Influence of annealing temperature on photoelectronic properties and wettability of TiO$_2$ nanotube arrays

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Abstract. TiO$_2$ nanotube arrays (TNs) were prepared by anodization of titanium foil and then annealed at different temperatures (300°C, 400°C, 500°C, 600°C, and 800°C). The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and ultraviolet-visible spectroscopy (UV-Vis). Effect of annealing temperature on crystalline structures, morphology, photoelectronic properties, and wettability has been investigated. The results indicate that low temperature (below 500°C) has no obvious influence on surface morphology, while amorphous phase changes into anatase phase and rutile phase. The ultraviolet absorbance decreases while the visible light absorbance slightly increases with the increase of annealing temperature. At 500°C, the TNs show the highest photocurrent and maximum light-induced contact angle change, which are ascribed to their good crystallization, mixed crystal structure, and nanotubular structure.

1. Introduction

Heterogeneous photocatalysis has received increasing attention since Fujishima’ work in 1972 [1]. Of the many semiconductor metal oxides, TiO$_2$ is regarded as the important photocatalytic candidate because of its high chemical and optical stability, nontoxicity, low cost, and corrosion resistance [2-9]. Therefore, in recent years, particularly TiO$_2$ nanotube arrays (TNs) have received considerable attention. [10].

It is well known that the physical and chemical properties of TiO$_2$ thin films strongly depend on the preparation methods and annealing conditions [11-13]. Therefore, it is necessary to investigate the effect of the annealing temperatures on the physical properties and photoelectronic properties of the films. So far, most of the works mainly focus on the effect of annealing conditions on the morphology and photocatalytic activity. In this work, TNs were prepared by anodization, and then annealed at various temperatures. The relation of crystalline structures, morphology, photoelectronic properties, and wettability were investigated systematically.

2. Methods

2.1 Preparation of TiO$_2$ nanotube arrays

TNs were prepared as the method described by Schmuki and co-workers [14]. Ti foil anode and a platinum foil cathode was connected to direct current power supply. The electrolyte contained 0.175 M NH$_4$F. All anodizations were performed at 30 V for 3 h. After fabrication, the samples were annealed at 300°C, 400°C, 500°C, 600°C and 800°C for 2h, respectively.
2.2 Characterization
The crystalline structures of the TNs were checked by XRD. The morphology observation was performed on a FE-SEM. Absorbance spectra of the samples were obtained by an ultraviolet-visible spectrophotometer.

2.3 Photoelectronic performance measurements
Photocurrent transient was measured in 0.1mol/L Na$_2$SO$_4$ solution with electrochemical workstation. The samples were irradiated with a high pressure mercury lamp ($\lambda$=365nm).

2.4 Contact angle measurement
The wettability of TNs was evaluated by contact angle measurements using a contact angle detect system (SCI3000, hengda), 5 μL deionized water droplets were dropped on three different positions and the digital images of the droplet were captured with a CCD camera, the average value was taken for accuracy. A 15 W UV (254 nm) lamp was used to study the contact angles of the TNs.

3. Results and discussion

3.1 Microstructure and morphology

Fig. 1 XRD patterns of TNs annealed at different temperatures

Fig. 1 shows the XRD spectra of the TNs annealed at various temperatures. It is can be seen that only the diffraction peaks of the titanium substrate for the unannealed sample (JCPDS No. 44-1294), which means it is amorphous. For the sample annealed at 300°C, two weak peaks at 2θ = 25.3° and 48.1°, corresponding to (101) and (200) plane diffraction of anatase TiO$_2$ (JCPDS No. 21-1272) can be observed. With increasing annealing temperature from 300°C to 500°C, the magnitude of the anatase peaks increases. Annealed at 500°C, a weak peak of rutile appears (JCPDS No. 21-1276) (too weak to calculate average crystalline size below). At 600°C, the intensity of the titanium peaks decreases, whereas the intensity of the rutile peaks increases. This indicates that atmospheric O$_2$ was diffusing through the oxide layer and oxidizing the remaining Ti substrate [15]. For the sample annealed at 800°C, the diffraction peaks of the titanium substrate almost vanish while anatase phase changes into rutile phase completely, which is well accordance with Grimes’ results [16].

3.2 Surface morphology analysis
Fig. 2 SEM images of TNs (a) unannealed and annealed at (b) 400°C, (c) 500°C, (d) 600°C, and (e) 800°C, (f) cross-sectional image of the unannealed TNs

Fig. 2 presents SEM images of TNs annealed at various temperatures. All samples exhibit highly ordered TNs except the sample annealed at 800°C. Annealing below 600°C, it has no obvious effect on morphology of TNs. At 800°C, the TNs are destroyed and dense rutile film is observed. This is accordance with the mechanism of TNs crystallization reported by Grimes et al. [16] The transformation of anatase to rutile is constrained by the tube walls whereas the transformation continues in the interface region. This condition persists until there is enough energy to form larger rutile crystallites and cause the tube walls to rupture.

3.3 Optical properties

Fig. 3 Absorption spectra of TNs annealed at various temperatures

Fig. 3 shows the absorption spectra of TNs. As shown, with the increase of annealing temperature, the UV absorbance decreases while the visible light absorbance slightly increases, which is ascribed to the increase of rutile content at higher annealing temperature [17]. The absorption spectra of the 800°C sample is the lowest, which may be attributed to the collapsing of the nanotubular structure.

