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 ($26\times24\times1$ mm^3) and Si ($25\times8\times0.5$ 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 λ = 365 nm.

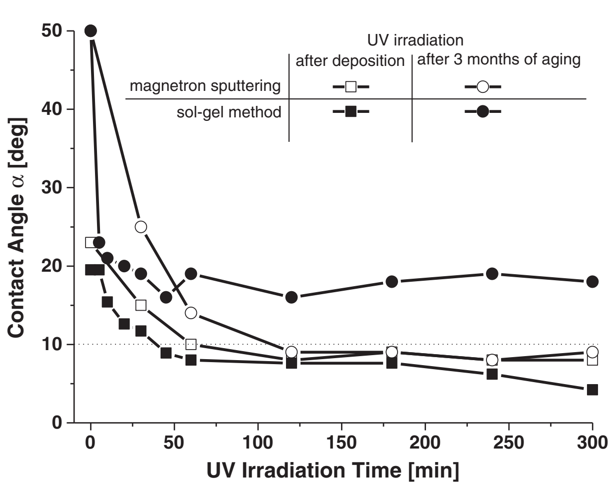

Fig. 1. Effect of UV irradiation (1.3 mW/cm^2) and aging on water contact angle of the sol–gel and magnetron sputtered TiO_2 films.

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

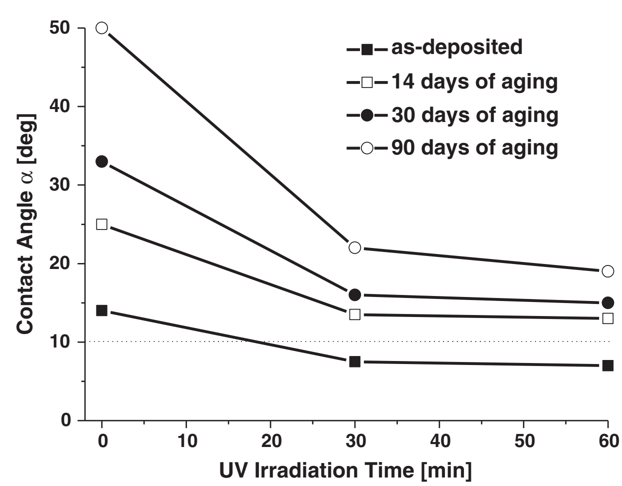

Fig. 2. Effect on the water contact angle of aging of sol–gel prepared TiO_2 films stored in the dark place for 1, 14, 30 and 90 days after deposition and UV irradiation (1.3 mW/cm^2).

effect of aging of the TiO_2 films was also evaluated. The aging effect was tested for the TiO_2 films stored in a dark box for 3 months. Obtained results are summarized in Fig. 1. From this figure, the following issues can be drawn:

1. TiO_2 films prepared by sol–gel method.
   a) The contact angle α decreases with increasing time of UV irradiation and achieves approximately 9° after 40 min of irradiation ($t_{UV} = 40'$), remains constant up to $t_{UV} = 180'$ and decreases again for $t_{UV} > 180'$ with $\alpha = 4°$ at $t_{UV} = 300'$
   b) The contact angle α decreases to ≈20° with no further decrease for UV irradiated TiO_2 films stored in black box for 3 months.
2. TiO_2 films prepared by magnetron sputtering.
   a) The contact angle α decreases with increasing time of UV irradiation t_{UV} more slowly than that on the TiO_2 films prepared by the sol–gel method.
   b) The contact angle α of the water droplet on both as-deposited TiO2 films and the stored in the black box for 3 months

