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Research Article

Influence of Annealing and UV Irradiation on Hydrophilicity of Ag-TiO_2 Nanostructured Thin Films

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Ag-TiO_2 nanostructured thin films with silver content of 5 vol% have been deposited on silicon, glass, and quartz substrates by RF magnetron sputtering and annealed in ambient air at 900°C for 15, 30, 60, 90, and 120 min. Their crystal structure, surface morphology, and hydrophilicity have been characterized by X-ray diffractometer, atomic force microscope, and water contact angle apparatus, respectively. The influence of annealing time and UV irradiation time on hydrophilic property of Ag-TiO_2 thin films have been studied in detail. It is shown that annealing time influences crystal structure of Ag-TiO_2 thin films. The unannealed film is amorphous and shows poor hydrophilicity. With the increase of annealing time from 15 to 120 min, the grain-size slowly increases and tends to uniformity. A suitable annealing time can significantly enhance the hydrophilic behavior of Ag-TiO_2 films. Water contact angle decreases with the increase of irradiation time. The mechanism of hydrophilicity has been proposed and can be attributed to the increase of oxygen anion radicals O_2^- and reactive center of surface Ti^{3+}.

1. Introduction

In 1997, Wang et al. [1] reported that ultraviolet illumination of TiO_2 surfaces could produce a highly hydrophilic surface which was named as super-hydrophilicity. Since then, hydrophilic titanium dioxide materials have been attracting attentions for many practical applications such as self-cleaning and antifogging materials. However, the hydrophilicity of TiO_2 thin films need to be further improved and enhanced for practical application. It was reported that the addition of noble metal to a photocatalytic semiconductor can change the semiconductor surface properties [2]. Although many attentions have been paid to the material doped with noble metals, such as Pt [3] and Au [4], to enhance photocatalytic activity of the TiO_2 thin films; a study on hydrophilic behavior of silver modified TiO_2 thin films has rarely been reported [5]. Ag-TiO_2 thin films can be prepared by numerous techniques such as chemical vapor deposition [6], ion assisted deposition [7], sol-gel processes [8], photoelectrochemical reduction method [9], and sputtering [10]. Among these techniques, RF magnetron sputtering method provides more advantages in controlling the microstructure and composition of the films. In a previous study [11], we found that a suitable amount (around 5 vol% Ag) of silver addition can significantly enhance the hydrophilic behavior of TiO_2 films. In this work, Ag-TiO_2 nanostructured thin films with silver content of 5 vol% were deposited on silicon, glass, and quartz substrates by RF magnetron sputtering at room temperature and annealed in ambient air at 900°C by changing annealing time. We report on the influence of annealing time and irradiation time of high-pressure mercury lamp on photo-induced hydrophilic property of TiO_2 thin films.

2. Experimental

2.1. Preparation of Samples. Ag-TiO_2 nanostructured thin films with silver content of 5 vol% were prepared by a high-vacuum multifunctional magnetron sputtering equipment (JGP560I) using Ag-TiO_2 composite targets ($\Phi = 60$ mm) on silicon ($10 \times 10\,mm^2$), glass ($10 \times 15\,mm^2$), and quartz ($25.1 \times 15.4\,mm^2$) substrates at room temperature. The targets were made [11] by sticking silver strips (99.99% purity) onto TiO_2 ceramic target (99.99% purity). Prior to deposition, the substrates were ultrasonically cleaned with acetone, absolute ethyl alcohol, and deionized water for 10 min, respectively. When the sputtering chamber was evacuated to a base pressure of 8×10^{-4} Pa, argon gas (99.99% purity) was introduced. Before the films were deposited, Ag-TiO_2 ceramic target was presputtered by argon ion for 3 min to weed out the surface adsorption. During sputtering, argon gas flow rate was kept at 30 sccm, the chamber pressure was maintained at 0.8 Pa, the sputtering power was 60 W, the distance between the substrate and the target was 60 mm, and the sputtering time was 24 min. The furnace was slowly ramped to 900°C with the sample inside it, and the as-deposited films were annealed in ambient air at 900°C for 15, 30, 60, 90, and 120 min.

