ÓPTICA PURA Y APLICADA
www.sedoptica.es

Type: Research Paper
Section: Sensors and Photonics Devices

Comparative analysis of TiO_2 layers grown by pulsed laser deposition at atmospheric pressure and pyrolitic nebulization.

Estudio comparativo de capas de TiO_2 depositadas por PLD a presión atmosférica y nebulización pirolítica.

M. R. Tejerina[1], M. Gamba[2], L. Ponce Cabrera[3], F. C. Alvira[4,5,*]

1. Centro de Tecnología de Recursos Minerales y Cerámica (CETMIC) (CIC-CONICET La Plata) Cno. Centenario y 506 M.B. Gonnet (1897), Buenos Aires, Argentina.

2. Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Diagonal 113 y 64, La Plata (1900), Buenos Aires, Argentina.

3. San Petersburg Electrotechnical University, Professora Popova 5, 197376 St. Petersburg, Russia

4. Laboratorio de Instrumentación, Automatización y Control. Dpto. de Ciencia y Tecnología, Universidad Nacional de Quilmes, Roque Saenz Peña 352, 1876, Bernal, Buenos Aires, Argentina.

5. Laboratorio de Biomembranas, Dpto. de Ciencia y Tecnologia, Universidad Nacional de Quilmes, Roque Saenz peña 352, 1876, Bernal, Buenos Aires, Argentina.

(*) E-mail:fernando.alvira@unq.edu.ar

Received: 10/04/2018 Accepted: 25/09/2018
DOI: DOI: 10.7149/OPA.51.4.50301

ABSTRACT

TiO_2 layers and nanolayers are widely studied due to its technological applications. This material could be used in solar cells, transmission, emission or selective reflection, among other applications. In this paper, we show a characterization of layers of TiO_2 grown by two different methods, Pulsed Laser Deposition (PLD) at atmospheric pressure and spray pyrolysis (SP). The samples were characterized by SEM, EDS, AFM, XRD and Raman Spectrometry.

Key words: TiO_2 layers, spray pyrolysis, air pulsed laser deposition

RESUMEN

Las nanocapas cerámicas son ampliamente estudiadas por su interés en aplicaciones tecnológicas. Estos recubrimientos pueden conformar celdas solares, superficies de transmisión, emisión o reflexión selectiva de luz, entre otras tantas aplicaciones. En este trabajo se presenta una comparación entre películas delgadas de TiO_2 depositadas por ablación láser pulsado (PLD) y por nebulización pirolítica (sol-gel spray-pyrolisis, SP). La caracterización de las nanocapas se realizó empleando diversas técnicas como microscopía electrónica de barrido (SEM), espectrometría de dispersión de energía de Rayos X (EDS), microscopia de Fuerza Atómica (AFM), Difracción de Rayos X y espectroscopia Raman.

Palabras clave: capas TiO_2, spray pirólisis, PLD en aire

REFERENCES AND LINKS / REFERENCIAS Y ENLACES

[1] F. C. Alvira, L. P. Cabrera, Y. Peñaloza Mendoza, M. L. Martinez Ricci, and F. Videla, "Pulsed laser deposition of PbTe under monopulse and multipulse regime," Optics and Lasers in Engineering **90**, 284-290 (2017).

[2] R. M. Gazoni, M. G. Bellino, M. Cecilia Fuertes, G. Gimenez, G. J. A. A. Soler-Illia, and M. L. M. Ricci, "Designed nanoparticle-mesoporous multilayer nanocomposites as tunable plasmonic-photonic

architectures for electromagnetic field enhancement," Journal of Materials Chemistry C **5**, 3445-3455 (2017).

[3] V. M. Sánchez, E. D. Martínez, M. L. Martínez Ricci, H. Troiani, and G. J. A. A. Soler-Illia, "Optical Properties of Au Nanoparticles Included in Mesoporous TiO2 Thin Films: A Dual Experimental and Modeling Study," The Journal of Physical Chemistry C **117**, 7246-7259 (2013).

[4] S. Ullah, E. P. Ferreira-Neto, A. A. Pasa, C. C. J. Alcântara, J. J. S. Acuña, S. A. Bilmes, M. L. Martínez Ricci, R. Landers, T. Z. Fermino, and U. P. Rodrigues-Filho, "Enhanced photocatalytic properties of core@shell SiO2@TiO_2 nanoparticles," Applied Catalysis B: Environmental **179**, 333-343 (2015).

