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Photodecomposition and bactericidal effects of TiO_2 thin films prepared by a magnetron sputtering

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TiO_2 thin films were deposited on either glass or Si wafer substrate using a reactive magnetron sputtering by varying the process conditions including $O_2/(Ar+O_2)$ ratio, working pressure, sputtering time and dc power, to examine the influence of surface morphology and crystallinity on photodecomposition efficiency of phenol and bactericidal activity of Escherichia coli (*E. coli 078*). The UV illuminated nanoporous anatase TiO_2 films with a higher roughness (205 Å) and crystallinity behaved as the best photocatalysts by 60% of phenol photodecomposition and 70% of bacteria cell (*E. coli*) destruction. Therefore, it was conceivable that the photocatalytic efficiency may be governed by the specific surface area, which was directly related to the crystallinity and the roughness of the films.

1. Introduction

TiO_2 thin film photocatalysts have been investigated extensively for environmental applications such as air, water treatment and deodorizer, because of its large specific surface area, strong oxidizing power, high photocatalytic activity, self-cleaning function, bactericidal and detoxification activity [1–3]. Among various film processes, such as thermal oxidation of metal [4], sol-gel and dip-coating [5, 6] and PECVD [7, 8], the use of a reactive magnetron sputtering [2] has many advantages over the other techniques because of low substrate temperature, high deposition rate and easy control of experimental parameters [9].

Our previous studies revealed that microstructure and morphology of TiO_2 thin film prepared by a reactive magnetron sputtering was primarily governed by $O_2/(Ar+O_2)$ ratio, working pressure, sputtering time and dc power, respectively [10]. The optimum sputtering condition for the nanoporous anatase TiO_2 film was 23% of $O_2/(Ar+O_2)$ ratio, 2×10^{-3} torr of working pressure, sputtering time (>10 min) and dc power (>150 W), respectively. Under this condition, an amorphous α-SiO_2 layer was firstly grown on Si substrate, an amorphous α-TiO_2 structure close to the α-SiO_2 phase was then formed and a columnar TiO_2 film normal to the amorphous α-TiO_2 was finally developed. The morphology of the film was a typical island structure consisting of fine particles of 10–30 nm. However, the influence of morphology on the photocatalytic activity of the films was not investigated.

It has been reported that TiO_2 under UV radiation can degrade most of the organic compounds [2–9], Escherichia coli (*E. coli 078*) and endotoxin efficiently from the cells [1] by its strong oxidizing power, resulting in bactericidal activities. The *E. coli 078* that cause disease in chickens are collectively known as avian pathogenic *E. coli* and mainly consist of enteropathogenic *E. coli* and enterotoxigenic *E. coli* serovars [11]. Endotoxins are part of the outer membrane of the lipopolysaccharide (LPS) cell wall of Gram-negative bacteria whether the organisms are pathogens or not. The biological activity of endotoxin is associated with the LPS. Toxicity is associated with the lipid component and immunogenicity is associated with the polysaccharide components. The cell wall antigens of Gram-negative bacteria are components of LPS. LPS elicits a variety of inflammatory responses in an animal. Because it activates complement by the alternative (properdin) pathway, it is often a part of the pathology of Gram-negative bacterial infections. Although endotoxin may be fatal to health due to pyrogenicity, lethal toxicity or Schwartzman reactivity, it can be used as means of immunoadjuvanticity and antitumor activity [1, 12, 13]. In the present study, TiO_2 thin film was

deposited on either glass or Si wafer substrates using a reactive magnetron sputtering technique to evaluate the influence of surface morphology and crystallinity on photodecomposition efficiency of phenol and survival ratio of *E. coli* (equivalent to the reciprocal of bactericidal activity).

2. Experimental procedures

The TiO_2 thin film was deposited on either glass or Si wafer substrate by using a reactive magnetron sputtering (Samhan Vacuum Tech. Co., Korea) with a titanium target of 99.9% purity [10]. The Si wafer and the glass were used as the substrate for XRD and photocatalytic activity measurements, respectively. Prior to the introduction of the sputtering gas, the pressure in the vacuum chamber was reduced to 5×10^{-6} torr. Presputtering was then performed for 5 min at a pressure of 1×10^{-2} torr, a power of 200 W and an Ar flow rate of 20 sccm to remove a small amount of carbon contamination as well as a moisture layer. Phase, morphology and microstructure of the films were analyzed by using XRD (MX-18HF, MacScience, Japan), AFM (M5, PSI, Japan) and SEM (Jeol 300FX, Japan). The optimum sputtering condition for the TiO_2 film, as shown in Fig. 1, was previously determined to be 23% of $O_2/(Ar+O_2)$, 2×10^{-3} torr of working pressure, sputtering time longer than 10 min and dc power higher than 150 W [10].