2.2. Characterization. The thickness of the films with silver content of 5.0 vol%, measured by a surface profiler meter (Ambios XP-1), is about 150 nm. The crystallization behavior of the films was analyzed by an X-ray diffractometer (MAC M18XHF) using Cu kα radiation. Surface morphological feature was observed by an atomic force microscope (AJ-IIIa).

2.3. Hydrophilicity Measurements. The photo-induced hydrophilicity of the films was evaluated by screening photos and measuring the contact angle of water droplet during irradiation by a 36 W-high-pressure mercury lamp, which emits visible light of 404.7 nm, 435.8 nm, 546.1 nm and 577.0~579.0 nm, and ultraviolet light of 365 nm. The distance between the sample and the high-pressure mercury lamp was 8.0 cm. The intensity of light striking the films was about 20.2 mW/cm^2 (the intensity is the overall one and not only the UVA part, which is usually given and proposed to be in the range of 2 to 4 mW/cm^2 for photo-induced superhydrophilicity studies). The UV source was turned on with the water droplet on the film surface, and the film was tested for contact angle measurements after the irradiation was over. The hydrophilicity photos were obtained by a home-made water contact angle apparatus, which was performed at ambient air (25°C, relative humidity (RH) 60%). By measuring the diameter and height of the spherical crown of 3 μL droplet dropped on the surface of the films from 2 mm height, the water contact angle can be calculated from

$$\theta = \arctan \frac{4HL}{L^2 - 4H^2}, \tag{1}$$

where θ is the water contact angle, L is the diameter of the spherical crown, and H is the height of the spherical crown, as shown in Figure 1. The experimental error of the measurements was ±0.1°. Water droplets were placed at four different positions for one sample and the selected hydrophilicity photo was the one its water contact angle being relatively close to the average value.

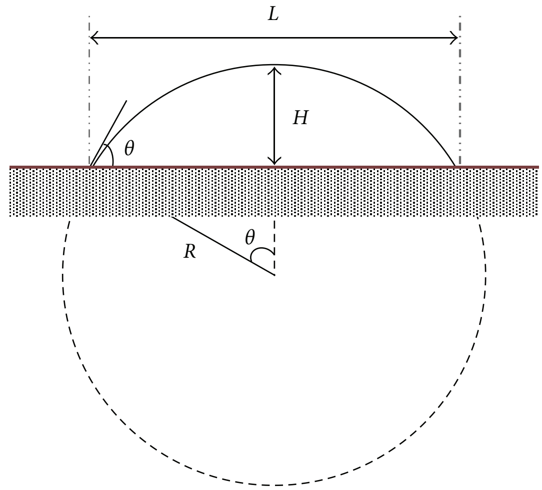

Figure 1: Geometric pattern for calculation of water contact angle.

