

Investigation of the Dependence of Thickness and Roughness of TiO₂ Thin Films Fabricated Using Pulsed Laser Deposition on the Laser Energy

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Abstract: In this work Titanium Dioxide thin films were successfully deposited on glass substrates at room temperature by pulsed laser deposition technique (PLD) using a Q-switch Nd: YAG laser to fabricate thin films. The target was an Anatase TiO₂ powder that converted to solid disks by compressing it. The disks were irradiated with different laser pulse energies (100, 150 and 200 mJ) with the same number of laser pulses (10 pulses) and the same laser repetition rate to fabricate three groups of thin film (I, II and III). An atomic force microscopy (AFM) was used for the characterization of the thickness and topography of these thin films. The results showed that the thickness of the films was in the range of hundreds nanometers and it is increased exponentially with the laser energy. The dependence of the root means square roughness (RMS) on laser pulse energy also was investigated and the results showed that the (RMS) increase exponentially as laser pulse energy to specific value, and then decrease exponentially that the whole curve looks like Gaussian shape.

Keywords: TiO₂ Thin Films, Pulsed Laser Deposition, Nano-Films, Roughness, AFM

1. Introduction

Titanium dioxide (TiO₂) is a fascinating material that has been intensively researched by worldwide researchers. (TiO₂) nanomaterials are known for their numerous and diverse applications, which range from common products, such as sunscreens, to advanced devices, such as photovoltaic cells, and include, among others, a series of environmental and biomedical applications, such as photocatalytic degradation of pollutants, water purification, bio sensing, self-sterilizing surfaces, antifogging surfaces, also used for surface anticorrosion optical or gas sensor and drug delivery. The importance and variety of these applications have spurred enormous interest and substantial advances in the fabrication, characterization, and fundamental understanding of TiO₂ nanomaterials in the past decades [1-8]. It is soluble in

sulfuric acid and alkalis and insoluble in water [9], thermally stable, non-flammable and cheap non-toxic material that has very good semiconducting properties [10]. TiO₂ is electrically insulating with an extremely high resistivity, but the suboxidized TiO₂ with an excess of titanium is an n type semiconductor with unique properties, indicating the defect disorder and O/Ti stoichiometry play an important role in the electrical properties [11]. Naturally it exists in three polymorphs namely Anatase, Rutile and Brookite which influence the sensing properties. The Anatase phase is preferred over rutile in gas sensing due to its higher photocatalytic activity. Anatase and Brookite are thermodynamically metastable forms of TiO₂ which irreversibly convert to rutile at high temperatures. This anatase-to-rutile transition

has a severe effect on the sensor's sensitivity [12]. Anatase and Rutile are tetragonal and Brookite is orthorhombic. In all polymorphs, titanium is coordinated octahedrally by oxygen, but the position of the octahedra differs between polymorphs [13].

Among the several methods for synthesizing and depositing titanium dioxide thin films and coatings which are available: chemical/ physical vapor deposition techniques (CVD/PVD), sol-gel methods, photo-deposition, pulsed laser deposition (PLD) and e-beam evaporation [14-16], PLD used in this work represents one of the physical vapor deposition techniques which provides a well adherent thin films with good mechanical rigidity and offers advantages such as stoichiometrically transferring material from target to the substrate [17]. It is a reliable method to fabricate oxide thin films in which Deposition parameters play an important role in achieving good-quality thin films [18]. The PLD deposition parameters include deposition temperature, laser pulse repetition rate, laser energy, and ambient gas pressure [19]. This technique was used in this work to fabricate TiO₂ thin films and the dependence of the thickness and roughness of the films on the laser energy was deduced.

2. The Experimental Procedure

Pulsed Laser Deposition process was carried out using frequency doubled Nd: YAG laser ($\lambda=532$) at room temperature and atmosphere pressure as shown in Figure (1). To fabricate TiO₂ thin films. (Anatase) Titanium dioxide powder with grain size (10 nm) and purity (99.5%) supplied from (Nanjing Mission Advanced Material Co., Ltd, republic of china) was compressed with mini press machine to form solid disks as targets. The distance between the target and the substrate was adjusted to (10 mm). The substrates used for the synthesizing of the films were high quality glass slides manufactured by (Ningbo Co., Ltd Hi-Tech zone people's republic of china). They were prepared with dimensions of (10x10 mm²), properly cleaned, rinsed multiple times with de-ionized water, dried and placed just up to the target by attaching it to low speed rotating motor. The laser beam was struck the target with (45°). Three groups of TiO₂ thin films were fabricated (I, II and III) based on varying laser pulse energy: I (100 mJ), II (150 mJ) and III (200 mJ). Laser pulse width and pulse repetition rate was kept the same (10 ns) and (10 Hz), respectively, for all the three groups.

