Influence of the variation of the experimental conditions when obtaining the TiO$_2$ antireflective thin film

**J.I. Montes-Monsalve$^1$, L. A. Florez$^1$, L. M. Mósquera$^1$, R. Dorantes-Rodriguez$^2$ and B. Cruz-Muñoz$^1$**

$^1$Physics Department, Universidad Tecnológica de Pereira, Pereira, C.P. 660003, Colombia

$^2$Energy Department, Universidad Autónoma Metropolitana, Unidad Azcapotzalco, Ciudad de México, C.P. 02200, México

bcrucz@utp.edu.co

The formation of thin films based on TiO$_2$ plays a fundamental role in research involving solar energy (solar cell and solar thermal collectors) and from the part environmental (photocatalysis-artificial photosynthesis as a source of clean energy). In this sense, our work has focused on the experimental details directed towards the method of obtaining, for which as a precursor salt Titanium Oxyacetylacetonate (IV) (Sigma Aldrich with 90% purity) it has been used dissolved in methyl alcohol (Fisher Chemical with 99.8% purity) in 0.05 M molar concentration. The effect on deposited films was studied by varying airflow (2 L/min - 6 L/min) and substrate temperature (150 °C - 450 °C). For the Optical and structural characterization was used UV-VIS spectroscopy and X-ray diffraction techniques. From the analysis of the results was determined the energy band gap with values around 3.5 eV for all films. The Anatase phase with tetragonal structure was find it, refined using the Rietveld method that determined network parameters of $a = 3.807617$ Å, $b = 3.807617$ Å, $c = 9.547797$ Å, the thickness of the films ranged in a range between 70 nm - 150 nm whose values depended on the deposit conditions. The previous evidence allows concluding that this material can be used as an anti-reflective layer to be implemented in solar collectors.

1. Introduction

To meet the challenges of the energy sector and in turn to the continuous deterioration of natural resources, both science and technology must converge into new systems to transform the way energy is produced and consumed, allowing a transition to sustainable energy systems. In particular, the integration of different types of materials (such as nanoparticles, thin films, etc.) to devices that use renewable energy can improve their efficiency and performance [1, 2]. TiO$_2$ thin films generally manufactured under a variety of techniques, have the potential to be designed according to the desired application, considering its various properties (optical, structural, morphological, etc.). The TiO$_2$ films are often used in gas and humidity sensors [3], as gate electrodes for metal-oxide devices [4], as semiconductors in solar energy [5, 6], photocatalysis [7] or as material for anti-reflective layers [8-10]. They can be implemented in solar cells as well as in solar thermal collectors. This work is focused on applications where it is necessary to capture as much light as possible, that is, it is necessary to add anti-reflective materials (for example TiO$_2$). Since a significant combination of optical losses on the selective
surface of solar collectors is due to the high contrast index, which results in a high reflection of the absorber surface, whose value is around 35% over the entire electromagnetic spectrum [11].

One of the methods of obtaining TiO$_2$ in the form of thin films is by means of the aerosol-assisted chemical vapor (AACVD) technique, which has advantages over other deposition techniques with higher cost (e.g. magnetron sputtering and other vacuum techniques), since it is a simple process and has a very low cost of implementation. In addition, the deposits can be made on substrates with complex geometries, acquire a uniform distribution of the precursor solution, forming high quality coatings [12]. The AACVD technique consists in atomizing a precursor solution in very fine drops that are then dragged by a flow of hot air through a mobile nozzle, towards a substrate with a certain temperature where the film is formed due to condensation of the atoms that move on the surface of the substrate [13]. The characteristics of the material deposited using this technique depend on variables such as the temperature of the substrate, the carrier air flow with the species to be deposited, the speed of the nozzle and the distance of the nozzle to the substrate (figure 1). In order to establish a deposit protocol and the optimization of the deposit process towards the manufacture of the anti-reflective layer (TiO$_2$), using the AACVD technique, the influence of the deposit parameters and the consequences of their variations on the coating were systematically investigated. Therefore, this work describes the experimental method of the technique, varying two process parameters: the substrate temperature and the speed of the nozzle, in order to find their influence on the structural and optical properties of the deposited material. From the diffractograms, analytical methods were used to determine the structure of the deposits using Rietveld refinement, which approximates the intensities to certain positions of the X-ray measurement in order to obtain the specific diffractogram [14]. While using the Swanepoel method, the refractive index was obtained in a range of wavelengths and film thickness. [15, 16]. The results obtained will help to optimize the manufacturing process of these coatings that will be the anti-reflective layers on the selective absorbent surfaces used in the manufacture of water heaters, air or solar energy installations of different types, like solar cells, photovoltaic panels, among others.

