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Substrate and Fe-doping effects on the hydrophilic properties of TiO_2 thin films

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Abstract

Titanium dioxide films are known for their hydrophilic and photocatalytic characteristics. Increasing specific surface area and doping can enhance their photocatalytic activity and hydrophilicity. We report here results regarding the enhancement of the photocatalytic properties of titania by both controlling surface morphology and the anatase/rutile ratio. The samples were deposited on glass, indium tin oxide covered glass, and $SrTiO_3$ by sputtering and laser ablation techniques. Film structure and surface morphology were investigated by X-ray diffraction and atomic force microscopy. Film hydrophilicity was assessed from contact angle measurements during- and post-irradiation with UV light. The contact angle data are discussed in terms of the synergic effects of surface morphology, structure and composition of the films.

Keywords: Titanium dioxide; Sputtering; Laser ablation

1. Introduction

Some of the world environmental problems are expected to be solved with the aid of photocatalysts. TiO_2 has focused a considerable attention during the last decades as a material with a strong oxidation power [1,2]. Self-cleaning titanium dioxide films feature excellent photocatalytic and hydrophilic properties, due to their wide band gap. A great deal of effort is now under progress to enhance the photocatalytic and hydrophilic properties of pure TiO_2 films, mainly by widening the wavelength sensitization range and by ensuring stable properties of the materials under severe environment conditions.

Results are presented in this paper on the influence of several factors on the induced hydrophilicity of TiO_2 thin films, such as: (a) preparation method: radio frequency (RF) sputtering vs. pulsed-laser ablation; (b) substrate nature: amorphous glass vs. polycrystalline indium tin oxide covered glass (ITO/glass) vs. single-crystal $SrTiO_3$ (STO) substrates; (c) iron doping.

2. Experimental

Different sets of pure titanium dioxide films were prepared by magnetron sputtering and laser ablation. The reactive RF sputtering of Ti was done in a conventional 13.56 MHz setup (Huettinger, model PFG 300RF). A series of films were deposited at 250 °C in the same deposition run onto glass and ITO/glass substrates (Merck Balzers). The thickness of the transparent indium tin oxide layer was 100 nm. Fe-doped TiO_2 films were deposited using a mosaic structure of Ti and Fe_2O_3. The total pressure of the $Ar + O_2$ gas mixture during deposition was set at 0.10 Pa with a partial pressure of O_2 of 0.03 Pa.

The pulsed-laser deposited (PLD) thin films were prepared in a UHV ablation chamber with a base pressure of 1.3×10^{-3} Pa. A sintered TiO_2 commercial target disk (Furuuchi Chemicals Co, 99.99% purity) was used as an ablation target under 15 000 laser shots (20 ns duration, 50 Hz repetition rate, 60 mJ/pulse) from a 308 nm XeCl excimer laser (Lambda Physik LPX 100). This pulse energy led to a low density of cluster/aggregates in the films. The laser beam was focused on a 2.5×1.5 mm^2 area of the target. The target-substrate distance was 2.5 cm. The ablation was performed under O_2 atmosphere ($p = 0.2$ Pa), to compensate the oxygen depletion in the films and thus keep material stoichiometry [3,4]. Single-crystal $SrTiO_3$ (STO) and glass (Corning 7740 Pyrex® borosilicate, 91% transmittance

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between 325 and 2000 nm) slides were used in this case as substrates. Samples were deposited on STO and glass substrates at 150 °C and 500 °C, respectively.

X-ray diffraction (XRD) patterns were plotted using the CuK_α radiation at 4° grazing incidence. Film thickness was measured using the profilometer technique (Sloan Dektak). Surface morphology has been investigated by atomic force microscopy (AFM) in non-contact mode. Elemental composition of Fe-doped thin films was derived from EDX measurements (JEOL 5600LV Oxford Instruments).

Film hydrophilicity was assessed from the measurements of the contact angle (CA) between the de-ionized water and film surface. A home-built goniometer, allowing semi-automatic advancing- and/or receding-angle measurements of a sessile drop was used in this case. The CA measurements were performed at room temperature under 65% environment humidity conditions. Drop volumes of 0.5 and 1 μL were chosen to avoid gravitation-induced shape alteration and to diminish the evaporation effects. The drop image was acquired using a digital camera (1280×960 pixels) attached to a microscope and processed by an image analysis software. Sample irradiation was done using a high-pressure 150 W mercury lamp, under a flux value of 100 mW/cm^2 at 366 nm at sample surface. The contact angle was monitored against the ultraviolet (UV) dose, until full photoactivation was reached. Subsequent CA measurements followed the photoactivation with a time step of 8 h to assess the time constant of the activation decay. Between measurements, the samples were kept in darkness, at room temperature and 65% relative humidity.