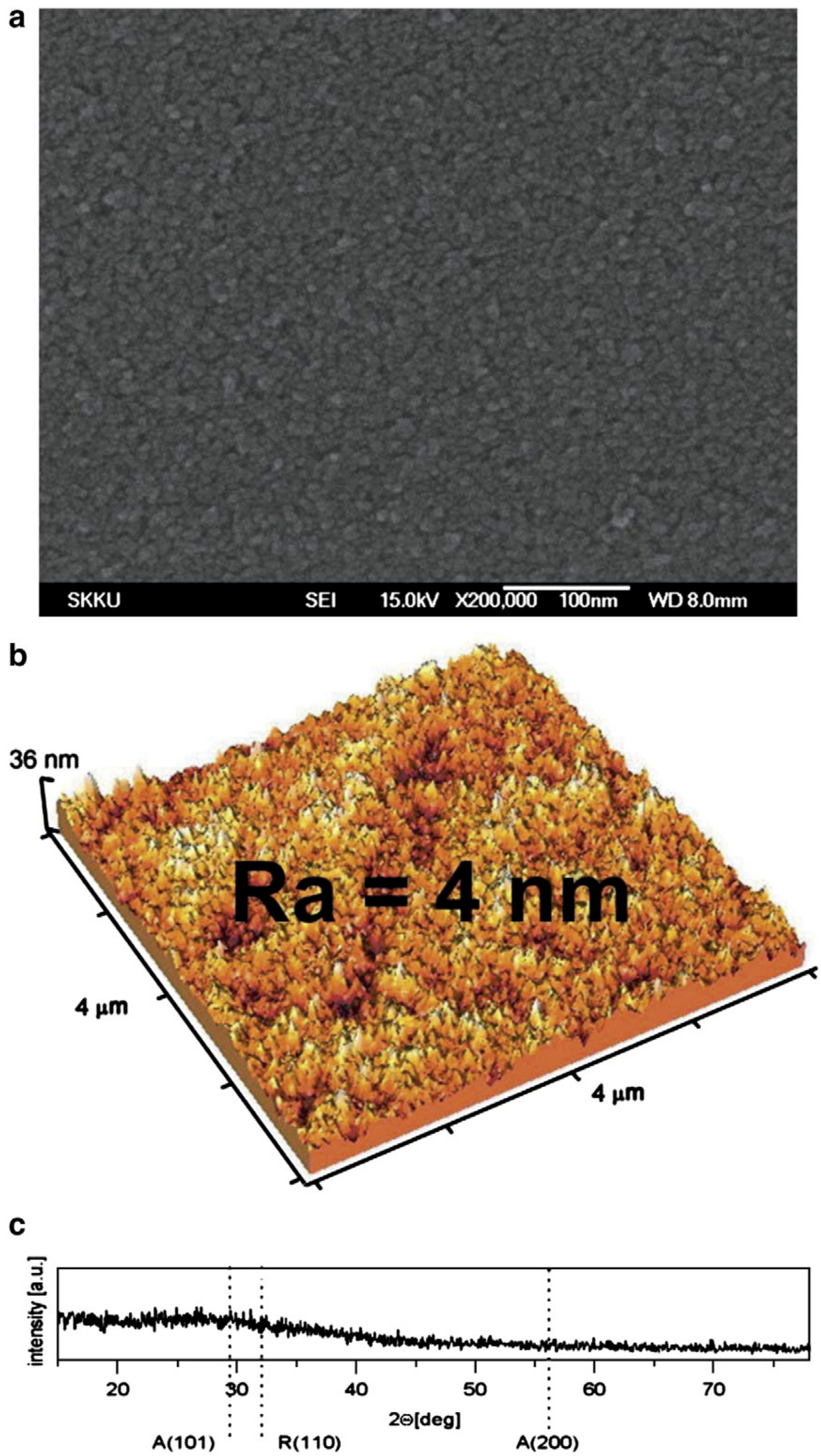

Fig. 3. SEM (a), AFM (b), and XRD (c) of the as-deposited TiO_2 film prepared by sol–gel method (the film thickness of 200 nm).

decreases to approximately the same value $\alpha \approx 8°$ after their UV irradiation for $t_{UV} \geq 120'$.

All obtained results are summarized in Table 1.

