Effect of annealing treatment on the photocatalytic activity of TiO$_2$ thin films deposited by dc reactive magnetron sputtering

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Abstract. Titanium dioxide (TiO$_2$) thin films have been deposited by DC reactive magnetron sputtering on silicon and quartz substrates with different Ar/O$_2$ ratios in the gas mixture. Substrate temperature was kept constant at 400 °C during the deposition process, and the TiO$_2$ thin films were later annealed at 700 °C for 3 h. The effect of the Ar/O$_2$ ratio in the gas flow and the annealing treatment on the phase composition, deposition rate, crystallinity, surface morphology and the resulting photocatalytic properties were investigated. For photocatalytic measurements, the variation of the concentration of the methylene blue (MB) dye under UV irradiation was followed by a change in the intensity of the characteristic MB band in the UV–Vis transmittance spectra. We report here that the as-grown TiO$_2$ films showed only the anatase phase, whereas after annealing, the samples exhibited both the anatase and rutile phases in proportions that varied with the Ar/O$_2$ ratio in the mixture of gases used during growth. In particular, the annealed TiO$_2$ thin film deposited at a 50/50 ratio of Ar/O$_2$, composed of both anatase (80%) and rutile phases (20%), exhibited the highest photocatalytic activity (30% of MB degradation) compared with the samples without annealing and composed of only the anatase phase.

1. Introduction
Titanium dioxide is a material known for its high refractive index, high transparency in the visible and near-infrared wavelength region [1], high dielectric constant, very good wear resistance and stability and a large semiconductor band gap, which has developed significant importance as a catalyst for the breakdown of organic substances under UV illumination. Due to these special properties, TiO$_2$ has become the subject of much research for applications in optical coatings, microelectronic devices, and protective layers [2]. Crystalline TiO$_2$ films are a focus of interest because of their specific properties compared to the amorphous phase. Titanium dioxide crystallizes in three structures: tetrahedral anatase, rutile and orthorhombic brookite. Rutile is primarily desirable for optical applications and is the thermodynamically stable phase; anatase has high kinetic stability and is more hydrophilic and photocatalytic [3], which allows the creation of products with new properties such as easy-to-clean surfaces, self-cleaning windows, as well as photocatalytic air and water purification devices. However, it has been argued that a mixture of anatase and rutile may show the highest photocatalytic activity; an example is the P25 powder from Degussa [4]. Many researchers [5–7] have investigated mixtures of the TiO$_2$ phases regarding their performance as photocatalysts. In this work, we deposited TiO$_2$ thin films by DC magnetron sputtering at 400 °C onto quartz substrates and studied the crystallinity, phase mixing, and photocatalytic properties, such as the dependence on the Ar/O$_2$ ratio in the gas mixture and the subsequent annealing treatment.

2. Experimental details
We grew TiO$_2$ films on quartz and silicon (100) substrates with a DC reactive magnetron sputtering system from a titanium target (99.9%) with 2.54 cm diameter that was placed inside a chamber with
an Ar/O$_2$ gas mixture. The Ar/O$_2$ ratio flow in the gas mixture was systematically varied (95/5, 90/10, 80/20, and 50/50) to study the influence of the oxygen partial pressure on the crystallographic structure and photocatalytic activity of the TiO$_2$ thin films. The base pressure was 4 x 10$^{-4}$ mbar, and the working pressure (2.4 x 10$^{-2}$ mbar), power applied to the target (150 W), distance from the substrate to the Ti target (8 cm), temperature (400 °C), and deposition time (2 h) were maintained constant for all samples. After the sputtering process, the TiO$_2$ films were annealed at 700 °C for 3 h.

![Figure 1](image_url)

**Figure 1.** TiO$_2$ XRD patterns of films deposited on quartz at different Ar/O$_2$ flow ratios: a) unannealed and b) annealed.

The crystal structure of the TiO$_2$ films was determined by using glancing angle X-ray diffraction (GAXRD) at a 2° incidence angle in the 2-theta mode over the range of 20°<2θ<80° with a Bruker
(Model D8 Advance) diffractometer using the Kα1 line of Cu (λ = 1.5406 Å, 25 kV and 16 mA). The crystallite size was deduced from the full width at half maximum of the XRD lines according to Scherrer’s equation [8]. Raman spectra were taken on a JobinYvon micro-Raman system. For the photocatalytic measurements, the variation of the concentration of the methylene blue (MB) dye was followed by the change (a decrease) of the characteristic band intensity of the MB, located at 665 nm, in the UV–Vis transmittance spectra, which was analyzed as a function of the UV irradiation time. The MB solution in a quartz cell was irradiated with ultraviolet light with a power of 4 W and the source was located 4 cm from the cell. The solution was bubbled with air before irradiation. From these measurements, we evaluated photocatalytic performance by analyzing the percentage of dye degradation when the films were used as a catalyst in a Shimadzu spectrophotometer (UV model 1601).

