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Crystallisation of TiO_2 thin films induced by excimer laser irradiation

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Abstract

Titanium dioxide thin films have been deposited by reactive magnetron sputtering on glass substrate and subsequently irradiated by UV radiation using a KrF excimer laser. In this work, we have study the influence of the laser fluence (F) ranging between 0.05 and 0.40 mJ/cm^2 on the constitution and microstructure of the deposited films. Irradiated thin films are characterized by profilometry, scanning electron microscopy and X-ray diffraction. As deposited films are amorphous, while irradiated films present an anatase structure. The crystallinity of the films strongly varies as a function of F with maximum for $F = 0.125$ J/cm^2. In addition to the modification of their constitution, the irradiated areas present a strongly modified microstructure with appearance of nanoscale features. The physico-chemical mechanisms of these structural modifications are discussed based on the theory of nucleation.

Keywords: Excimer; Anatase; TiO_2; Thin films

1. Introduction

Since decades, titanium dioxide (TiO_2) thin films have drawn a lot of interests for numerous technological applications [1]. Nowadays, TiO_2 thin films are expected to play a significant role in nano- and microtechnologies. Therefore, more and more efforts are performed in order to develop methods for nano- or micro-structuring of TiO_2 thin films. One of the suitable candidates to modify in a controllable way the coating microstructure is the laser treatment [2]. It is widely accepted that interaction of laser with thin films causes various processes such as melting, ablation, texturing, and hardening [3]. For example, in the semiconductor technology, laser crystallization has been widely used because it presents selective absorption and low processing temperature [4]. Indeed, the irradiation area can be freely selected without heating other regions, and no substrate heating is needed.

TiO_2 posses three polymorphous structures namely, anatase, rutile and, brookite. Anatase TiO_2 presents a lot of interest because of its excellent photocatalytic behaviour [5]. Unfortunately, in comparison to rutile, the anatase phase is more difficult to synthesize because it is thermodynamically less stable [6]. Therefore, efforts have still to be realized to optimize the synthesis of anatase TiO_2 thin films. In this work, we report on excimer laser induced crystallization of TiO_2 thin films deposited on glass. The goal of the present work is to evaluate the effect of the laser irradiation on the constitution and the microstructure of the films.

2. Experimental details

TiO_2 films are deposited by reactive magnetron sputtering in an Ar/O_2 mixture. The deposition chamber consists on an industrial system (TSD 400-CD HEF R&D). Titanium target (99.9% purity) with an area of 45 cm × 15 cm and a thickness of 0.8 cm is sputtered in DC mode using an ENI RPG 100 generator. The maximum power is 10 kW with a maximum voltage of 800 V. 208 nm thick TiO_2 coatings are deposited on 180 cm^2 glass substrate. No intentional heating of the substrate is performed.

After deposition, the films are irradiated in air using a Lambda Physik (Model Compex 205) excimer laser (248 nm wavelength, 25 ns pulse duration). The laser fluence (F) is modified by varying the distance between an UV lens (250 mm focal length) and the sample.

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Structural characterization has been performed by using D8 Discover goniometer equipped with HI-STAR 1024 × 1024 pixels 2D detector (Bruker-AXS Inc). Cu Kα source was used with acceleration voltage and current of 40 kV and 40 mA, respectively. The detector to sample distance was 15 cm. The goniometer was equipped with a pinhole collimator, a laser and a camera for focusing on the area of the sample to be measured. The incident angle was 5° with a frame width of 32° and a measurement time 240 s per frame.

Thickness and roughness (average values calculated from three different positions on the sample) of the irradiated films are evaluated by means of a DEKTAK 3030ST profilometer. Finally, the microstructure of the coatings has been evaluated by scanning electron microscopy (SEM) by using a Philips XL20 microscope.

3. Results

Fig. 1 presents a top view SEM picture of as deposited (left side) and irradiated (right side, $F = 0.075$ J/cm^2) TiO_2 films. After irradiation, the morphology of the film is significantly modified with appearance of ''bumpers'' and ''holes''. X-ray diffraction (XRD) of the sample reveals that the as deposited film (left side) is amorphous while the irradiated part (right side) presents evidences of anatase diffraction peaks. In order to estimate the crystallinity of the irradiated coatings, we have fitted the strongest anatase peak, namely the (1 0 1) diffraction peak with a pseudo-Voigth function [7]. Fig. 2 shows the evolution of the intensity of the (1 0 1) anatase diffraction peak (I_{101}) as a function of F. For $F < 0.075$ J/cm^2, I_{101} is close to 0 meaning that the film remains amorphous. For $F > 0.075$ J/cm^2, I_{101} strongly increases until a maximum value is reached for $F = 0.125$ J/cm^2. Finally, I_{101} decreases linearly with F and no diffraction peak are detected for $F \geq 0.35$ J/cm^2. This experiment has been performed for different total energy values namely, 0.4 J and 0.68 J. Both set of data follow the same trends as a function of F.

