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Ceramics International 37 (2011) 2781–2788

CERAMICS INTERNATIONAL

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Study on the photocatalytic activities of TiO_2 films prepared by reactive RF sputtering

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Received 20 January 2011; received in revised form 4 April 2011; accepted 18 April 2011

Available online 25 April 2011

Abstract

Titanium oxide (TiO_2) films were deposited on non-alkali glass by reactive radio frequency (RF) magnetron sputtering using a Ti metal target in this study. The deposition parameters employed to realize the photocatalytic activities of TiO_2 films include RF power, deposition time, argon–oxygen ratio ($O_2/(Ar + O_2)$) and substrate temperature. The orthogonal array and analysis of variance (ANOVA) were adopted to determine the effect of the deposition variables on characteristic properties and the optimal conditions. The results indicated that a higher photocatalytic activity of TiO_2 films could be achieved under RF power of 150 W, deposition time of 3 h, argon–oxygen ratio of 40% and substrate temperature of 80 °C. RF power and argon–oxygen ratio had a higher effect on the methylene blue (MB) absorbance. The validation experiments show an improved photocatalytic activities of 5% when the Taguchi method is used.

Keywords: Titanium oxide; Photocatalytic activities; Reactive radio frequency magnetron sputtering

1. Introduction

Over the past decades, photocatalyst materials are increasing their importance as one of the most interesting groups of materials due to unique properties such as restrains virus activity, catches and eliminates the planktons in the air, provides the function of anti-pollution, deodorization, dust-proof, and self-clean. Titanium dioxide (TiO_2) with a band gap of 3.2 eV is one of the most important photocatalyst materials and it has started to be applied for the photocatalytic purification/disinfection of water and air. When TiO_2 is irradiated by ultraviolet (UV) light, it produces pairs of electrons and holes. Such excited electrons or holes can diffuse to the TiO_2 surface and generate various radicals or ions which can decompose organic compounds adsorbed on the TiO_2 surface. TiO_2 exhibits three distinct polymorphs in nature (i.e., anatase, brookite and rutile). In particular, anatase and rutile are commonly used as photocatalyst [1–7]. However, anatase shows a greater photocatalytic activity for most reactions [1,2]. Besides, the photocatalytic activities of TiO_2 materials strongly depend on surface morphology, crystal structure and crystallization of the concerned TiO_2 photocatalyst [8]. Numerous studies on deposition techniques of TiO_2 thin films used sol–gel [9,10], metalorganic chemical vapour deposition (MOCVD) [11,12], and sputtering [13–17]. However, sol–gel and MOCVD are of great disadvantage compared with sputtering in deposition of TiO_2 thin films, such as low deposition rate, high crystallization temperature, compositional non-uniformity over large substrates, rough surface morphology, lack of appropriate precursors in gas phases, and poor reproducibility. Sputtering technique, either using direct current (DC) or radio frequency (RF) currents, has attracted extensive interest in recent years due to TiO_2 thin film possess very smooth surface by sputtering. The technique mainly uses the plasma consisting of argon and oxygen. Several approaches had been devoted for investigating the effects of sputtering power, O_2 partial pressure, depositions time and substrate temperature on the crystallization of TiO_2 films [18–22].

Oxygen is supplied from the sputter gas to fill up the oxygen lack of deposited film during the TiO_2 sputtering. The supplied oxygen is thought to be in an excited state. So, the sputter gases with various O_2 concentrations play an important role as it

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0272-8842/$36.00
doi:10.1016/j.ceramint.2011.04.030

Table 1
Setting of factors and levels in TiO_2 deposition conditions.

Substrate	Non-alkali glass
Target	Ti: 99.99% purity
Gas	Ar (99.995%), O_2 (99.995%)
Base pressure	0.67×10^{-3} Pa
Substrate-to-target distance	80 mm
Working pressure	0.67 Pa
Substrate rotate vertical axis	10 rpm

Symbol	Control factor	Level 1	Level 2	Level 3
A	RF power (W)	50	100	150
B	Deposition time (h)	2	3	4
C	Argon-oxygen ratio $(\frac{O_2}{Ar+O_2})$%	40	60	80
D	Substrate temperature (°C)	Room	80	120

Table 2
Experimental results and S/N ratios for the MB absorbance with the TiO_2 photocatalytic films after 240 min UV irradiation.