3.1. Effect of aging on hydrophilicity of TiO_2 films prepared by the sol–gel method

The hydrophilicity of films was characterized by the water droplet contact angle α. The contact angle α was measured for the as-deposited film and films stored in the dark box for 14, 30 and 90 days, see Fig. 2. For all TiO_2 films prepared by the sol–gel method the water contact angle α decreases with increasing t_{UV} approximately to 30 min and saturates at a constant value α_S at $t_{UV} \geq 30'$. The value α_S increases with increasing storage time t_S and achieves $\approx 20°$ after storage for $t_S = 90$ days and 60 min of UV irradiation.

Our experiments show that the as-deposited TiO_2 film prepared by sol–gel method exhibits a better hydrophilicity than the as-deposited TiO_2 film prepared by magnetron sputtering. Moreover, the TiO_2 films prepared by sol–gel method exhibit a significant aging effect, which was not observed for the magnetron sputtered film. To explain this different behavior of the TiO_2 films prepared by magnetron sputtering and sol–gel method, the characterization of surface morphology of these films by SEM and AFM method and their structure using XRD was carried out.

3.2. Surface morphology and structure of TiO_2 films

Fig. 3 shows SEM and AFM images and XRD pattern of as-deposited TiO_2 film prepared by sol–gel method. Fig. 3a and b shows a smooth surface with no cracks and low roughness value $R_a \approx 4$ nm.