2. Methodology

2.1. Deposit conditions
Thin films of TiO$_2$ were obtained using the aerosol-assisted AACVD deposit technique, whose scheme with each of the electrical and mechanical components is shown in figure 1. Details about the configuration of the deposition system can be surveyed elsewhere [17, 18]. All deposits were made on glass slides substrates with dimensions 2.5 cm x 7.5 cm. These were subjected to a cleaning treatment in an ultrasonic bath consisting of an immersion of acetone and subsequently methanol that lasted 40 minutes, in order to remove any grease from the surface. Titanium oxide (TiO$_2$) was obtained from the precursor salt Titanium Oxyacetylacetonate (Sigma Aldrich, 99% purity) dissolved in methyl alcohol (Fisher Chemical 99.8%) with a molar concentration of 0.05 M. Filtered compressed air was employed as carrier gas it was fed at 5 L/min, the distance between the mobile nozzle and the substrate was 1 mm, the mobile nozzle scrolled across the substrates, applying 4 layers. Coatings were deposited in two stages: (a) Variation of substrate temperature from 150 °C to 450 °C in steps of 50 °C; (b) Variation of the speed of the mobile nozzle from 0.6 cm/min to 0.8 cm / min and substrate temperature of 400 °C. Table 1 summarizes the deposit parameters used for both stages.
Figure 1. Descriptive diagram of the aerosol-assisted (AACVD) technique where each of the components that composed the system is presented (own authorship).

Table 1. Deposit parameters, experimental conditions on two stages: temperature and speed variation.

| Deposit parameters          | Temperature variation experiment | Speed variation experiment |
|-----------------------------|----------------------------------|---------------------------|
| Temperature (°C)            | 150 - 450                        | 400                       |
| V_N-Nozzle speed (cm/min)  | 0.6                              | 0.6 - 0.8                 |
| Air flow (L/min)            | 4                                | 5                         |
| Nozzle-substrate distance (mm) | 1                             | 1                         |
| Air flow temperature (°C)  | 30                               | 30                        |
| Layers or passes            | 4                                | 4                         |

2.2. Characterization methods

The thermal stability of the precursor salt was studied by Thermogravimetric analysis (TGA). Simultaneously, a TGA-DSC device (TA Instruments SDT-650) was used, with an alumina tray of 90 ul. The curves were measured up to 800 °C at a heating rate of 10 °C/min under a constant nitrogen flow. The crystalline structure was analyzed by grazing incidence x-ray diffraction. For this purpose, a Diffractometer XPERT-PRO system was used, operating at 45 keV and 20 mA that works with Cu Kα radiation (0.1540 nm and 0.1544 nm). The parameters used to make the measurements were: scanning range 2Θ from 20° to 100°, a scanning time of 14 s, a step size of 0.04° and a grazing incidence angle set at 0.5°. Phase identification and Rietveld refinement were done using X-pert High Score Plus and GSAS software with a Pseudo-Voigt function, respectively [19]. The transmittance and reflectance spectra were measured in the UV-Vis interval using a Thermo Scientific - Evolution 220.
spectrophotometer equipped with integrating sphere accessory. The Swanepoel method was used by adjusting the envelopes of the interference bands of the transmission spectrum in order to obtain the refractive index and the film thickness [15, 16].