Experimental no.	Control factors				MB absorbance	S/N (dB)
	A	B	C	D		
1	1	1	1	1	0.831	1.618
2	1	2	2	2	0.841	1.514
3	1	3	3	3	0.825	1.618
4	2	1	2	3	0.905	0.819
5	2	2	3	1	0.782	2.158
6	2	3	1	2	0.709	2.975
7	3	1	3	2	0.683	3.350
8	3	2	1	3	0.579	4.731
9	3	3	2	1	0.684	3.350

Note: A = RF power; B = deposition time; C = argon–oxygen ratio; D = substrate temperature, the experiments were repeated three times.

affects the deposition rate during TiO_2 film deposition. Ohno et al. showed that the oxygen amount is proportional to applied power density [14]. Song et al. reported that the content of rutile and anatase phase correlated closely with atomic mass of the sputtering gas [15]. The crystallinity and photocatalytic activity of TiO_2 films decrease with increasing substrate RF bias during TiO_2 film deposition [16]. Besides, the effect of crystallization of sputtered TiO_2 films correlated with substrate temperature on TiO_2 film deposition [19,23,24]. A high substrate temperature results in good crystalline structure, and low substrate temperature leads to an amorphous TiO_2 structure [25]. In general, brookite and anatase are stable at low temperature and will transform into rutile at the temperature above 900 °C [26,27]. Zhang et al. found that the crystallization of TiO_2 films followed as: anatase → anatase + rutile → anatase, when the substrate temperature was increased from 50 to 600 °C [28]. However, most of them focused on the TiO_2 film structure and photocatalytic activity, and detailed research on the optimize processes parameters of the sputter deposited TiO_2 films has not been reported.

Taguchi method is very useful tool to solve the complex and confused problem with the least variables and fewer tests in many areas of manufacturing processes [29,30]. It uses orthogonal arrays and ANOVA to determine the effect of the variables on characteristic properties and the optimal conditions of selected variables. Kim et al. obtained the optimization for the synthesis of TiO_2 nanoparticles by Taguchi method [31]. Cheng et al. showed the feasibility to prepare the optimal the photocatalytic thin film reactor by Taguchi method and to quantify the photocatalytic activity using the formation of hydroxyl radical [32].

Table 3
ANOVA results for the MB absorbance with the TiO_2 photocatalytic films.

Factors	Level (dB)			Degree of freedom	Sum of squares	Variance	Percentage of contribution (%)
	1	2	3				
A	1.584	1.984	3.810	2	8.453	4.227	69.85
B	1.929	2.801	2.648	2	1.301	0.650	10.74
C	3.108	1.894	2.375	2	2.242	1.121	18.52
D	2.375	2.613	2.390	2	0.107	0.053	0.88
Total				8	12.103		
Optimize deposition condition ($A_3B_2C_1D_2$)					MB absorbance 0.553		

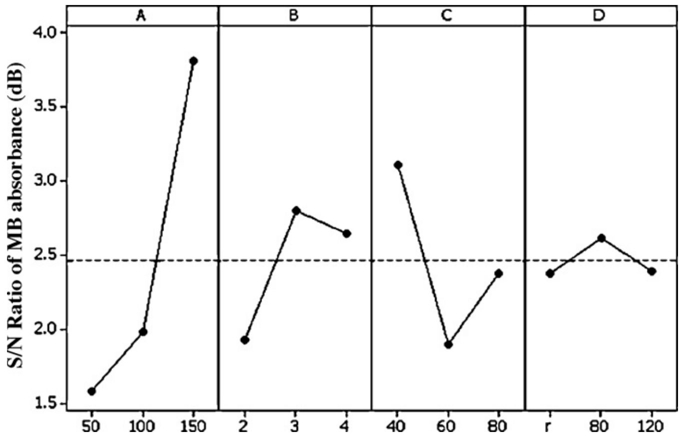

Fig. 1. S/N response graph for the MB absorbance.