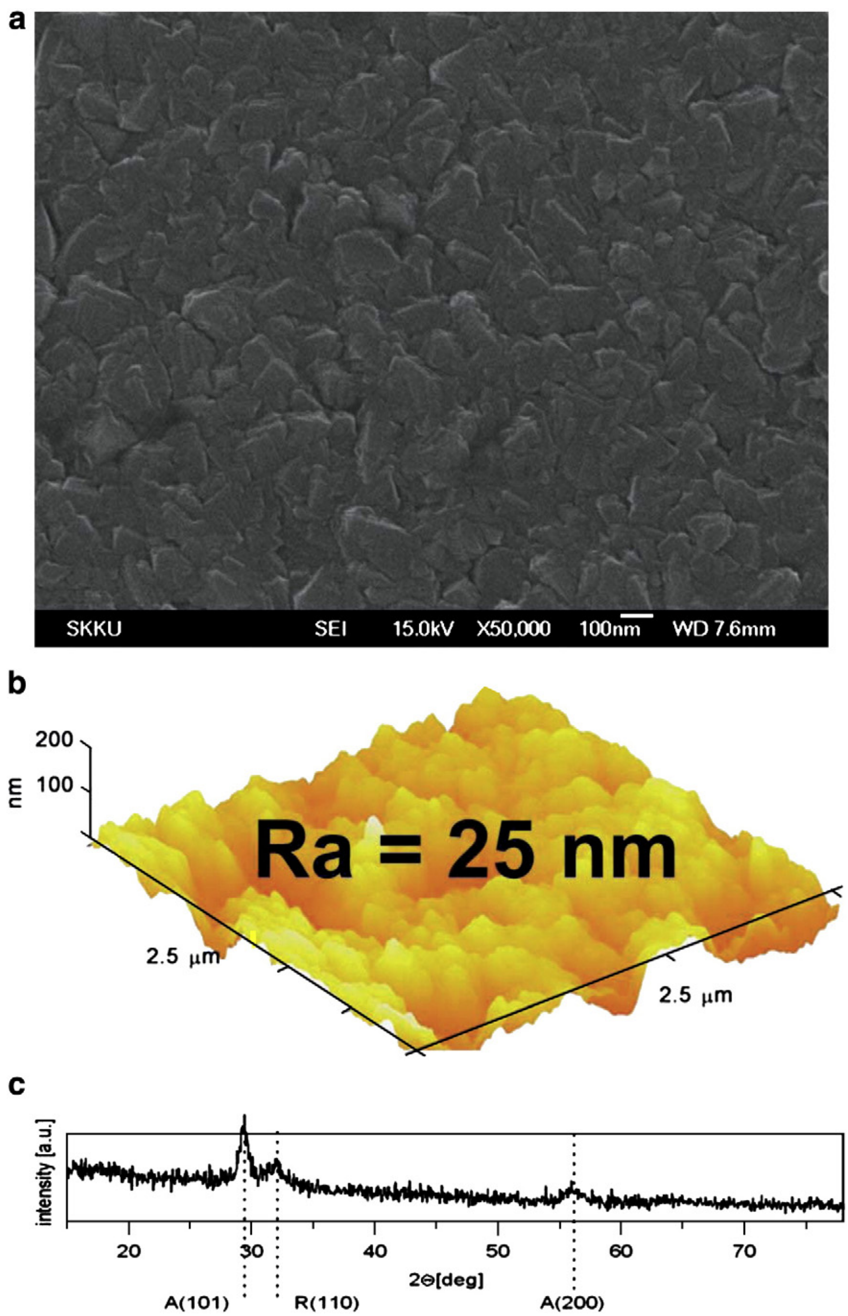

Fig. 4. SEM (a), AFM (b), and XRD (c) of the as-deposited TiO_2 film prepared by sol–gel method (the film thickness of 1500 nm).

Table 2
Comparison of properties of TiO_2 films prepared by sol–gel method and reactive magnetron sputtering.

	Sol–gel non-treated film	Sputtered film
Thickness [nm]	200	1500
XRD structure	Amorphous	Anatase and rutile
RMS [nm]	≈4	≈25
Cluster/grain size [nm]	≈10	≈200

The SEM image (Fig. 3a) shows that the film is composed of small clusters with average size of about 10 nm. The XRD pattern in Fig. 3c shows that the structure of TiO_2 film prepared by the sol–gel method is amorphous. SEM and AFM images an XRD pattern of the magnetron sputtered TiO_2 film are given in Fig. 4. The surface of film is rougher compared to TiO_2 film prepared by sol–gel method ($R_a \approx 25$ nm and 4 nm respectively); compare Figs. 3a and b and 4a and b. The SEM image (Fig. 4a) shows that the film is composed of large (≈200 nm) grains. The XRD pattern exhibits one strong, sharp peak corresponding to (101) anatase structure and two broader peaks corresponding to (200) anatase and (110) rutile structure. The significant differences in the surface morphology and structure of TiO_2 films prepared by the sol–gel method and magnetron sputtering are summarized in Table 2.

The aging of TiO_2 films prepared by sol–gel method and stored in the dark box results in strong changes of the water contact angle α (Fig. 1). These significant changes seem to be caused by changes in the surface morphology and/or chemical state of the film surface. Therefore, the surface morphology of these films was investigated in detail, see Fig. 5. In this figure the surface morphology of TiO_2 films stored in a dark box for 14 days is displayed. A comparison of this measurement with that given in Fig. 3a and b, however, shows no difference in the surface morphology of the as-deposited TiO_2 films and those stored in a dark box for 14 days.

