Fabrication of superhydrophilic and amphiphilic TiO_2 thin films by glancing angle RF magnetron sputtering at low substrate temperature

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Abstract: TiO_2 thin films of different surface properties have been fabricated by RF reactive magnetron sputtering on various glancing angles of the unheated glass substrates. The smaller angle (0^o-60^o) deposited films are hydrophobic and become superhydrophilic after a short UV irradiation time. The variation of the glancing angle from 60^o to 75^o induced high porosity and roughness and the high glancing angle deposited films exhibited persistent superhydrophilicity for several days and very low stabilized water contact angle.

Keywords: TiO_2, GLAD, sputtering, roughness, porous, superhydrophilic, amphiphilic

1. Introduction

Advanced nanomaterials with special wetting characteristics attract a great research interest, both for practical and academic reason. Depending on the desired functionality, stable hydrophilic, hydrophobic, or amphiphilic thin films with the ability to alternate from hydrophobic to hydrophilic by an external stimulus may be required. TiO_2 is a wide band gap semiconductor and photocatalyst which also exhibits the photoinduced superhydrophilicity phenomenon (PSH), i.e. reversible wettability from hydrophobicity to superhydrophilicity upon exposure to UV irradiation [1], [2]. Due to their chemical inertness, low toxicity, robustness and transparency, TiO_2 thin films which also exhibit special wetting properties are considered to be perfect candidates for self-cleaning and antifogging surfaces, channel coatings for micro-droplet manipulation, automated valves and/or capillary pumps on microfluidic devices, for biomedical applications etc [3-5].

However, the realization of an intrinsically hydrophilic TiO_2 surface with persistent superhydrophilicity, without the requirement of UV irradiation, as well as the rate and the extent of the hydrophobic/hydrophilic conversion of the amphiphilic TiO_2, depend on the specific structure, surface morphology, roughness and/or porosity of the films.

The glancing angle vapor deposition (GLAD), i.e. vapor deposition on a substrate which is tilted with respect to the evaporation source, is an appropriate technique for the fabrication of nanostructured thin films. The vapor particle flux arrives on the substrate at an incident angle and due to atomic scale shadowing, several nanostructures, surface morphologies and enhanced porosity can be accomplished by GLAD [6]. GLAD technique is mainly applied with electron beam evaporation sources, as the e-beam vapor flux is well collimated. However, the choice of the deposition method should be made under consideration of many other factors such as mass productivity, cost effectiveness and applicability limitations. RF magnetron sputtering is a versatile vapor deposition method exhibiting remarkable results in the low-temperature deposition of high quality, crystalline TiO_2 thin films while it is also suitable for large scale production.

In this work, we present the fabrication of TiO_2 thin films by the combined glancing angle RF magnetron deposition at low substrate temperature. The effect of the variation of glancing angle of the substrate is investigated in terms of the surface morphological characteristics and the resulting wetting states of the TiO_2 films.

2. Experimental

A homemade high vacuum RF (13.56 MHz) magnetron sputtering system was used for the fabrication of the TiO_2 films. A 2 inches' diameter circular Ti (99.99%) target accommodated on a balanced magnetron source (ST-20, AJA Int.) was the sputtered material. Pure Ar (99.999%) and O_2 (99.999%) were used as the sputtering and the reactive gas, respectively. Before each deposition the chamber was evacuated to a base pressure of $4x10^{-7}$ Torr and consequently the Ti target was presputtered by Ar for 4 min in order to remove any surface oxide. All the depositions were carried out with a nominal power input of 300 W. The partial oxygen pressure $P_{O_2}/(P_{O_2}+P_{Ar})$ was 50% and the total working pressure was 2.2 mTorr . The TiO2 thin films were deposited on unheated glass substrates at the normal a = 0o substrate angle and at glancing substrate angles (GLAD) of 60^o, 75^o, and 87^o with respect to the cathode axis. The target to substrate distance was 5 cm.

Film thickness and the deposition rate were determined by contact profilometry (Dektak XT). The TiO_2 thin films structure was identified by confocal UV–vis micro-Raman spectroscopy (Horiba Jobin-Yvon LabRam HR800, Horiba, Kyoto, Japan) at 441.6 nm excitation line of the HeCd laser (Kimmon Electric Co., Itabashi-Ku, Japan). The morphology and surface roughness of the films was characterized by atomic force microscopy (Dimension Fast Scan, Bruker Corporation, Billerica, MA, USA). The wettability of the TiO_2 thin films surface was studied by contact angle goniometry (Kruss DSA100) of the 2 μL static distilled water droplets placed on the

TiO_2 surfaces. The UV-vis transmittance spectra were recorded by Lambda900 UV–vis–nIR spectrophotometer. The refractive index of the TiO_2 films was estimated by simulating the recorded UV-vis transmittance data with P.U.M.A. computational method [7].