Fig. 3 shows the evolution of the roughness as a function of F. The roughness presents a maximum value for $F = 0.25$ J/cm^2. On the other hand, the thickness of the irradiated area measured by profilometry slightly increases as a function of F (Fig. 4). This suggests an inflating regime under laser irradiation.

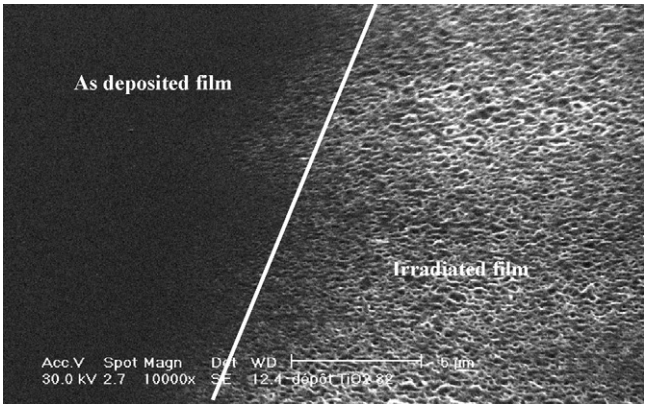

Fig. 1. Top view scanning electron microscopy picture of the as deposited TiO_2 film (left side) and of the irradiated film with $F = 0.075$ J/cm^2 (right side).

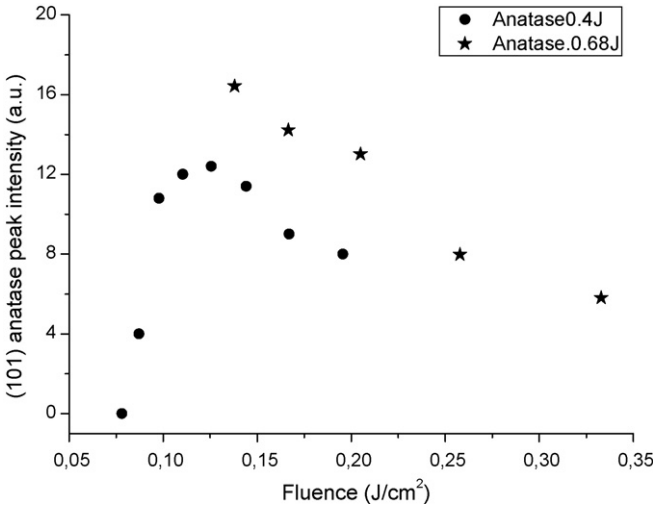

Fig. 2. Evolution of the (1 0 1) anatase diffraction peak as a function of the laser fluence. The results are presented for two values of the total energy of the laser.

4. Discussion

In order to understand the origin of the observed transformations, we have evaluated the temperature rise induced by the laser irradiation [8]. A fluence of 1 J/cm^2 corresponds to a temperature of 3200 K. This implies that the laser-induced transformations observed in the present work take place at temperatures ranging between 240 and 1120 °C. Since it is accepted that post annealing of TiO_2 thin films leads to anatase phase at temperatures smaller than 800 °C [9], our results are consistent. Nevertheless, it has to be noted that, F values used in this work are still too low to evaporate the film [10]. Therefore, the film crystallization occurs without complete melting.

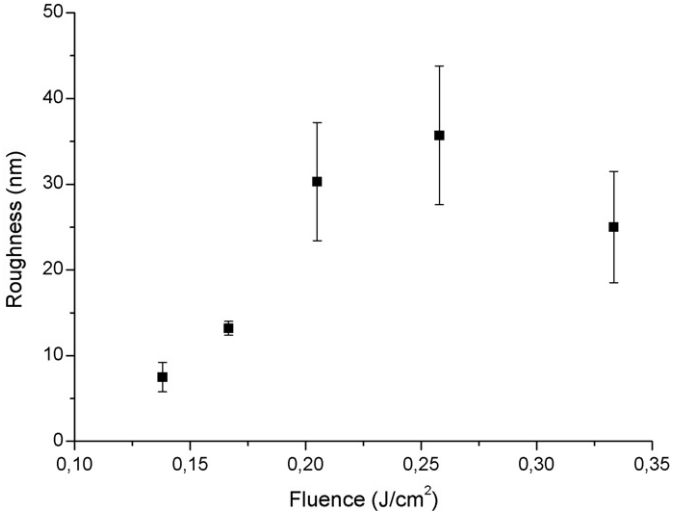

Fig. 3. Evolution of the roughness of the film as a function of the laser fluence.