[5] S. T. Sundari, N. C. Raut, T. Mathews, P. K. Ajikumar, S. Dash, A. K. Tyagi, and B. Raj, "Ellipsometric studies on TiO_2 thin films synthesized by spray pyrolysis technique," Applied Surface Science **257**, 7399-7404 (2011).

[6] A. Giberti, M. C. Carotta, C. Malagù, C. M. Aldao, M. S. Castro, M. A. Ponce, and R. Parra, "Permittivity measurements in nanostructured TiO_2 gas sensors," physica status solidi (a) **208**, 118-122 (2011).

[7] Y. Peñaloza-Mendoza, and L. Ponce-Cabrera, "Comparison on Morphological and Optical Properties of TiO_2 Thin Films Grown by Single-Pulse and Multi-Pulse Laser Ablation," Journal of Surface Engineered Materials and Advanced Technology **5**, 17-23 (2015).

[8] M. Giarola, A. Sanson, F. Monti, G. Mariotto, M. Bettinelli, A. Speghini, and G. Salviulo, "Vibrational dynamics of anatase TiO_2: Polarized Raman spectroscopy and ab initio calculations," Physical Review B **81**, 174305 (2010).

[9] L. Reimer, *Scanning electron microscopy : physics of image formation and microanalysis* (Springer, 1998).

[10] A. G. Manohari, S. Dhanapandian, K. S. Kumar, and T. Mahalingam, "Optimization of Deposition Parameters on the Physical Properties of TiO_2 Thin Films by Spray Pyrolysis Technique," International Journal of Thin Films Science and Technology **3**, 1 (2014).

[11] A. Nakaruk, D. Ragazzon, and C. C. Sorrell, "Anatase thin films by ultrasonic spray pyrolysis," Journal of Analytical and Applied Pyrolysis **88**, 98-101 (2010).

[12] I. Oja, A. Mere, M. Krunks, R. Nisumaa, C. H. Solterbeck, and M. Es-Souni, "Structural and electrical characterization of TiO_2 films grown by spray pyrolysis," Thin Solid Films **515**, 674-677 (2006).

[13] N. C. Raut, T. Mathews, S. T. Sundari, T. N. Sairam, S. Dash, and A. K. Tyagi, "Structural and Morphological Characterization of TiO_2 Thin Films Synthesized by Spray Pyrolysis Technique," Journal of Nanoscience and Nanotechnology **9**, 5298-5302 (2009).

1. Introduction

TiO_2 is an n-type semiconductor that has emerged as an extremely valuable oxide for numerous technological applications because of its unique electrical and optical characteristics. It is mostly used as thin films because of its unusual properties such as high refractive index and high dielectric constant. Due to these properties, TiO_2 thin films can be used in several applications such as microelectronics, solar energy conversion, photo-catalysis, photovoltaic, optical systems such as multilayer structures that can be anti-reflective or exhibit high reflectivity at a specific wavelength and, organic light emitting diodes. Also, thin films made of TiO_2 are frequently used for optical coatings due to their unusual optical properties, wide energy band gap, transparency throughout the visible spectrum and a high refractive index over a broad spectral range that spans from ultraviolet to the far infrared region.[1-3]

Many methods such as electron beam evaporation, chemical vapor deposition, magnetron sputtering, pulsed laser deposition (PLD) among others have been successfully developed to synthesize transparent TiO_2 thin films. However, these processes need moderate to high vacuum atmospheric conditions to be carried out and therefore, require expensive equipment. Moreover, these methods are not suitable for deposition over a large surface area. We focus the present study on the comparison of coatings made by inexpensive techniques: atmospheric pressure PLD and sol-gel spray-pyrolysis (SP).