3. Results

The as prepared TiO_2 thin films exhibited very good adhesion with the substrate even though they were deposited on unheated glass. The self-heating temperature of the substrate due to ion bombardment was $T_s<150^oC$. The TiO_2 films also showed good transparency at the visible wavelength range at the order of 70% to 80% as confirmed by the UV-vis transmittance spectra (not shown here).

The change of the substrate angle caused the reduction of the deposition rate from 7.5 nm/min to ~ 3 nm/min. There can be observed two regimes. The variation of the glancing angle of the substrate from 0^o to 60^o does not severely affect the deposition rate. However, the transition from 60^o to 75^o leads to about ~50% decrease of the deposition rate which remains almost constant even for the film deposited on the extreme glancing angle of 87^o. During high glancing angle deposition, the substrate area facing the sputtering flux is limited and thus the incident particles available for nucleation and growth per unit time are less, resulting in lower deposition rates. Nevertheless, considering that the depositions were conducted with an oxygen rich gas mixture, the deposition rate is relatively high, even for the high glancing angle regime.

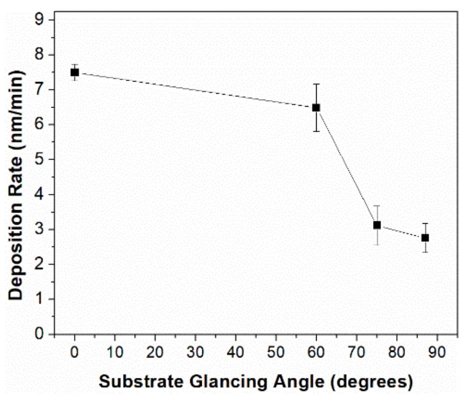

Fig. 1. Deposition rate of RF magnetron sputtered TiO_2 thin films versus glancing angle of the substrate

In our previous work [8], we observed a similar decrease of the deposition rate, along with phase transition as a result of the inclination of the substrate from 0^o to 87^o of the TiO_2 films deposited at greater substrate to target distance. The micro-Raman spectra of the films deposited at the normal orientation of the substrate (0^o) exhibited the rutile peaks superimposed with the peaks that correspond to the glass substrate, indicating a rutile structure in an amorphous matrix. The change of the glancing angle to 87^o degrees induces the phase transformation to the anatase structure as it can be concluded from the well-defined anatase Raman peaks for the depositions at both 10 cm and 5 cm. The effect of the glancing angle on the crystallinity and phase will be further investigated.

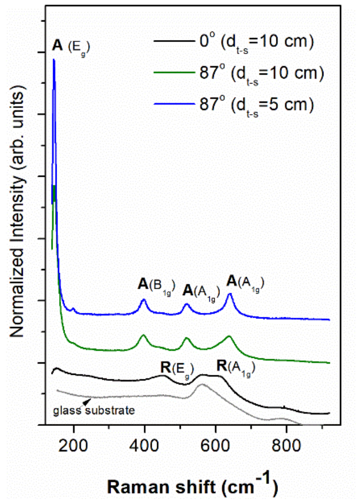

Fig. 2. Raman spectra of the TiO_2 films deposited at the normal 0^o angle of substrate and at the 87^o glancing angle

The as deposited films were superhydrophillic. The initial superhydrophillic state of the sputtered TiO_2 can be attributed to the plasma UV induced hydrophilization and the ultra-clean surface of the films. Nevertheless, the hydrophillicity deteriorates with films storage in dark and ambient conditions. The variation of the water contact angle of the GLAD TiO_2 films was recorded for a long storage time in dark until it reached a steady value and is presented in Figure 3.

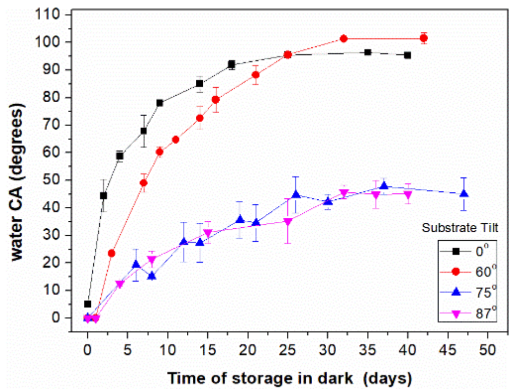

Fig.3 Water contact angle variation with time of storage of the TiO_2 films in dark

Remarkably, the high glancing angle deposited TiO_2 thin films exhibited persistent superhydrophilicity with water $CA<15^o$-20^o for over a week of dark storage after the deposition, while the contact angle of the normal angle deposited film had already reached a value of ~70°. Despite the slower rate towards hydrophobicity compared to the 0^o deposited film, the 60^o GLAD film's stabilized contact angle was >100^o.