3. Results and Analysis

3.1. X-Ray Diffraction (XRD) Analysis. Figure 2 shows XRD patterns of Ag-TiO_2 thin films with silver content of 5 vol% on silicon substrate (a) as-deposited and annealed at 900°C for (b) 15, (c) 30, (d) 60, (e) 90, and (f) 120 min. We can see that the crystal structure of the films changes with the increase of annealing time. The as-deposited Ag-TiO_2 thin film possesses just one slight diffraction peaks of 37.74 deg, which is corresponding to anatase (1 1 2). It is suggested that unannealed film is amorphous. When annealing time is 15 min, there are diffraction angles of 36.93, 64.31, 27.43, 33.13, 44.35, 48.14, 54.42, and 56.7 deg, which are corresponding to rutile (1 0 1), rutile (3 1 0), rutile (1 1 0), $Ag_2Ti_4O_9$ ($\bar{6}$ 0 3), Ag (2 0 0), anatase (2 0 0), rutile (2 1 1), and rutile (2 2 0), respectively. When annealing time increases to 30 min, the diffraction peaks of $Ag_2Ti_4O_9$ (0 0 4) at 31.04 deg and silver (1 1 1) at 38.07 deg appear, but anatase (2 0 0) disappears. When annealing time increases to 60 min, the diffraction peaks of rutile (1 0 1) and silver (2 0 0) disappear, the diffraction peak of rutile (3 1 0) obviously weakens, but the diffraction peaks of $Ag_2Ti_4O_9$ (2 0 5) at 43.78 deg and rutile (3 0 1) at 69.44 deg appear. When annealing time increases to 90 min, the diffraction peaks of rutile (1 1 1) at 41.87 deg, silver (2 0 0) at 44.16 deg, and AgO (2 2 0) at 53.47 deg appear, but $Ag_2Ti_4O_9$ (2 0 5) disappears. With further increase of annealing time to 120 min, the diffraction peaks of $Ag_2Ti_4O_9$ ($\bar{6}$ 0 3) and rutile (1 0 1) appear again, the diffraction peak of rutile (3 1 0) obviously boosts up again, but rutile (1 1 1), AgO (2 2 0), and rutile (3 0 1) disappear. Evidently, all these analyses suggest that annealing time influences crystal phases of Ag-TiO_2 thin films.

3.2. Atomic Force Microscope (AFM) Analysis. Figure 3 presents AFM images of Ag-TiO_2 thin films with silver content of 5 vol% on silicon substrate (a) as-deposited and annealed at 900°C for (b) 15, (c) 30, (d) 60, (e) 90, and (f) 120 min. From Figure 3(a), it can be seen that unannealed sample

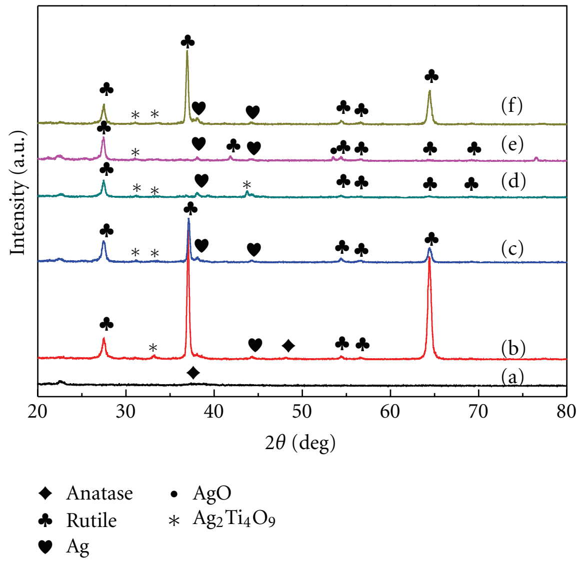

Figure 2: XRD patterns of Ag-TiO_2 films on silicon substrate (a) as-deposited and annealed at 900°C for (b) 15, (c) 30, (d) 60, (e) 90, and (f) 120 min.