In the case of SP, deposition route works under open atmospheric conditions and is therefore, highly suitable for relatively large surface area coatings. High dense non-porous anatase titania films have been synthesized by sol-gel technique. Films of nominal porosity find applications as gas sensors and UV sensors. Films of optimized porosity are imperative for gas sensor applications as the number of

interactions of gas molecules increases with the film's surface area thereby increasing its response and sensitivity. Films of controlled porosity synthesized by spray pyrolysis technique have been applied for large area deposition and are ideally suitable for gas sensing applications.[4]

PLD is a technique which uses focused pulses of laser energy to remove material from the surface of a target. The vaporized material, containing neutrals, ions and electrons is known as a laser-produced plasma plume and expands rapidly away from the target surface (velocities typically $\sim 10^6$ cm s^{-1} in vacuum). Film growth occurs on a substrate upon which some of the plume material condenses. In practice, many variables affect the properties of the film, such as laser fluence, background gas pressure and substrate temperature. These variables allow the film properties to be manipulated somewhat, to suit individual applications. PLD has been applied with multiple experimental variations like different types of laser (all the Nd:YAG harmonics have been tested as excitation source), micro, pico, nano and femtosecond laser pulses have been applied. Also, laser emitting single or multiple pulses were performed in previous works[1]. To the best of our knowledge, a variant of PLD unexplored until these days is the implementation of PLD without a vacuum chamber that is so says PLD in air or under atmospheric pressure. This variant has the simplicity that uses neither vacuum pump nor chamber, which significantly simplifies the manufacturing process. One possible drawback of this approach is regarding the quality of the layers obtained. However, not all the applications need a high-quality smooth layer: regarding photocatalysis and photovoltaic applications of TiO_2 coatings, the most critical limitation is its low absorption in the visible region. Thus there are extraordinary efforts in sensitizing TiO_2 with visible absorbing materials or by producing non-stoichiometric TiO_2, i.e., TiO_{2-x} which is usually known as "black" TiO_2. On the other hand, in photocatalysis and photovoltaic applications anatase is the phase of choice because of its higher photoelectron yield, while rutile is most used in optical devices because of its higher stability.[2-6]

This paper aims to report a comparison between TiO_2 coatings obtained by the two previously mentioned inexpensive techniques. We analyze the following properties of samples generated by PLD and SP: porosity (useful to gas sensing), composition (regarding for photocatalyst) and crystalline phase throughout well-known Raman spectrum of TiO_2. We also propose possibly applications for these manufacturing methods according to the obtained results.

2. Material and experimental set-up.

The deposition by PLD was done on soda-lime glass substrates using a commercial TiO_2 target (Kurt J. Lesker with a purity of 99.99%). In the ablation process, a home-made Nd:YAG laser was employed; the laser emitted a Gaussian beam with a nearly negligible hot spot in the focus region, the wavelength emitted was 1064 nm and was operated at a frequency of 10 Hz. The deposition was performed under atmospheric pressure, with a target-substrate distance of 1 cm and without heating the substrate. The total energy for each emission was adjusted to 104 mJ, which fixed the working fluence at 2 $J.cm^{-2}$. More details of the laser can be found elsewhere.[1, 7] The laser beam was rastered over the target, and it was rotated. The deposits were made with nearly 4000 laser pulses.

The coating made by SP was fabricated from a precursor solution containing titanium butoxide as a titanium source (TB), acetylacetone (AcA) as a stabilizer and ethanol as a solvent. A TB concentration of 6% v/v and a TB:AcA molar ratio of 1:2 were employed. This solution was stirred for 30 min at a temperature of 60 ºC. The solution was atomized through a conventional airbrush using pressurized nitrogen (between 150 and 200 Kpa) at a rate of 350 l/h. The film was generated by manually atomizing the solution over a heated (350-400 °C) glass slice (soda lime) employed as a substrate. After this, the coated substrate was annealed for 30 min at 600ºC employing heating and cooling slope less than 2 ºC/m.

Before the deposition, the substrate was cleaned with detergent, distilled water, ethanol and acetone. The morphology of the samples was evaluated by scanning electron microscopy (SEM) (JEOL 6000) and atomic force microscopy (TT AFM Workshop) with a Si tip in the contact mode. The chemical composition of the films was determined by energy dispersive X-ray spectroscopy (EDS) (Apollo XL-SDD, EDAX). To perform X-Rays Diffraction technique (XRD), A Bruker XRD D2 Phaser was employed.

3. Results and discussions

3.a. Morphological and compositional determination.

