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Characterization of Titanium Dioxide thin films produced by RF plasma sputtering technique for photocatalytic applications

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Abstract

In the present work Titanium Dioxide thin films were successfully prepared both on FTO and (1 0 0) Silicon substrates by means of radiofrequency plasma sputtering technique. AFM, XRD, SEM and contact angle measurements were performed in order to characterize the samples. XRD measurements revealed a crystalline structure for all the samples, with a mean globular size in the range of 20 - 30 nm. All samples showed a reversible hydrophilic behavior due to UV irradiation, that can be correlated with their photocatalytic properties.

Introduction

Search of clean fuels is a primary objective in research activity devoted to the development of new technologies and innovative materials for energy applications. Among the clean fuels, hydrogen is a promising candidate, because it is energy-efficient, environmentally friendly and abundant in nature. Looking for a new way to produce it, not depending on steam reforming process and fossil fuels, photocatalytic water splitting seems to be a good alternative. This process uses solar energy to decompose water into hydrogen and oxygen in the presence of a photocatalyst. A photocatalyst is a semiconductor which absorbs solar energy and creates an electron - hole pair. These charge carriers migrate on the semiconductor surface without recombination and promote redox reactions in the water. The net effect is the hydrogen production with a clean process. TiO_2 is a well-known semiconductor intensively investigated in the fields of photocatalysis since 1970s [1], because of its high photo-oxidation, photostability, low cost and non-toxicity [4, 5]. However, because of its wide band gap (≈ 3,2 eV) [4], it shows a weak photoresponse to the visible light region, as well as a high electron-hole pair recombination rate greatly reducing the quantum efficiency. The method most often used to synthetize titanium dioxide thin films is a sol-gel technique [6, 7, 8], but other ways have been demonstrated to be interesting: reactive magnetron sputtering [9], ion beam sputtering [10], chemical vapor deposition [11]. Lately, a different method has been investigated [12, 13, 14]: plasma enhanced chemical vapor deposition technique. The principal feature of this method lies in the effective use of radio frequency induced plasma to enhance and catalyze chemical reactions during the deposition process. On the basis of the discussion above, we report a first experimental approach of characterization of thin films of TiO_2 deposited with RF plasma sputtering, in order to identify experimental parameters able to produced thin films with relevant photocatalytic properties.

Experimental Setup

Two experimental campaigns were carried out. Thin films of TiO_2 were prepared by means of RF (13,56 MHz) plasma sputtering, both on (1 0 0) Silicon and FTO substrates. Substrates were carefully placed on the grounded substrate holder under the RF powered electrode. The vacuum before deposition was less than 1 x 10^{-6} mbar and the substrate temperature was monitored by using a thermocouple placed in contact with the sample. The sample holder had the possibility to perform deposition both at T_{Room} and with the substrate heated by a heating system: temperature achieved in this way was in the range 340-360 °C. Argon (99.999%) and Oxygen (99.999%) gases were introduced into the chamber through a mass flow controller with different percentages: Argon plasma in a reactive Oxygen environment promotes sputtering of Titanium target. Different film thicknesses were achieved, depending on Argon and Oxygen quantities and on target-substrate distance. Working pressure was fixed at 10^{-2} mbar and the upper electrode was kept at 1500 V. Subsequently samples have been characterized by means of Atomic Force Microscope (AFM), X-Ray Diffraction (XRD), Contact Angle (CA) Measurement and Scanning Electron Microscopy (SEM). AFM measurements were made in air by a Nano-RTM AFM System (Pacific Nanotechnology, Santa Clara, CA, USA) operating in contact mode. Silicon conical tips of 10 nm radius mounted on silicon cantilevers of 125 m length, 42 N/m force constant and 320 kHz resonance frequency were used. Images were processed and analyzed by means of the NanoRule+TM software provided by Pacific Nanotechnology. The structural properties studied by X-ray diffraction measurements were performed with a wide angle Siemens D-500 diffractometer (WAXD) equipped with a Siemens FK 60-10 2000W tube. The radiation was a monochromatized Cu Kα beam with wavelength λ = 0.154 nm. The operating voltage and current were 40 kV and 40 mA, respectively. The data were collected from 20 to 80 2θ° at 0.02 2θ° intervals by means of a silicon multi-cathode detector Vortex-EX (SII). The morphological properties and physical structure of the films were investigated through Scanning Electron Microscopy (SEM). Measurements were performed by using a HR SEM SU70 with Schottky electron source by Hitachi with an acceleration voltage of 20 kV. Taking into account the demonstrated relationship between photohydrophilicity and photocatalysis [2, 14], measures of contact angle were carried out. Static contact angle measurements after UV irradiation (2 h time, 3 mW/cm^2) were taken with an Optical Contact Angle Measuring Instrument (Model OCA 20, Dataphysics Instruments GmbH, Filderstadt). Samples were positioned on a support and illuminated by a light source with an electronic dosing system; water droplet was dispensed over the samples taking care not to press too and deform the droplet itself to avoid measurement errors. In order to measure contact angle, a dedicated camera captured a picture of the droplet deposited on the sample. With specific software analysis the droplet profile was automatically extracted by the analysis of grey level of image pixels and then contact angle was measured using an ellipse fitting.

