 1 a), where the diffractograms show well defined peaks.

In Table 1 the XRD results of the films are summarized, the rutile phase mainly appears when the thermal annealing is made with one-step temperature segment (1RTT), this could be related to the synthesis process, since other works report that the Sputtering technique tends to form rutile or disordered TiO$_2$, then a thermal annealing rutile form [16]. Nonetheless, increasing the number of steps reduces the rutile phase percentage and increases the anatase phase percentage, where the percentage values are like the 2RTT or 3RTT, in agreement with the behavior seen in Raman spectra intensities. However, the three-step temperature segment film tends to decrease the grain size of the rutile, while the anatase remains relatively the same. Due to the use of steps in temperatures lower than 500 °C, where the formation of anatase is favored, this is why this phase begins to increase with the addition of steps [16]. This phase change could be explained by the low temperature values of the thermal annealing, due to the reported optimal temperature for anatase formation being between 400 and 500 °C [15], the fact that the rutile formed at that temperature depends more on the synthesis process rather than the thermal treatment [1, 17].
Table 1. XRD phase percentage and crystal (tetragonal) size for the thin films with thermal annealing

|        | Rutile            | Anatase           |
|--------|-------------------|-------------------|
| Phase %| Crystal Size (nm) | Phase %           | Crystal Size (nm) |
| 1R-TT  | 82.66%            | 20.4              | 17.34%            | 28.2               |
| 2R-TT  | 68.4%             | 11.8              | 31.6%             | 37.1               |
| 3R-TT  | 69.67%            | 8.7               | 30.33%            | 31.5               |

3.2 Photoluminescence and AFM

The photoluminescence spectrum is shown in Figure 2 a) in the energy range of 2.0 and 3.5 eV and shows three main peaks: one at 3.2 eV related to the Band Gap of the TiO$_2$ and another two peaks at 2.1 and 2.8 eV, which could be related to oxygen defects [18]. The Band Gap peak does not change between the films with different step temperature segments, neither in position nor intensity, which could indicate that while there is a microstructural change, the band gap remains relatively the same. On the other hand, the peaks related to the oxygen defects tend to diminish as the number of steps increases; this behavior could be attributed to a better crystalline quality shown in the microstructural studies, as it can be observed that they have the same behavior with Raman Figure 1 b) and in X-ray diffractogram Figure 1 a), since the slow increment in temperature allowed the oxygen atoms to have more time to rearrange into a more stable structure [8].

Using Gwyddion software, the surface images of the thin films were obtained, where the RMS roughness values could be calculated in an area of 1 µm$^2$. In Figure 2 b), the AFM images show the surface topography of the thin film with 1RTT, where all films evinced a good homogenization with a surface than deepened less than 10 nm. The rugosity values are depicted of the films, there, the film without heat treatment (WTT) has an RMS rugosity of 1.25 nm, 1RTT films 1.30 nm, 2RTT 1.42 nm, and this increases as the number of step temperature segments reaches 1.68 nm for 3RTT. This may be due to the increased crystallinity level of the films, as observed in the Raman and XRD data, as they have shown in some articles [1].

Figure 2. a) Photoluminescence spectrum of the thin films with thermal annealing in the range from 2.0 to 3.5 eV, and b) Topography of the thin films: 1RTT.

3.3 Morphology

Figure 3 shows surface morphology without thermal annealing and 1R TT, in which a relatively large area is observed and where a very uniform surface is observed in images a) y b), the other samples show a similar morphology, so they were not placed. The formation of two different sizes of nanometric grain can be seen, one around 30 nm and the other approximately at 15 nm, all very similar and uniform sizes on the surface of the respective thin films. This corroborates the grain sizes calculated in the XRD analysis of Table 1, where two different crystalline phases are identified. In all the SEM images of the surface of the thin films, the morphology shown of the material does not shows apparent changes regarding what has been reported in several studies [16].
Figure 3. Image of the SEM where morphology of the surface samples can be observed: a) films without thermal treatment (WTT), and b) 1RTT.

3.4 Hardness and thickness.
Figure 4 a) shows the comparison of hardness vs rugosity of the films with different TT; the hardness values were adjusted applying the Korsunsky work-of-indentation approach model, which is a method of extracting a value of hardness [12]. Results of the Vickers Microhardness showed a clear behavior that increased the hardness values as the number of steps increased, reaching hardness values of 14.74, 18.09 and 19.82 GPa for the 1RTT, 2RTT and 3RTT respectively. This enhanced hardness of the films at higher temperature steps could be related to the reduction of the grain size of the rutile phase seen in the XRD results [13], additionally, it is possible that the hardness increase could be because they have better crystalline quality, as can be verified with Raman spectra and Photoluminescence. While hardness above 18 GPa could seem too high for TiO$_2$ two films, other studies have archived similar results [19-20] and some similarities can be observed between the reported works and our work, the grain sizes are very similar, and is also influenced by the type of substrate (silicon) [21], that have reached hardness values of 19 GPa. It is visible that the effect of the step temperature segments is favorable for improving the hardness and crystal quality on the rutile due to the reduction in the crystal size that is shown in Table 1. This could be related to the fact that when steps were used, a greater homogeneity of the temperature is ensured within the furnace, and therefore the thin films, before reaching the final temperature of the thermal treatment. Finally, the thickness was measured in cross section, as shown in Figure 4 b), the micrograph of the cross section of the 1RTT film, where it shows a thickness of 400 nm, where a type of columnar growth of the material is observed, the thickness of thin films does not vary.

Figure 4. a) Vickers measurements plot of hardness and rugosity vs steps in thermal treatment, and b) cross- sectional SEM of the 1RTT thin film.
4. Conclusions
Thin films of TiO$_2$ were fabricated by co-sputtering technique on silicon wafer (100) substrates and post-deposition thermal annealing treatments were made at 500 °C for 3 hours, varying the number of steps to reach maximum temperature. The thin film with the best crystalline quality corresponds to the 3RTT film, this is demonstrated by the Raman and PL spectrum. For hardness and rugosity, this film reached maximum hardness values of 19.8 GPa, AFM revealed the highest RMS roughness value to be 1.68 nm in its topography, being the best values of all films. It has been established that the crystalline quality, hardness and rugosity improve as the number of temperature steps increases, but the band gap does not change with it. With the proposed conditions in this study to implement the TiO$_2$, thin films have reached hardness values similar to 19 GPa compared to those reported in other studies between 16 GPa and 19 GPa. In other hardness studies, Vickers have reported similar hardness values for this material, TiO$_2$ shows a similar hardness for microhardness measurements or Vickers hardness.

5. References
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