3. Results and Discussion

3.1. Thermal stability: Influence of substrate temperature

In order to determine the influence of the temperature on the formation of thin films of TiO₂, the thermal behavior (TGA–DSC) of the precursor salt (TiO(acac)₂), Titanium(IV) Oxyacetylacetonate) was analyzed up to a value of 800 °C. The purpose was to obtain information about the temperatures of reaction and products during the thermal decomposition. However, it is important to take into account that this result is only an indicator of the possible precursor transformations, due to the different thermal conditions during the synthesis of the films in the AACVD [20]. For this reason, deposits were made in the temperature range between 150 °C and 450 °C and additionally the transmittance spectra in the UV-Visible were analyzed.

Figure 2 shows the TGA curve (continuous line) and the DTG curve (dotted curve) of the precursor salt of Titanium Oxyacetylacetonate. From the TGA curve, the reagent decomposition can be observed, while the DTG curve can accurately identify the two steps in which mass loss occurs. There is an initial slow endothermic mass loss of approximately 1% up to 152 °C, related to the loss of water present in the reagent. The first decomposition step for Oxyacetylacetonate corresponds to the temperature range between 162 °C - 284 °C (endothermic reaction), that results in a mass loss of 54%, which is equivalent to the maximum mass loss rate. This first decomposition can be tentatively explained with the loss of mass of the chelated ligands and the burning point corresponding to acetylacetone [21, 22]. The second step of mass loss occurs in the range of 439 °C - 502 °C that begins as a rapid endothermic reaction with a constant mass change of (3%). The decomposition of the reagent is completed practically from 480 °C. Figure 3 shows the DSC curve of the same salt, where only one endothermic peak is observed between 200 °C and 250 °C, which can be attributed to the onset of Oxyacetylacetonate decomposition. According to the results obtained, it is concluded that the temperature range to make the deposits is above 350 °C since at lower values of this temperature there is both an irreversible transition and a greater loss of mass (TGA), which is observable in the DSC thermogram and the greater loss of mass (TGA) that the reagent has.

![Figure 2. Thermal decomposition curves of titanium Oxyacetylacetonate: TGA - thermogravimetric curve (blue continuous line) and DTG - derivative TGA curve (dotted line).](image1)

![Figure 3. DSC curve of titanium Oxyacetylacetonate: Endothermic peak observable between 200 °C and 250 °C](image2)
One way to corroborate that the films correspond to TiO$_2$ and that they also comply with the properties to be implemented as antireflective layers is through the study of their optical characteristics. Figure 4 shows the layers transmittance spectra in the Uv-Visible range, of layers for different substrate temperatures. It is observed that as the temperature increases, the transmittance decreases depending on the absorption zone, that is, either in the zone of strong absorption (Uv-Visible) or the zone that goes from the mean to the weak absorption (400 - Near-InfraRed), this fact is given by the interference bands that is a well-known optical phenomenon [23]. The transmittance measurements allowed to determine the energy of the band gap $E_g$ using the square of the product of the absorption coefficient ($\alpha^2$) and the energy of the incident photons ($(h\nu)^2$), as a function of the energy ($h\nu$), such as it shown in Figure 5. From the high absorption region, the graph of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) and extrapolating the linear region of this curve $(\alpha h\nu)^2 = 0$ get it the energy value of the band gap $E_g$ is calculated for each thin film. In all cases, it can be seen that a direct transition takes place and, in addition, the presence of different $E_g$ values according to the substrate temperature.

In the case of deposit temperatures in the range of 150 °C - 350 °C, values between 1.5 eV and 2.7 eV are obtained (figure 5a), which are below of the values reported in the literature for TiO$_2$ (3.4 eV [24]) as a potential antireflective layer. However, this behavior could be explained based on the results reported from the thermal study, where it was observed that at temperatures below 350 °C the TiO$_2$ formation is not stable producing changes in mass loss, even induced other phases. In the case of deposit temperatures between 400 °C and 450 °C (Figure 5b), the $E_g$ values found are 3.5 eV, which are around the values reported in the literature [24]. The $E_g$ value obtained, allows to establishing that for temperatures between 400 °C and 450 °C, the layers of TiO$_2$ with antireflective characteristics can be achievable and deposited using a versatile and low-cost technique such as AACVD.