First experimental campaign

Two experimental campaigns were carried out. In the first campaign the target-substrate distance was kept at 7 cm. In order to find the right experimental parameters, different samples were prepared varying Oxygen percentage. The first time 20 sccm of gas entered inside the camera, 18 sccm of Argon and 2 sccm of molecular Oxygen. The thickness achieved (estimated by SEM and profilometer) was 140 nm (Dep. Rate ~ 0.6 nm/min), both on FTO and Silicon substrates. During the second deposition the percentage composition was changed: 19 sccm of Ar and 1 sccm of Oxygen were inserted. The greater mass of Argon enhanced the sputtering rate and the as-deposited samples achieved a thickness of about 160 nm (Dep. Rate ~ 0.7 nm/min).

X-ray diffraction analysis

In fig. 1 is shown the X-ray diffraction (XRD) pattern of a representative TiO_2 coating deposited on Silicon substrate. The most intense peak comes from the Silicon substrate in the region of 2θ ≈ 65-75°. As-deposited film shows an intense line at 25.4° and less intense lines at 38.9° and 48.1°, which correspond to the (1 0 1), (0 0 1) and (2 0 0) plane reflections of the phase anatase, respectively. In addition to the peaks associated with anatase, there is also a weak peak at 2θ ≈ 28° which confirms the presence of the rutile (1 1 0) reflection, able to extend the absorption of samples in the visible light region. The narrow peaks suggest a well-defined crystalline structure. XRD analysis was also conducted with sample holder heated to a temperature below 360-370 °C. As expected, no signals from TiO_2 were observed, implying that the prepared coatings were amorphous.

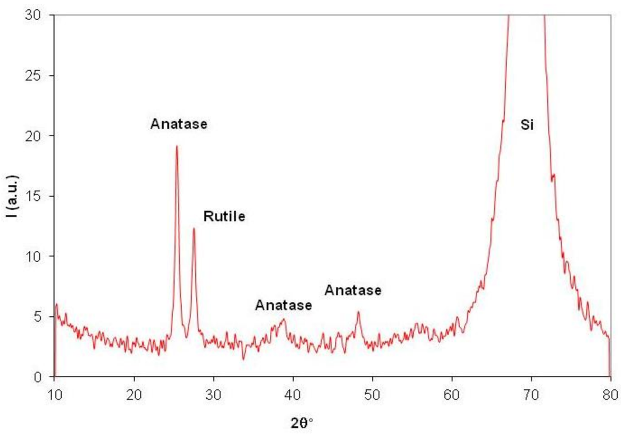

Fig. 1. XRD pattern of TiO_2 deposited on Silicon substrate (19 sccm of Ar and 1 sccm of O_2).

Scanning electron microscopy and atomic force microscopy analysis

Surface morphology, roughness parameters, and globular sizes of TiO_2 films were analyzed. Fig. 2 shows representative SEM images of TiO_2-films deposited onto silicon substrates. The roughness of the coatings have been investigated by AFM, all films were very flat and the rms roughness was found in the range of a few nanometers (Tab. 1). SEM imaging allowed us to observe the microstructure of the films to estimate the globular size. The globular size was found in the range 20-30 nm. All coatings showed a typical columnar feature (Fig. 2, right). The interface between the TiO_2 coatings and the substrates was sharp and flat with a good interlayer contact. The morphology was relatively uniform for all films.

SAMPLES	ROUGHNESS AVG. SQ.	AREA of analysis
FTO + TiO_2	5,2 nm	3 μm^2
	1,67 nm	5 μm^2
Si + TiO_2	2,65 nm	2 μm^2
	2,75 nm	3,5 μm^2
	3,15 nm	5 μm^2

Tab. 1. Roughness of TiO_2 films deposited onto Si and FTO substrates.

