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Synthesis of TiO_2 Films on Glass Substrates for Hydrophilicity Applications

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In this work, the TiO_2 films were deposited on glass substrates using a paste mixture by spin coating method and heat treatment at temperature of 400°C and 500°C for 3hrs, respectively. The crystal structure, optical property, composition and surface morphology of the films thus prepared were characterized by x-ray diffractometry (XRD), UV–Vis spectra, X-ray photoelectron spectroscopy (XPS) and atomic force microscope (AFM). In addition, the hydrophilicity of the films was evaluated by optical contact angle measurements (OCA). The XRD results indicate that the sample post-annealed at 500°C has higher quality of crystallization. The UV–Vis spectrum shows that absorptions of the three samples in visible light region are almost the same. The band gaps of samples without post-anneal, post-annealed at 400°C and 500°C calculated from UV-Vis spectra is 3.1eV, 3.17eV and 3.19eV, respectively. The surface of sample annealed at 500°C is smoothed, post-anneal also increases the size of particles and changes the shape of particles. Then, the sample post-annealed at 500°C has better hydrophilicity than the other samples.
Key words: TiO_2 film, hydrophilicity, optical contact angle (OCA).

1. INTRODUCTION

It is well known that, when exposed to UV radiation, titanium oxide (preferentially in its anatase polymorphic form) shows photocatalytic properties. Since Fujishima and Honda [1] discovered that a TiO_2 electrode can decompose water into hydrogen and oxygen under UV light in 1972, various applications based on the photo-induced activity of TiO_2 have been demonstrated. The self-cleaning property is one of the most fascinating applications. It is based on two kinds of photo-induced mechanisms, namely a photocatalytic oxidative decomposition and/or photo induced hydrophilicity, which arise both from the photo-generation of electron-hole pairs. The former is caused by active oxidizing radicals ($\cdot O_2^-$, $\cdot OH$) able to decompose the organic compounds adsorbed at the TiO_2 surface. These radicals are formed by redox reactions with photoelectrons and holes generated by the titanium oxide under UV irradiation. The latter is based on the trapping of adsorbed water on surface oxygen vacancies (Vo), which are created by a photo-reduction of TiO_2 ($Ti^{4+} + e^- \rightarrow Ti^{3+}$ and $2O^{2-} + 2h^+ \rightarrow O_2 + 2Vo$), resulting in the formation of a superhydrophilic surface [2,3].

The previous studies have found that the TiO_2 film will change from hydrophobicity to hydrophilicity after irradiated by UV light, which can be used to anti-wetting, anti-frost, self-cleaning, and anti-fogging [4,5]. So far, the way to use this property of TiO_2 is mainly TiO_2 film coating on various materials, and the main fabrication methods are PVD (physical vapour deposition) [6], CVD (chemical vapour deposition) [7], SPD (spray pyrolysis deposition), and etc.[8,9].

In this work, transparent TiO_2 films have been prepared with paste solution by spin-coating on glass substrate. And the effect of heat treatment temperature on the photo-induced hydrophilic properties of the prepared TiO_2 films have been investigated

2. EXPERIMENTAL

2.1 Sample preparation

Using titanium lactate, isopropyl alcohol (IPA) and urethane acrylic oligomer as titania source, solvent and stabilizer, respectively. The concentration of titanium deoxide was 5wt%, and the quantity ratio of titanium lactate and IPA was maintained to be 31:57 in weight. The mixed solution was prepared at room temperature and stirred for 1h to yield a clear and homogeneous solution. Then, it was coated on quartz glass substrate at 3000rpm for 60s. The precursor films were heated at 200°C for 10min to remove the solvent and organic residuals. The coating and heating process repeated for 10 times. The sample without post-anneal is named as sample A. The prepared films were then post-annealed at 400°C (sample B) and 500°C (sample C) for 3h in the air, respectively.

2.2 Characterizations

The crystalline phase of TiO_2 films was studied by X-ray diffraction (XRD) with Cu Ka radiation. The optical properties of prepared samples were investigated by UV-Vis spectra (V-570, JASCO) at room temperature. The composition and ratio of Ti/O were measured by XPS (SSX-100, Surface Science Instruments). The surface morphology was observed by atomic force microscope (AFM, JEOL, JSPM-5200TM).

