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Titanium Dioxide Thin Films Deposited By Pyrolytic Spray And Their Structural And Electrical Characterization

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ABSTRACT
Films of titanium dioxide (TiO_2) were synthesized by pyrolytic spraying, using a precursor solution of titanium diisopropoxide stabilized with 75% acetyl – acetonate in isopropanol dissolved in methanol. This solution was sprayed on glass substrates in a reaction chamber at 30 psi pressure at different temperatures (380, 430 and 480 and 380 annealed at 500 °C). X–ray diffraction (XRD), studied, the grain size, microtension and lattice parameters. The four-point collinear team studied the voltage – current relationship. At 380 °C, the film is amorphous and the others presented anatase phase with a predominant peak (101). The film grown at 480 °C shows the rutile peak (211). The grain size decreases and the microtension increases with temperature. The voltage – current graph is linear for samples grown at 480 °C.
KEYWORDS *titanium dioxide; thin films; spray pyrolysis; diffraction; microtension.*

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I. INTRODUCTION

We are immersed in a world made up of different types of materials, materials of a metallic, polymeric, ceramic nature and all their possible combinations. These materials support our present well-being and enable our continued progress. In this context, the investigation of new materials, such as thin films, arouses much interest locally and worldwide, as their applications are increasingly being explored. In the world, the first vestiges of processes related to thin films can be traced back to the Iron Age with metallic coatings, which have been used for at least the last four millennia [6]. At the local level, the Chavín culture and later the Mochica culture, by cold hammering gold and copper, converted these into sheets, and later, for ornamental purposes, transformed them into crowns, earmuffs, nose rings, belts and bracelets, among others [7]. The term thin film does not have a precise definition; In general, it refers to films whose thickness ranges from 0.1 µm to about 300 µm, and is not normally applied to coatings such as paints or varnishes, which are usually much thicker. For a thin film to be useful, it must possess all or almost all of the following properties: (a) it must be chemically stable in the environment in which it will be used; (b) it must adhere well to the surface it covers (the substrate); (c) it must have a uniform thickness; (d) must be chemically pure or have a controlled chemical composition; and (e) it must have a low density of blemishes. In addition to these general characteristics, they may require special properties for certain applications. For example, the thin film might have to be insulating or semiconductive, or possess special optical or magnetic properties. These films can be manufactured from different materials such as: metals, metallic oxides and organic substances [25]. Said films when synthesized with PLD (Pulsed Laser Deposition) can also be doped with rare earths and / or nanocrystalline materials [4].

In general terms, thin films are used for two purposes: the simplest, to optimize one or more of the properties of the substrates they cover or even to provide them with new properties. In this case, we often refer to thin films by the term "coating." The second general application is the manufacture of devices with specific and unique physicochemical properties, which bear little or no relation to the initial properties of the substrate, which here behaves as a mere physical support. For this second type of application, simple layers are not used, but layered multilamellar systems.

Currently, in Peru and in the world, the demand for electronic products, such as Flash memory, to cite one example, is growing. A conventional Flash memory device works by storing data in a transistor containing a floating gate (Floating Gate or FG) and this is separated from the control circuit by a thin oxide film. Said layer, to ensure data retention for at least 10 years, cannot be less than 8 nm thick[3]. Computer systems store the programs to be executed in a central memory RAM (Random Access Memory), these programs are stored in a permanent or massive storage device, such as the magnetic disk. For this reason, hard disk drives have a thin film of magnetic material on the surface of the disk to achieve storage[20].

Focusing our interest on the thin films of titanium dioxide, TiO_2, we can say that these are among the most versatile and widely used materials, they are used as homogeneous catalyst, gas sensors, in optically active protective supports; as a pigment in paints, inks, textiles; as filler material in plastics, rubbers, paper; and in solar cells [18], disinfection of hospital environments and in antibacterial applications when it is doped with Zn [1], self-cleaning and anti-fog [16]. TiO_2 is considered a transparent conductive oxide (TCO) material, it is also of great interest due to its distinctive physical, chemical, optical and optoelectronic properties, for this reason it plays a very promising role in various areas of research due to its high and efficient photocatalytic activity, high refractive index, resistance to photocorrosion, chemical stability, low cost and non-toxicity [26]. TiO_2, is a compound of great technological interest, it has four crystalline phases: rutile (tetragonal structure), anatase (octahedral structure), brookite (orthorhombic structure) and a high-pressure α-PbO_2 type [28]. Although its main application is that of pigment, it is currently being the subject of research and development due to its good photochemical properties, sometimes in the form of nanoparticles[25]. TiO_2 is also used successfully in the photodecomposition of water, purification of environmental pollutants, antireflection coatings, ceramic membrane and waveguide [10].