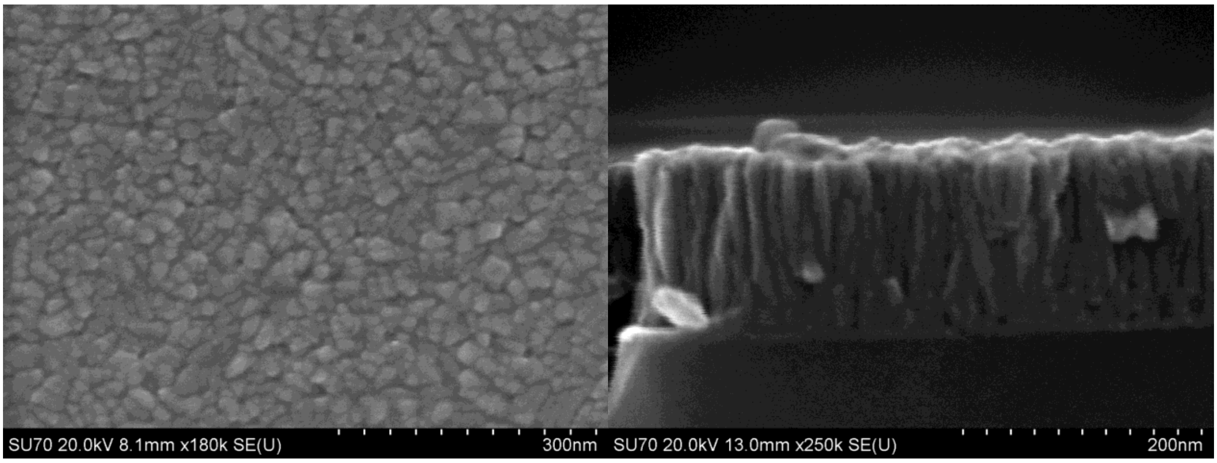

Fig. 2. Top (left) and cross-section (right) view SEM images of a TiO_2 coating.

Contact angle analysis

Surface wettability of samples was investigated with contact angle measurements. From literature [14] we found that as-deposited titanium dioxide thin films show a water contact angle in the range 70°-90°. With respect to this, samples deposited with our work conditions show since the first time a lower contact angle, which is symptomatic of a better surface wettability. The irradiation with UV light can significantly reduce this angle, enhancing the surface wettability of samples. The variation of contact angle as a function of illumination time was also studied. In order to be sure that no capillary effects arise, the volume of liquid droplets used in the measurements was 4 µl [3]. Measurements were made with different timing: tab. 2 shows the sequence. All the samples showed a reversible hydrophilic behavior due to UV irradiation, more evident for samples with Si substrate, probably due to the smoother surface. Fig. 3 shows this reversible trend.

SAMPLES	AGEING	CONTACT ANGLE
1) FTO glass + TiO_2	2 h after deposition	27°
	48 h after deposition	32,5°
	48 h after deposition + 2 h under UV	18°
2) Si + TiO_2	2 h after deposition	18,7°
	48 h after deposition	29,6°
	48 h after deposition + 2 h under UV	7°
3) Si + TiO_2	1 week stored in the dark	57°
	1 week in the dark + 2 h under UV	18°

Tab. 2. Contact angle of three samples measured in different moments.