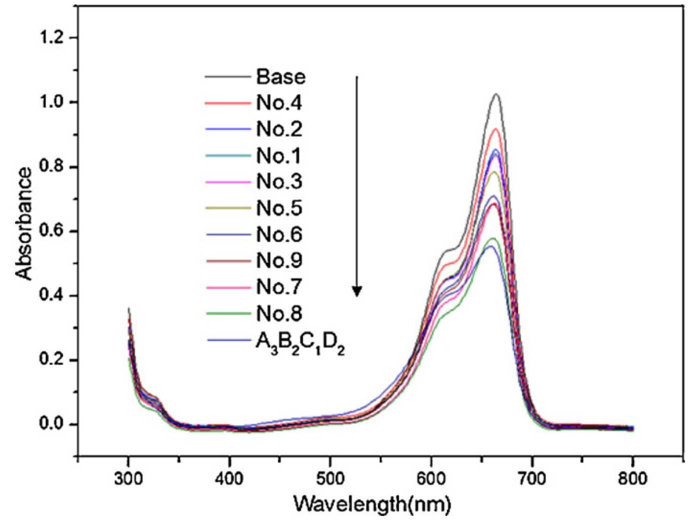

Fig. 2. Absorption spectrum of the MB aqueous solution (10 μM) degraded by TiO_2 photocatalytic film for the orthogonal arrays from No. 1 to No. 9 and the optimal deposition condition ($A_3B_2C_1D_2$) with 240 min UV irradiation.

2. Experimental

2.1. Film preparation

TiO_2 thin films were deposited on non-alkali glass substrates by reactive RF magnetron sputtering with a base pressure of 0.67×10^{-3} Pa, using Ti metallic target. Reactive and sputtering gases were O_2 (purity: 99.995%) and Ar (purity: 99.995%), respectively. The size of substrates was $20 \times 20 \times 1$ mm^3. Before coating, these specimens were ultrasonically cleaned in acetone, methanol and distilled water for about 15 min, then nitrogen gas was dried and placed into the magnetron sputtering chamber. Before each deposition event, the vacuum chamber was evacuated to a residual pressure lower than 3.99 Pa rough. During this time, the substrates were uniformly heated by quartz heaters, which were symmetrically positioned within the chamber. The temperature of the substrates was kept at about 100 °C. Once the chamber was pumped down to 6.65×10^{-4} Pa, it was back-filled with argon to a working pressure of 1.33×10^{-1} Pa. The sputtering power was controlled at 20 W. Before deposition, the target was pre-sputtered for about 5 min to remove any contaminants from the surface. In the chamber, all the substrates were mounted at the mid-point of a circle planetary substrate holder, which rotated at a speed of 10 rpm during deposition.

2.2. Film characterization

The film thicknesses were measured using a surface profilometer (α-step, AMBIOS XP-1). Surface morphology was analyzed using a JEOL JSM-6500F field emission scanning electron microscope (FESEM). The crystal structures of the films were determined by X-ray diffraction (Rigaku-2000 X-ray Generator) with automatic data acquisition using Cu Kα radiation with grazing incidence angle of 1°. The scanning rate was 5°/min. The topographic images measurement was performed with a SPA-400 atomic force microscope (AFM). The black light (UVP UVL-225D) lamp of main wavelength of 365 nm (1:5 mW/cm^2 at the film surface) was used as the UV light source.