3.4 Transient photocurrent response

Photocurrent transients of the TNs were measured in a three-electrode system, shown in Fig. 4(a) (The photocurrent values of the TNs unannealed and annealed at 800°C are too small to superimpose). It can be seen that the photocurrent values rapidly decrease as soon as the light turns off, and then increase to a value when the light turns on, which have a good reproducibility. The photocurrent fluctuations can be ascribe to surface species absorption/desorption and appearance of defects [18].
is generally accepted that oxygen molecules are adsorbed onto the TNs surfaces by capturing free electrons \([ O_2(g) + e^- \rightarrow O_2^-(ad) ]\), leading to a low-conductivity depletion region near the surface [19-20]. Upon UV illumination, e\(^-\)-h\(^+\) pairs are generated. The h\(^+\) migrate to the surface and combine with oxygen ions, inducing desorption of oxygen from the TNs surface \([ h^+ + O_2^-(ad) \rightarrow O_2(g) ]\).

This leads to an increase of the conductivity [20-21]. As shown in Fig. 4(a), the photocurrent increases with increasing annealing temperature, nevertheless, it decreases when the temperature exceed 500°C. At 500°C, the sample shows the biggest photocurrent due to its good crystallization, and nanotubular structure. At 600°C, with anatase turn into rutile, the photocurrent rapidly decreases. According to Seto [22], there are a large number of defects at the grain boundary due to incomplete atomic bonding. These defects will result in the formation of trapping states, which have the ability to trap carriers and immobilize them, hence reduce the number of free carriers for electrical conductivity. Therefore, the decrease of photocurrent may be attributed to the increase of to the grain boundary between anatase and rutile and the decrease of anatase content. At 800°C, there is a very low photocurrent due to the formation of dense rutile film.

In order to further investigate the effect of annealing on electrical conductivity, the photocurrent response curves of TNs unannealed and annealed at 800°C were replotted, as shown in Fig. 4(b), the photocurrent of unannealed TNs is about 0.02 μA, which is about 300 times lower than that annealed at 500°C. It indicates that there are a large number of localized states in the amorphous TNs which act as traps and recombination centers. This reduces the TNs’ photo-electronic performance [23-24]. It is noteworthy that the photocurrent of the TNs annealed at 800°C has a fast growth and decay while the response duration of the unannealed TNs is relatively long. This indicates that apart from the exchange process for carrier trapping due to oxygen absorption or desorption on the surface of TNs, there is another slower electron recombination at the native defects which are vanish after heating [25]. Thus, slow response and decay of the photocurrent occurs for unannealed TNs [26].

### 3.5 Wettability of TNs
Fig. 5 Photographs of water droplets on the TNs annealed at different temperatures before and after UV irradiation for 4 hours

The water droplets showing the completely spread for each as-prepared TNs, this means the intrinsic state of TiO\textsubscript{2} film is hydrophilic [27]. After the samples stored in the dark for several weeks, they gradually transformed into hydrophobic. This wetting behavior may be ascribed to the adsorption of organic contaminants and the replacement of the chemisorbed OH group with oxygen in air [28-29]. As shown in Fig. 5, before UV irradiation, the water contact angle (WCA) of samples annealed below 600°C has no significant difference, within the range of 123°~130°. At 800°C, the WCA decreases to 89°. On illumination, the WCA value for TNs annealed at 800°C gave the least change whereas the WCA decreases significantly from 123° to 35° for TNs unannealed, from 130° to 25° for TNs annealed at 300°C, from 130° to 15° for TNs annealed at 400°C and from 126° to 17° for TNs annealed at 600°C. It is noticeable that maximal change was observed when TNs were annealed at 500°C, the change rate of WCA decreased 94.3%. It is known that wettability is related to the surface morphology and crystalline structure of films. At 800°C, the nanotubes are completely destroyed, a large number of compact rutile particles prevent the liquid permeates the surface result in the least change of WCA. It can be observed in Fig. 1 and 2, annealing below 600°C, it has no obvious effect on surface morphology, however, the crystal structure changed obviously. A widely accepted mechanism for the wettability is that, under UV illumination, photoexcited e\textsuperscript{−} is excited from the valance band to conduction band. These e\textsuperscript{−} will reduce Ti\textsuperscript{4+} to Ti\textsuperscript{3+}, in this process, oxygen atoms are desorbed, and oxygen vacancies are created. These oxygen vacancies are favorable for hydroxyl adsorption than oxygen adsorption that make the surface hydrophilic [30]. At 500°C, due to its good crystallization and nanotubular structure, the sample shows the most obvious hydrophobic-to-hydrophilic transition.

4. Conclusions
Highly ordered TNs were prepared by anodization of titanium foil in a mixed electrolyte solution of glycerol and NH\textsubscript{4}F. The annealing temperature has significant influence on morphology, crystal structure, and photoelectronic properties. Photocurrent and photoinduced hydrophilicity increase with increasing annealing temperature, nevertheless, they decrease when the temperature exceeds 500°C. At 500°C, the sample shows the biggest photocurrent and the most remarkable hydrophobic-to-hydrophilic transition due to its good crystallization and nanotubular structure. At 800°C, the lowest photocurrent was observed, which can be attributed to the formation of full rutile phase and the collapsing of ordered nanotube. The photocurrent of the unannealed TNs has a slow growth and decay. This indicates that apart from the exchange process for carrier trapping due to oxygen absorption/desorption on the surface of TNs, there is another slower electron recombination at the native defects.

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