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Improvement in the heat-induced hydrophilicity of TiO_2 thin films by doping Mo(VI) ions

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Abstract

Undoped and Mo ions doped TiO_2 thin films were prepared by a sol–gel method on soda lime glass substrates. The obtained films were characterized by ultraviolet–visible spectroscopy, X-ray diffraction and atomic force microscopy. The heat-induced hydrophilicity of the film is enhanced by doping Mo(VI) ions. After being heated at 400 °C for 1 h, the 0.75 wt.% Mo(VI)-doped TiO_2 film shows superhydrophilicity.

Keywords: Titanium dioxide; Surface morphology; Superhydrophilicity; Molybdenum

1. Introduction

Since Fujishima and Honda found the electrochemical photolysis of water at a titania semiconductor electrode in 1972, the application of titania has been paid much attention [1]. As for titania thin films, there are actually two distinct phenomena: one is the well-known photocatalytic phenomenon, which leads to the decomposition of organic compounds, sterilization, cancer treatment, etc.; the other is superhydrophilicity which was actually discovered by accident in work that was being carried out at the laboratories of TOTO Inc. in 1995. It was found that, if a TiO_2 film is prepared with a certain percentage of SiO_2, it acquires superhydrophilic properties after ultraviolet (UV) light illumination [2]. The superhydrophilic surface could be obtained by UV light irradiation, high-temperature annealing and Ar^+ sputtering in a vacuum [3]. Many transition metal/metal ion dopants have been investigated for TiO_2 [4–9], but most of such works were concentrated on improving the photocatalytic activity and on understanding the mechanisms, while few works were reported on the change of hydrophilicity of a TiO_2 film with the addition of metal ions. In this paper, we reported the effect of doping different amounts of Mo ion on hydrophilicity of TiO_2 thin films induced by high-temperature annealing.

2. Experimental details

2.1. Preparation of TiO_2 thin films

Colloidal titania was prepared by a sol–gel method. In a typical experiment, 0.30 g Poly(*N*-vinyl-2-pyrrolidone) (PVP, K-30, average molecular weight 40,000) was added to a 50 mL of distilled water and the pH of the solution was adjusted to 1.5 with nitric acid. Then, a desired volume (e.g., 0.18 mL for 0.75 wt.% Mo(VI) doping) of 0.02 g/mL $(NH_4)_2MoO_4$ solution was added. The obtained mixture was added dropwise to a 21 mL of $Ti(OBu)_4$ anhydrous isopropanol solution (volume ratio $Ti(OBu)_4$/isopropanol = 1:20) under vigorous stirring at room temperature for about 6 h, resulting in a transparent colloidal solution. Likewise, a set of transparent TiO_2 colloids with different amounts of Mo ions were prepared by varying the volume of $(NH_4)_2MoO_4$ solution added in the above preparation.

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A cleaned substrate (soda lime glass, quartz glass and single crystalline silicon) was dipped into a transparent colloid prepared above for half an hour. Following that, the substrate was withdrawn at a constant rate of 1.5 mm s^{-1}. After drying in air, it was finally calcined at 200, 300 or 400 °C for 1 h.

2.2. Characterization

Ultraviolet–visible (UV–Vis) absorption spectra of the TiO_2 thin films were measured by a TU-1800 UV–Vis spectrophotometer. X-ray diffraction (XRD) was performed on a DMAX-3C Rigaku X-ray diffractometer with Cu Ka radiation, where the accelerating voltage and the applied current were 30 kV and 25 mA, respectively. The particle size and uniformity of the prepared TiO_2 thin films with and without Mo doping were characterized by an atomic force microscopy (AFM) using a Digital Instruments Nanoscope IIIa (Santa, Barbara, CA) with a silicon cantilever in the tapping mode. The hydrophilicity of the thin films was evaluated by measuring the contact angle of water with a Dataphysics OCA-20 contact angle meter.

