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Comparison on Morphological and Optical Properties of TiO_2 Thin Films Grown by Single-Pulse and Multi-Pulse Laser Ablation

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Abstract

TiO_2 thin films were prepared on glass substrates using the PLD (Pulsed Laser Deposition) technique. In order to carry out the ablation process, a Nd:YAG laser was used emitting in 1064 nm wavelength at 10 Hz repetition rate, set up for operating in both single-pulse and multi-pulse regimes. A comparison of the deposition rate, the optical and morphological properties of the layers obtained from both ablation regimes was made, which showed that the multi-pulsed ablation produced layers with a higher surface quality and better optical properties.

Keywords

Pulsed Laser Deposition, Single-Pulse Ablation, Multi-Pulse Ablation, TiO_2 Thin Film

1. Introduction

Titanium dioxide (TiO_2) has become an extremely valuable metallic oxide for many technical applications in different uses due to its unique electrical and optical properties and the fact that it is not toxic and has a low cost [1]. TiO_2 thin films have a wide spectrum of applications in photocatalysis, photovoltaic and optical systems, especially in multilayer structures that can be anti-reflecting or have a high reflectance level at a specific wavelength [2].

Previously, many techniques as sol-gel [2], spray pyrolysis [3], sputtering [4] and chemical vapor deposition [5], have been applied to prepare TiO_2 thin films. A technique that has been increasingly applied for obtaining thin layers is the so-called Pulse Layer Deposition (PLD) [6]-[8]. Due to its versatility, this technique has extended to include the deposition of a great number of materials, ranging from pure elements to multicomponent

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compounds [9] [10]. Compared to other physical deposition techniques, PLD has the advantage of easily and amply controlling the physical, chemical and structural properties of many materials [11], as well as in many cases the capacity to preserve the stoichiometry.

An important characteristic of PLD is the use of a pulsed laser as the source of excitation for ablating the target material, which under high vacuum conditions moves to the substrate, forming the layer with the desired thickness, ultimately proportional to the flow and amount of pulses.

Recently, Nd:YAG lasers with Q-Switch device based on saturable absorbers have been used for the purpose of exciting samples for elementary analysis by Laser Induced Breakdown Spectroscopy (LIBS). In this regime, the Q-Switch consists of a Chrome-doped YAG crystal (Cr^{4+}:YAG), which is clarified during the pumping process, emitting one or several pulses in the course of a one lamp's excitation pulse [12] [13]. **Figure 1** shows the temporary structure of the pulses for both types of excitation, which we will call single-pulse and multi-pulse, respectively. Jedlinszki and Galbács show in [14] that in principle it is possible to reach higher levels of plasma ionization when the laser emits multi-pulse regime. This can be a very interesting point in the PLD technique, as higher plasma ionization levels, with the presence of very energy-rich species, may contribute to the growth of the film by transferring energy to the process.

This paper describes the use of the PLD technique for producing TiO_2 thin films with the two ablation regimes: single-pulse and multi-pulse, and the optical and morphological properties, as well as the deposition rates are evaluated for the purpose of establishing the potential of the multi-pulse regime as an excitation source in PLD.

2. Experimental Procedure

A Nd:YAG laser with 1064 nm wavelength and 10 Hz repetition rate was used for the ablation process; it was set up with saturable Cr^{4+}:YAG absorbers for operating in single-pulse and multi-pulse operation regimes. In the multi-pulse regime, each laser shot is made up of three micro-pulses with an interpulse separation of 45 μs, where each micro-pulse has an average duration of 60 ns, as shown in **Figure 1**. The separation is 100 ms between each shot.

For the purpose of obtaining the single-pulse emission, a second Cr^{4+}:YAG Q-Switch was added to the optical cavity, which had the same dimensions and transmittance. This second Q-Switch increases the loss in the optical cavity, thus rendering the resupply process less efficient [15], reducing the emission (previously multi-pulse) to just one laser pulse. **Figure 2** shows the temporary structure of micro-pulse for single-pulse regimes, we observe that the pulse width was 40 ns. When compared to the multi-pulse regime, the reduction of the pulse width arises because when the second Q-Switch is incorporated, the total dimension of the saturable absorber increases, allowing a higher level of population inversion to be reached.