The extent of photodecomposition was investigated by monitoring the degradation of phenol (C_6H_5OH) using a spectrophotometer (UV-1601S, Shimadzu, Japan) to determine the concentration of phenol. The film was positioned in 300 ml (50 ppm) phenol solution in beaker. Black light UV lamp (365 nm) was illuminated along the vertical direction and air (30 cc/min) was supplied, which is shown in Fig. 2. The beaker was shaken to make oxygen in the air dissolve naturally in the solution and to increase the contact of the contaminants with the films sufficiently. The water cooling system was used to keep the solution at room temperature. The concentration of phenol was analyzed by withdrawing a sample of 10 ml periodically at 20 min interval.

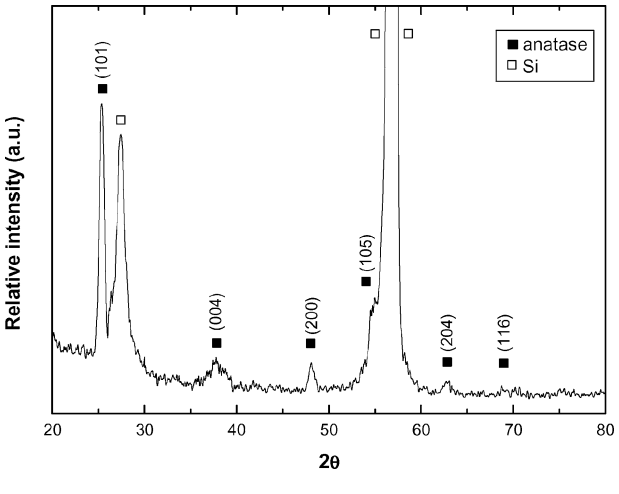

Figure 1 XRD patterns of TiO_2 thin films prepared on Si wafer. The films were sputtered for 30 min at a working pressure of 2×10^{-3} torr, 23% of $O_2/(Ar+O_2)$ ratio and 399 W.

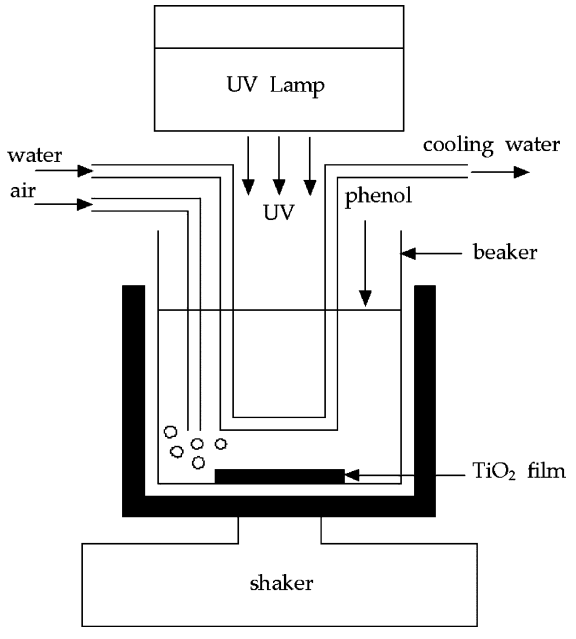

Figure 2 Schematic diagram of the photodecomposition experimental system.

The survival ratio of *E. coli* was examined by the standard plate count method to determine the efficiency of photocatalytic degradation, which counted the number of viable cells (colonies) in terms of colony forming units (CFUs), as reported by Sunada *et al.* [1]. CFUs are relatively undifferentiated cells of the same lineage that retain the ability to divide and cycle throughout postnatal life. Reagent endotoxin (*E. coli 078*), precultured in latose broth (LB) for 14–24 h at 37°C, was used. Both 10 ml of sterilized LB and 50 μl of *E. coli* were pipetted into the petri-dish, which was illuminated with UV lamp (350–400 nm) for 30 min. A 50 μl of *E. coli* suspension was sampled, and the appropriate dilutions were plated on LB medium and incubated for 24 h prior to analysis.

