Thin Solid Films 519 (2011) 6944–6950

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Comparison of hydrophilic properties of TiO_2 thin films prepared by sol–gel method and reactive magnetron sputtering system

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ARTICLE INFO

Available online 30 April 2011

Keywords:
TiO_2 films
Sol–gel
Reactive magnetron sputtering
Photocatalytic property
Oxygen plasma treatment

ABSTRACT

This article reports on preparation, characterization and comparison of TiO_2 films prepared by sol–gel method using the titanium isopropoxide sol (TiO_2 coating sol 3%) as solvent precursor and reactive magnetron sputtering from substoichiometric TiO_{2-x} targets of 50 mm in diameter. Dual magnetron supplied by dc bipolar pulsed power source was used for reactive magnetron sputtering. Depositions were performed on unheated glass substrates. Comparison of photocatalytic properties was based on measurements of hydrophilicity, i.e. evaluation of water contact angle on the film surface after UV irradiation. It is shown, that TiO_2 films prepared by the sol–gel method exhibited higher hydrophilicity in the as-deposited state but has significant deterioration of hydrophilicity during aging, compared to TiO_2 films prepared by magnetron sputtering. To explain this effect AFM, SEM and high resolution XPS measurements were performed. It is shown that the deterioration of hydrophilicity of sol–gel TiO_2 films can be suppressed if as-deposited films are exposed to the plasma of microwave oxygen discharge.

1. Introduction

Today the photocatalytic technology is becoming more and more attractive to industry, because a global environmental pollution has recognized to be a serious problem that needs to be addressed immediately. TiO_2 is an inexpensive, non-toxic, and biocompatible material which exhibits also a high photocatalytic activity. As a result, TiO_2-based photocatalytic process proved to be very effective in removing many air and water pollutants [1]. Also, TiO_2 is a good optical material with high transmittance from the ultraviolet (UV) to visible (vis) light. These properties can be used in many applications, for example, the dissolution of hazardous volatile organic compounds (VOC), the removal of endocrine disrupters, the recovery of heavy metal, the anti-fogging, decontamination and self-cleaning, etc. [2].

At present, the TiO_2 photocatalytic thin films can be prepared by a number of methods such as dip-coating, sol–gel method, thermal oxidation of metal or reactive magnetron sputtering [3–9]. Sol–gel process is one of the most common methods used for producing photocatalytic TiO_2 material in the form of powder or coatings. Recently, a special attention is focused on a plasma treatment for thin TiO_2 films with the aim to improve photocatalytic activity for the decomposition of organic and inorganic pollutants under UV light [10]. Besides, the plasma treatment is also used for the creation of hydrophobic or hydrophilic surfaces on metals, plastics or polymers [11].

The photocatalytic efficiency of TiO_2 photocatalytic films depends on many parameters. For instance, the TiO_2 film should exhibit crystalline anatase structure [12–14]. The aim of this article is to compare properties of photocatalytic TiO_2 films prepared by the sol–gel method and the reactive magnetron sputtering. An enhancement of the photocatalytic activity of TiO_2 films prepared by the sol–gel method with the microwave plasma treatment is also discussed.

2. Experimental details

2.1. Sol–gel deposition of TiO_2 films

The deposition of thin TiO_2 films was carried out with a dip-coating method using the titanium isopropoxide sol (TiO_2 coating sol 3%) used as a solvent precursor. The isopropoxide sol for TiO_2-based photocatalysts was prepared from titanium tetraisopropoxide, HNO_3 acid and water. The titanium tetraisopropoxide was slowly dropped into the 0.4% nitric acid solution which was stirred vigorously for 2 h at room temperature (RT), and then heated at 80 °C for 24 h. During reaction the isopropanol was removed by distillation and the originally coarse-milky solution was gradually changing to a blue fine-milky solution. Prior to the deposition of TiO_2 photocatalysts, the glass substrates were at first degreased, thoroughly cleaned and dried. Then the substrate was dipped into the viscous TiO_2-precursor sol and several times pulled out at a uniform pulling rate of 5 mm/s (2, 4, 6 dip-coatings were formed) and dried at room temperature (RT) for 24 h.

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doi:10.1016/j.tsf.2011.04.144

2.2. Magnetron sputtering of TiO_2 films

Thin TiO_2 films were prepared by dc reactive magnetron sputtering using a dual magnetron system equipped with the substoichiometric TiO_{2-x} targets of 50 mm in diameter. The dual magnetron system consists of two unbalanced magnetrons tilted at 20° to the vertical axis perpendicular to the surface of the substrate holder. The magnetrons are operated in symmetric bipolar mode at a floating potential and are connected to the dc pulse unit. Each magnetron alternatively acts as the anode and the cathode during the positive and negative pulse, respectively. The magnetrons were supplied by a dc-pulsed Advanced Energy 5-kW power supply. A mixture of argon (99.999%) and oxygen (99.995%) was used as the sputtering gas. The TiO_2 films were deposited under the following conditions: average pulse magnetron discharge current was $I_{da1,2} = 3$ A, substrate to target distance $d_{s-t} = 100$ mm, substrate bias $U_s = U_{fl}$ (floating potential), substrate temperature $T_s = RT$ (unheated substrate), total working pressure was $p_T = p_{Ar} + p_{O2} = 1.0$ Pa, oxygen partial pressure $p_{O2} = 0.026$ Pa, repetition frequency of pulses $f_r = 100$ kHz and duty cycle $t_1/T = 0.5$; here $T = 1/f_r$ is the period of pulses and t_1 pulse-on time. The pressure p_T was kept constant using argon and oxygen MKS Type 247 gas flow meters. More details are given in [15,16]. The films were sputtered on glass ($26 \times 24 \times 1$ mm^3) and Si ($25 \times 8 \times 0.5$ mm^3) substrates. The film thickness was measured by a profilometer Dektak 8 of the Veeco Instruments and its structure was characterized by X-ray diffraction (XRD) analysis using an XRD spectrometer Dron 4.07 in the Bragg–Brentano configuration with CuKα radiation. The contact angle α of a water droplet on the film surface was evaluated using Surface Energy Evaluation System containing the CCD camera connected to a computer. The droplet of distilled water with the volume of 4 μl was transported on the film surface from a zero falling height.