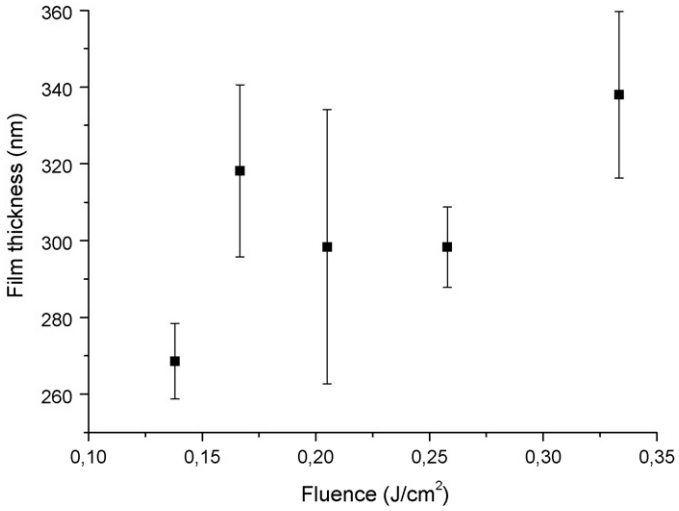

Fig. 4. Evolution of the apparent thickness of the film as a function of the laser fluence.

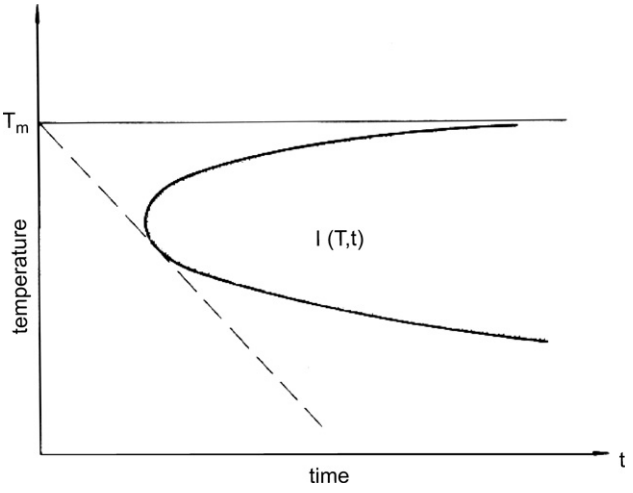

Fig. 5. Temperature, time, transition diagram.

Crystallization of thin films is generally described by the nucleation theory [11]. To crystallize the film it is necessary to overcome the nucleation barrier which corresponds in our data to $F = 0.075$ J/cm^2. This energy barrier is given by Eq. (1) [12]:

$$\Delta G_c = \frac{4 f^3 \gamma^3}{27(G_2 - G_1)^2}, \quad (1)$$

where f is a geometric factor, γ the surface tension and G_1 and G_2 are the energy for an atom in the phase 1 and 2 corresponding, in the present case, to amorphous and anatase TiO_2. The probability to get nucleation depends of the probability to find a critical size nucleus. The number of such nucleus is given by Eq. (2):

$$N^* = N \exp\left(\frac{-\Delta G_c}{kT}\right), \quad (2)$$

where N is the total number of atoms of the system, k the Boltzmann's constant, and T is the solidification temperature. N^* appears to be negligible when $(G_2 - G_1)$ is close to 0, but increases strongly for small values of $(G_2 - G_1)$. The strong increase of crystallization within small range of F namely between $F = 0.075$ J/cm^2 and $F = 0.1$ J/cm^2 could be associated with this explanation (Fig. 2).