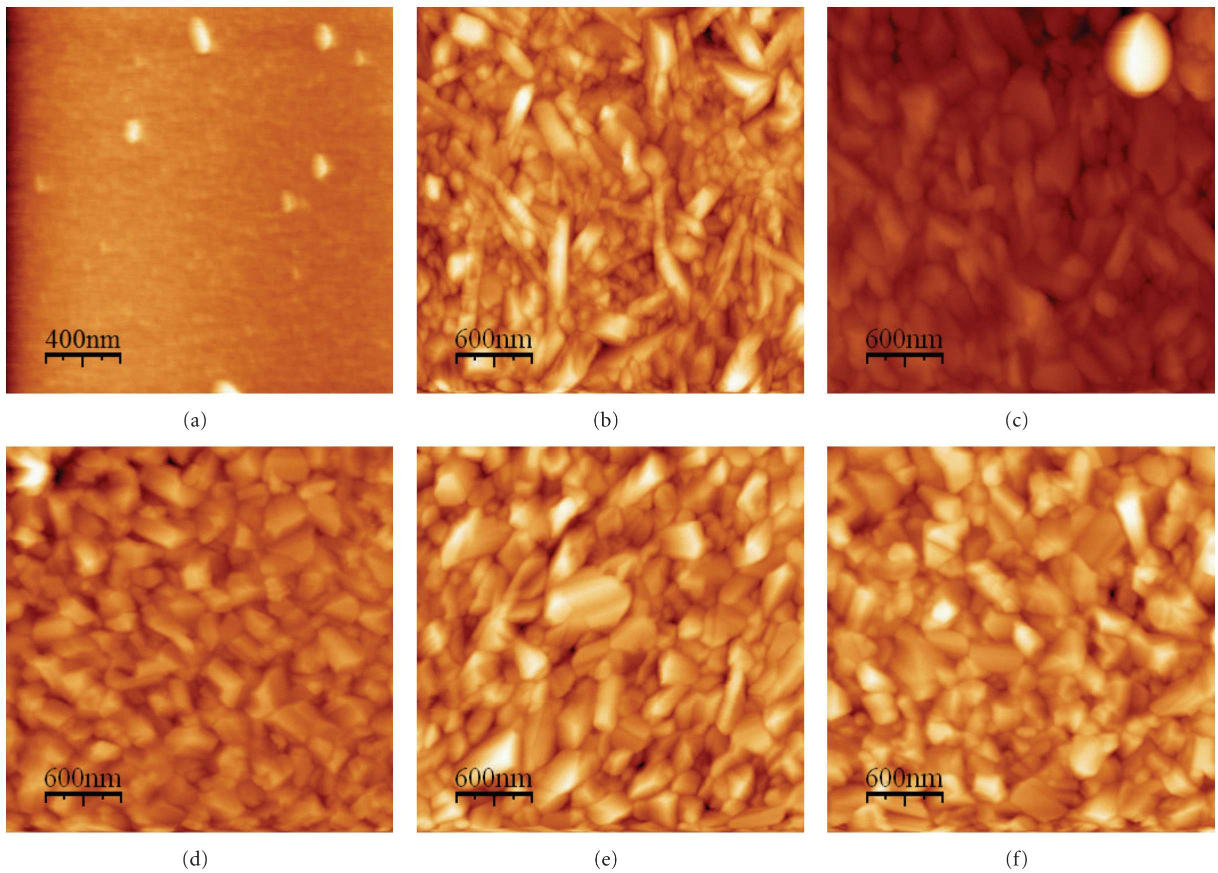

Figure 3: AFM images of Ag-TiO_2 films on silicon substrate (a) as-deposited and annealed at 900°C for (b) 15, (c) 30, (d) 60, (e) 90, and (f) 120 min.

has a small amount of grains, these grains maybe silver grains. Annealed at 900°C for 15 min, the surface of the film is rough and has much fine-grains. Combining XRD analysis with AFM image, it can be seen that Ag-TiO_2 thin film changing from amorphous to rutile phase but a small amount of anatase. With the increase of annealing time from 15 to 120 min, the grain-size slowly increases and tends to uniformity.

Figure 4 shows the influence of annealing time on grain size of Ag-TiO_2 films deposited on silicon substrate. It can be seen that average grain-size gradually increases with the increase of annealing time up to 30 min and then tends to a constant. The maximum grain-size sharply increases with the increase of annealing time up to 60 min and then slowly decreases. Since maximum grain-size increases apparently at long annealing time, growth of fine-grain is restricted, therefore minimum grain-size slowly decreases with increasing annealing time up to 90 min and then slowly increases to some extent. From Figure 4, it can be reasonably deduced that the maximum and minimum grain-sizes would eventually come closer to the value of average grain-size, at longer annealing times, that is, the Ag-TiO_2 films would achieve a narrow grain-size distribution at longer annealing times.