Likewise, TiO_2 in recent years has been applied to self-sterilizing surfaces and its implementation in hospitals due to its greater reliability and stability under irradiation [30]. It is also widely used to kill different groups of microorganisms, including bacteria, fungi, and viruses, due to its high photoreactivity, broad-spectrum antibiosis, and chemical stability[11]. Currently, thin TiO_2 films are prepared using various techniques, such as sputtering [23], sol-gel [13], pulse laser deposition [29], chemical bath deposition [22], and pyrolytic spraying [34], spin coating [19] among others.

At present, in the world and especially in Peru, research is being done on thin TiO_2 films, but not enough, and above all, having so much potential of application to solve such real and urgent problems. Investigating TiO_2 films also involves selecting the most appropriate synthesis technique and once the technique is selected, each of the variables that, in turn, each technique involves must be managed in order to understand a little more. the morphological, optical and electronic properties, which are what really give them such powerful and diverse application potential. Size problem is a challenge that leads us to be committed to research on this topic.

In this research, thin TiO_2 films were synthesized by pyrolytic spraying and characterized to verify their morphological and electrical properties using X–ray diffraction and electrical resistivity measurement techniques respectively.

II. MATERIALS AND METHODS

Thin films of titanium dioxide (TiO_2) were manufactured by pyrolytic spraying from a solution of Titanium diisopropoxide (precursor reagent) stabilized with acetyl acetonate 75% in isopropanol dissolved in methanol, and deposited on 76x26x1 mm glass substrates. dimension.

2.1 Crystal structure

The determination of the crystalline structure of the TiO_2 films was made by analyzing the X–ray diffraction spectra that were obtained using a BRUKER brand, D8 ADVANCED ECO (Figure 1a). To identify the phase of the crystal structure of the TiO_2 films, the data from the diffractogram obtained was compared with the team's ICSD–1997 database. The sweeps were carried out with angles of 2θ, with values between 15 and 70 °, with a typical step of 0.02 °.

The interplanar distance (d), determined using the following equation 1 (Bragg's Law):

$$\text{sen}\,\theta = \frac{\lambda}{2d_{hkl}} \quad (1)$$

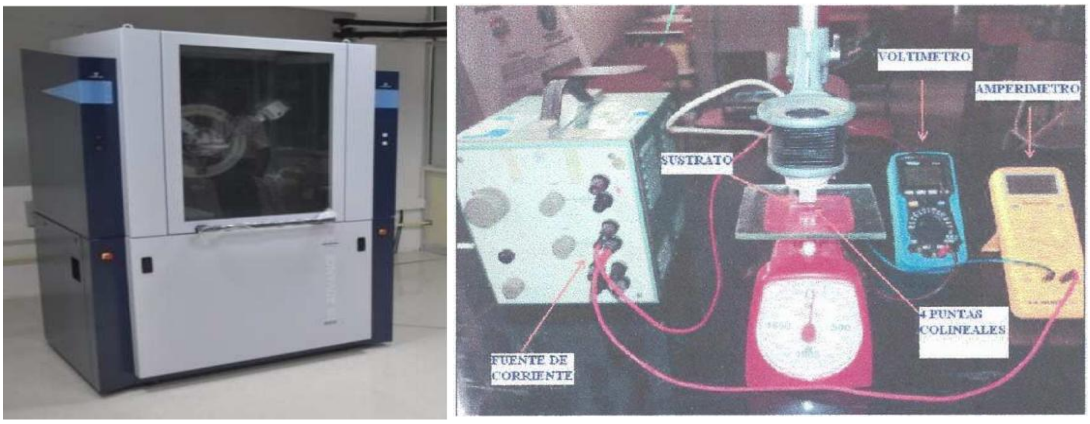
where λ is the wavelength of the X-rays, $\lambda = 0.15418$ nm and θ is the angle of the peak of maximum intensity.

The grain size (D) was obtained through equation 2:

$$D = \frac{k\lambda}{\beta_{hkl}\cos\theta} \quad (2)$$

where k takes the value of 0.90; β is the mean width of the maximum X-ray peak (FWHM). β must be taken in radians.