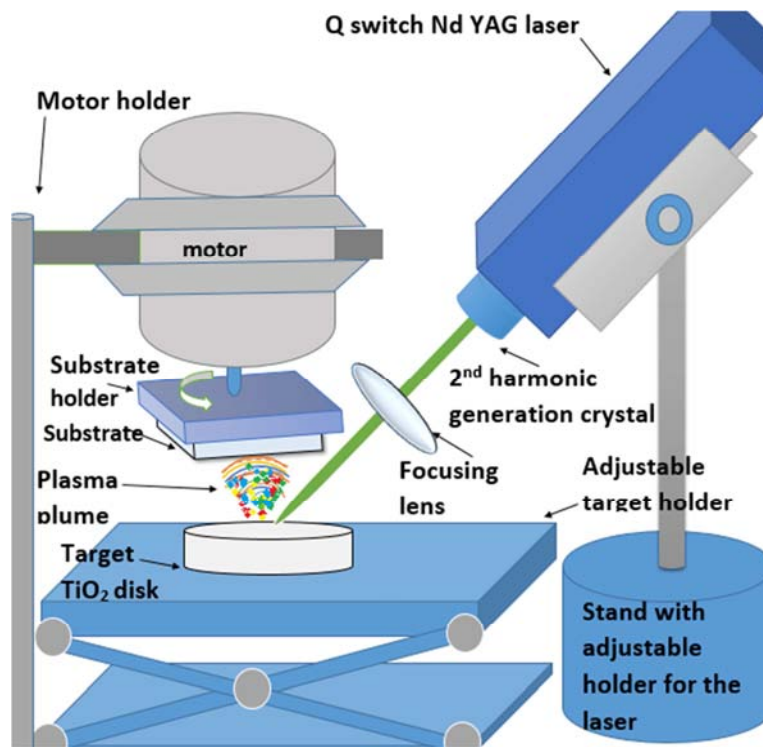


Figure 1. The pulsed laser deposition setup used in this work.

The thickness and the surface topography roughness of the fabricated films were observed using atomic force microscopy (AFM) (SPA-400 microscope, Seiko Instruments Inc., Japan). The images were taken under contact mode with a scan Rate of (2.0 Hz). The film thickness and surface roughness were deduced using software (Nano Navi Station version 5.60 A copy right 2005-2010, SII Nano Technology Inc).

3. Results and Discussion

Figure (2- I, II and III) shows three (AFM) images of the fabricated TiO₂ thin films grown on glass substrates with the same number of laser pulses (10 pulses) and the same repetition rate (10 Hz) at various laser pulse energies: I (100 mJ), II (150 mJ) and III (200 mJ).