3. Results and discussion

As previously reported [5,6] the temperature plays a crucial role on the structure of the as-deposited films. A threshold temperature value of approximately 200 °C is specific for the TiO_2 thin films prepared by both sputtering and laser ablation [5–7]. Below this threshold, the deposited films are amorphous, while above it, they feature a polycrystalline structure with anatase and/or rutile polymorphs. The average grain size values were calculated from XRD patterns according to the procedure described in Ref. [6].

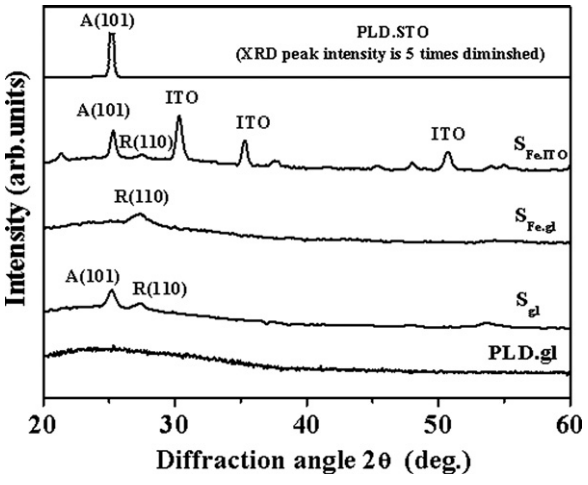

Fig. 1. The XRD patterns of the investigated samples (CuK_α radiation, λ=1.54178 Å).

Table 1
The main characteristics of the investigated films

Sample	Deposition technique	Substrate	d (nm)	W_A/W_R	R_{AFM} (nm)	E_g (eV)
S_{gl}	RF sputtering	glass	270	7/3	5.5	3.15
$S_{Fe.gl}$	RF sputtering	Glass	270	Rutile	2.5	3.00
$S_{Fe.ITO}$	RF sputtering	ITO/glass	270	17/3	4.5	3.18
PLD.gl	PLD	Glass	250	Amorphous	13.5	3.33
PLD.STO	PLD	STO	250	Anatase	14.5	3.22

d is the sample thickness, W_A/W_R is the percentage ratio of anatase/rutile phases, R_{AFM} is the average surface roughness, and E_g — the optical band gap.

Film structure of the investigated samples is dependent on the nature of the substrate and Fe-doping degree (Fig. 1). The undoped sample deposited on glass (S_{gl}) contains a mixture of anatase–rutile phases, with anatase predominating over rutile. The anatase average grain size is about 16 nm.

As seen in the XRD plots, the sputtered Fe:TiO_2 films onto glass contain a pure rutile phase (sample $S_{Fe.gl}$). On the contrary, the development of the anatase phase is enhanced in Fe-doped samples deposited onto ITO/glass substrates, as a combined effect of both doping and substrate nature (sample $S_{Fe.ITO}$). This result is in good agreement with the facts reported in Ref. [6]. The ratio of the weight percentage of the anatase/rutile phases (W_A/W_R), calculated according to Spurr's formula [8], is given in Table 1. As observed from the XRD patterns, the rutile peak R (110) is wide for both doped samples, indicating that rutile grain size is in the 10 nm range.

The PLD samples deposited on glass (PLD.gl), at 150 °C, are amorphous, since the substrate temperature is below the above-mentioned threshold. When deposited at higher temperature, the samples deposited on STO (denoted as PLD.STO) are pure anatase, with a sharp A (101) peak. This is a consequence of the excellent matching between the film- and substrate-atomic spacing. The average grain size in this sample is about 30 nm, almost twice the value of the anatase phase in the Fe-doped films.

Based on the energy dispersive X-ray measurements, the chemical formulas of the samples $S_{Fe.gl}$ and $S_{Fe.ITO}$ may be approximated as $Fe_{0.01}Ti_{0.99}O_2$ and $Fe_{0.03}Ti_{0.97}O_2$, respectively. These results certify that the solubility of iron ions in anatase is higher than in the rutile phase [9].

To indirectly check the grain size in the films, AFM measurements have been done, and the results are depicted in Fig. 2. As shown in Table 1, mean average roughness of the surface, R_{AFM}, of the sputtered TiO_2 films is quite low. A special remark is worth for the Fe-doped samples, which are smoother than the undoped ones, mainly when deposited on glass. The mean roughness of the PLD TiO_2 films is larger by a factor of three compared with their sputter-deposited counterparts. In spite of the lack of crystallographic ordering in the sample PLD.gl (as suggested by the XRD measurements) the AFM image of this sample depicts a polycrystalline-like structure (Fig. 2C) with grains smaller than the detection limit