Figure 1. (a) BRUKER brand X-ray diffractometer (XRD), Model D8 ADVANCED ECO with Cu - α Cathode (λ = 0.15418 nm). **(b)** Set of 4 collinear points, indicating its components. Available at the Materials Physics



(a) **(b)**

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The lattice parameters: a, b and c; in which it is true that a = b, where c is different; since titanium has a tetragonal structure (both in anatase and rutile), they were obtained with equation 3.

$$\frac{1}{d_{hkl}^2} = \left[h^2 + k^2 + l^2\left(\frac{a}{c}\right)^2\right]\frac{1}{a^2} \quad (3)$$

on the other hand, the microtension (ε) was calculated using the following equation (Cullity, 1978):

$$\varepsilon = \left(\frac{1}{\mathrm{sen}\theta}\right)\left[\left(\frac{\lambda}{D}\right) - (\beta\cos\theta)\right] \quad (4)$$

Furthermore, the dislocation density (δ) was calculated using the following equation [21]:

$$\delta = \frac{1}{D^2} \quad (5)$$

Also the unit cell density (ρ) for anatase using the following equation [32]:

$$\rho = \frac{4 \times M}{N \times a^2 \times c} g \cdot cm^{-3} \quad (6)$$

where "M" is the molecular mass of TiO_2 (79.87 g/mol), N is Avogadro's number (6.022x1023 entities / mol), finally a and c are the lattice parameters in cm.

2.2 Electrical characterization

The determination of the electrical resistance of the TiO_2 films was made by means of the 4 collinear tips equipment, (Figure 1b). To determine the resistance of the film, the linear adjustment of the Voltage–Current data obtained was used, which allowed obtaining the slope of the line that corresponds to the value of the electrical resistance of the material, applying Ohm's Law.

III. RESULTS AND DISCUSSION

The film formation was produced through thermal decomposition of the precursor subjected to oxygen:

$$C_{16}H_{28}O_6Ti + 21O_2 \rightarrow TiO_2 + 16CO_2 + 14H_2O$$

This leads to colorless and clear films, while films obtained in the absence of oxygen contain carbon, such as occurs by the method of manufacturing thin films by Aerosol Pyrolysis of a similar metallic organic precursor [33].

3.1 Diffractograms of thin films of titanium dioxide

X–ray diffraction showed that the film deposited at substrate temperature of 380 °C is totally amorphous and does not show a TiO_2 diffraction peak (black curve in Figure 3a). But, when subjected to annealing up to 500 °C for 2 hours, the anatase crystalline phase is presented, as shown by the diffraction peaks (101), (004), (200) and (211) clearly detected in the graph (red color in figure 2a). The peaks mentioned correspond to the diffraction angles of 25.277 °, 37.884 °, 48.019 ° and 54.990 ° respectively.

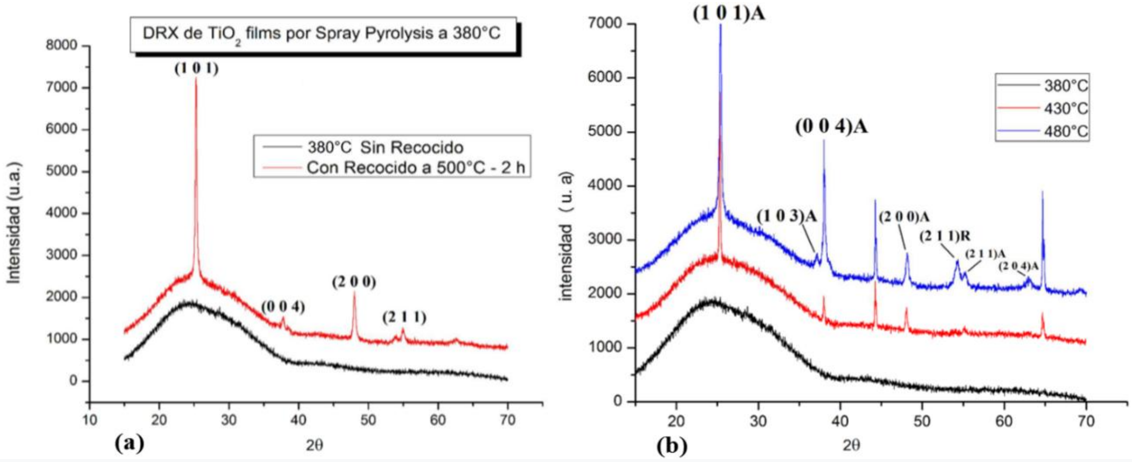


Figure 2. (a) Samples deposited at 380 °C without annealing (black curve) and with annealing at 500 ° C for two hours (red curve). The annealed sample shows the anatase phase of TiO2. **(b)** X–ray diffraction pattern thin films of TiO_2 deposited and prepared at temperatures of 380 °C, 430 °C and 480 °C without annealing.