![Figure 4](image.png)

Figure 4. Transmittance spectra in the UV-Visible range for a deposit temperature range between 150 °C and 450 °C, in 50 °C steps compared to the uncoated substrate.
3.2. Influence of speed mobile nozzle

The study of the influence of the parameters of the deposition process, showed that the temperature to obtain the films should be above 400 °C on glass substrates. In fact, the structural characteristics and the validation of the optical properties that have been studied when varying the speed of the nozzle confirmed it. In this sense, two TiO₂ films were deposited by varying the speed of the mobile nozzle at a substrate temperature of 400 °C with speeds of 0.6 cm/min and 0.8 cm/min and whose other parameters are shown in table 1.

3.2.1. X-Ray diffraction. Figure 6 shows the standard diffraction patterns for films deposited at speeds of 0.6 cm / min and 0.8 cm / min. In both cases it is observed that they have a polycrystalline structure and to which 10 planes can be associated, two of them of high intensity and eight planes of low intensity. The planes with higher intensity in the diffractogram are oriented in 2θ around the values 25.31 ° - plane (101) and 48.05 ° - plane (200). The other eight planes can be seen in figure 6. It should be noted that the planes around 2θ in 36.85 ° - plane (103), 37.86 ° - plane (004) and 38.68 ° - plane (112), only appear in the deposited film with a nozzle speed (VN) equivalent to 0.6 cm /min. All above crystalline planes correspond to TiO₂ with tetragonal structure and anatase phase, according to the ICSD database card No. 9852 [26]. It is important to note that at the higher nozzle speed of (0.8 cm/min), the crystallinity of the film decreases, showing planes with very low intensity and even some planes do not appear at all. This behavior could be taken as a technology indicator for the optimization of the deposit parameters, in order to improve antireflective layers. After exposing the latter information, it could be said that the most appropriate speed with the conditions used in table 1 is likely 0.6 cm/min.
Figure 6. Grazing incidence diffraction patterns of samples with speeds of 0.6 cm/min and 0.8 cm/min

The Rietveld refinement was performed for both samples in order to corroborate the atomic positions and find evidence of possible structural changes with respect to the reference pattern and also calculate the crystallite size using the parameters obtained from the refinement. The phase and structure formed for each velocity were determined using the unit cell (tetragonal - referenced from the database) and the known spatial groups (I41/amd-141) for TiO$_2$, whose values are shown in table 2. Figure 7 shows the experimental diffraction pattern and its respective refinement for the sample with speed 0.6 cm/min, with values of ($\chi^2$) = 1.5 and R ($F^2$) = 0.77.

Figure 7. Rietveld refinement from the diffractogram corresponding to sample deposited at 0.6 cm/min
Table 2. Phase and structural information of TiO$_2$ samples

| Sample | TiO$_2$ Structure | Phase | Crystal size (nm) | Lattice parameter (Å) |
|--------|------------------|-------|------------------|-----------------------|
| $V_N=0.6$ cm/min | Tetragonal | Anatase | 20 | $a = b = 3.79$, $c = 9.80$ |
| $V_N=0.8$ cm/min | Tetragonal | Anatase | 21 | $a = b = 3.81$, $c = 9.78$ |
| ICSD: 9852 $[26]$ | Tetragonal | Anatase | -- | $a = b = 3.78$, $c = 9.50$ |

3.2.2. Optical properties. To validate that at temperatures around 400 °C and when the nozzle speed is changed, the optical properties do not vary. The values of the energy band gap ($E_g$) were determined with the transmittance measurements and, in addition, applying the Swanepoel method $[15, 16]$ the thickness of the films and the refractive index were calculated according to the wavelength, whose results will confirm that TiO$_2$ is obtained by the AACVD technique successfully.

Figure 8 shows the transmittance spectra for the samples run at the speed of 0.6 cm/min (figure 8a) and 0.8 cm/min (figure 8b). The Swanepoel method allowed to calculate the envelopes of maximum (TM) and minimum (Tm) interference.

