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PREPARATION AND CHARACTERIZATION OF TIO2 THIN FILMS BY PLD AND HIPIMS

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TiO_2 thin films were deposited on Si (100) and SiO_2 substrates using two different techniques: high-power impulse magnetron sputtering (HiPIMS) and pulsed laser deposition (PLD). The structure and morphological differences of the obtained thin films were analyzed and compared, along with the optical properties. The comparison shows strengths and weaknesses of each deposition technique, pointing to different applications.

Keywords: pulsed laser deposition, high-power impulse magnetron sputtering, TiO_2, thin films, XRD.

1. Introduction

Titanium dioxides (TiO_2) is an intensive studied compound, mainly due to his large energy gap, refractive index, mass density and dielectric constant. TiO_2 thin films are usually used for photovoltaic devices [1], capacitors [2-3], optical elements [4-6] and antibacterial devices [7-8]. Even in bulk form titanium dioxide is widely used in food industry as food coloring or in cosmetics for sunscreen creams. The optical properties makes TiO_2 thin films useful in waveguides, filters or gas sensing applications [9-12]. TiO2 exists in three crystal phases: rutile, anatase and brookite. The most common one is rutile (tetragonal crystalline). The next most common phase is anatase (tetragonal crystalline), which is not as thermodynamically stable as rutile and brookite (orthorhombic crystalline). By heat treatment of rutile we can obtain anatase or brookite and the transition is irreversible.

TiO_2 thin films were deposited by various techniques such as pulsed laser deposition [13], chemical vapor deposition [14], sol–gel [15] or magnetron

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sputtering [16]. Magnetron sputtering (MS) process and in particular HiPIMS is a competitive method for the development of medical prostheses or gas sensors, but not so competitive when it comes to optical coatings or photovoltaic devices. MS allows a good control of the interface layer between the substrate and the thin film, which is a very important aspect that can be used to substantially improve the film adhesion to substrate. PLD, on the other hand, has numerous advantages over the other deposition methods, because it allows for the control of crystalline status and stoichiometry of the synthesized material. Also, the incorporation of contaminants is drastically reduced.

In this paper, we report the successful growth of pure anatase phase TiO_2 thin films by PLD and also high quality crystalline films by HiPIMS.

2. Experimental method and results

The thin film deposition was performed inside a cylindrical stainless-steel irradiation chamber. For the PLD experiment we have used a UV KrF* (λ = 248 nm, τ_{FWHM} aprox.25 ns) excimer laser source, operated at 3.1 J/cm^2 incident fluence value, target diameter 1”. The targets were prepared from titanium dioxide powder by pressing at 3 MPa and sintered at 1100^{o}C for 4 h. Before each deposition procedure, the vacuum chamber was evacuated down to a residual pressure lower than 10^{-4} Pa. The distance between the target and the substrate was set at 5 cm. The target was rotated during the laser irradiation with a frequency of 3 Hz. During the deposition, high purity oxygen (99.999%) was inserted into the interaction chamber and the dynamic pressure was keep constant with an MKS 100 controller. The substrates were carefully cleaned in ultrasonic bath in acetone. Additional target cleaning was performed by applying 3000 laser pulses to the rotating target. During this step, a manual shutter was placed between the target and the substrate. The interaction chamber was heated up to 70^o for 15 minutes with the help of matrix of heating cables that had surrounded the chamber. The used substrates were Si (100) and SiO_2. The dynamic oxygen pressure was set to 1 and 10 Pa, the laser pulses were varied from 10000 to 20000 and the substrate was heated up to 500^{o}C. (Table 1).

Table 1

Deposition conditions for the PLD experiment

Name	Temp.(^{0}C)	O_2 pressure [Pa]	Number of pulses
$TiO_2$1P	500	10	20000
$TiO_2$2P	500	1	20000
$TiO_2$3P	500	1	10000
$TiO_2$4P	500	10	10000