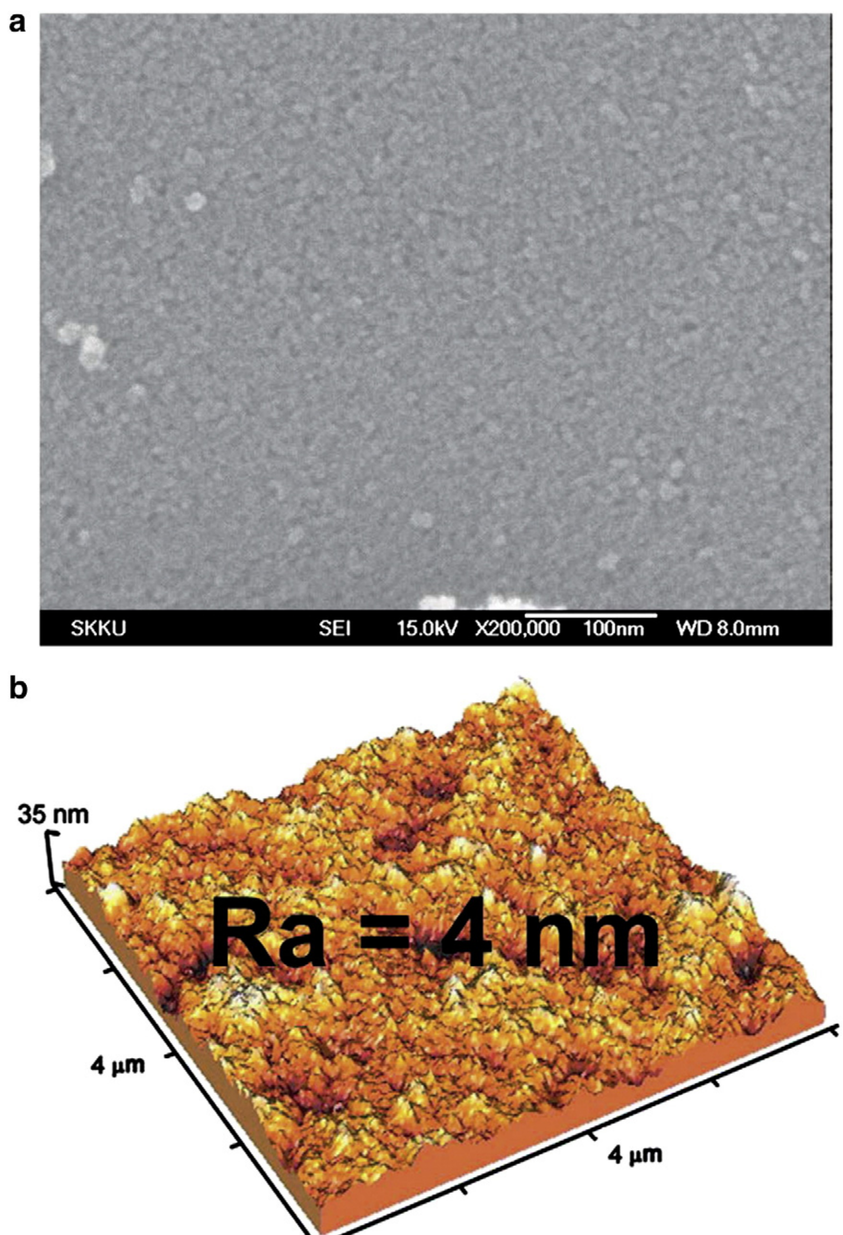

Fig. 5. SEM (a) and AFM (b) of the TiO_2 film prepared by sol–gel method and after 14 days of aging (the film thickness of 200 nm).

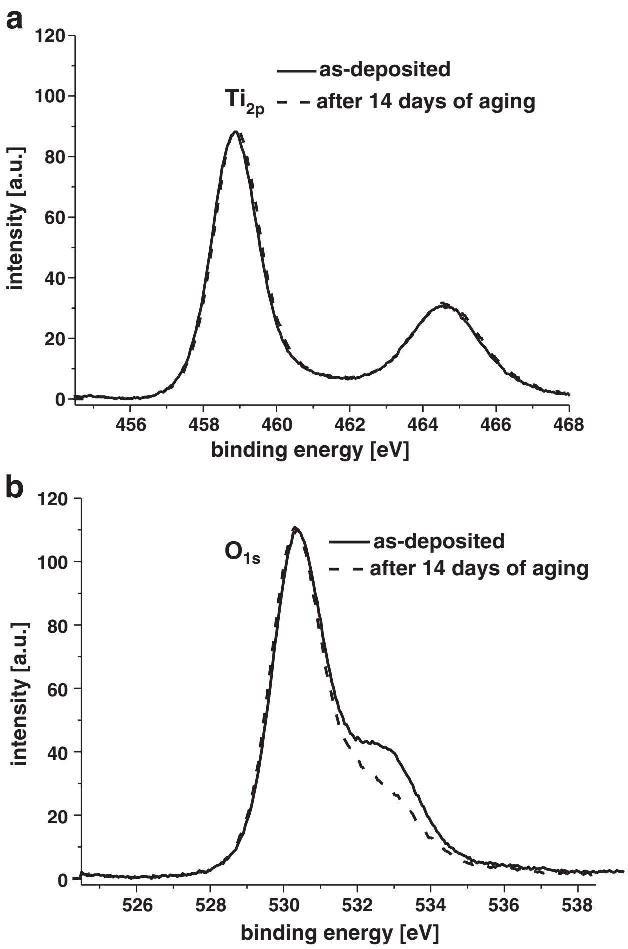

Fig. 6. XPS Ti_{2p} (a) and O_{1s} (b) spectra of the as-deposited sol–gel TiO_2 films before (solid curve) and after 14 days aging (dashed curve).