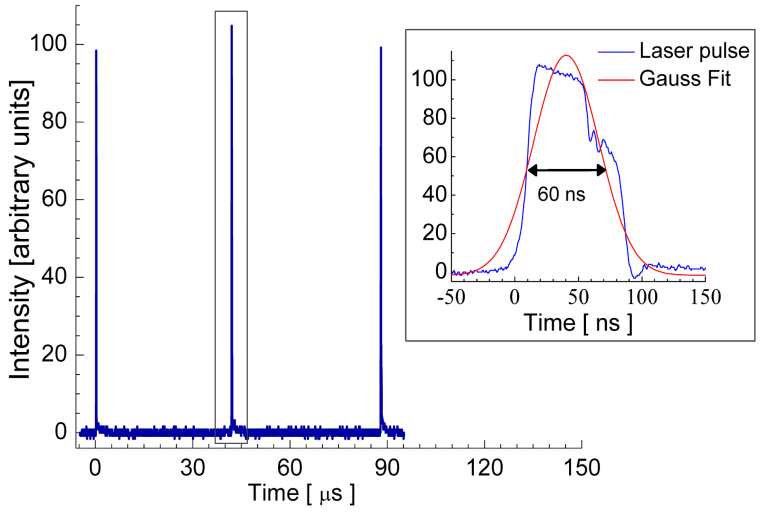


Figure 1. Temporary pulse profile and duration in the multi-pulsed ablation regime.

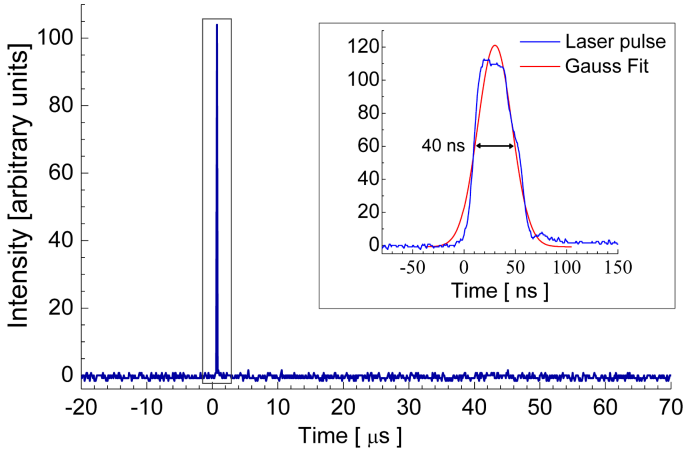


Figure 2. Temporary pulse profile and duration in the single-pulsed ablation regime.

The total energy of the pulse was set at 100 mJ for both regimes, obtaining 3.3×10^7 W·cm^{-2} and 5×10^7 W·cm^{-2} of irradiance, for multi-pulses and single-pulses respectively. The depositions were made on glass substrates in a high vacuum atmosphere, 2 - 5 × 10^{-5} Torr, at a constant flow and temperature, 2 J·cm^{-2} and 130˚C. The target-substrate distance was set at 5 cm.

Depositions were made at different pulse quantities ranging from 3000 to 1200 pulses for the purpose of obtaining different layer thicknesses. The first characterization stage consisted of evaluating the morphology of the film by Atomic Force Microscopy (AFM), and also the roughness and the thickness. In a second stage an evaluation was made of the optical characteristics, comparing the absorbance of the films which had a similar thickness in the two regimes.

3. Results and Discussion

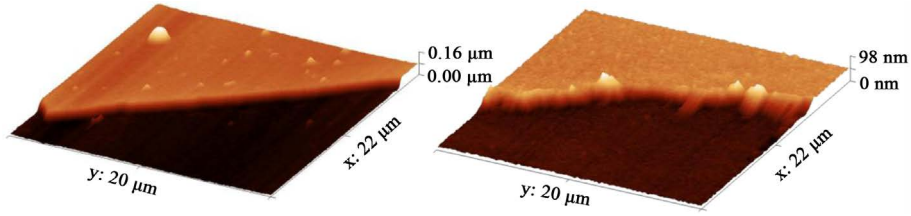
The first criterion of the comparison was based on the morphological characteristics: roughness and thickness. In order to measure the thickness, small areas were removed after the deposition process was completed; this was done using laser pulses with the necessary irradiance for producing the complete ablation of the film on the area of the spot, without damage the substrate. This created a crater whose wall represents a reference step for thickness measuring, **Figure 3**, which was done with an atomic force microscope (TT-AFM Workshop) in contact mode.

Figure 4 shows the thickness as a function of the number of shots employed to make the thin films. Once the thickness measurements were available the deposition rates were calculated at 0.1 ± 0.01 Å/pulse and 0.04 ± 0.006 Å/pulse, for the single-pulse and multi-pulse regimes respectively.