3. Results and discussion

Photodecomposition efficiency of phenol as a function of illumination time was evaluated for the TiO_2 thin films sputtered for 30 min at a working pressure of 2×10^{-3} torr, 399 W and various $O_2/(Ar+O_2)$ ratios (10%, 23%, 41%) and is shown in Fig. 3. At 10% of $O_2/(Ar+O_2)$ ratio, the degradation efficiency was less than 10% after 20 min UV illumination. However, the efficiency increased gradually as the illumination time rose. At 23% of $O_2/(Ar+O_2)$, the efficiency was superior to the film prepared at 10% of $O_2/(Ar+O_2)$ ratio, due to the improved crystallinity of the film [2, 10]. On the other hand, the photodecomposition effect was not observed for the film sputtered at 41% of $O_2/(Ar+O_2)$ ratio, probably due to the insufficient crystallization of the films caused by collisions as a result of higher oxygen partial pressure [2, 10]. This observation indicated that the photodecomposition efficiency was governed by the crystallinity and the surface morphology of the films because the films prepared at 23% ratio had

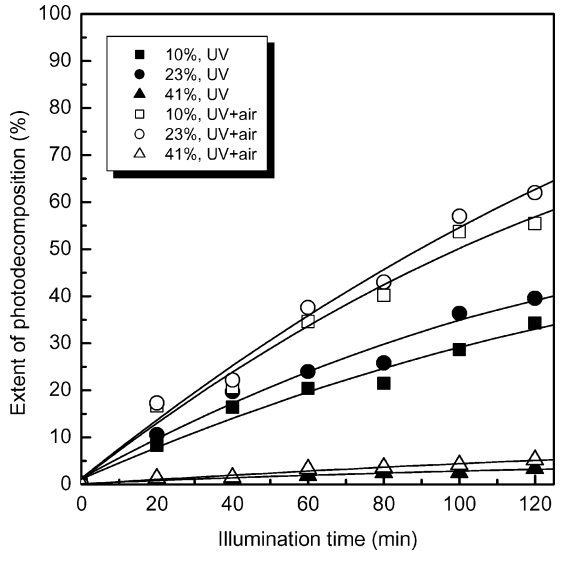

Figure 3 Photodecomposition of phenol for TiO_2 thin films with various $O_2/(Ar + O_2)$ ratios. The film was sputtered for 30 min at a working pressure of 2×10^{-3} torr and 399 W.

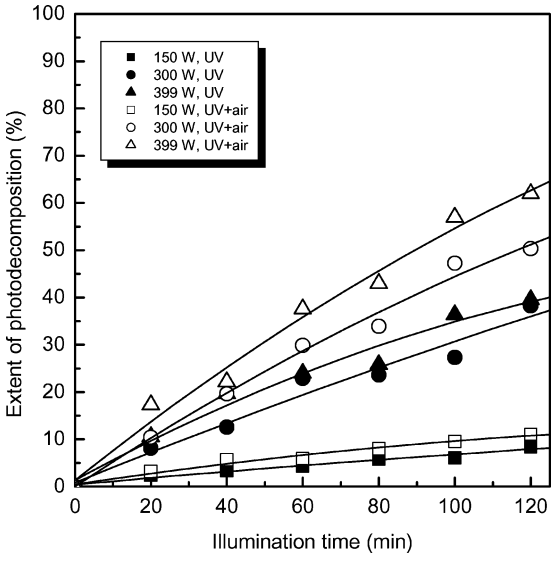

Figure 5 Photodecomposition of phenol for TiO_2 thin films with different power. The films were sputtered for 30 min at a working pressure of 2×10^{-3} torr and 23% of $O_2/(Ar+O_2)$ ratio.

excellent crystallinity and large specific surface area among the films investigated [10], which was prerequisite for the photodecomposition efficiency. The efficiency was further improved from 40 to 60% when UV radiation and air were used simultaneously, as verified in Fig. 3. The oxidation of hydroxyl radicals formed by TiO_2 photocatalyst under UV irradiation may be the main reaction of the photodecompositon of phenol [1, 9, 14]. The oxygen supply may delay the recombination time of electrons and holes, resulting in the longer lifetime of hydroxyl radicals and effective photocatalytic oxidation of the films.

The dependence of sputtering parameters, such as sputtering time and power, on the degradation of phenol was also investigated as shown in Figs 4 and 5. As both sputtering time and power increased, the photodecomposition efficiency of the films rose because of well-developed crystallinity (Fig. 1) of the TiO_2 films [10, 12]. The contribution of air flow to the efficiency of the films was also observed as expected.