The surface hydrophilicity was evaluated by the in-time variation of the water contact angle, which was

performed at ambient conditions (i.e., 298K) using a commercial contact angle meter (OCA20, dataphysics). The ultraviolet (UV) illumination was carried out using a 9W Handy UV lamp (LUV-6) with the wave wavelength 365nm and the distance between the UV light and the sample was 10 cm.

3. RESULTS AND DISCUSSION

3.1 XRD pattern

XRD patterns of samples without post-annealed (a), post-annealed at 400°C (b) and 500°C (c) are shown in Fig. 1. The film without post-anneal shows only a broad peak and is amorphous. TiO_2 films post-annealed at 400°C and 500°C show the 101 and 004 peaks of anatase phase. However peaks of sample annealed at 400°C are very weak. The sample post-annealed at 500°C has the higher crystallinity. The post-annealing at 500°C benefits the crystal growth of anatase-type TiO_2 film.

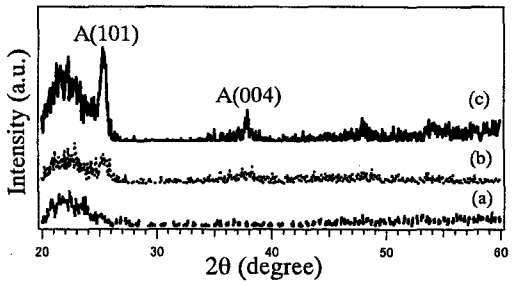

Fig. 1 XRD patterns of TiO_2 films.
(a) sample A, (b) sample B, and (c) sample C

3.2 UV–Vis spectra

Fig. 2 shows UV–Vis spectra of three prepared TiO_2 films in the wavelengths range from 250nm to 700nm. The absorbance in the visible light range (>500nm) is almost the same for all three samples. For the two samples post-annealed at 400 and 500°C, the absorbance is almost the same in the whole wavelength range. The absorption edge of sample post-annealed at 500°C is sharpest, which should attribute to the higher quality of crystallization. And that of sample without post-anneal is smoothest, it should be due to its lowest quality of crystallization. That agrees with the result of XRD. So the quality of crystallization can influence the UV-Vis absorption. The band gaps of samples without post-anneal, post-annealed at 400°C and 500°C calculated from UV-Vis spectra is 3.1eV, 3.17eV and 3.19eV, respectively.

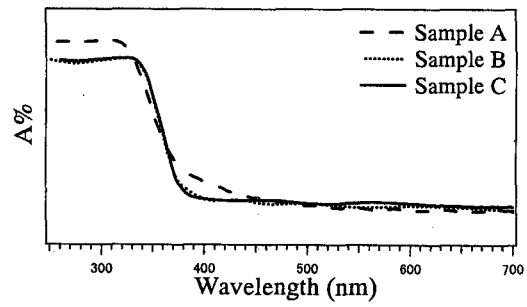

Fig.2 UV-Vis spectra of samples

3.3 XPS spectra

XPS analyses are shown in Fig. 3(a) and Fig. 3(b). In order to further characterize the oxide films, the samples of titanium dioxide film are sputtered with Ar^+ ions for 5min. In the survey spectra, peaks assigned to C(1s), Ti(2p) and O(1s) are observed. The C(1s) peaks should originate from the residual organics. For both samples, the spin orbit components of Ti(2p) state are clearly seen as two peaks at 459.3eV for $Ti(2p_{3/2})$ and 465.0eV for $Ti(2p_{1/2})$, respectively. The Ti (2p) peaks of sample C are stronger than that of sample A, which may be due to the sample C has higher quality of crystallization. The result agrees with the result of XRD. The area ratio between the Ti and O components of sample A and sample C is 3.0 and 1.7. The reduction of the ratio should attribute to the evaporation of residual organics in sample A.

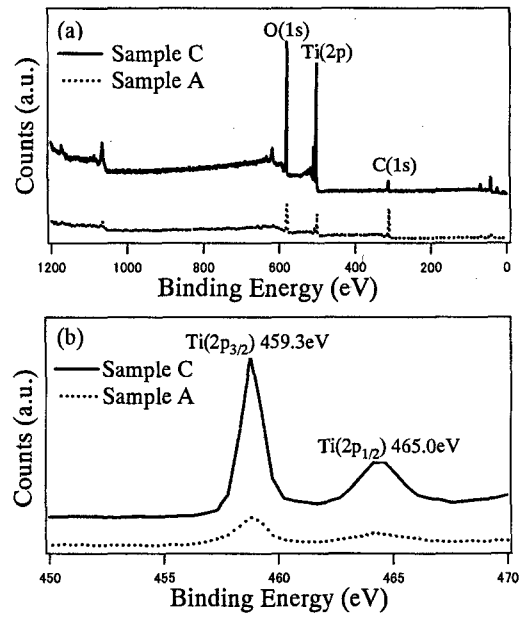

Fig.3 XPS spectra of TiO_2 films (sample A and C). (a) survey spectra, (b) high resolution spectra for Ti(2p) region