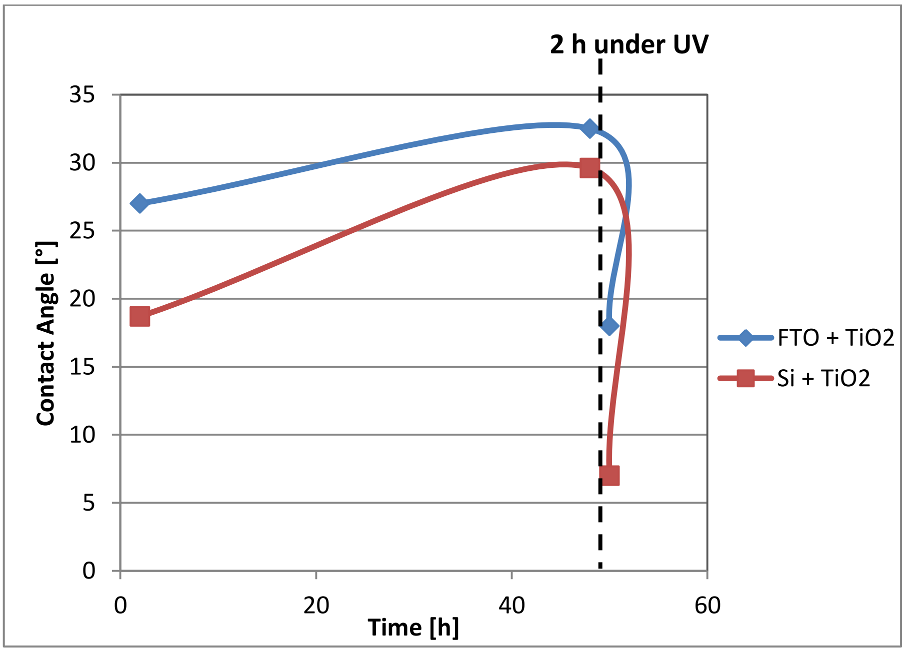

Fig. 3. Reversible trend of TiO2 due to UV irradiation.

Good photocatalytic properties can be expected from this hydrophilic behavior. The correlation between the two effects [2] can be easily explained: more OH groups can be adsorbed on the surface due to the hydrophilicity, and this mechanism enhances the photocatalytic activity. In fact, OH^- groups can trap more photogenerated holes and avoid recombination of electrons and holes, thus improving the quantum efficiency.

Second experimental campaign

In order to test new experimental conditions, different samples (with different Oxygen percentage) were deposited with target-substrate distance of 4,4 cm. No difference in the sputtering rate was observed. Also the other measurements did not reveal significant differences. In fig. 4 is reported the XRD pattern of sample with 5% Oxygen and heated substrate. This set of parameters already confirms the possibility to obtain both anatase and rutile phase.

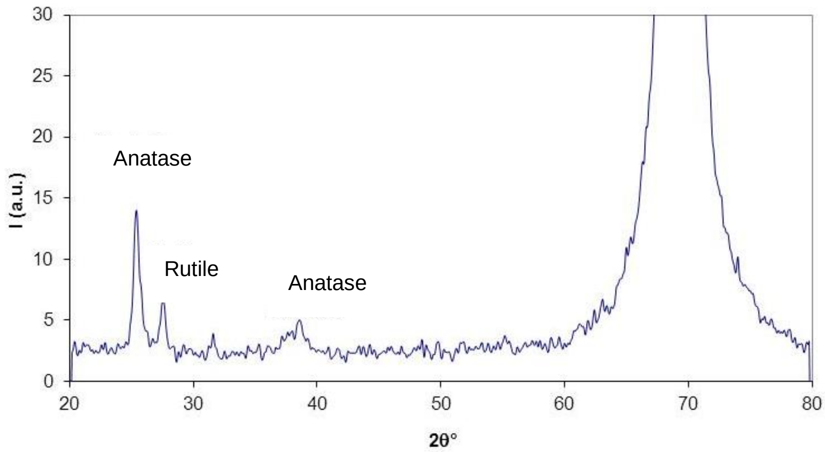

Fig. 4. XRD pattern of TiO_2 deposited on Silicon substrate (19 sccm of Ar and 1 sccm of O_2).

Fig. 5 shows SEM images of a 5% Oxygen sample: a typical columnar feature is evident with average globular size in the range of 20-30 nm.

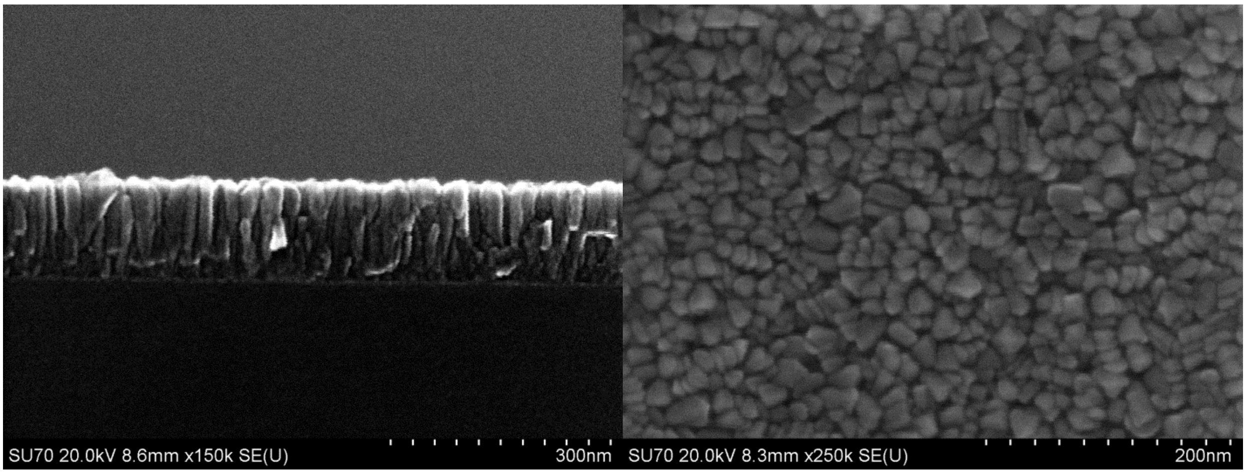

Fig. 5. Top (left) and cross-section (right) view SEM images of a TiO_2 coating.