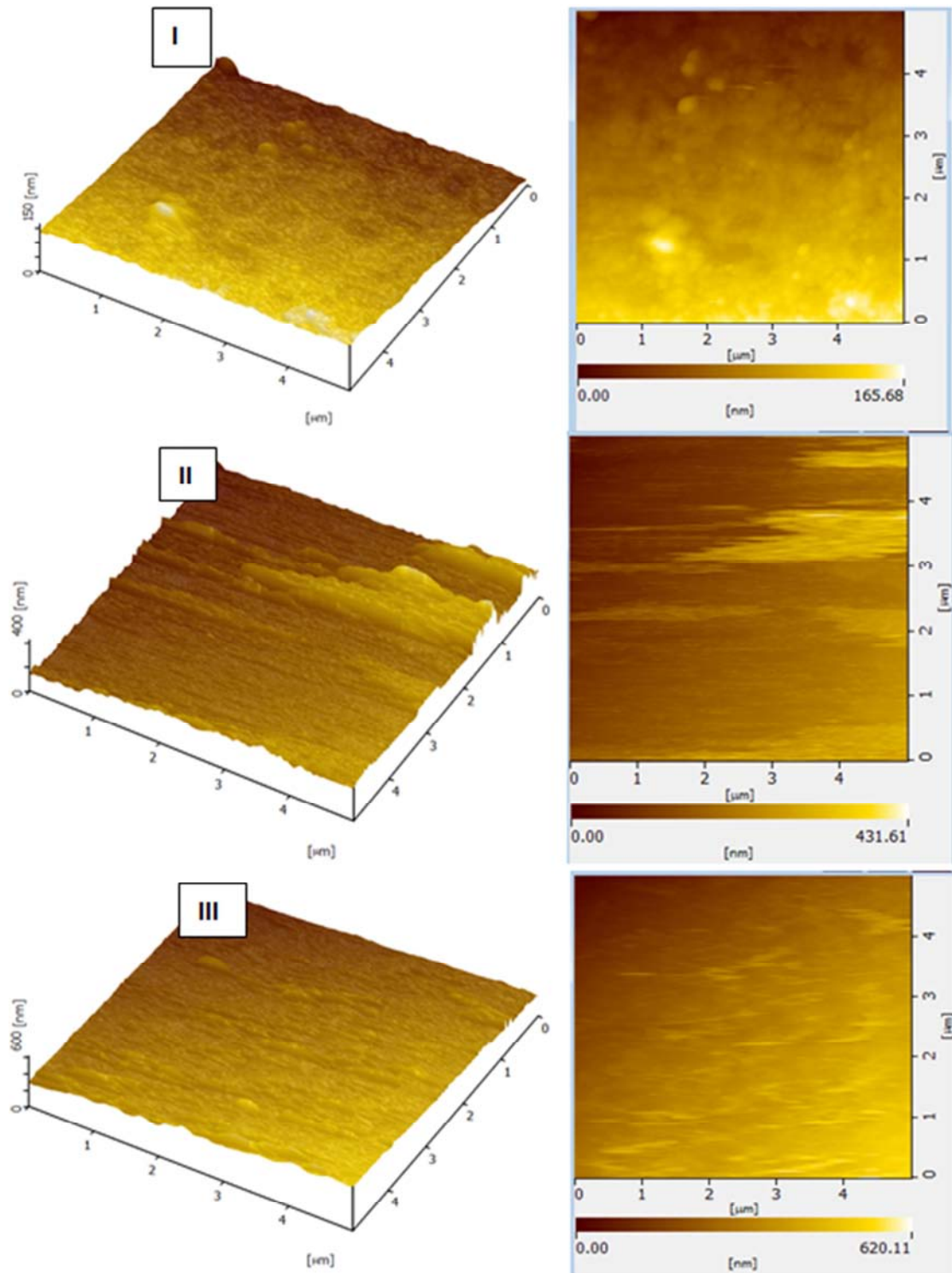


Figure 2. Three dimensional and Top view AFM images of the fabricated TiO_2 thin films -synthesized onto glass substrates using pulsed laser deposition technique PLD grown on at various laser pulse energies [I]. (100 mJ) [II]. (150 mJ) [III]. (200 mJ).

Figure 3 illustrates that the film thickness is in the range of hundreds nanometers and it is increased exponentially with the laser pulse energy. It is clear that the ablation deposition rate logarithmically dependent upon the laser pulse energy threshold $> (25 \text{ mJ})$, below which ablation does not occur, above it the rate of the growth of the film thickness at the

beginning increased slowly after that the rate of growth become relatively fast at energy greater than (100 mJ) then the growth rate again slow down till it become nearly zero at energy $> (200 \text{ mJ})$ and the thickness become almost stable without a considerable increase.

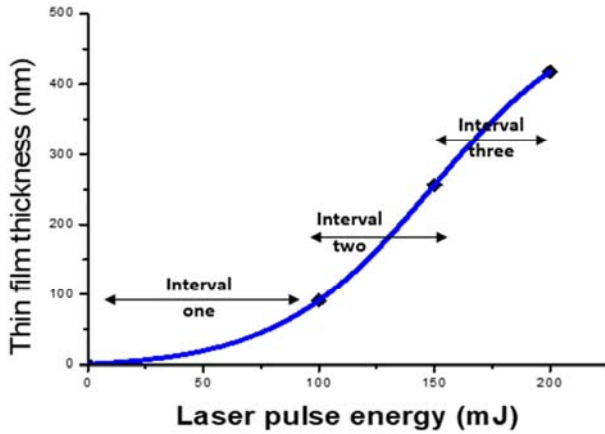


Figure 3. Thickness of the fabricated TiO₂ thin films as a function of the laser pulse energy.