3.4 AFM images

AFM images of the samples without post-anneal (sample A) and post-annealed at 500°C (sample C) are shown in Fig. 4. It can be found that, in scanned area, the surface roughness of sample A and C is 96nm and 50nm, respectively. The particle shape of sample A and C are oval and spherical-like, respectively. The average particle sizes are about 30nm and 80nm, respectively. So the surface of sample annealed at 500°C has been smoothed, post-annealing also increases the size of particles and changes the shape of particles.

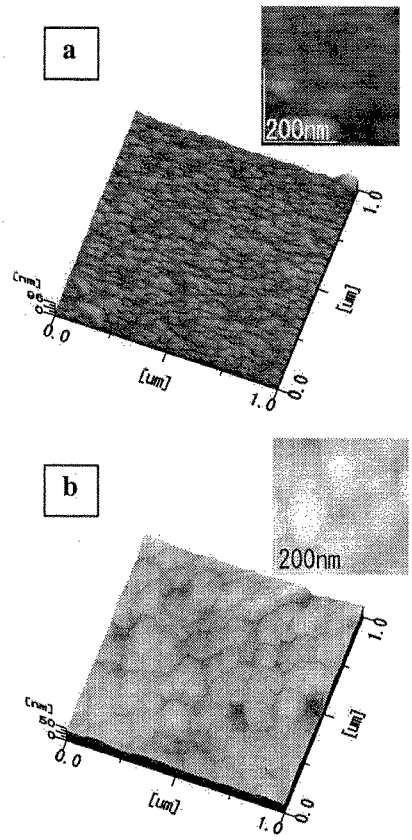

Fig. 4 AFM images of (a) sample A and (b) sample C.

3.5 OCA measurement

The effects of UV irradiation time on the OCA of prepared samples are shown in Fig. 5 and 6. Before the UV irradiation, the OCA of film without post-anneal (A), post-annealed at 400°C (B) and 500°C (C) are 70°, 30°, 25°, respectively. The UV irradiation for the sample A does not cause so much reduction of OCA; from 70° to 60° after the 60 min UV irradiation. On the other hand, for sample B and C, the UV irradiation for 30 min causes the large reduction of OCA; from 30° to 15° for sample B and from 25° to 11° for sample C. After the irradiation for 60 min, the OCA is reduced to be 10° for both samples B and C. It can be concluded that well crystallized anatase type TiO_2 films show better hydrophilicity.

Sample	Before UV irradiation	After UV irradiation for 1h
A		
B		
C		

Fig. 5 Images showing effect of UV irradiation on OCA

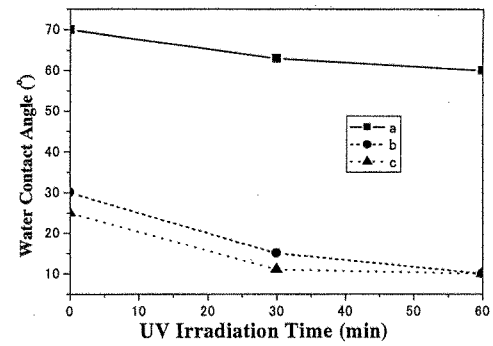

Fig. 6 Water contact angle variations following the UV irradiation time for the films. (a) sample A, (b) sample B and (c) sample C

4. CONCLUTIONS

Crystalline titanium oxide films with hydrophilic properties were prepared on glass substrate using a paste routes. The results suggest that hydrophilic properties primary require a good film crystallization degree. XRD and XPS results indicate that films deposited on glass during a high temperature heat-treatment (500°C) exhibit better crystallization than the others. The UV–Vis spectrum shows that the absorption edge of sample post-annealed at 500°C is sharpest, which should attribute to the higher quality of crystallization. And that of sample without post-anneal is smoothest, it should be due to its lowest quality of crystallization. The surface of sample annealed at 500°C has been smoothed. The post-annealing increases the size of particles and changes the shape of particles. Then, the sample post-annealed at 500°C has better hydrophilic than the other samples.

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