In fig. 6 is reported the behavior under UV activation: with respect to the first experimental campaign, as-deposited samples have a higher contact angle (well in agreement with the value reported in the literature), but respond positively to the UV irradiation. The hydrophilic behavior is confirmed.

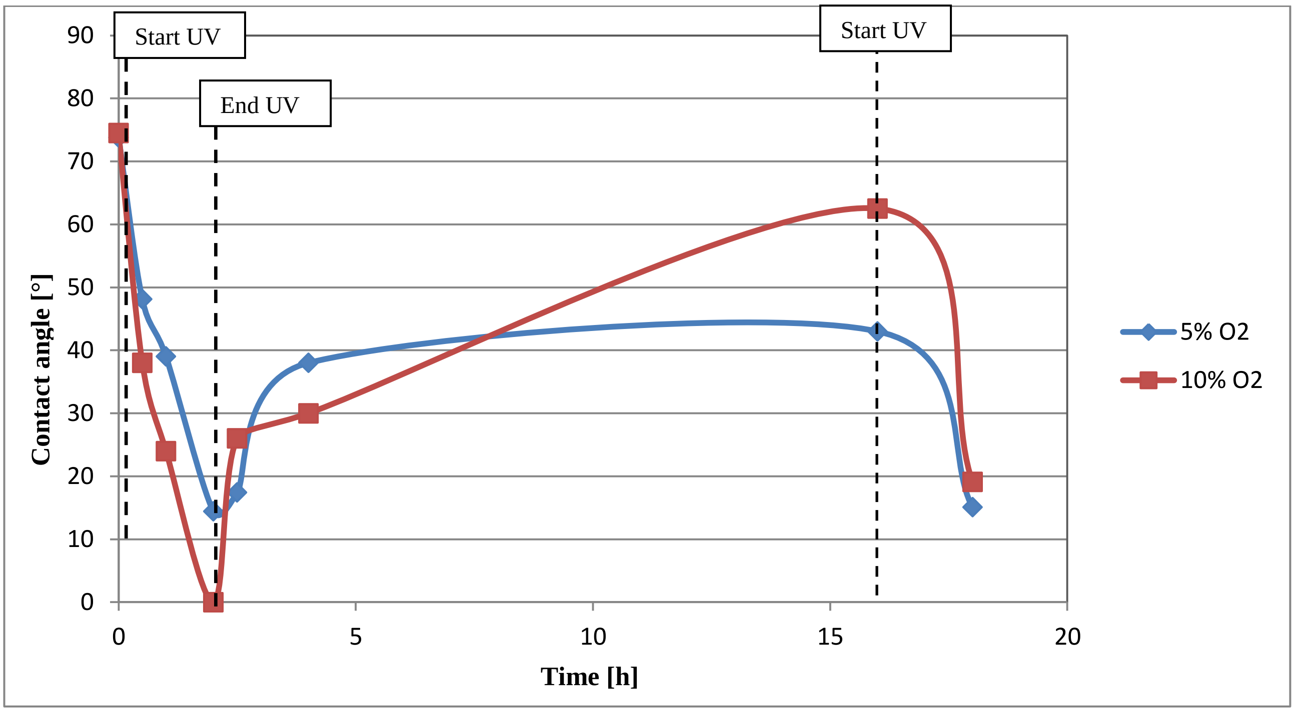

Fig. 6. Evolution of contact angle under UV illumination.

Conclusions

TiO_2 thin films have been deposited using RF plasma sputtering technique. This technique has been proved to be suitable with respect to the goal of this study. Varying Oxygen percentage has been possible to obtain different thickness. The heating system during the deposition allows us to deposit films with rutile phase, obtainable usually at higher temperature. From SEM and XRD measurements all samples show a columnar and well-ordered structure, typical of crystalline film. The most interesting feature about these films is the switchable behavior under UV irradiation. Such a feature opens interesting perspectives for the subsequent photocatalytic applications.

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