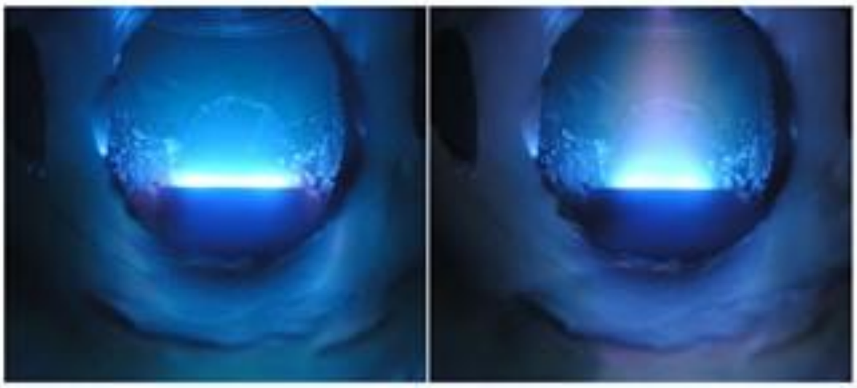
Using the HiPIMS technique, we have deposited titanium dioxide thin films using a circular magnetron, target diameter 2”, magnetic field induction at the target surface of 1000 Gauss, a high voltage pulse generator for HiPIMS technology with a power density between 0.5 and 10 kW cm^{-2}. The power generator has the capability to adjust the pulse duration between 2 and 50µs and also to adjust the pulse period between 0.2 and 6 ms, with a response time of less than 500 nanoseconds. The target was made from high purity titanium dioxide powder. 2” pellets were pressed at 3 MPa and put into a furnace for 4h at 1100°C. The experiment was performed in a uniform dynamic flow of 2 Pa monitored by an MKS 50 controller. We have used two gases, Ar and O_2 at different ratios 50:1 and 4:1. The deposition was performed at 1 and 2 kHz frequencies at a fixed pulse duration of 5 µs. The average power was set to 50 and 100 W and the deposition time was 180 minutes. During the deposition, the substrates were heated up to 500°C and placed at a distance of 50 mm from the target. The external magnetic fields, was created by the exterior coils. We had one coil surrounding the target, which was set to 300 Gauss and another one surrounding the substrate that was set to 100 Gauss. (Table 2)

Table 2

Deposition conditions for the HiPIMS experiment

Name	Ar/O_2	Frequency [kHz]	Average power [W]
$TiO_2$1H	50/1	1	50
$TiO_2$2H	50/1	2	100
$TiO_2$3H	4/1	2	100
$TiO_2$4H	4/1	1	50

The magnetic field induce by the two coils are confining the plasma (Fig.1) and doing so the deposition rate is improved and the losses to the chamber walls are reduced [17-18].



Bs=0, Bj=0 **Bs 300 Gauss, Bj= 100 Gauss**

Fig. 1 Plasma confinement due to the magnetic field

According to the diffraction patterns from Fig. 2 we managed to obtain pure anatase phase. Anatase is present in all of the samples, but Rutile is present only where the dynamic pressure is set to 1 Pa. The reason is that if we are to increase the dynamic pressure, then the energy of the atomic species that are deposited on the substrate will decrease. For the TiO_2 HiPIMS thin films, only sample $TiO_2$2H has Anatase and Rutile present and the rest of the samples are amorphous (Fig. 3).

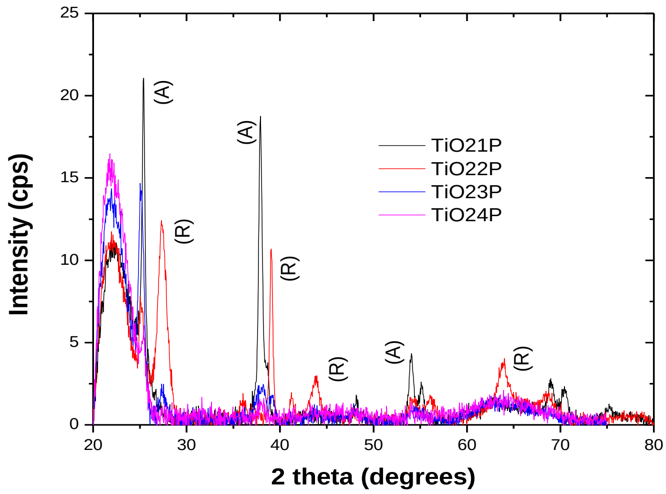


Fig. 2. XRD diffraction pattern for PLD films

Using the Scherrer equation FWHM = 0,94 λ / (R cosθ) [18] we will see that in both cases, for pulsed laser deposition and for magnetron deposition, the grain sizes are between 16 and 30 nm. The XRD patterns were obtain using a Shimadzu D6000 system.