Figures 1(a) and (b) show SEM micrographs for the films deposited by PLD and SP, respectively. The appearance of the samples is entirely different: the coating manufactured by PLD presents a large opacity, while the sample obtained by SP is entirely transparent for normal incidence angle. From observation with optical microscopy and a submicron positioner stage, it was determined a thickness of around 9 μm for PLD layer and a thickness of less than 300 nm for SP layer.

On one hand, the large particles in PLD coatings were produced by the splashing effect which is typical of this method. Also, for this coating the surface seems irregular, and some pits are observed. This was confirmed by AFM images (see Figure 2(a)) where a highly inhomogeneous surface with valleys and top can be seen. It was not possible to measure the distance between a valley and top because it was out of range for the AFM instrument (it is higher than 3 μm). On the other hand, the SEM image of TiO_2 layers obtained by SP shows a smooth surface, with very little splashed material and mainly without pits. This was also confirmed by AFM image presented in Figure 2(b), a smooth surface with a few pits of at least 50 nm thick. In summary, by examining both AFM and SEM images, it was concluded that the layer obtained by PLD is less homogeneous and presents a higher degree of roughness (more than 3 μm) than the layer obtained by SP technique (less than 80 nm).

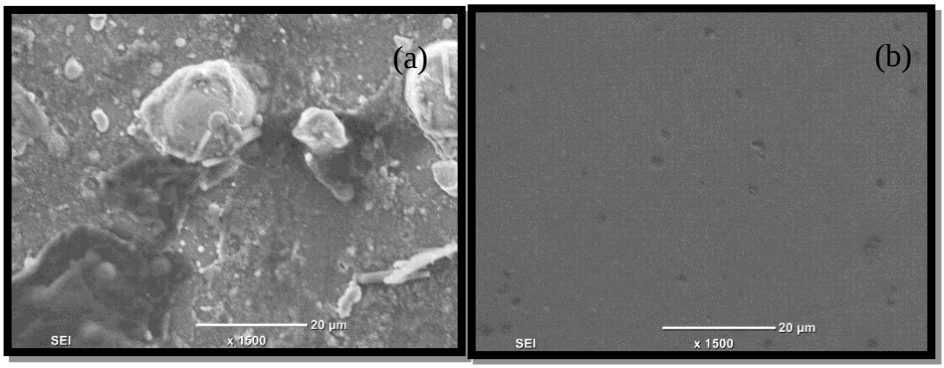

Fig 1: (a) TiO_2 layers obtained by PLD at atmospheric pressure. (b) TiO_2 layers obtained by SP.

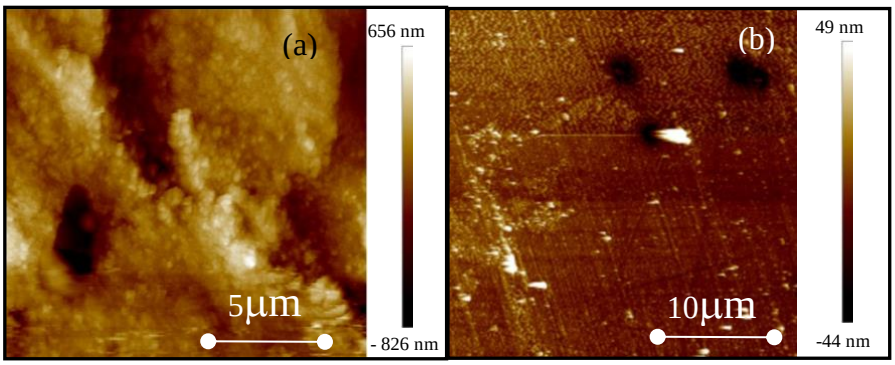

Figure 2: (a) AFM height images of layers grown by PLD and (b) SP (figure B).

The composition of samples was estimated employing EDS measurement and well-known ZAF semi-quantitative correction method[8]. In Figure 3, the measured spectrum for SP and PLD films is shown. On one hand, Ti and O, which belong to the deposited layer, were detected. On the other hand, Si, Na, Mg, Ca and a portion of O atoms correspond to the glass substrate and were also present in both samples. This is because the electronic beam penetrates more in-depth than the width of the films. To analyze the composition of thin films which are composed of Ti and O, the percentage of O atoms corresponding to the substrate was subtracted from each composition. To this end, an EDS spectrum and quantification was performed for each substrate employing the same experimental conditions used for each layer and the ratio