The chemical state of TiO_2 films surfaces was characterized by XPS measurements. All measurements were done before the film UV irradiation.

1 Sol–gel TiO_2 films — typical high resolution XPS Ti_{2p} and O_{1s} spectra measured by regional scans of the as-deposited sol–gel prepared TiO_2 films and those for film stored for 14 days in dark box are given in Fig. 6a and b. Ti_{2p} spectra exhibit no changes with aging of TiO_2 film, see Fig. 6a. However, the aging of TiO_2 film influences O_{1s} spectra, see Fig. 6b. For as-deposited TiO_2 film prepared by the sol–gel method exhibiting water contact angle $\alpha \approx 8°$ after 60 min of irradiation $t_{UV} = 60'$, the O_{1s} binding energy of the main peak appears at 530.0 eV together with the shoulder peak of 532.0 eV (OH species peak). The shoulder OH species peak at 532.0 eV decreases with TiO_2 aging. This is demonstrated for TiO_2 film stored for 14 days in dark box, which exhibited higher water contact angle $\alpha \approx 13°$ after 60 min of UV irradiation $t_{UV} = 60'$, see Fig. 6b. This indicates that the amount of OH species at the film surface is higher for the as-deposited film and decreases during its aging. Due to no differences in the surface morphology during aging, as shown in Figs. 3 and 5, it has been suggested that surface hydroxyl groups contribute to better hydrophilic behavior of as-deposited TiO_2 films.

2 Magnetron sputtered TiO_2 films — high resolution XP O_{1s} spectra obtained for TiO_2 film prepared by the magnetron sputtering method and stored for 3 months in a dark box is given in Fig. 7. There is no shoulder OH species peak at 532.0 eV for this TiO_2 film. We haven't observed any aging effect for this TiO_2 film compared to TiO_2 film prepared by the sol–gel method ($\alpha_{5h} \approx 9°$ and $\alpha_{5h} \approx 20°$ after 3 months of aging), as shown in Fig. 1 and Table 1. Obtained results show that the chemical state of surface, especially the OH species density, is apparently the dominant factor affecting the hydrophilic behavior of TiO_2 films prepared by the sol–gel method. On the contrary, the hydrophilicity of the magnetron sputtered TiO_2 film is not affected by the intensity of the OH species peak. This indicates that there are different mechanisms which activate the hydrophilicity of TiO_2 films prepared by sol–gel and magnetron sputtering method.

Table 3
Plasma conditions for treating TiO_2 films prepared by sol–gel method.

	Ar plasma treatment	O_2 plasma treatment
MW power [W]	300	300
Ar flow rate [sccm]	100	0
O_2 flow rate [sccm]	0	100
Exposure time [min]	5	5
Discharge pressure [Pa]	21	21

Changes of TiO_2 films prepared by the sol–gel method induced by aging can be reduced by a plasma treatment in a microwave (MW) discharge. Treatment conditions are listed in Table 3. As-deposited TiO_2 films were treated in Ar or O_2 plasma. The water contact angle α on the surface of the plasma treated TiO_2 film irradiated by UV was measured after 3 months of aging, see Fig. 8. The water contact angle