3. Results and discussion

3.1 XRD analysis

The XRD patterns of TiO₂ films deposited on quartz substrates at ratios of 95/5, 90/10, 80/20, and 50/50 of Ar/O₂ are displayed in Figure 1a). We can observe that all of the TiO₂ films show a preferred (211) orientation (denoted as A211) of the anatase crystalline structure; however, the more commonly reported anatase phase orientation is the (101) orientation. This behavior can be attributed to the fact that different surface free energies are associated with the different diffraction planes [9]. In our case, the applied sputtering power density (~300 kWm⁻²**) activates TiO₂ film growth from a relatively lower surface free energy to a higher surface free energy [10]. The crystallite size of the samples calculated from the Scherrer equation were 18.6, 18.6, 17.9, and 17.7 ± 0.1 nm for the films deposited at ratios of 95/5, 90/10, 80/20 and 50/50 of Ar/O₂, respectively. The XRD patterns of the films subjected to heat treatment at 700 °C for 3 h are shown in Figure 1b). In the patterns, increased film crystallinity with annealing and change to the anatase-rutile phase mixture can be observed. The films deposited at 80/20 and 90/10 crystallized in completely different manner, with peaks predominately in the rutile phase with preferred orientations in the 301 and 110 planes (peaks noted as R301 and R110) and less appearance of the anatase peaks. From Figure 1b), it is clear that the structure of the films after annealing is strongly influenced by the Ar/O₂ ratio, presenting a tendency.

![Figure 2](image2.png)  
**Figure 2.** Raman spectra of unannealed TiO₂ films deposited at different Ar/O₂ flow ratios

![Figure 3](image3.png)  
**Figure 3.** Raman spectra of TiO₂ films annealed for 3 h at 700 °C at different Ar/O₂ flow ratios
for the rutile phase to increase when the Ar/O<sub>2</sub> ratio decreases. We can conclude that for unannealed TiO<sub>2</sub> films, the crystallite size of the anatase phase remains almost constant (~18 nm) with increasing oxygen percentage, whereas for the annealed films, the crystallite size of the anatase and rutile phases decreases from 58.9 to 28.2 and from 49.4 to 31.7 nm, respectively; in both cases, it is higher than the crystallite size in the unannealed TiO<sub>2</sub> films.

**Table 1.** Percentages of anatase and rutile phases for the annealed samples, calculated from the Raman analysis

| Ar/O<sub>2</sub> ratio | Anatase (%) | Rutile (%) |
|------------------------|-------------|------------|
| 95/5                   | 29          | 71         |
| 90/10                  | 42          | 58         |
| 80/20                  | 65          | 35         |
| 50/50                  | 80          | 20         |

**Table 2.** Photocatalytic degradation of MB in presence of annealed TiO<sub>2</sub> films

| Ar/O<sub>2</sub> ratio | Degradation % | Anatase/Rutile relation | Crystallite size (nm) |
|------------------------|---------------|--------------------------|-----------------------|
| 95/5                   | 13            | 71/29                    | 49.4/38.9             |
| 90/10                  | 25            | 58/42                    | 47.3/33.3             |
| 80/20                  | 29            | 35/65                    | 36.6/29.4             |
| 50/50                  | 30            | 20/80                    | 31.7/28.2             |

**3.2 Raman analysis**

To study how the Ar/O<sub>2</sub> flow ratio affects both the anatase and rutile phase formation in the TiO<sub>2</sub> films, we measured the Raman spectra of the films deposited on quartz substrates without annealing. Figure 2 displays these spectra. All spectra show the presence of an intense peak at the 142.2 cm<sup>-1</sup> wavenumber associated with the TiO<sub>2</sub> <sup> Eg</sup> band of anatase, as previously reported [11]. Similarly, all of the spectra display three smaller peaks at 394.9 (associated with the B<sub>1g</sub> mode of the anatase phase), 515.5 and 637.4 cm<sup>-1</sup>, which agree with those reported for the structure of the anatase phase [10]. Moreover, the intensity for each peak increases, and the peaks become narrower with decreasing oxygen partial pressure in the Ar/O<sub>2</sub> gas mixture. This behavior indicates that the samples organize into microstructures with better crystallinity as the partial pressure of oxygen decreases [12]. Considering the phase diagram proposed by Zeman et al. [13], the TiO<sub>2</sub> film deposited at 2.4 Pa working pressure and at a smaller oxygen amount in Ar/O<sub>2</sub> ratio (95/5) has an anatase phase crystallization higher than those of the other samples, as shown in Figure 2. To induce the appearance of the rutile phase in samples reaching the anatase phase, we subjected them to annealing at 700 °C for 3 h. Figure 3 shows the Raman spectra after heat treatment. We can clearly observe that the anatase phase is transformed into the rutile phase in different proportions depending on the as-grown Ar/O<sub>2</sub> ratio flow. The percentages of the corresponding phases were obtained by performing the decomposition of the anatase and rutile peaks for each sample. Decomposition was performed by calculating the percentage of each of the areas with a combination of Lorentzian and Gaussian fits. Table 1 presents the corresponding calculated percentages of the phases. According to the phase diagram presented by Löbl et al. [14], the samples with a higher degree of crystallization in the anatase phase are expected to be transformed more easily to the rutile phase after the annealing process. Indeed, under our conditions, this effect occurred for the samples deposited at the 95/5 ratio of Ar/O<sub>2</sub>, as observed in Figure 3 and Table 1.