between Si and O was determined. With this information the proportion of oxygen atoms corresponding to glass substrate was subtracted to the sample composition using Si atoms as a reference. After this procedure, Ti and O ratios in the samples were determined and the results are presented in Table 1. According to the well-known stoichiometry, it is expected a mass ratio O:Ti of about 0.7. The stoichiometry obtained by both of the deposition methods gave satisfactory results, taking into account the uncertainty of the semi-quantitative analysis [9]. On one hand, the composition obtained by SP almost matched the expected stoichiometry, which is in accord with previously published results[10]. On the other hand, layers grown by PLD have an excess of oxygen, which could be generated by a selective ablation process. This consists of the enrichment of the gas phase formed immediately after the ablation by one of the components and plays a crucial role in the stoichiometry.

Table 1. Mass proportion estimated by EDS semi-quatitative ZAF method for SP and PLD samples

	Ti (Mass %)	O (Mass%)	O:Ti
PLD	55.2 +/- 5.0	44.8 +/- 4.2	0.8 +/- 0.1
SP	59.93 +/- 4.8	40.07 +/- 4.7	0.7 +/- 0.1

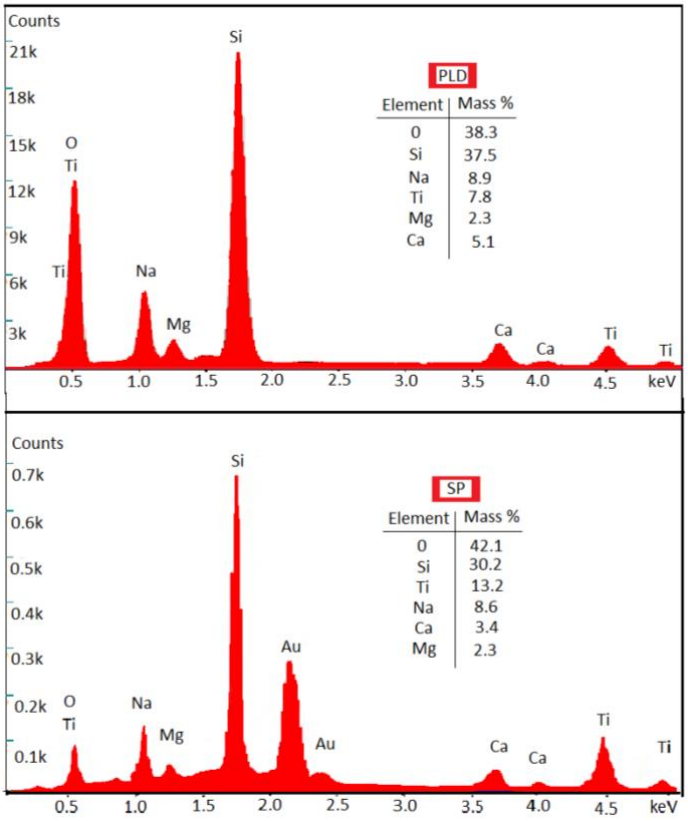

Figure 3. EDS spectrum for (a) PLD sample and (b) SP sample.

The degree of crystallinity in the studied samples was tested using Raman Spectroscopy. The anatase phase has a well-known Raman spectrum, and the vibrations are widely characterized in bibliography. [8, 11-13] The Raman spectrum showed in Figure 4 (a) corresponds to the layers grown by PLD. In this spectrum only the most intense peak corresponding to the anatase phase can be seen, and the other usual peaks are missing. Presumably, this is due to a low degree of crystallinity. By another way, the spectrum showed in Figure 4 (b), corresponds to the nanolayer grown by SP where all the peaks corresponding to the anatase phase were labeled. This means that this sample should have a high degree of crystallinity.