2.3. Post deposition treatment

As-deposited TiO_2 film prepared by the sol–gel method exhibited no hydrophilic effect. Therefore, it was treated in the plasma generated by microwave and with a gas mixture of Ar and O_2 for 5 min. The microwave plasma was generated at frequency $f_r = 2.45$ GHz, microwave power 300 W, and total pressure $p_T = 21$ Pa. The TiO_2 film exhibited hydrophilic effect even without UV irradiation, after 5 min of the treatment. Best results were obtained in the case when the TiO_2 film was treated in microwave discharge generated in pure oxygen. The TiO_2 films were irradiated in a system containing five Philips TLD 36 W/08 black lamps located 35 mm above the substrate holder. The average intensity of UV irradiation was 1.3 mW/cm^2 at the peak wavelength $\lambda = 365$ nm.

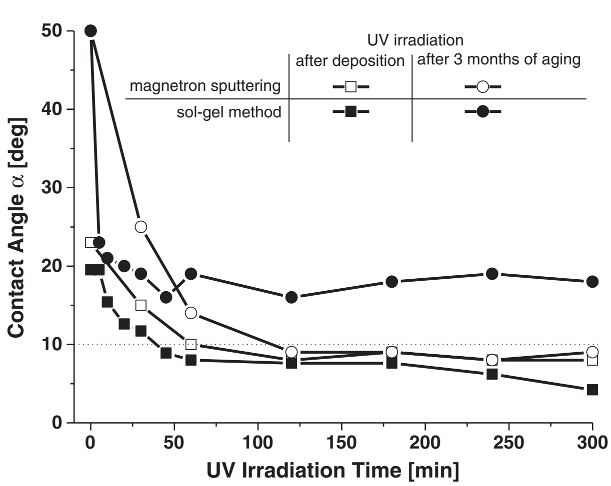

Fig. 1. Effect of UV irradiation (1.3 mW/cm^2) and aging on water contact angle of the sol–gel and magnetron sputtered TiO_2 films.

Table 1
Water droplet contacts α on surface of TiO_2 films prepared by sol–gel method and reactive magnetron sputtering.

	Sol–gel non-treated film	Sputtered film
As-deposited	35°	50°
1 h of UV irradiation	8°	10°
5 h of UV irradiation	4°	8°
3 months of aging and 5 h of UV irradiation	20°/[a]7°/[b]5°	9°

[a] First measured sample.
[b] Second measured sample.

2.4. Analysis methods

The field emission scanning electron microscope (FE-SEM; JEOL, JSM7000F) and the atomic force microscope (AFM; THERMOMICROSCOPE™, AP-0100) were used to study on TiO_2 surface. The grain size of each TiO_2 film was measured by FE-SEM. The surface morphology was investigated by AFM. AFM Images were obtained using Thermo Microscopes with silicon nitride probe mounted on a cantilever. AFM imaging was performed in contact mode. The ex-situ X-ray photoelectron spectroscopy (XPS; VG microtech, ESCA2000) measurement of each TiO_2 film was performed using MgKα X-ray source (1253.6 eV) and concentric hemispherical analyzer. XP spectra showed the content ratio changes and the chemical binding types. The X-ray diffraction (XRD; Rigaku, D/max-RC) spectra were used to study the structure of TiO_2 film. The wettability surface was characterized by the contact angle meter (Surface and Electro-Optics, SEO 300A). Deionized (DI) water was used as a liquid in the measurement. A pendent water drop that was formed at the tip of the syringe and the specimen was raised until it touched the bottom of the drop. After the DI water drop was dropped onto the surface of TiO_2 substrate, the advancing contact angles were measured immediately by a sessile drop method.

3. Results and discussion

To compare the hydrophilicity of the TiO_2 films prepared by the sol–gel method and the magnetron sputtering, the water contact angle α on the film surface was measured after UV irradiation. The

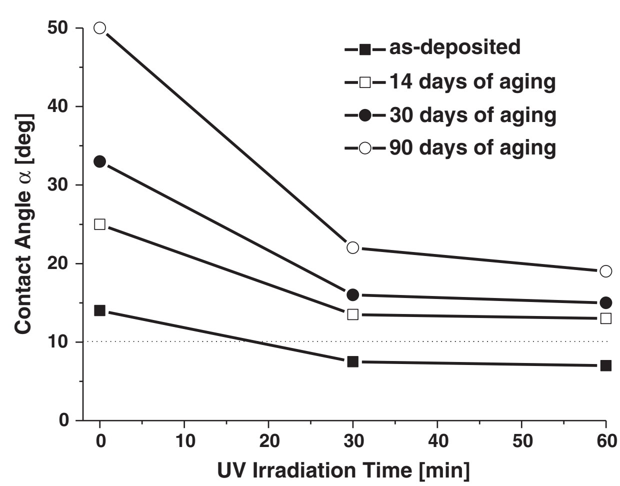

Fig. 2. Effect on the water contact angle of aging of sol–gel prepared TiO_2 films stored in the dark place for 1, 14, 30 and 90 days after deposition and UV irradiation (1.3 mW/cm^2).