**3.3 Photocatalytic activity evaluation**

Evaluation of the photocatalytic activity was initially carried out by irradiating the TiO<sub>2</sub> samples with ultraviolet light. Figure 4a) displays the relative concentration reduction of MB as a function of the UV irradiation time for unannealed TiO<sub>2</sub> films deposited at different Ar/O<sub>2</sub> ratios. We observed the degradation of the MB compound. The percentage of relative degradation of MB in the unannealed films was approximately 26%, considering that all unannealed samples showed only the anatase phase and had almost the same gap value [15] and a very similar crystallite size. The
anatase phase has a band gap of 3.2 eV and an affinity adsorption of organic compounds much higher than the rutile phase [16]. Additionally, the anatase phase has a lower recombination rate than the rutile phase because its hollow capture rate is 10 times higher [17]. In contrast, the thermodynamically stable rutile phase has a smaller gap of 3.0 eV, which allows excitation by wavelengths extending into the visible range at 410 nm. However, the anatase phase of TiO₂ is generally considered the most active phase of photochemistry, most likely due to the combined effect of a lower recombination rate and higher adsorption capacity on the surface. Other research has investigated TiO₂ anatase and rutile phases mixing and found that these have a higher photocatalytic activity than does either individual pure phase [18]. Therefore, because our TiO₂ samples initially presented only the anatase phase, the appearance of the rutile phase was induced by annealing at 700 °C for 3 h. Figure 4b) shows the results of photocatalysis tests of the annealed samples. The percentage of relative degradation of MB varies from 13% for the 90/5 grown film with 71% rutile and 29% anatase relative composition up to 30% for the 50/50 with 20% rutile and 80% anatase relative composition. The results are shown in Table 2. Based on reports in several papers [20-22], the rutile phase has low photocatalytic activity; therefore, no test samples have been made on a 100% rutile phase sample. As mentioned above, the two polymorphs of the TiO₂ photocatalysts in the mixed phase can effectively reduce the recombination of photogenerated electron-hole pairs to improve photocatalytic activity. In addition, photoactivity depends on crystallite size and, as noted above, the region where the potential barrier is generated should be in the order of the crystallite size. If the crystallite is very small, the carriers easily reach the surface to participate in photoactivity. In large crystallites, the separated charges undergo recombination outside the barrier region. Therefore, the probability of recombination is high, as reflected in the photoactivity. The radiation absorbed outside the barrier region behaves similarly to the pure anatase and rutile phases, in a manner unaffected by the effects of the interface. Samples containing 65 and 80% of the anatase phase have higher photoactivity than do samples containing only the pure anatase phase. According to Tanaka et al. [19], the photocatalytic activity of TiO₂ is determined by the anatase phase content and crystallite size. These authors reported [19] a proportional increase in photocatalytic activity with increased TiO₂ crystallite size. However, in our case by comparing the crystallite sizes for both phases (Table 2), we can conclude that decreased crystallite size increases photocatalytic activity. The higher photocatalytic activity occurs in the sample with a rutile-anatase ratio of 80/20, and this photocatalytic activity is similar to the commercial TiO₂ powder Degusa 25 [23, 24] that is widely used for photocatalysis. We can also conclude that increasing the content of the anatase phase in the sample increases the photocatalytic activity. Regarding the rutile phase, this result may be related to the increased affinity of absorption of organic compounds with this phase.

Figure 4. Relative concentration versus degradation time of MB in the presence of TiO₂ a) unannealed and b) annealed films deposited at different Ar/O₂ ratios.
Conclusions
We found that the oxygen content in the Ar/O\textsubscript{2} ratio in the gas mixture during growth using a sputtering technique strongly influences the deposition rate, the structure of the films after annealing, and the photocatalytic activity. After thermal treatment, higher oxygen content in the Ar/O\textsubscript{2} ratio improves the crystallinity of the as-grown TiO\textsubscript{2} films, and the samples exhibit a tendency to decrease their rutile phase content. We also found that the phase mixture improves photocatalytic activity compared to samples exhibiting only the anatase phase. The best percentage of MB degradation (30\%) was for the sample with an anatase to rutile ratio of 80/20.

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