Figure 5 plots the influence of annealing time on area scans roughness of 5 vol% Ag-modified TiO_2 thin films deposited on silicon substrate. From Figure 5, the roughness increases with the increase of annealing time up to 60 min, which is possibly because of the growth of fine-grain, but then abruptly turns around with the increase of annealing time to 90 min, which is possibly because of anatase changes into rutile phase completely annealed at 900°C for 90 min. With further increase of annealing time to 120 min, the roughness increases again to some extent.

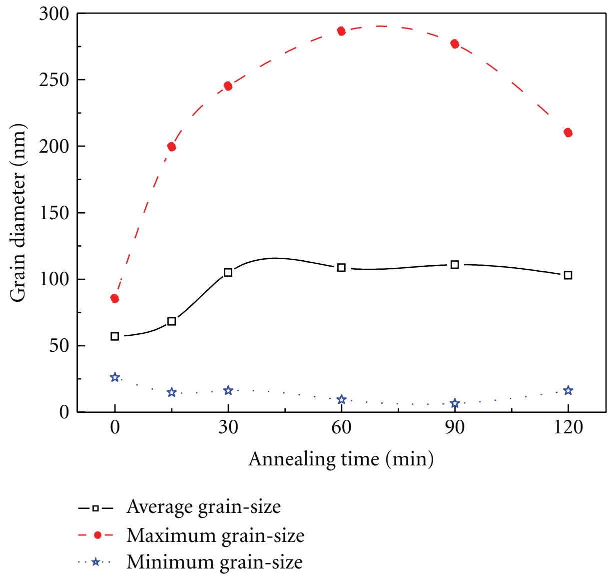

Figure 4: Influence of annealing time on grain-size of Ag-TiO_2 films deposited on silicon substrate.

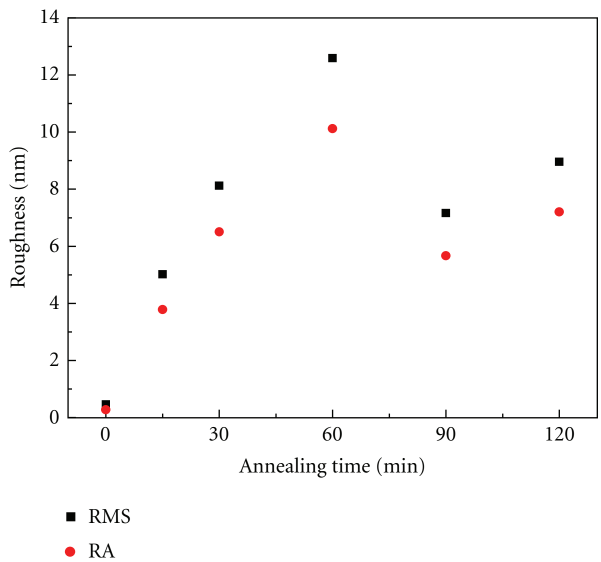

Figure 5: Influence of annealing time on area scans roughness of Ag-TiO_2 films deposited on silicon substrate. (Note: RMS stands for root-mean-square roughness and RA stands for arithmetic mean roughness.)

3.3. Hydrophilicity. Figure 6 shows hydrophilicity photos of 5 vol% Ag-modified TiO_2 thin films on silicon substrate (a) as-deposited and annealed at 900°C for (b) 15, (c) 30, (d) 60, (e) 90, and (f) 120 min. Relationship of water contact angle of the films and annealing time is shown in Figure 7. From Figures 6 and 7, it can be seen that un-annealed sample possesses the biggest water contact angle of 81.3°. When annealed at 900°C for 15, 30, 60, 90 and 120 min, the water contact angles of the films are 59.0, 64.5, 62.7, 62.4, and 62.2°, respectively. Obviously, water contact angle slowly decreases and tends to a constant with the increase of annealing time. Therefore the optimal annealing time for hydrophilicity is around 15 min. Combine XRD with AFM analysis, it can be seen that amorphous shows poor hydrophilicity. With the increase of rutile phase and roughness, the hydrophilicity enhances to some extent. The anatase/rutile mixture obtained by annealing at 900°C for 15 min may induce optimal hydrophilicity.