On the other hand, the maximum of crytallinity observed for $F = 0.125$ J/cm^2 (Fig. 2) could be explained by considering the crystallized TiO_2 volume fraction (I) produced by the irradiation treatment. Assuming spherical crystallites, the following equation can be written [12]:

$$I(T,t) = \frac{4}{3}\pi n(T) v^3(T) t^4, \quad (3)$$

where t is the time, $n(T)$ the nucleation rate (related to N^*) and v the velocity of the interface between phases 1 and 2. The corresponding transformation–temperature–time (TTT) diagram for crystallization of every crystal phase competing with glass formation is presented in Fig. 5. The bold line drawn on this diagram corresponds to the border between phase 1 (left side, amorphous TiO_2) and phase 2 (right side, anatase TiO_2). This limit is often calculated for $I = 10^{-6}$ [11]. Considering this curve and $t = 0$, the evolution of I as a function of T presents a maximum for a given T value. In our case, it corresponds to a given F value which has been determined to be 0.125 J/cm^2.

Although the nucleation theory explains qualitatively the behaviour of the crystalline fraction (the anatase phase) with F, it disagrees quantitatively with the experimental results. Under thermal annealing, it is shown experimentally that, around 600 °C, it takes minutes to hours to obtain transformations [13]. In our cases, the transformations is in the 25 ns range, i.e. more than 10 orders of magnitude quicker. The origin of this very large discrepancy is attributed to electronic effects. Indeed, the amorphous-to crystal transition requires the rearrangement of covalent bonds. This can only be achieved via creation, migration and recombination of dangling bonds sites [14] which leads to a strong increase of the entropy of the transformation as well as to a strong decrease of the formation and migration energy of dangling bonds and hence to a significant increase of the crystal rate formation. More theoretical works are needed to support this explanation.

As suggested by SEM data (Fig. 1), the film microstructure is significantly modified by the laser treatment. Additionally, an already reported ''inflating'' regime of the film under laser treatment is observed [8]. Anatase crystallization which only occurs for 0.125 J/cm^2 $\leq F \leq$ 0.25 J/cm^2 cannot explain this phenomenon since the latter is observed in the all range of F. Actually, it is likely that the inflating regime is a measurement artefact associated with the low lateral resolution of the profilometry technique. Fig. 1 suggests that laser treatment results in rough and porous structure instead of the smooth one observed for as deposited film. As schematically described by Fig. 6, it is likely that, for the irradiated sample, the profilometer tip has a too large diameter (2.5 μm) to penetrate the valleys between the hills. As a consequence, the film appears to be thicker than the as deposited one. Atomic force

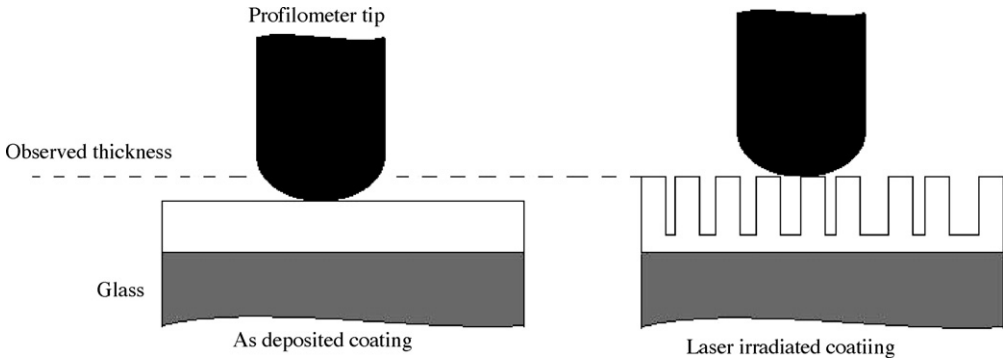

Fig. 6. Schematic description of the profilometry measurements before and after laser treatment.

and transmission electron microscopy, which will be carried out in the future, might resolve this issue.

5. Conclusion

In this work, we have shown that it is possible, in a controlled manner, to crystallize amorphous TiO_2 into anatase TiO_2 by laser irradiation. The evolution of crystallinity as a function of the laser fluence is understood based on the theory of nucleation. In addition of crystallization, under laser irradiation, we have observed a strong modification of the films microstructure as well as an inflating behaviour of the films. The latter is not related to the crystallization mechanism. Actually, based on SEM imaging, the inflating regime seems to be an artefact due to the too low lateral resolution of the profilometer tip. Indeed, after irradiation, the films appear restructured with valleys and hills at the nano-scale level. Combination of anatase structure and high surface to volume ratio obtained by laser irradiation could be of great interest for photocatalytic applications of such a kind of films.

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