The effect of working pressure on the photodecomposition of phenol was displayed in Fig. 6. The highest degradation efficiency (50%) of phenol was observed for the film prepared at a working pressure of 1×10^{-2} torr. Kim and coworkers [10] reported that the pressure (3×10^{-2} torr) was so high that the energy of the particles arriving at the substrate decreased due to collisions with other particles, resulting in the decrease in XRD peak intensity, the broadening of peak width and the extinction of XRD peaks except (101) and (105) planes. SEM results revealed that a typical island morphology consisting of fine particles (10–20 nm) was observed when the working pressure was 3×10^{-2} torr as demonstrated in Fig. 7c. However, TiO_2 particles with diameters of 20–30 nm and with the highest

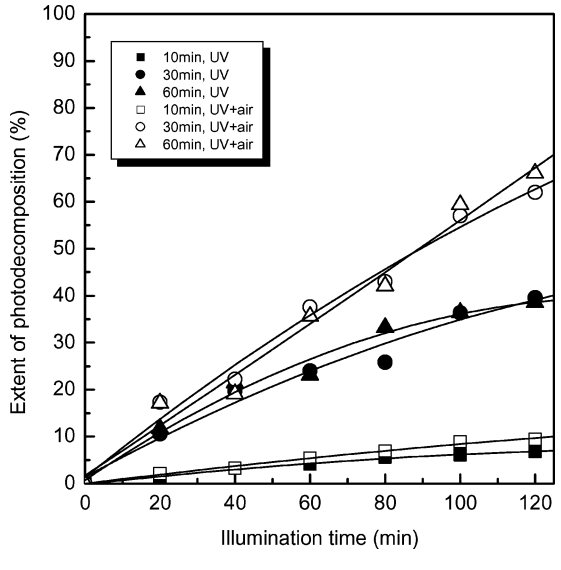

Figure 4 Photodecomposition of phenol for TiO_2 thin films with different sputtering time. The films were sputtered at a working pressure of 2×10^{-3} torr, 23% of $O_2/(Ar+O_2)$ ratio and 399 W.

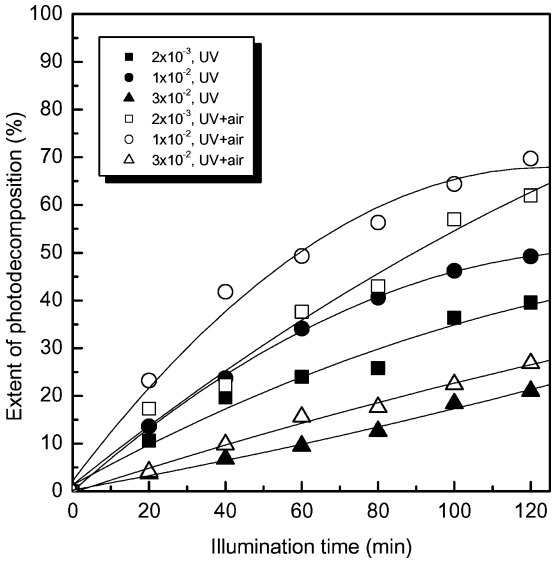

Figure 6 Photodecomposition of phenol for TiO_2 thin films with different working pressure. The films were sputtered for 30 min at 23% of $O_2/(Ar+O_2)$ and 399 W.

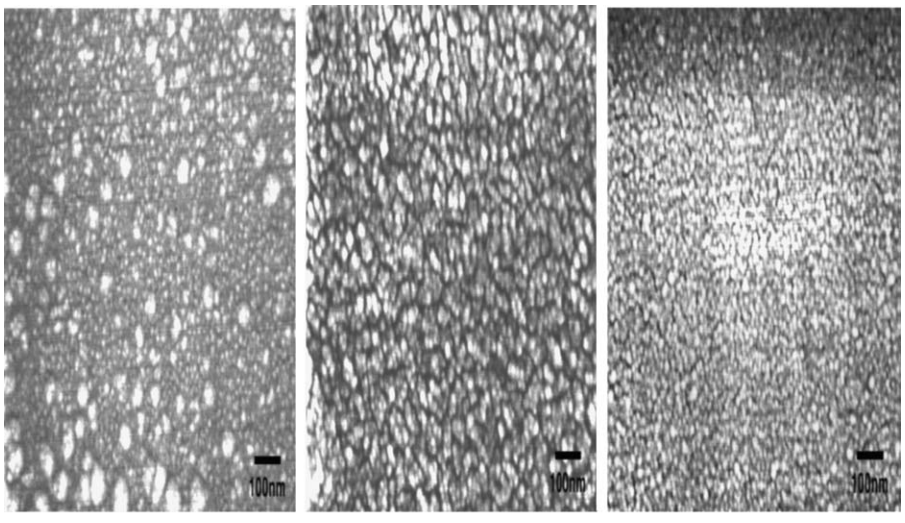

Figure 7 Photodecomposition of phenol for TiO_2 thin films with different working pressure: (a) 2×10^{-3}; (b) 1×10^{-2}; (c) 3×10^{-2} torr. The films were sputtered for 30 min at a 23% of $O_2/(Ar+O_2)$ and 399 W.