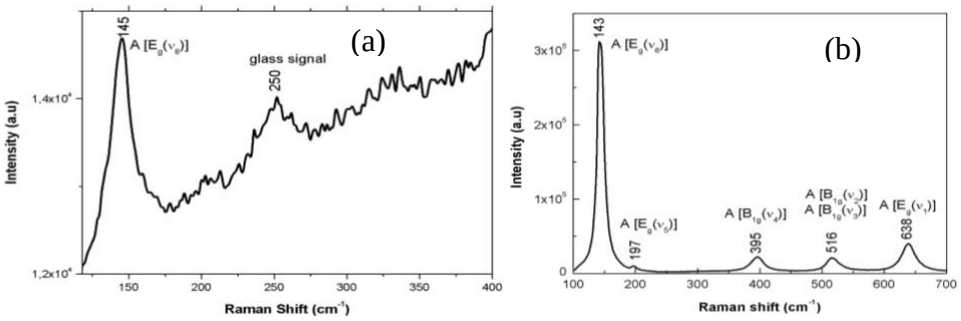

Figure 4: Raman spectrum of (a) PLD deposited coating and (b) SP deposited coating.

Typical XRD measurement was performed for both samples, and the results are presented in Figure 5. In Figure 5(b), for the SP sample, only the most intense peak corresponding to the anatase phase (at 25.4 ºC) was observed. The other peaks cannot be distinguished from the noise, in agreement with previously reported works.[10] In the case of PLD sample (Figure 5(a)) anatase peaks were not observed because this TiO_2 film has a low degree of crystallinity, as was determined by Raman measurement.

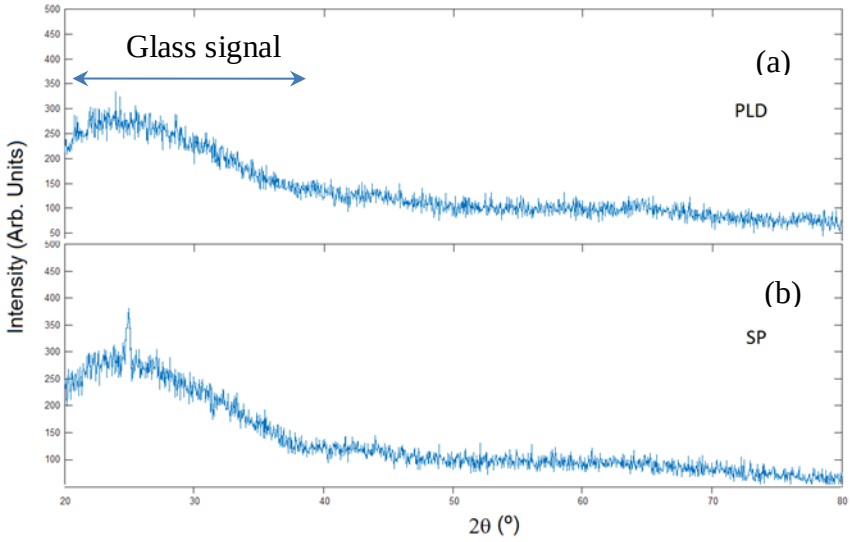

Figure 5 (a) XRD measurements for PLD sample and (b) SP sample.

4. Conclusions

TiO_2 films were deposited by PLD and by SP; both techniques were performed under atmospheric pressure. The structure, composition, and surface roughness were studied to compare morphological aspects and stoichiometry of the samples. The morphology of the layers was smooth in the case of the SP samples and definitively inhomogeneous in the case of PLD samples. Therefore, the homogeneous roughness of SP films makes them appropriate for high refractive index coatings over lens and mirrors, for example, for selective optical reflection or transmission. Considering the composition of samples manufactured by PLD and SP, both have an acceptable stoichiometry, within the uncertainty of quantification.

Also, to the best of our knowledge, layers of TiO_2 grown by PLD at atmospheric pressure are firstly reported and characterized.

In the future, thermal treatment will be applied to the samples obtained by PLD under atmospheric conditions to increase their crystallinity. In this sense, it is also required an exploration of the characteristics

of deposited films as a function of the relevant parameters that governs physiochemical process (i.e., the wavelength of the pump laser, time of deposition, the energy of pulse, among others).

Acknowledgments

This research paper was partially supported by Quilmes National University under Programs entitled: "Biotecnología de Lípidos y Proteínas", and "Estrategias de Ingeniería en Automatización, Computación y procesos industriales aplicadas a la resolución de problemas tecnológicos".
This work was also partially supported by the Agencia de Promoción Científica y Tecnológica under contract PICT-2010-2575 and PICT 2015-0452.
M.R.T. wants to thank Dr. R. Parra (INTEMA, Mar del Plata, Argentina) for providing spray-pyrolysis deposited film and its Raman spectrum.