![Figure 8](image)

Figure 8. Transmittance spectra for samples with a speed variation of: (a) 0.6 cm/min and (b) 0.8 cm/min. The TM and Tm envelopes of the maximum and minimum interference, respectively are shown $[15]$. 

In the spectra of figure 8, it can be observed that the films are highly transparent in the range of Visible - NIR (Near InfraRed) with transmittance values around 70 % and that they also have an absorption edge of around 350 nm, which is equivalent to the edge obtained for the deposited films when varying the temperature (figure 4). The highly transparency in that range, is a good indicator of the characteristics of an antireflective material, considering that the interference fringes along the electromagnetic spectrum, may contribute as optical traps when the antireflective layer is on top of the absorbent layer, causing the light to be absorbed again, this due to top surface to be out of phase with
the wave reflected from the another surface [5]. Another optical property that confirms the obtaining of TiO₂ is the refractive index (n), which was determined with the envelope method (Swanepoel) and is shown in figure 9.

The variation of n for the film obtained at a nozzle speed equal to 0.6 cm/min has a nearly constant value between 400 nm and 800 nm with n = 2.2, such value is in accordance with the values reported in the literature [27, 28]. For the sample obtained at a speed of 0.8 cm/min a value is even below n = 2.0, which can be attributed to lower crystallinity and the presence of possible defects such as dislocations possibly caused by the higher speed, showing that the speed of the nozzle is a decisive parameter to obtain TiO₂ layers with optimal values. The calculated thickness value was approximately 470 nm for the speed of 0.6 cm/min and 505 nm for the speed of 0.8 cm/min.

![Figure 9. Index refraction for the samples deposited at V_N = 0.6 cm/min– 0.8 cm/min.](image)

Finally, Figure 10 shows the graph of (αhν)² as a function of the energy of the photons (hν) from which values of the energy band gap were calculated, E_g = 3.5 eV for both speeds 0.6 cm/min and 0.8 cm/min. These values are equivalent to those obtained when varying the substrate temperature. Therefore, it can be said that the technological parameters of the process have been varied successfully. Both the temperature and the speed of the mobile nozzle, provide reproducible results and ideal characteristics that are conditions necessary to meet, so that the TiO₂ can be employed as an antireflective layer and incorporated into the absorber surface of a flat solar collector.
Figure 10. Plot of $(\alpha h)^2$ vs $h$ for the samples deposited at 0.6 cm/min – 0.8 cm/min.

Conclusions
The variation of the speed of the mobile nozzles during the deposit via AACVD, has allowed to determine that there is a speed limit equivalent to 0.6 cm/min, in order to obtain polycrystalline TiO$_2$ with a well-defined structure, with a crystallite size around 20 nm, optimal refractive index, a value of the energy band gap $E_g = 3.5$ eV that confirms that the proposed material was obtained, and fundamentally, that allows the crossing of up to 70% of the light in the Visible-NIR range, working as optical traps with well-defined interference fringes, which make it have the ideal deposit conditions to be used as antireflective material to be integrated into a solar collector.

Acknowledgements
The authors would like to thank Ph.D. Mario Miki Y., M.Sc. Pedro Pizá R. and Ph.D. Patricia Amézaga M. from the Centro de Investigación en Materiales Avanzados, S.C. (CIMAV-Chihuahua) for their support in the development of this work. In addition, we are grateful to CONACYT for the partial funding received through project 249855, to the Universidad Tecnológica de Pereira with project 3-18-5 and COLCIENCIAS for the postdoctoral stay under announcement 811 of 2018 and young researcher under announcement 712 of 2018.