3. Results and discussions

3.1. UV–Vis absorption spectra

Fig. 1 shows the UV–Vis absorption spectra in the wavelength range 300–800 nm for undoped TiO_2 and 0.75 wt.% Mo-doped TiO_2 films deposited on quartz glasses. The absorption edge of the doped TiO_2 is observed at a longer wavelength than that of the pure TiO_2. This could be attributed to the perturbation of Mo^{6+} doping on the electronic structure of TiO_2. By Mo^{6+} doping, an impurity level is generated in the band gap, near the bottom of the conduction band. The photon energy needed to excite electrons into the impurity band is lower than to excite electrons to conduction band from valence band. Hence a "red shift" is observed when the catalyst is doped with Mo^{6+} ions.

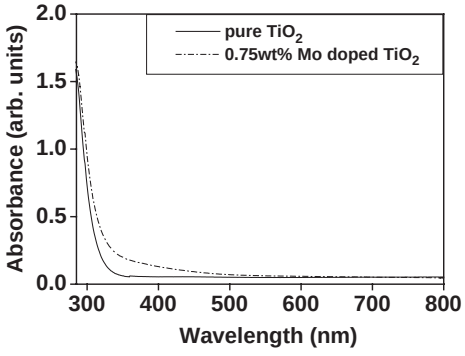

Fig. 1. UV–Vis spectra of undoped and 0.75 wt.% Mo(VI)-doped films.

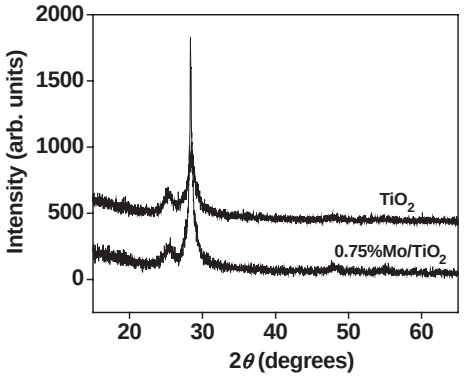

Fig. 2. XRD patterns of undoped and 0.75 wt.% Mo(VI)-doped TiO_2 films heated at 400 °C.

3.2. XRD patterns

In this measurement, the single crystalline silicon was used as a substrate. Fig. 2 shows XRD patterns of undoped and Mo(VI)-doped TiO_2 films calcined at 400 °C. As evidenced by the typical XRD peaks at 25.3° (Fig. 2), TiO_2 particles with and without Mo doping possess the same crystalline modification, anatase. Considering that the content of Mo ions is very low (~0.75%), any XRD peaks arisen from molybdenum oxide (such as MoO_3) are hardly to be detected. As the radius of Mo^{6+} (62 pm) is close to that of Ti^{4+} (68 pm), Mo ions are apt to enter into the lattices of TiO_2 and displace Ti^{4+} ions.

3.3. AFM

AFM was used to characterize the uniformity and particle size of undoped and doped films. As shown in Fig. 3, the TiO_2 particles contained in the two films both exhibit spherical shapes. In the undoped film, TiO_2 has a particle size of 50–90 nm, while in the 0.75 wt.% Mo ions doped thin film, TiO_2 has the particle size of 30–60 nm (Fig. 3b). The particle size in the TiO_2 thin films increased significantly during the calcining process. For the Mo ions doped samples, the grain growth of TiO_2 is inhibited and the particle size is much smaller.

The factors of surface roughness, represented by a root mean square (RMS), are estimated to be 38 nm and 14 nm for undoped and doped TiO_2 films, respectively. Films with different amounts of Mo ions doping have similar surface morphologies. The RMS values of undoped and 0.75 wt.% Mo(VI)-doped TiO_2 films heated at different temperatures are listed in Table 1.

3.4. Hydrophilicity

Fig. 4 shows the contact angle of water on TiO_2 films that were doped with different amounts of Mo ions and calcined at different temperatures. When calcined at 200 °C, water contact angles for all the samples are larger than 30°. As the heating temperature increases, the contact angles all