The three different growing intervals as depicted in figure (3) refers to that at first one, in the beginning, the adsorbate possess enough kinetic energy and thermally accelerated travel well and diffuse deep into the bulk inside of the substrate and growth upward. This diffused inside part of the film and will not appear at the measurement of the film thickness. In the second interval the film already grew from inside the substrate and exceed the substrate surface and now will appear in the thickness measurement. Hence the growth rate looks faster cause all the deposited species will be measured. Increasing energy of the laser which is converted into thermal, chemical, and mechanical energy [20] leads to increase the thermal and kinetic energy of the plume species Eq (1) and the incoming particles will have more energy to dislodge tens to hundreds of atoms with each pulse, thus instead of increasing the growth rate of the film, it starts to drop due to the sputtering of the film itself by the bombardment with the target energetic particles [21].

$$N_{\text{pulse}} f_s = E_{\text{thermal}} + E_{\text{chemical}} + N_{\text{particle}} \left(\frac{1}{2} m v^2 \right) \quad (1)$$

Where: N_{pulse} is the total number of pulse, S : the cross-section area of the laser, m : the mass of a single particle, E_{thermal} : proportional to f : the fluence, while E_{chemical} : proportional to N_{particle} : the total number of particles ablated and deboned from the target, which relates with the number of particles deposited onto the substrate N'_{particle} .

Another reason contributes in reduction rate of the growth as clear from equation-(1) is the thermal energy buildup as the pulse energy increment leads to expansion of the vapor randomly in all directions [22, 23] which prevents some of the laser beam reaching the target either by absorption of it in the plume or reflection of the laser due to plasma oscillation with specific frequency, thus the volume of ablated target will be reduced also and hence the deposition rate will decrease.

Figure (4) Depicts the dependence of the root means square of surface roughness (RMS) of the fabricated TiO₂ thin films on the laser pulse energy. As indicated in the curve, the (RMS) increase with energy and have maximum value at pulse energy of (150 mJ) after that decrease, this behavior is

due to that at low pulse energies the resultant heat and kinetic energy of the plume species is relatively low which result to formation of coarse film due to the less mobility and lateral diffusion of particles on the substrate to coalesce and make continuous smooth film, on the other hand the film become smoother due reduction of the particulates reaching the substrate resulted from increase in the laser pulse energy which leads to vaporization of particulates contributing in roughness also increasing the laser pulse energy increase the mobility of the particles and enhance the film quality with relatively low roughness. Also the ionic content in the plume rises due to the increment of incident laser energy and this higher ionic content helps the crystalline growths [24].

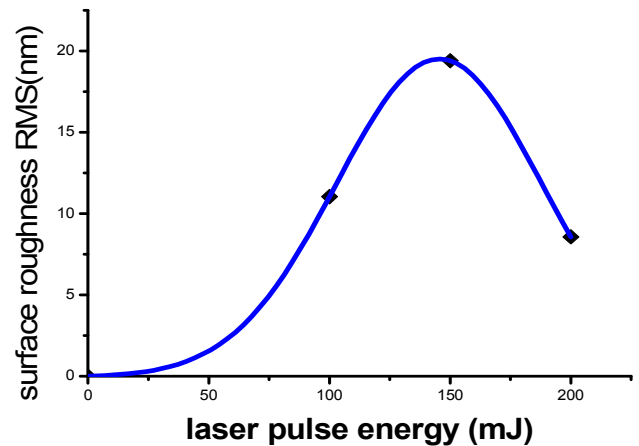


Figure 4. The dependence of root means square Surface roughness (RMS) of the fabricated TiO₂ thin films on the laser pulse energy.

4. Conclusions

In this work TiO₂ thin films are fabricated on glass substrates by pulsed laser deposition technique (PLD) and the effect of laser pulse energy on the thickness and surface root means square roughness of deposited films has been investigated using atomic force microscopy. The obtained results showed that the laser pulse energy has a significant influence on the thickness and roughness of the TiO₂ thin films, that there is a threshold pulse energy after which deposition starts and the film thickness increase exponentially. The roughness behaves in a different manner that it starts to increase till reaches the maxima when the laser pulse energy around (150) mJ and falls down again, due to this manner we recommend using specific energy to obtain specific thickness and smooth films. Also we conclude that: it is possible fabricating Nano-structure TiO₂ thin films those are suitable for optical components, gas sensors, photocatalytic degradation of pollutants, sun screens and photo voltaic cells. We recommend in the present researches the same study done under vacuum or inert gases, deduce effect of other laser parameter such as pulse duration and repetition rate, substrate conditions on the properties of the films.

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