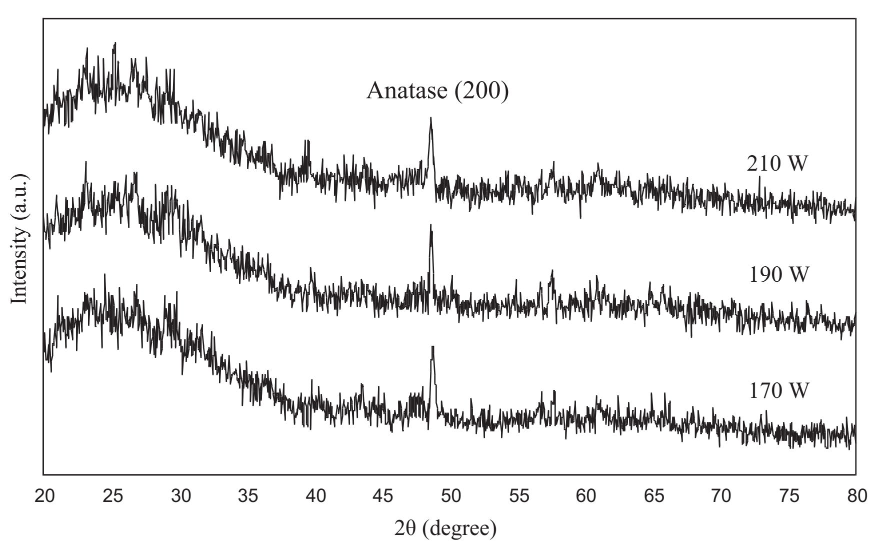

Fig. 3. The XRD patterns of TiO_2 thin films prepared at 170, 190 and 210 W.

2.3. Decomposition of methylene blue (MB)

The aqueous solution of 10 μM/l methylene blue (MB) was prepared and used in this study. The decomposition of methylene blue was examined with pretreated TiO_2 specimens. TiO_2 specimen immersed in the solution was irradiated by a 1.5 mW/cm^2 UVP UVL-225D lamp for 4 h in the dark without agitation to avoid possible complicating effects of illumination. TiO_2 specimens were taken at designated times and analyzed according to the change in the concentration of methylene blue, which was measured with a UV/vis/NIR spectrometer (Jasco V-670) at 365 nm. The measured absorption was converted to a concentration using a standard calibration curve for methylene blue. The decolorizing ratio (ξ) was calculated as following [33]:

$$\xi = \frac{\beta_I - \beta_T}{\beta_I} \times 100 \tag{1}$$

where β_I and β_T represent the absorbance of the methylene blue solution for the initial (without treatment) and test samples, respectively.

2.4. Taguchi method

In this study, Taguchi method with a L_9 orthogonal array robust design was implemented to optimize experimental conditions for the photocatalytic activities of TiO_2 films prepared by reactive RF magnetron sputtering, under various deposition parameters (i.e., R.F. power, deposition time, argon–oxygen ratio and substrate temperature) to find the optimum deposition conditions to obtain high photocatalytic activities. Table 1 show the factors and levels settings in TiO_2 deposition conditions.

Experiments are repeated three times and the mean values of each output were subsequently used for analyzing the results. The optimization of observed values was determined by comparing the signal-to-noise (S/N) ratio, based on Taguchi method. In this investigation, the photocatalytic activity of TiO_2 films was selected to optimize the deposition parameters to get the smaller the better characteristics. The S/N ratio of the smaller the better characteristic can be expressed as

$$(\mathrm{S/N})_S = -10 \log \frac{1}{n} \sum_{i=1}^{n} y_i^2 \tag{2}$$

where n is the number of repetitions of the experiment and y_i is the average measured value of the experimental data i.

Table 4
Effect of RF power on MB absorbance with the TiO_2 photocatalytic films.

Unchange deposition parameters	3 h deposition time, 40% argon–oxygen ratio and 80 °C substrate temperature	
	RF power (W)	MB absorbance
Change deposition parameter	170	0.538
	190	0.512
	210	0.509

3. Results and discussion

3.1. ANOVA

Experimental results and the corresponding signal-to-noise (S/N) ratios for the MB absorbance with the TiO_2 photocatalytic film after 240 min UV irradiation were shown in Table 2. From Table 2, the best experimental result to get lower MB absorbance with the TiO_2 photocatalytic film is No. 8. The percentage contribution of various deposition parameters for the selected performance characteristic can be obtained by