Figure 8 shows hydrophilicity photos of as-deposited 5 vol% Ag-modified TiO_2 thin films on (a) glass, (b) silicon, and (c) quartz substrate as a function of irradiation time of high-pressure mercury lamp. Figure 9 presents the relationship of UV irradiation time and water contact angle of as-deposited Ag-TiO_2 thin films with silver content of 5 vol% on (a) glass, (b) silicon, and (c) quartz substrate. From Figures 8 and 9, we can see that water contact angle decreases with the increase of irradiation time, which means the surface converts to hydrophilic state. And it seems that for the films deposited on quartz substrate, the high hydrophilic property could be achieved easily after irradiation of high-pressure mercury lamp.

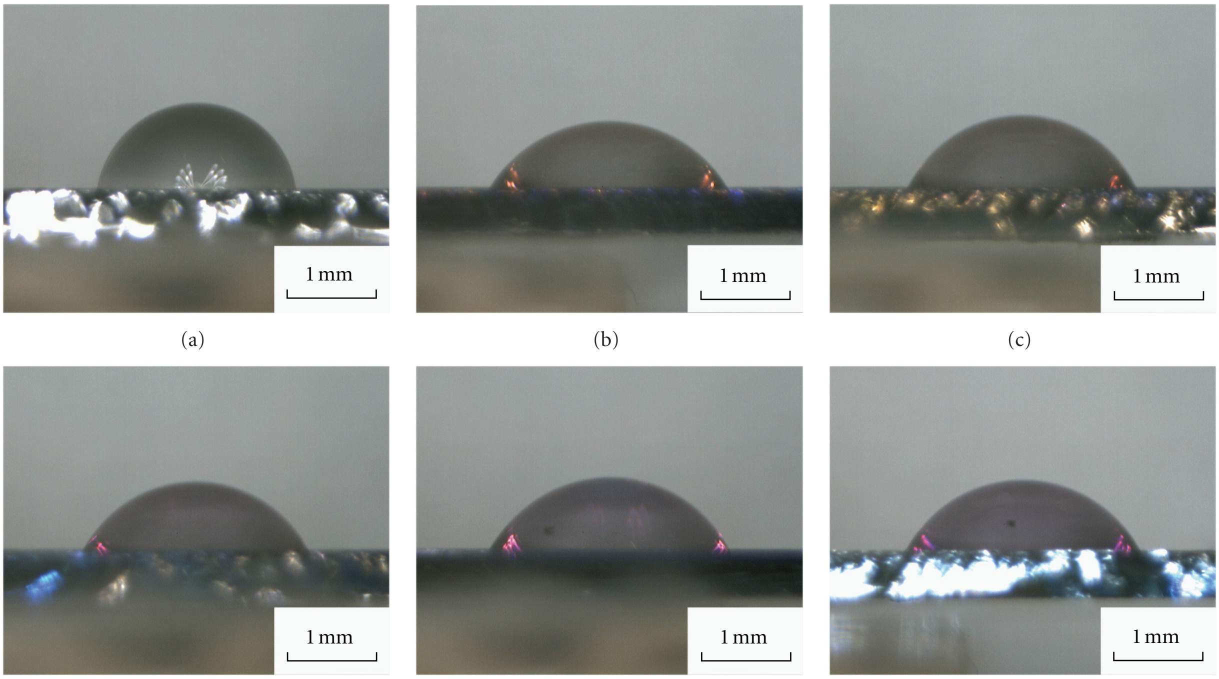

FIGURE 6: Hydrophilicity photos of Ag-TiO_2 films on silicon substrate (a) as-deposited and annealed at 900°C for (b) 15, (c) 30, (d) 60, (e) 90, and (f) 120 min.