The wetting behavior of the normal angle deposited and GLAD TiO_2 films is correlated with their surface morphology and porosity. In Figure 4, we present the 5x5 μm images of the films surface as obtained by atomic force microscopy analysis, along with the corresponding images of the stabilized water contact angle.

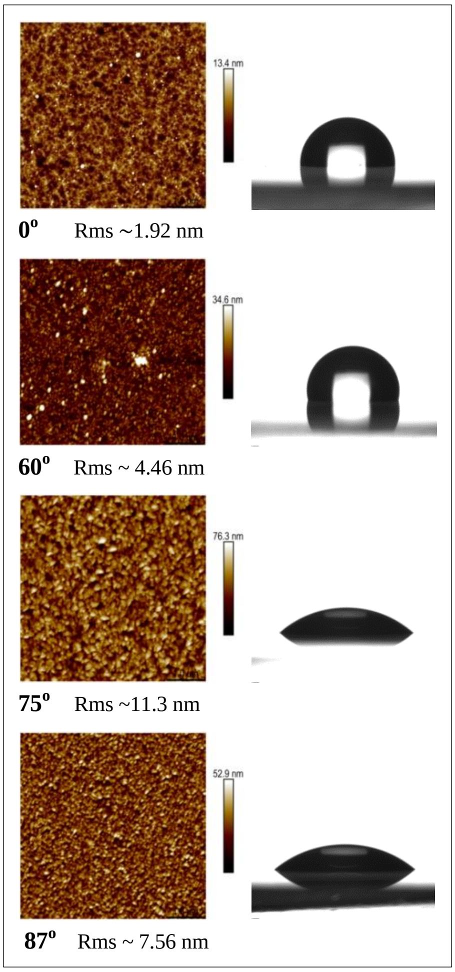

Fig. 4. AFM images (5x5μm), surface roughness and the corresponding stabilized water contact angle after long term storage in dark ambient conditions of the TiO_2 films deposited at a d_{t-s}=5 cm and at normal and glancing substrate angles. From top to bottom: Glancing angle 0o, 60^o, 75^o, 87^o

The porosity of the films was also evaluated using the relation [9]:

$$P\% = \left[1 - \frac{n_f^2 - 1}{n_d^2 - 1}\right] \cdot 100 \qquad (1)$$

where n_f and n_d are the refractive indices of the deposited film (calculated from the UV/VIS spectra) and that of the dense crystalline rutile TiO_2 (n_d=2.76), respectively.

Even for the normal angle deposited film (0^o) the estimated porosity was relatively high in the order of 35%, as a consequence of the limited surface diffusion length on the cold glass substrate. Nevertheless, at the 0^o angle deposition, the range of the angle of incidence of the ad atoms is wide and therefore they distribute evenly across the substrate area resulting eventually in a smooth surface (Rms~1.92 nm). The inclination of the substrate to higher angles with respect to the target surface from 0^o to 60^o, promoted the enhancement of the surface roughness to 4.46 nm, but the degree of porosity was lower (~25%). The roughness enhancement combined with low porosity leads eventually to a more hydrophobic surface with a contact angle >100^o. On the other hand, the films deposited at the high GLAD regime (a>60^o) are characterized by significantly higher surface roughness (7.5–11.5 nm), as well as high porosity (45-52%). These TiO_2 surfaces exhibit a persistent long term highly hydrophilic character in dark ambient conditions.