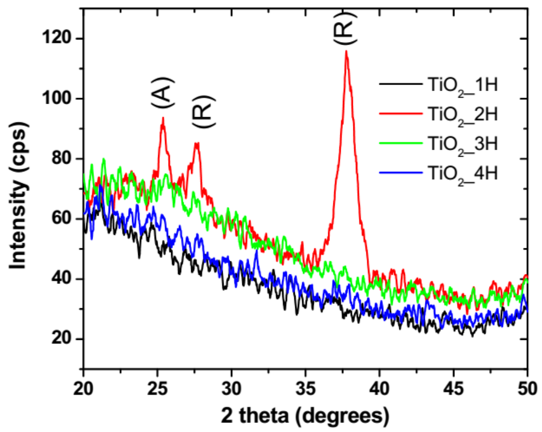


Fig. 3. XRD diffraction pattern for HiPIMS films

The SEM investigations was performed with a FEI model Inspect S. For Fig. 4 we can see that some samples have granular structure, which refers to the crystalline thin films, while the other samples have a smooth surface. At the same time, we can observed spherical particles or large irregular shaped particles that might be the result of (i) the instability of the hydrodynamic development over the entire melted surface (ii) the pressure generated by the plasma recoil (iii) the overheating of the target area or (iv) following the blast-wave-type explosions that occur at liquid-solid.

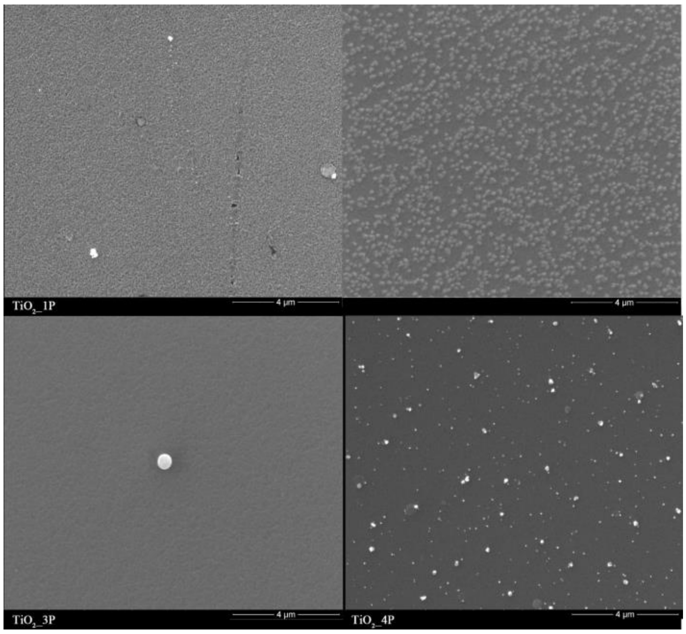


Fig. 4. SEM images for the PLD films

The SEM analysis of the HiPIMS samples shows similar morphological characteristics. Sample TiO_2_2H has a granular structure, similar with TiO_2_1P and the rest of the HiPIMS thin films have smooth surfaces with droplets on them (Fig. 5). The films were mainly composed of small spherical particles.

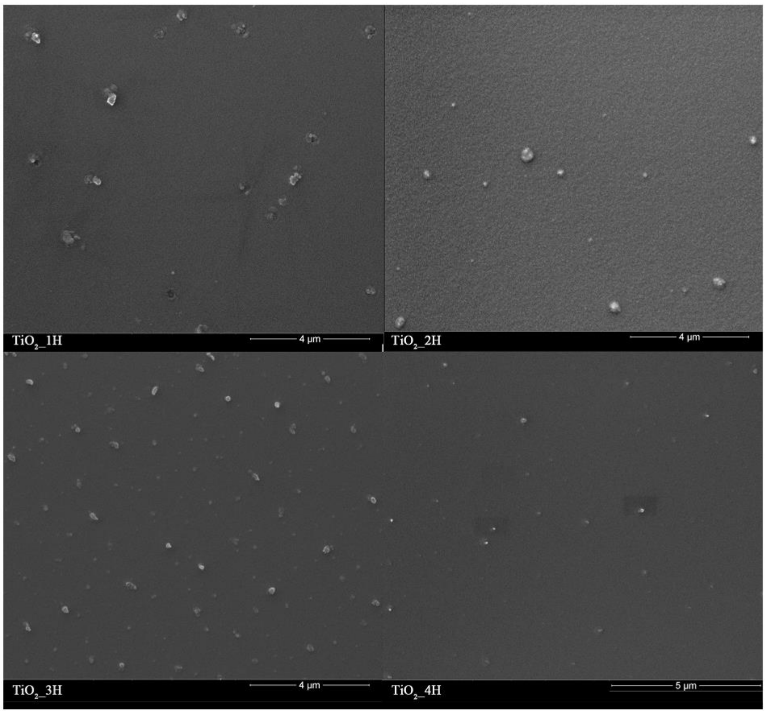


Fig. 5. SEM images for the HiPIMS films

The optical characteristics were evaluated with an Evolution 300 UV-Vis spectrophotometer equipped with a holographical diffraction grating with 1200 lines/mm. For the samples deposited by PLD we have a good transparency. For TiO_2_1P for example, we have areas with transparency over 85% in the VIS-NIR range. (Fig. 6).