References
[1]. Cai J and Qi L 2015 M. Horizons Royal Society of Chemistry 2 p 37–53.
[2]. Leonid A Kosyachenko 2012 Solar Cells - Silicon Wafer-Based Technologies. In: Silicon Wafer-Based Technologies. InTech; 2012
[3]. Dai J, Yang J, Wang X, Zhang L and Li Y 2015. Appl Surf Sci. 349 p 343–52.
[4]. Diebold U 2003 Surface Science Reports 48 p. 53–229
[5]. Kim S, Jahandar M, Jeong JH and Lim DC 2019 Recent progress in solar cell technology for low-light indoor applications Curr Altern Energy
[6]. Voroshilov PM, Simovski CR, Belov PA and Shalin AS 2015 J Appl Phys. 117 20
[7]. Scanlon DO, Dunmill CW, Buckeridge J, Shevlin SA, Logsdail AJ, Woodley SM, et al. 2013 Nat Mater 12 9 p 798–801.
[8]. Cao F, McEnaney K, Chen G and Ren Z 2014 Energy and Environmental Science Royal Society of Chemistry 7 p 1615-27
[9]. Keshavarz Hedayati M and Elbahri M 2016 Antireflective Coatings: Conventional Stacking Layers and Ultrathin Plasmonic Metasurfaces, A Mini-Review. *Materials (Basel)* 9 6 p 497

[10]. Cao F, Kraemer D, Sun T, Lan Y, Chen G and Ren Z 2015 Enhanced Thermal Stability of W-Ni-Al 2 O 3 Cermet-Based Spectrally Selective Solar Absorbers with Tungsten Infrared Reflectors. *Adv Energy Mater* 5 2

[11]. Chee KWA, Tang Z, Lü H and Huang F 2018 *Energy Reports* 1 4 p 266–73

[12]. Filipovic L, Selberherr S, Mutinati GC, Brunet E, Steinhauser S, Köck A, et al. Proceedings of the World Congress on Engineering 2013 Vol II

[13]. Malik O, Hidalga-Wade FJD La and Amador RR. *Spray Pyrolysis Processing for Optoelectronic Applications*. In: Pyrolysis. InTech; 2017.

[14]. Young R 2002 *The Rietveld method* (Oxford: Oxford Univ. Press) p 111 - 64

[15]. Swanepoel R 1983 *J Phys E* 16 12 p 1214–22

[16]. Manifacier JC, Gasiot J and Fillard JP 1976 *J Phys E* 9 11 p1002–4

[17]. Castrillón González EY, Hicapie Zapata JM, Cruz Muñoz B, Dorantes Rodriguez RJ and Medina Barreto MH 2019 *DYNA*. 86 210 p 52–7

[18]. Hincapie JM, Castrillon EY, Olarte W, Dorantes RJ and Muñoz BC 2019 *Journal of Physics: Conference Series* (Institute of Physics Publishing)

[19]. Larson A.C. and Von Dreele R B 2004 General Structure Analysis System (GSAS) Report LAUR 86-748 (University of California Los Alamos National Laboratory)

[20]. Pizá-Ruiz P, Sáenz-Trevizo A, Verde-Gómez Y, Amézaga-Madrid P and Miki-Yoshida M. 2019 *Ceram Int*. Jan 1;45 p 1156–62.

[21]. Lee CW and Lee JS 2006 *J Ceram Soc Japan* 114 1335 p 923–8

[22]. Acik IO, Madaras J, Krunks M, Tõnsuaadu K, Pokol G and Niinistö L 2009 *J. of Thermal Analysis and Calorimetry* p 39–45

[23]. Pankove JI and Kiewit DA 1972 *J Electrochem Soc.* 119 5 p 156C.

[24]. Spiridonova J, Katerski A, Danilson M, Krichevskaya M, Krunks M and Oja Acik I 2019 Effect of the Titanium Isopropoxide:Acetylacetone Molar Ratio on the Photocatalytic Activity of TiO2 Thin Films. *Molecules* 24 23 p 4326

[25]. Dundar I, Acik IO, Krichevskaya M and Katerski A 2019 *R. Society of Sci.* 6 2

[26]. Kristin P 2014 *Materials Data on TiO2 [Internet]. Materials Project*

[27]. Möls K, Aariik L, Mändar H, Kasikov A, Niilisk A, Rammula R, et al. 2019 *Opt Mater* (Amsterdam) 1 96

[28]. Hassanien AS and Akl AA 2019 *Phys B Condens Matter* 1 576