roughness (205 Å) were visible for the film sputtered at 1×10^{-2} torr (Figs 7b and 9a). It should be noted that the extent of photodecomposition is a strong function of the specific surface area, which is in agreement with the results given by Wang *et al.* [2]. Therefore, it is evident that the optimum condition of the TiO_2 films having the highest extent of photodecomposition was 23% of $O_2/(Ar+O_2)$ ratio, 1×10^{-2} torr of working pressure, 30 min of sputtering time and 399 W of dc power, respectively.

The survival ratio of *E. coli* was measured and depicted in Fig. 8. Specimens prepared by different processing conditions are listed in Table I. Under UV illumination without TiO_2 film, CFU was 3.94×10^2. CFU of 3.94×10^2 was assumed as 100, which is referred to as the control in Fig. 8. The survival ratio of *E. coli* decreased down to 30% when the illuminated TiO_2 films were used, implying that the bactericidal effect of TiO_2 films was pronounced because of the nullification of the viability of the bacteria and the destruction of the bacteria cell [1]. Sunada *et al.* [1] reported that the decomposition of endotoxin from the *E. coli* cells implied the destruction of the outer membrane of the *E. coli* cells. The bactericidal efficiency of the SG-4 specimen was above 70% as can be seen in Fig. 8. Therefore, the SG-4 specimen was the most effective to the phenol photodecomposition (60%) effect as well as the bactericidal activity (70%).

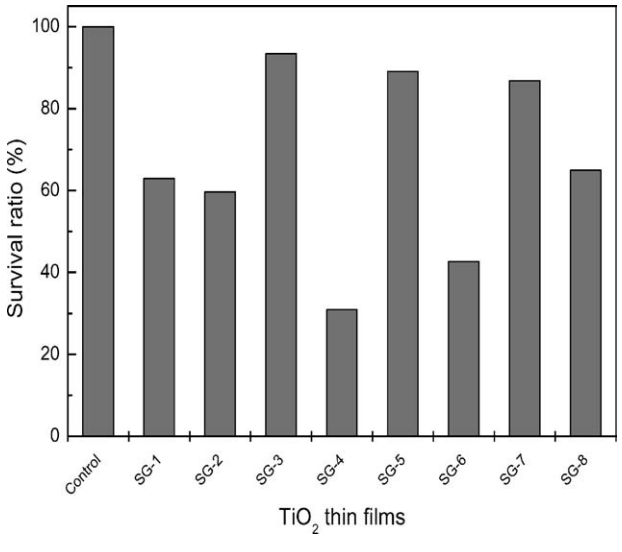

Figure 8 Survival ratio of *E. coli* for the illuminated TiO_2 thin films. Under UV illumination without TiO_2 film, CFU was 3.94×10^2. CFU of 3.94×10^2 was assumed as 100, which is referred to as the control.

The surface morphology and the roughness of TiO_2 film were examined by SEM and AFM to correlate the surface morphology and the photocatalytic efficiency, which is shown in Fig. 9. The SG-4 specimen (Fig. 9a) showed a typical island morphology consisting of nanoporous fine particles with a roughness of 205 Å. As the photocatalytic reactivity of the films decreased (Fig. 8, SG-4 → SG-2 → SG-7), the gap between the spherical particles was densified, indicating insufficient crystallization of anatase caused by the collisions (Fig. 9) [10]. The low mobility caused by a large number of oxygens and the subsequent collision and the inadequate energy (150 W, SG-7) for surface diffusion may result in the deficiency of crystallinity of the TiO_2 films. The surface roughness of the films became smooth and flat, resulting in a roughness of 65 Å for the SG-7 specimen. Therefore, it is conceivable that crystallinity and roughness of the films are critical to the photocatalytic efficiency.