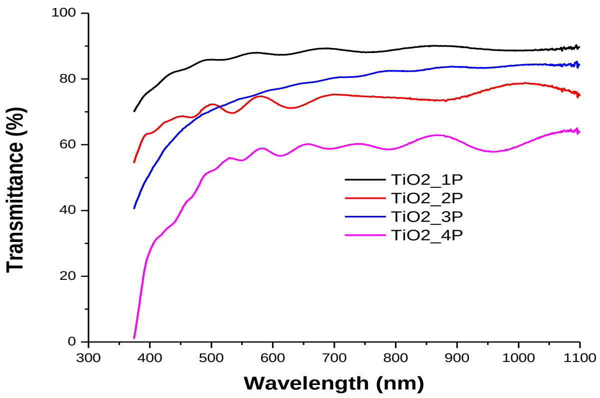


Fig. 6. Transmittance spectra of TiO_2 films grown by PLD

Figure 7 clearly shows that the thin films deposited by HiPIMIS have a lower transparency. TiO_2_1H and TiO_2_3H shows a drastic drop starting with 550 nm, while TiO_2_1H has an increase in transparency starting with 600 nm.

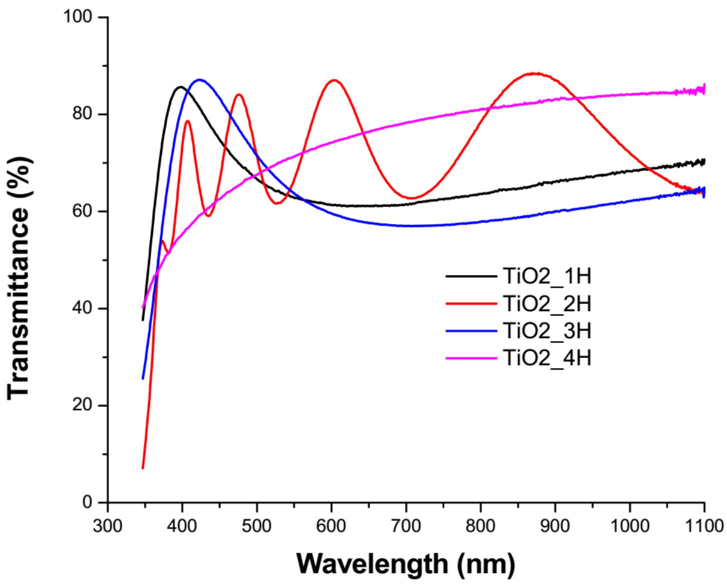


Fig. 7. Transmittance spectra of TiO_2 films grown by HiPIMS

Sample TiO_2_2H has a sinusoidal form and this is due to the crystalline structure, since this is the only thin film deposited by HiPIMS that is showing Anatase and Rutile forms.

3. Conclusions

The films that have only the Anatase phase has a higher transmittance that the ones with Anatase and Rutile phase and this is because Anatase has a higher catalytic activity than Rutile. If we are to compare the thin films obtain by pulsed laser deposition with the ones obtain by magnetron sputtering we will clearly see that for gas sensing applications PLD will be the right choice.

The PLD thin films are therefore good candidates for active layers in a new type of integrated optical gas sensor.

We obtained titanium dioxide anatase single phase thin films by PLD by ablation of TiO_2 targets in an oxygen atmosphere.

The SEM images shows that in both cases we have high quality films, with smooth surfaces and is some cases a granular structures, so we can say that the TiO_2 thin films exhibited uniform and smooth surfaces in this work.

The surface roughness and grain for the TiO_2 thin films deposited by HiPIMS changes with increasing O2 amount in O2/Ar reactive gas mixture, but the differences are not extremely obvious. XRD studies show that the films are amorphous except the case when we have high power and high Ar concertation.

The carried work tells us that both thin films deposition techniques, PLD and the newly developed HiPIMS system are versatile thin film sintering methods that brings an outstanding added value to the research and development of current technologies in terms of physical area or material engineering.

Both techniques shows a remarkable flexibility, with the ability for fine tuning of a large number of key parameters, providing precise control of the properties and functionalities of the deposited thin films.

Although HiPIMS is a very promising techniques there are areas where PLD and HiPIMS do not overlap. Future developments will surely bring this two techniques closer, but for the moment, there are advantages in using one technique instead of the other.

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