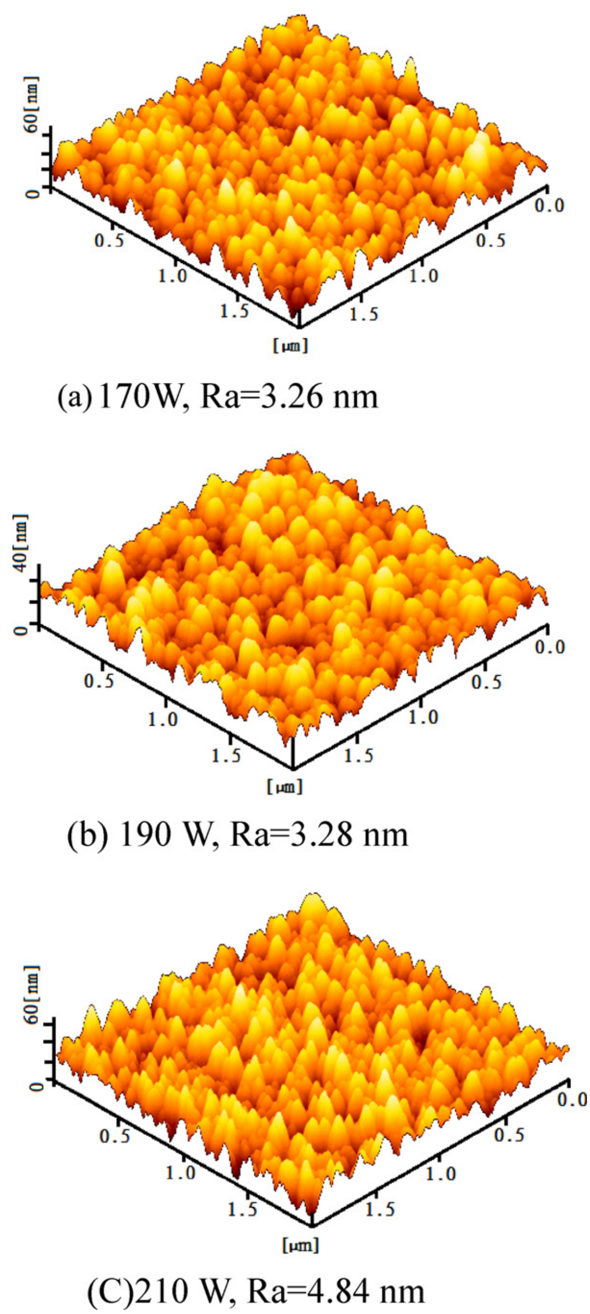

Fig. 4. The 3D AFM images of TiO_2 photocatalytic thin films deposited on the non-alkali glass by varying the RF power in the range of 170, 190 and 210 W. (a) 170 W, Ra = 3.26 nm, (b) 190 W, Ra = 3.28 nm, (c) 210 W, Ra = 4.84 nm.

ANOVA. The ANOVA results for the MB absorbance with the TiO_2 photocatalytic film were listed in Table 3. In Table 3, the RF power ($P = 69.85\%$), argon–oxygen ratio ($P = 18.52\%$) and deposition time ($P = 10.74\%$) had a higher effect on the MB absorbance. Substrate temperature had little effect on the MB absorbance. Fig. 1 shows the S/N response graph for MB absorbance. As shown in Table 3, the optimal TiO_2 photocatalyst films deposition performance for the MB absorbance was obtained at 150 W RF power (A_3), 3 h deposition time (B_2), 40% argon–oxygen ratio (C_1) and 80 °C substrate temperature (D_2) settings. Fig. 2 shows the absorption spectrum of the MB aqueous solution degraded by TiO_2 photocatalytic film for the orthogonal arrays from No. 1 to No. 9 and the optimal deposition condition ($A_3B_2C_1D_2$), after 240 min UV irradiation. It was found that the MB absorbance of the No. 8 (0.579) is higher than MB absorbance of optimal deposition condition (0.553). So, the performance characteristics of MB absorbance can be improved through Taguchi method.