The films deposited at 430 °C (red color in figure 2b) show the presence of TiO_2 in the anatase phase in their composition, according to planes (101), (004), (200) and (211), with (101) being the predominant. The films deposited at 480 °C (Blue color in figure 2b) also have the presence of anatase in the diffraction planes (101), (103), (004), (200), (211), (204) but also show the peak (211) R which undoubtedly belongs to the rutile phase according to XRD. With increasing deposition temperature, the films showed greater crystallinity, which is manifested by the corresponding increase in the intensity of the peaks in diffractograms[14].

In addition, while increasing the deposition and/or annealing temperature, the appearance of characteristic peaks of the rutile phase is promoted, which usually forms as a single phase at annealing temperatures above 700 °C [8]. But despite the fact that films deposited at 480 ° C reveal two additional anatase peaks (103) at 37.148 ° and (204) at 62.914 ° respectively, and reveal a rutile peak (211) at 54.209 °. The peak depends on the deposition parameters of the films manufactured in the present work. This is not surprising since for (Escobar et al., 1999), by the laser ablation method and[5] by the cathode arc method; the formation of films that reveal the presence of rutile is possible at substrate temperature even lower than 300 °C, and thus begins the appearance of an anatase-rutile phase transition state that according to the literature generally occurs from 600 °C [5].

Table 1. Structural parameters of thin films of TiO_2 for different substrate temperatures.

Temperature of substratum (ºC)	Grainsize D (nm)	Lattice parameters a and b of the peak (101) (Å)	Lattice parameter c of peak (101) (Å)	β = FWHM $x10^{-3}$ (rad)	Micro tension (ε) $x10^{-4}$	Dislocation density δ x 10^{14} (líneas/m^2)	Density of Anatasa (g/cm^3)
430	51.910	3.785	9.470	2.74	13.54	3.71	3.910
480	30.790	3.778	9.496	4.62	22.78	10.55	3.915
380annealed to 500	35.990	3.794	9.499	3.96	19.21	7.72	3.880

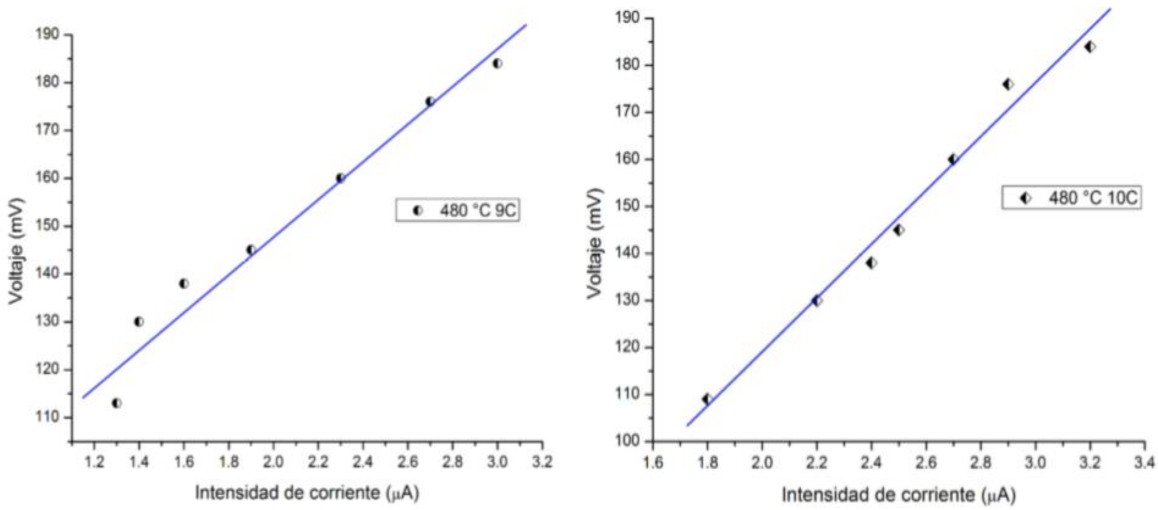
In Table 1 it is also noticeable that when there is an increase in temperature, the microtension increases considerably. This result contrasts with the one found by [15],. But it agrees with what was reported by[21] in their work report on the manufacture of films by the pyrolytic spray method. The change in this type of microtension may be due to the predominant recrystallization process in polycrystalline thin films. On the other hand, reported values of the dislocation density vary with temperature as reported [21]. Furthermore, the density data are in the order of the standard values for crystallized titanium dioxide in the anatase phase. In Table 1, the total width of the half of the maximum peak FWHM has an inverse relationship with the size of the grain.