The difference in the deposition rates may be because, taking into account the energy and vacuum conditions used, the separation between the micro-pulses in a multi-pulse shot is similar to the average life-time of the plasma [16]. The ablation process starts with the incidence of the first pulse on the target. When the second pulse is emitted, 45 μs later, the plasma is still in the extinction process, thus generating a pulse-plasma interaction. During this interaction, fraction of the energy of the pulse can be absorbed by the species still present in the plasma. Consequently, the energy impacting on the target is less and, therefore, the amount of extracted material is also less. This pulse-plasma interaction is unlikely in single-pulse regimen, because the separation between one pulse and next is 100 ms (10 Hz), a time largest than plasma life time (the range of μs).

Figure 5 reveals that for growths done with a lower number of shots (up to 6000 shots), the roughness level is similar in both regimes. On the other hand, for thicker layers (9000 and 12,000 shots), the roughness increased with the single-pulsed ablation.

Based on the pulse-plasma interaction described above, the species that absorbed part of the energy of the 2nd and 3rd pulse of the multi-pulse shot will increase their kinetic energy. This energy increase represents a longer diffusion time for the species because they are absorbed by the substrate surface. As the diffusion time increases, the probability that the atoms/molecules reach points of maximum absorption energy also increases, thus favoring an orderly growth of the nanolayers [6] [17] [18]. This process is evident in **Figure 5**, which shows that the



(a) (b)

Figure 3. AFM images of TiO_2 thin films surface and reference step, made with: (a) 6000 shots in single-pulsed regime; (b) 12,000 shots in multi-pulsed regime.

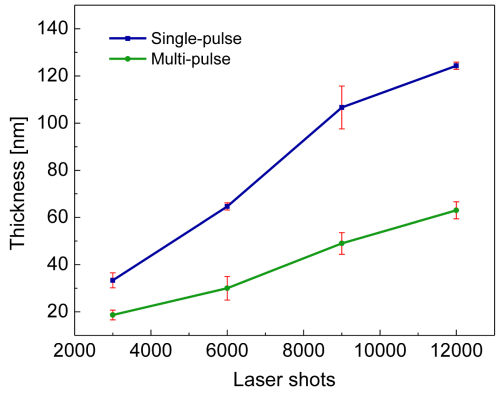


Figure 4. Thickness as a function of the number of shots of TiO_2 thin films made by single-pulse and multi-pulse ablation regimes.

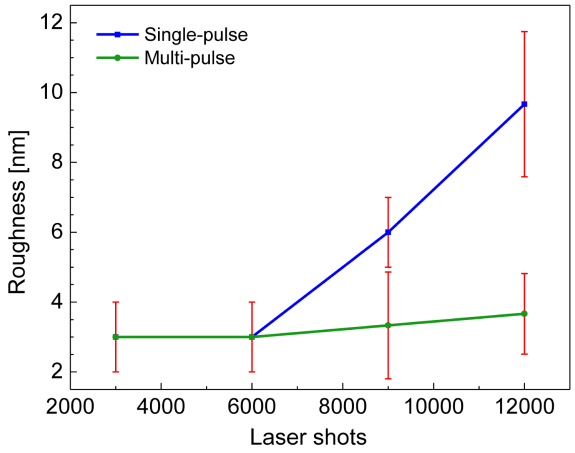


Figure 5. Roughness as a function of the number of shots of TiO_2 thin films made by single-pulse and multi-pulse ablation regimes.

roughness of the films grown with micro-pulses reveals very small variations when the deposition time increases, 0.5 Å/min, as compared to layers grown with multi-pulses, whose roughness grows 2.3 Å/min.

The increase in the roughness with the single-pulse regime can be the result of two factors: first of all, as the deposition rate increases, the surface diffusion of the atoms decreases, and this could generate flaws on the surface of the nanolayers. The second factor is the presence of particulates or splashing, which as **Figure 3** shows, is bigger in the films grown with multi-pulses. The presence of these micrometric particles in the initial stages of growth of the nanolayers may bring about an accumulative effect of defects on the final surface of the film, thus causing an accelerated increase in the roughness. In addition, it was suggested that the film roughness is influenced by strain induced in the film by a lattice mismatch with the substrate [19], this affect the roughness both ablation regimens.

Figure 6 shows images obtained by scanning electron microscopy (SEM) of the films grown with 6000 and 12,000 shots, with a single-pulse and multi-pulse regime, respectively. The films are similar in thickness, 65 nm and 63 nm, and have the same roughness, 3 nm. The thin films shown splashing, which are seen as small "drops", for both regimens. It should be noted the peculiar "elongated drop" shape of the bigger particles in the thin film grown with single-pulses, whose origins are still being determined. The thin films made by multi- pulse ablation have a higher density of particles that the single-pulse ablation regime, but these are smaller, the particles size are between 30 - 280 nm, with 50 nm of average size. While in single-pulse thin film the particle size is between 30 - 600 nm, with average size of 100 nm. A quantitative size distribution is unviable, due to irregular form of the particles in thin films made with single-pulse ablation.