TABLE I Specimens prepared by different processing conditions

Specimens	$O_2/(Ar+O_2)$ ratio (%)	Working pressure (torr)	Sputtering time (min)	dc power (W)
SG-1	10	2×10^{-3}	30	399
SG-2	23	2×10^{-3}	30	399
SG-3	41	2×10^{-3}	30	399
SG-4	23	1×10^{-2}	30	399
SG-5	23	2×10^{-2}	10	399
SG-6	23	2×10^{-3}	60	399
SG-7	23	2×10^{-3}	30	150
SG-8	23	2×10^{-3}	30	300

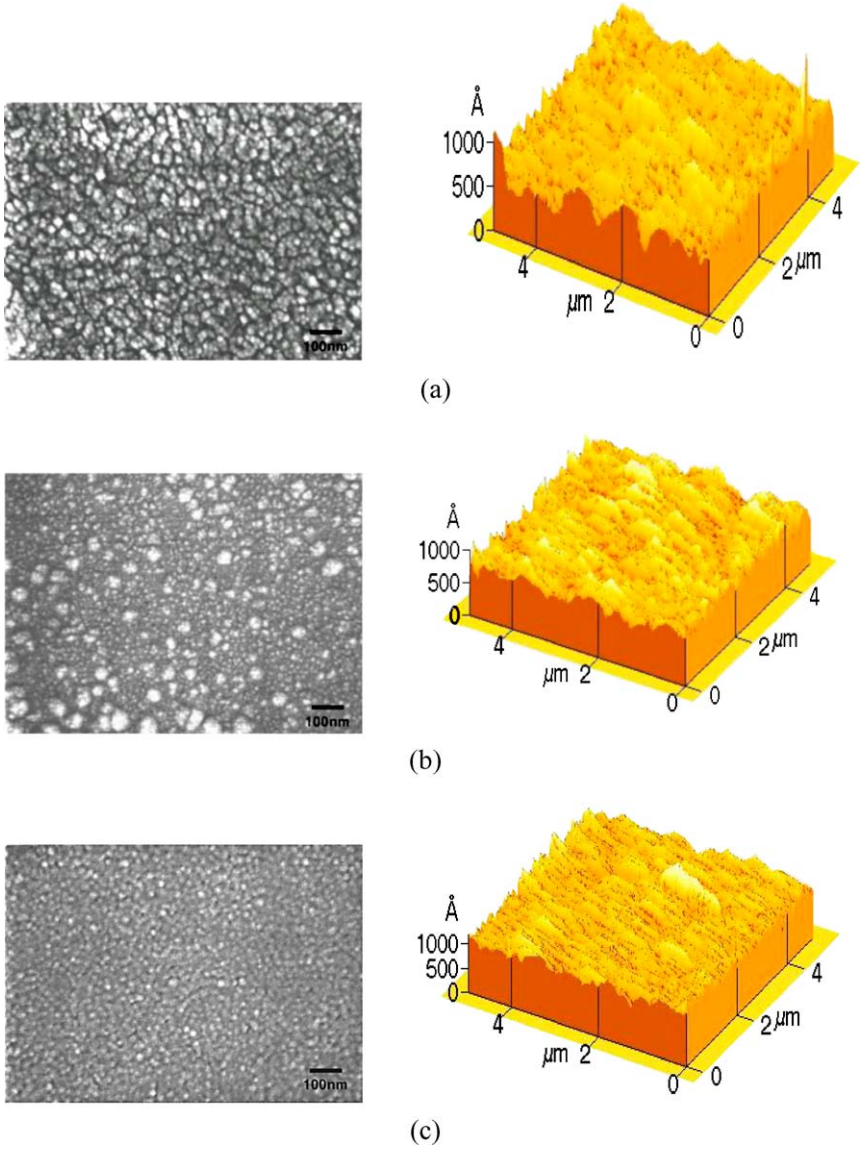

Figure 9 SEM and AFM images of TiO_2 thin films prepared by different conditions: (a) SG-4, (b) SG-2, and (c) SG-7.

4. Conclusions

Photodecomposition and bactericidal efficiency of the TiO_2 thin films prepared by sputtering were examined to determine the influence of surface morphology and crystallinity on photocatalytic effect of the films. TiO_2 thin films with a higher roughness and crystallinity showed the best photocatalytic efficiency and the optimum sputtering conditions of the TiO_2 films were 23% of $O_2/(Ar+O_2)$ ratio, 1×10^{-2} torr, 399 W and unheated substrate, respectively. Crystallinity and roughness of the films is likely to be functions of the photocatalytic efficiency, implying that the specific surface area may govern the photodegradation efficiency.

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