3.2. Deposition parameters analysis

The RF power and argon–oxygen ratio shows statistical and physical significance for the MB absorbance with the TiO_2 photocatalytic film. When the deposition time (3 h), argon–oxygen ratio (40%) and substrate temperature (80 °C) were kept constant, and the varied RF power were 170, 190 and 210 W, respectively, the MB absorbance of as-deposited films is 0.538, 0.512 and 0.509, respectively, as shown in Table 4. The RF power increases, the MB absorbance of TiO_2 photocatalytic films decreases. The XRD spectra of TiO_2 films deposited at different RF power are shown in Fig. 3. The XRD results indicated that (2 0 0) preferred oriented anatase polycrystalline structure at 2θ–48.0°. In addition, the photocatalytic activities of TiO_2 materials were related with surface morphology. Fig. 4 illustrates the AFM images of the surface morphologies of TiO_2 thin films deposited on the non-alkali glass by varying the RF power in the range of 170, 190

Table 5
Effect of argon–oxygen ratio on MB absorbance with the TiO_2 photocatalytic films.

Unchange deposition parameters	150 W RF power, 3 h deposition time, and 80 °C substrate temperature	
	Argon–oxygen ratio (%)	MB absorbance
Change deposition parameter	30	0.617
	35	0.363
	45	0.640
	50	0.504

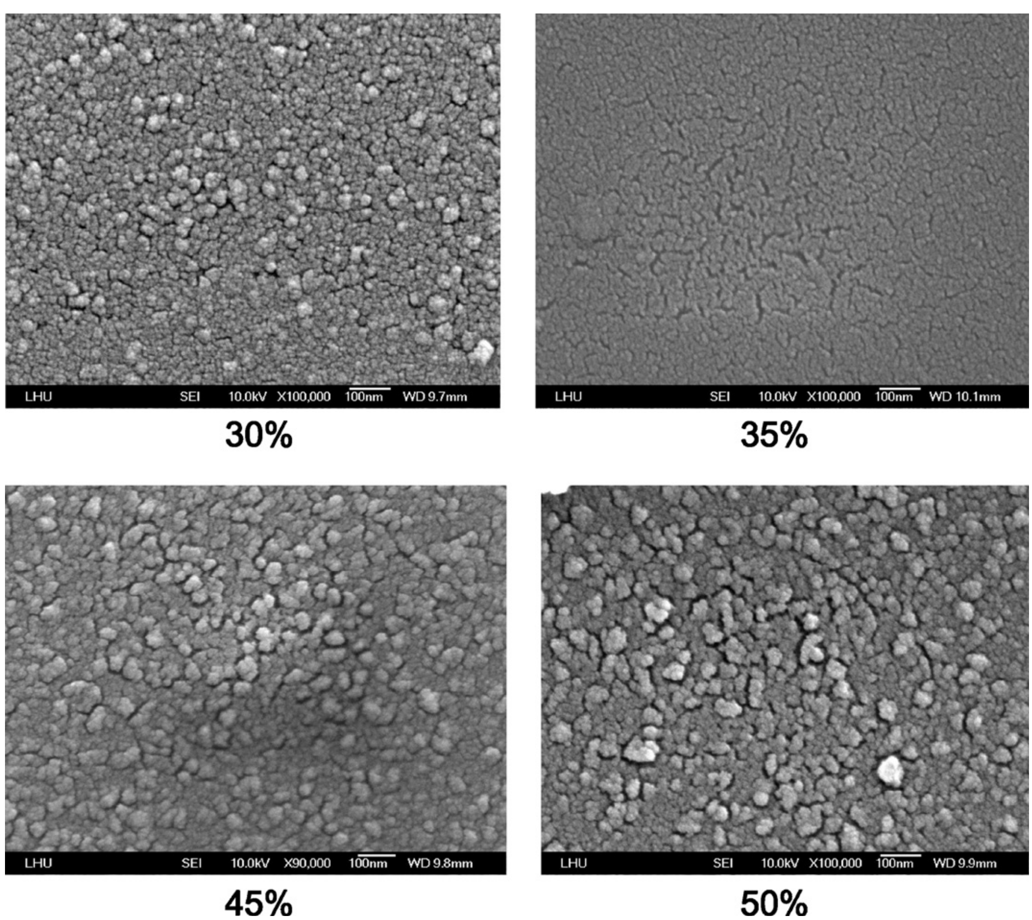

Fig. 5. The SEM surface morphologies of TiO_2 thin films deposited on the non-alkali glass by varying the argon–oxygen ratio in the range of 30, 35, 45 and 50%.