The second stage of the comparison consisted in evaluating the optical transmittance of the films. These were done using the transmittance technique in the UV-VIS-NIR range. The measurements were performed with a lambda 40 Perkin Elmer spectrometer. **Figure 7** shows the transmittance spectra of the thin films grown by both regimens. The films corresponding to 6000 and 3000 multi-pulses, with thicknesses of 65 nm and 34 nm respectively, have a significant absorption rate in the infrared region, especially between 800 - 1200 nm. This can be due to the vacancies of oxygen in the films as a result of the vacuum conditions used in the deposition [20]. These vacancies of oxygen can favor the inclusion of very small proportions of metallic titanium in the films, which would give rise to the absorption in the infrared-visible region. On the other hand, the films made with 6000 and 9000 multi-pulses, with 30 and 63 nm of thickness respectively, show an absorption close to zero in the infrared region of the spectrum. This could indicate that films grown with multi-pulses allow an improved conservation of the stoichiometry, as reported in [21].

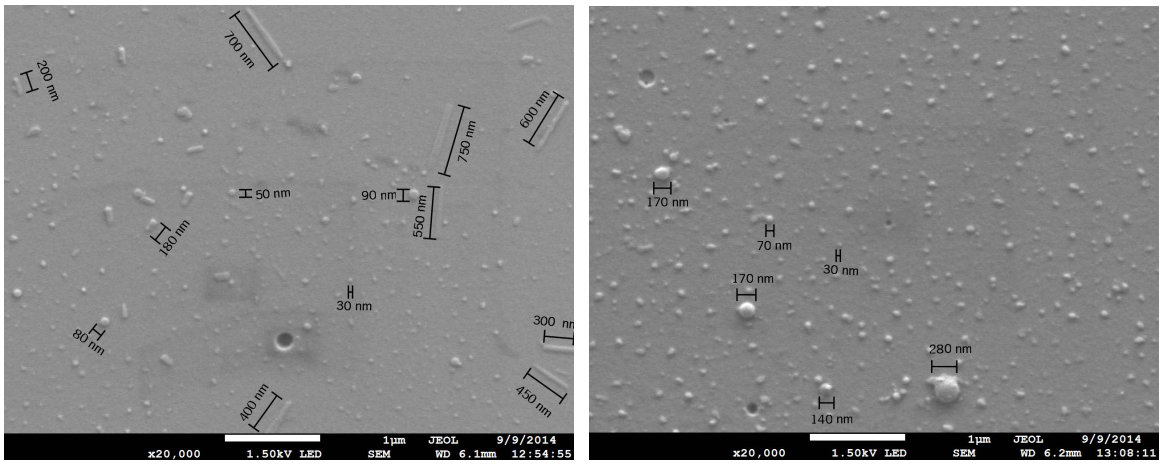


Figure 6. SEM micrography of TiO_2 thin film made with: (left) 3000 single-pulses and (right) 6000 multi-pulses.

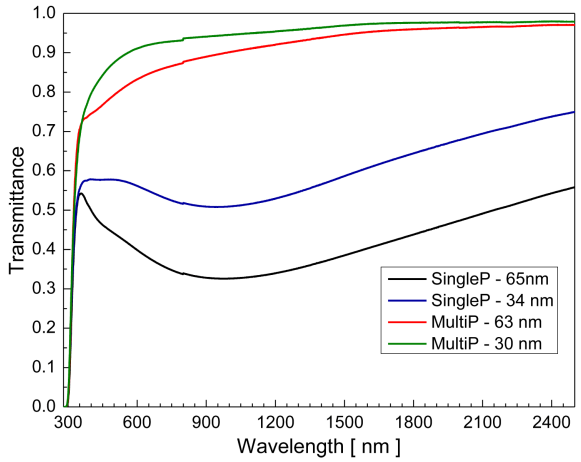


Figure 7. Transmitance spectra of TiO_2 thin films made with mono-pulse and multi-pulse laser ablation.

4. Conclusion

Single-pulsed ablation provided a 2:1 higher deposition rate than multi-pulsed ablation; consequently it can be stated that ablation in single-pulse regime is more efficient in terms of the extraction of material per pulse. However, for similar layer thicknesses, multi-pulsed ablation provided films that were not as rough and with particle size less. The films obtained with multi-pulses also have a transmittance greater level, which is desirable for most of the optical applications of TiO_2 thin films.

Acknowledgements

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