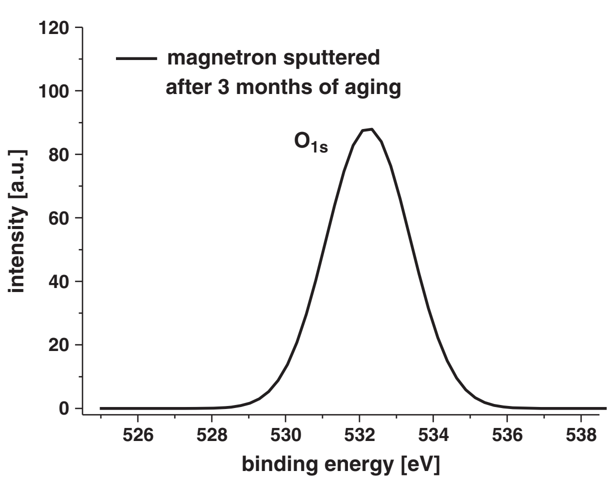

Fig. 7. XPS O_{1s} spectra of magnetron sputtered TiO_2 film after 3 months of aging.

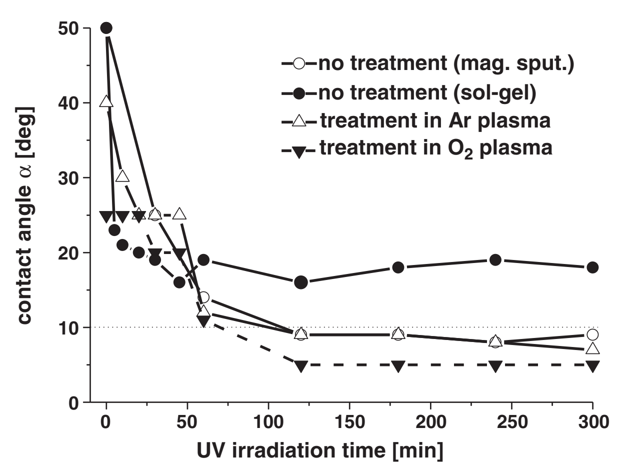

Fig. 8. Effect of UV irradiation (1.3 mW/cm^2) on the water contact angle α on magnetron sputtered TiO_2 film and sol–gel prepared TiO_2 films with/without treatment in Ar and O_2 MW discharge after 3 months of aging.

α measured on TiO_2 film treated in Ar plasma is $\alpha_{\ 2h} \approx 9°$ and that on TiO_2 film treated in O_2 plasma only 5° after irradiation of these films by UV for 2 h. Longer UV irradiation time resulted in further reduction of α. Experiment shows that this new approach using the MW plasma treatment in Ar and O_2 plasma enhances the hydrophilic properties of TiO_2 films.

4. Conclusions

The article presents a critical comparison of the properties and hydrophilicity of TiO_2 films prepared by sol–gel method and reactive magnetron sputtering. Obtained results can be summarized as follows:

The TiO_2 films prepared by the sol–gel method are amorphous and the water contact angle α decreases with increasing time of UV irradiation more rapidly than that on the anatase TiO_2 film prepared by reactive magnetron sputtering. The water contact angle α measured after 5 h of UV irradiation on the sol–gel prepared TiO_2 film is also lower (4°) than that (8°) on magnetron sputtered TiO_2 film. The aging has no effect on the hydrophilicity of TiO_2 films prepared by magnetron sputtering. The same water droplet contact angle $\alpha \approx 9°$ is measured for both the as-deposited TiO_2 film and TiO_2 film stored for 3 months in the dark box and UV irradiated for 5 h. On the contrary, the angle α on the surface of sol–gel TiO_2 film increases with storage time and for 3 months storage achieves ≈20° after UV irradiation for 5 h. This increase in α is connected with decrease of OH species density (binding energy 532 eV in XPS O_{1s} spectra) when the storage time (aging) increases. The surface roughness of the TiO_2 film prepared by magnetron sputtering is higher (25 nm) than that prepared by the sol–gel method (4 nm). Treatment of as-deposited sol–gel TiO_2 films in oxygen microwave discharge enhances their hydrophilicity, especially the aging effect.

Acknowledgments

This research was supported by grants NRF-20100025481 (Basic Science Research Program), NRF-20100029699 (Priority Research Centers Program), and NRF-20100029417 (Plasma Bioscience Research Center, SRC Program).

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