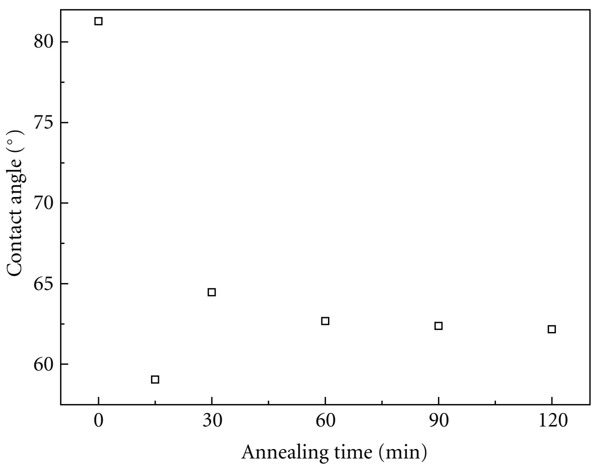

FIGURE 7: Relationship of annealing time and water contact angle of Ag-TiO_2 films on silicon substrate.

The mechanism of photo-induced hydrophilicity of TiO_2 has been intensively investigated by many researchers [12, 13]. As a result, it was revealed that preferential adsorption of water molecules on the photo-generated surface defective sites led to the formation of highly hydrophilic TiO_2 thin films surface [14]. Photo-generated electron-hole pairs could either recombine or move to the surface to react with species adsorbed on the surface. Some of the electrons react with lattice metal ions Ti^{4+} to form Ti^{3+} defective sites [15]. The formation processes of defective sites on TiO_2 surface can be expressed [16] as follows:

$$\begin{gathered} TiO_2 \xrightarrow{h\nu} e^- + h^+, \\ O^{2-} + 2\,h^+ \longrightarrow \frac{1}{2}O_2 + V_O \text{ (oxygen vacancy)}, \\ Ti^{4+} + e^- \longrightarrow Ti^{3+} \text{ (surface trapped electron)}. \end{gathered} \tag{2}$$

In air, the surface trapped electrons tend to react immediately with O_2 adsorbed on the surface to form ${O_2}^-$ or ${O_2}^{2-}$ ions. Meanwhile, water molecules may coordinate into the oxygen vacancy sites (V_O), which leads to dissociative adsorption of the water molecules on the surface [17, 18]. This process gives rise to the increase of hydroxyl content on the illuminated TiO_2 thin film surfaces. It was likely that the number of defective sites increases with the increase of annealing time and irradiation time and these led to the improvement of hydrophilicity. Water contact angle measurements show that the amount of defective sites increases with the increase of annealing time up to 15 min and then slowly increases and gradually tends to a constant.

4. Conclusion

In summary, water contact angle of the films decreases with the increase of annealing time and UV irradiation time. The optimal annealing time for hydrophilicity is around 15 min. With the increase of annealing time from 15 to 120 min, average grain-size slowly increases and tends to uniformity.