The above mentioned characteristics of GLAD films are attributed to the atomic self-shadowing effect leading to nanostructured TiO_2 thin films of different surface properties. Correlation of surface roughness with the different wettability states of the GLAD TiO_2 films, imply that the surface of the films follows the Wenzel model [10] which is described by Equation 2:

$$cos\Theta_a = rcos\Theta_i \qquad (2)$$

where Θ_a is the apparent contact angle on a real rough surface, r is the roughness factor indicating the ratio of the real surface area to the projected area, and Θ_i is the Young contact angle of the corresponding ideal rigid surface. According to Wenzel's approach increased surface roughness and surface area (r) promotes the wettability of an intrinsic hydrophilic surface, leading to lower apparent contact angle, while on the other hand the hydrophobicity of a hydrophobic surface will be also enhanced. The Wenzel type surface is more clearly identified by the behavior of the enhanced roughness- low porosity 60^o GLAD TiO_2 film. Compared to the smooth 0^o angle film, this film presents substantially lower values of the contact angles for the first 25 days after deposition. At this point, both films reach the hydrophobic state with CA≈90^o, but hydrophobicity is again favored only for the increased roughness 60^o GLAD film. On the other hand, it is the synergistic effect of high degree of porosity along with the rougher surface, that is responsible for the persistency of the superhydrophilic character of the high glancing angle (75^o, 87^o) deposited TiO_2.

In order to examine the reversible wettability property, we subjected the TiO_2 films to UV irradiation (256 nm, 8 mW/cm^2) and measured the water contact angle as a function of the exposure time (Figure 4a). The UV irradiation of all TiO_2 result to superhydrophilic films within several minutes, regardless of the initial value of the stabilized contact angle. The films deposited at 75^o and 87^o glancing angle turn to superhydrophilic within only 2 minutes. Despite the initially hydrophobic state of both 0^o and 60^o GLAD films, the change of the glancing angle, promotes the rate of the hydrophobic to superhydrophilic conversion due to the increased surface roughness. After the superhydrophilization the films were stored in dark and the contact angle recovery was also recorded during a month (Figure 4b). The hydrophilic to hydrophobic switching after the UV-induced superhydrophilization is due to the dehydroxylization of the surface and not due to the adsorption of contaminants, therefore the augmentation rate of the contact angle is greater than the corresponding rate of the aging process. The lowest porosity and rougher 60^o GLAD exhibits the greater CA variation from 0^o to >100^o, but the CA recovery rate is relatively slow. The recovery rate could be enhanced by application of mechanochemical methods [11]. On the other hand, the highest roughness porous 75o GLAD film exhibits the smaller variation of the contact angle from superhydrophilicity to a stabilized CA~ 32^o, which is even lower than the initial one.

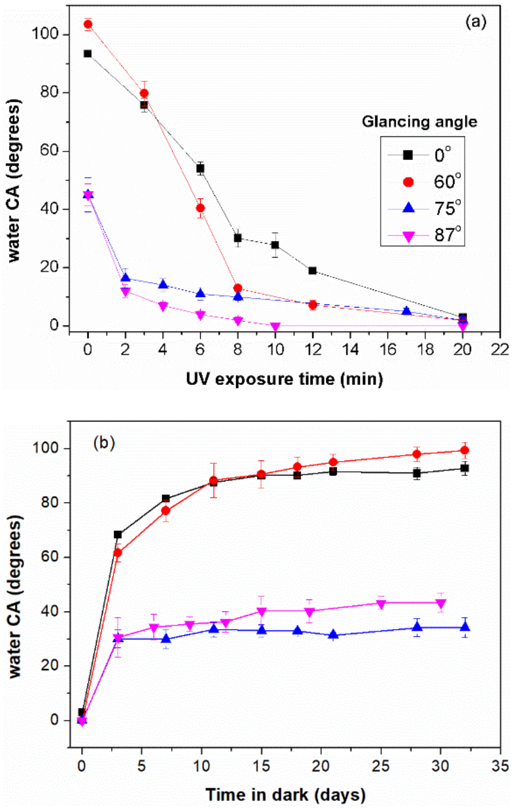

Fig.4 Variation of the water contact angle of the RF sputtered TiO_2 films deposited on different glancing angle of the substrate as a function of the UV irradiation time (a), and during the storage time of the samples in dark and ambient conditions (b).

4. Conclusions

High quality TiO_2 thin films with different microstructure and wettability were obtained by the combined GLAD RF reactive magnetron sputtering. Depending on the choice of the glancing angle, fabrication of either persistent superhydrophilic or hydrophobic/amphipilic TiO_2 thin films can be realized on thermosensitive substrates. Deposition at small glancing angle (0^o-60^o) resulted in hydrophobic TiO_2. The glancing angle variation from a=60^o to a=75^o induces high surface roughness and porosity and also causes a transition from hydrophobic TiO_2 (CA>100^o) to a highly hydrophilic TiO_2 surface with a stabilized CA<45^o. These high glancing angle deposited TiO_2 films also maintained superhydrophilicity for several days after deposition. Finally, the GLAD nanostructured films exhibit very fast conversion to superhydrophilic if exposed to UV irradiation for a few minutes.

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