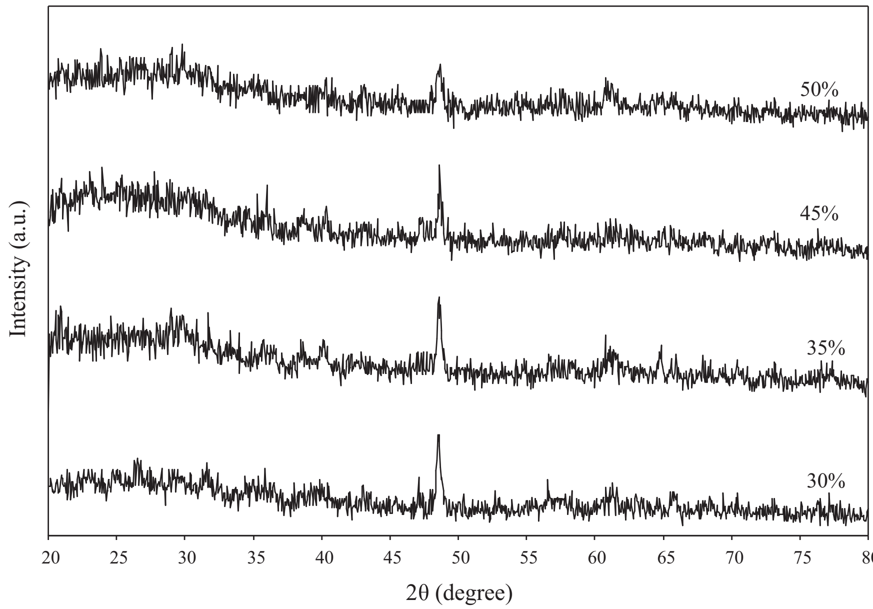

Fig. 6. The 3D AFM images of TiO_2 photocatalytic thin films deposited on the non-alkali glass by varying the argon–oxygen ratio in the range of 30, 35, 45 and 50%.

and 210 W. Moreover, the RF power (150 W), deposition time (3 h) and substrate temperature (80 °C) were kept constant, and the varied argon–oxygen ratio were 30, 35, 45 and 50%, respectively, the MB absorbance of as-deposited films is 0.617, 0.363, 0.640 and 0.504, respectively, as shown in Table 5. It was observed that the MB absorbance of TiO_2 films were different at various argon–oxygen ratios. The film deposited at 35% argon–oxygen ratio had the lowest MB absorbance of the four. Fig. 5 shows the SEM surface morphologies of TiO_2 thin films deposited on the non-alkali glass by varying the argon–oxygen ratio in the range of 30, 35, 45 and 50%. It was found that the film deposited at 35% argon–oxygen ratio had a