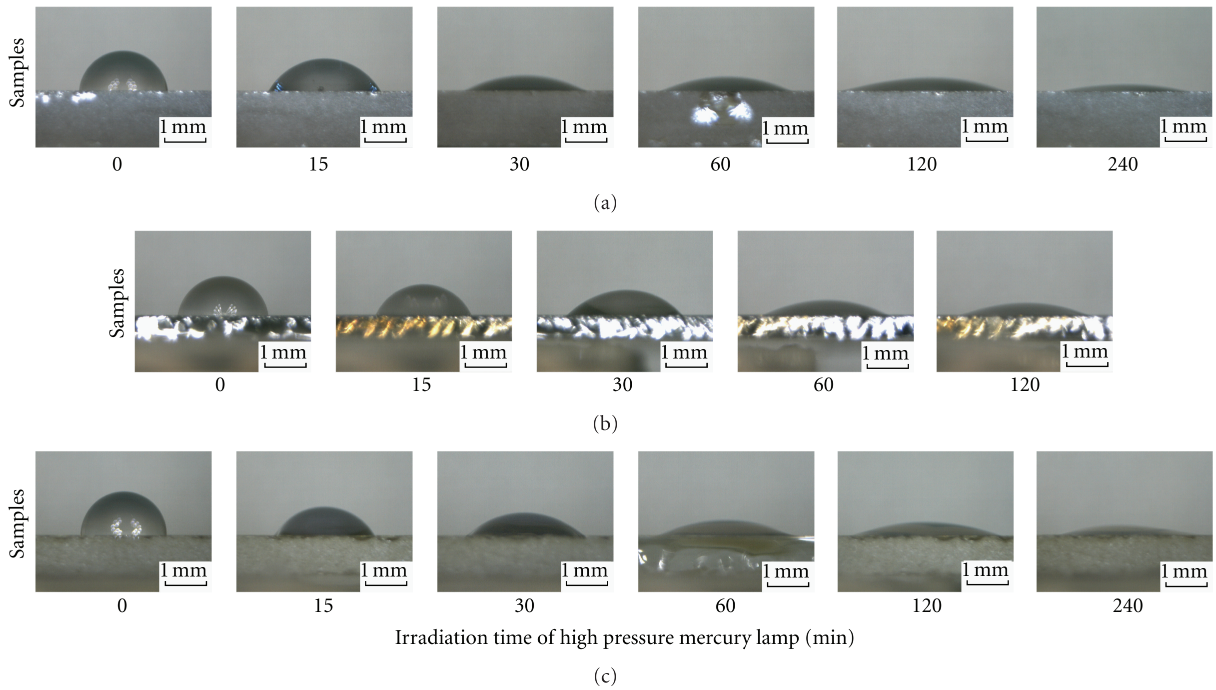

Figure 8: Hydrophilicity photos of as-deposited Ag-TiO_2 films on (a) glass, (b) silicon, and (c) quartz substrate as a function of irradiation time of high pressure mercury lamp.

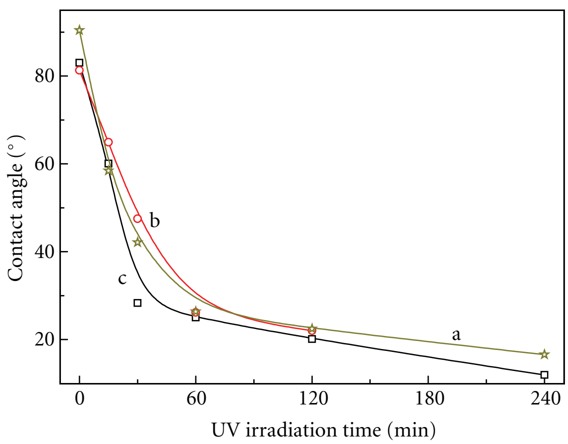

Figure 9: Relationship of UV irradiation time and water contact angle of as-deposited Ag-TiO_2 films on (a) glass, (b) silicon, and (c) quartz substrate.

The roughness increases with the increase of annealing time up to 60 min, which is possibly because of the growth of fine-grain, but then abruptly turns around with the increase of annealing time to 90 min, which is possibly because of anatase changes into rutile phase completely annealed at 900°C for 90 min. With further increase of annealing time to 120 min, the roughness increases again to some extent. The anatase/rutile mixture obtained and annealed at 900°C for 15 min may induce optimal hydrophilicity. The increase of O_2^- and Ti^{3+} on the films' surface are the main causes for enhancing hydrophilicity of Ag-TiO_2 films.

Acknowledgments

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