Likewise, it is observed that microtension and dislocation density increase as grain size decreases. The microtensions that affect the network of the films also influence the results of the spectrometry, producing a broadening of the diffraction peaks. This is verifiable with the data in Table 1, the higher the microtension, the smaller the grain size and therefore the greater the broadening of the diffraction peak. This explains why the film grown at 430 °C has the sharpest predominant peak (101) of the three, since it experiences the lowest microtension value.

It is important to note that the films annealed at 500 °C present valuesthat do not mark a trend with respect to the other two that were not annealed. It should be noted that they were initially manufactured at 380 °C, and by annealing they crystallized, in a post-growth process, up to a temperature of 500 °C. We could say that its entire growth process was interrupted for a period of time and after cooling it down to room temperature it was heated until it was finished at 500 °C. This change in the growth process is likely to be the basis for the emergence of a new manufacturing parameter.

3.2 Voltage - current graph

For 3-layer films manufactured at substrate temperature of 380, 430 and 480 °C, current and voltage data are not shown applying when subjected to measurement by the four-collinear method because the value of the electrical resistance is very high and not within the measurable range of the instrument. In other words; the intensity of the current that passes through the films could be below the instrument's measurement limit and, consequently, its value could not be correctly estimated [8]. The reason why the resistance of these films is high can be attributed to the low oxygen vacancy present in the structure [29]. However, to increase oxygen vacancy, films with double concentration were manufactured and the number of layers were increased to 10 and 9 with a substrate temperature of 480 °C, obtaining current and voltage data which graphically present contact characteristics. Ohmic between thin films and silver metallic contact, from 1.4 μA applied. Therefore, the linear adjustment of the data obtained allowed to obtain the slope of the line that corresponds to the value of the electrical resistance of the material.



(a) **(b)**

Figure 3. Graph of Voltage vs. Current of samples manufactured at 480 °C at double concentration with 9 and 10 layers where their linear trends are shown.

It should be taken into account that, to make the voltage and current measurements, the films were not exposed to any type of ultraviolet excitation. They were simply measured in air at room temperature in the absence of UV radiation. The 9–layer sample, from 1.4 μA applied, has linear behavior and the slope of the graph corresponds to the electrical resistance whose value is approximately 38 KΩ. On the other hand, the 10-layer sample also shows a linear behavior whose slope value is its electrical resistance, which is around 57 kΩ. It can be noted that the number of layers influences the voltage-current characteristics.

IV. CONCLUSIONS

According to the results obtained, at 380 °C substrate temperature, the TiO_2 films are totally amorphous. However, increasing the deposition temperature or subsequent heat treatments improve the oxidation of the film, contributing to the diffusion of the atoms through the network, which presents an anatase phase from 430 ° C. Even at 480 °C a rutile peak (211) is shown, initiating the formation of anatase-rutile phase transition states. When it comes to the manufacture of thin TiO_2 films by pyrolytic spraying, the presence of the rutile phase at 480 °C is an uncommon fact or it is not reported in the literature, which usually presents rutile peaks at substrate or annealing temperatures. above 600 °C. It is a little known fact in the manufacture of thin films by pyrolytic spray, but it occurs as a result of other manufacturing methods such as laser ablation and cathodic arc deposition. The grain size of the films shows a tendency to decrease with the substrate temperature and has its smallest value at 480 ° C which is 30.79 nm. The electrical resistance valuesof the films are strongly dependent on the number of layers deposited to form the film. This follows from the significant change in the calculated resistance values (38 and 57 kΩ) due to a difference of one layer only in manufacturing.

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