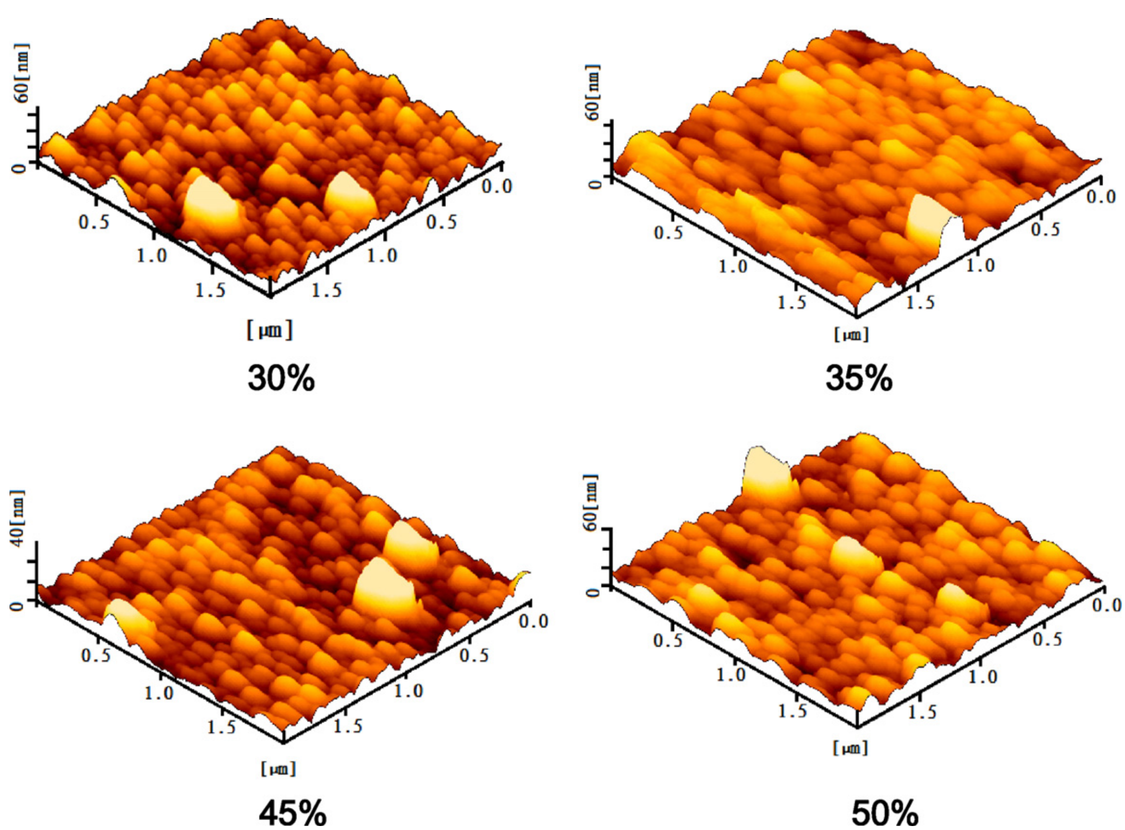

Fig. 7. The XRD patterns of TiO_2 thin films prepared at 30, 35, 45 and 50% argon–oxygen ratio.

Table 6
Effect of argon–oxygen ratio on surface roughness with the TiO_2 photocatalytic films.

Argon–oxygen ratio (%)	Surface roughness, Ra (nm)
30	2.224
35	1.538
45	3.467
50	2.575

fine and flat microstructure texture. Fig. 6 shows the XRD patterns of TiO_2 thin films by varying the argon–oxygen ratio. The XRD results showed that (2 0 0) preferred oriented anatase polycrystalline structure at 2θ–48.0°. Fig. 7 shows the 3D AFM images of TiO_2 photocatalytic thin films deposited on the non-alkali glass by varying the argon–oxygen ratio in the range of 30, 35, 45 and 50%. The film deposited at 35% argon–oxygen ratio had a granular microstructure and flat texture, had the lowest surface roughness as shown in Table 6.

4. Conclusions

Titanium dioxide (TiO_2) thin films were deposited on glass substrates by reactive RF magnetron sputtering under various conditions. The RF power was found to be the major factor affecting the MB absorbance, and the argon–oxygen ratio and deposition time were the second and third ranking factor, respectively. An optimal $A_3B_2C_1D_2$ parameter setting (150 W RF power, 3 h deposition time, 40% argon–oxygen ratio and 80 °C substrate temperature) to enhance TiO_2 films with high photocatalytic activities was proposed. The validation experiments show an improved photocatalytic activities of 5% when the Taguchi method is used. Besides, higher RF power and moderate argon–oxygen ratio produce a higher photocatalytic activity of TiO_2 films.

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