

Preparation and Characterization of TiO₂ Nanotube Arrays via Anodization of Titanium Films Deposited on FTO Conducting Glass at Room Temperature

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Abstract: Self-organized TiO₂ nanotube arrays with micro-scale length were prepared on fluorine-doped tin oxide (FTO) conducting glass in NH₄F/glycerol electrolyte by electrochemical anodization of pure titanium films deposited by radio frequency magnetron sputtering (RFMS) at room temperature. The samples were characterized by means of field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), and photoelectrochemistry methods. The results showed that Ti films prepared at the condition of Ar pressure 0.5 Pa, power 150 W, and 0.5 h at room temperature possessed the zone T model structure with good homogeneity and high denseness. When the anodization time was prolonged from 1 to 3 h at the voltage of 30 V, the pore diameter of TiO₂ nanotubes increased from 50 to 75 nm, and the length increased from 750 to 1100 nm and then gradually decreased to 800 nm, while their wall morphology changed from smooth to rough. Also with increasing the anodization voltage, the pore diameter became larger, and the remaining oxide layer reduced, which could be easily removed by ultrasonic- chemical cleaning in 0.05% (w, mass fraction) diluted HF solution. Moreover, the photocurrent response curves and electrochemical impedance spectroscopy (EIS) results indicated that UV-illumination clearly enhanced the effective separation of the electron-hole pairs and the crystallized electrodes from the annealing treatment of as-anodized electrodes at 450 °C exhibited a better photoelectrochemical performance.

Key Words: Radio frequency magnetron sputtering; Room temperature; FTO conducting glass; TiO₂ nanotube arrays; NH₄F/glycerol

The growth of metal film in vacuum is a deposition process of massive atoms or atomic groups arriving on the substrate, which is affected by the deposition parameters, such as substrate temperature, sputtering pressure, and power. The micro-structure of the films is dominated by the relative substrate temperature and the energy of deposition atoms^[1–4]. Mainly, there are evaporation method and sputtering method to prepare metal films by vacuum deposition. The former easily conducted in simple equipment can manufacture the films with poor compactness and several bubbles. The latter can produce firm and dense films with good homogeneity and reproducibility in a large area owing to high-energy bombarding particles. Therefore sputtering method has become an important way that has been used very widely.

Recently, titanium film has drawn extraordinary attention

for its applications in microelectronics, machinery, aerospace, and medical industry owing to its remarkable photoelectric performance and corrosion resistance. Mor group^[5] has successfully developed the technology to grow TiO₂ nanotube arrays from titanium thin films deposited on glass substrates at 500 °C by anodization. The well-orderly and perpendicularly-oriented TiO₂ nanotubes possessed not only large specific surface area and strong absorption capacity, but also superior electron lifetimes owing to providing excellent pathways for electron percolation. Thus they exhibited high photoelectric conversion efficiency^[6–8] and good photocatalytic properties^[9,10]. Some other groups^[11–16] also used the same way to deposit Ti films at high temperature on a variety of substrates (e.g. silicon). However, the length of nanotube arrays prepared in the electrolytes was less than 700 nm since the increasing of

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the thickness of Ti-sputtered films resulted in the degradation of the films' quality^[5,6]. Obviously, it is not appropriate to deposit Ti film at high temperature on flexible and temperature-nonresistant substrates, e.g. polyethylene terephthalate (PET) or polyethylene naphthalate polymer (PEN). Moreover, to prepare TiO₂ nanotubes on transparent substrates (e.g. conducting glass, PET substrate) can enhance the light-converting efficiency of optical-electric devices based on the TiO₂ nanotubes and make these devices microminiaturized and flexible. Although Eu^[17] and Neale^[18] *et al.* have prepared the porous titania films on the transparent substrate, the distribution of the pores is not ordered and highly oriented. According to our previous work^[19], the quality (dense, uniform) of the titanium film and the anodization parameters are critical to the formation process of titania nanotubes. Therefore, on the basis of the fabrication of high-quality Ti films, it is necessary to select an electrolyte with low chemical dissolution rate to increase the thickness-conversion ratio of Ti film. In this study, we attempt to deposit compact and uniform Ti films on conducting glass at room temperature, and then fabricate large aspect ratio TiO₂ nanotube layer (1100 nm) in NH₄F/glycerol electrolyte. Additionally, the growth process and photoelectrochemical characteristics of the TiO₂ nanotubes are investigated, and a method for eliminating the cover layer on the nanotube surface is also discussed.

1 Experimental

1.1 Deposition of the titanium film at room temperature on conducting glass

Ti films (ca 1.47 μm) were deposited on fluorine-doped tin oxide (FTO) conducting glass at room temperature by RFMS (radio frequency magnetron sputtering) (JPG500, China). A Ti disk (99.9% purity, TianYuan Co., Ltd., Shenzhen, China) with 60 mm diameter and 5 mm thickness was used as the target. The base chamber pressure was below 7.0×10^{-4} Pa and the distance between the target and sample was 60 mm. To remove pinhole defects in the titanium film, the specimen was cleaned by ultrasonic in acetone, ethanol, and deionized water for 15 min, respectively. Before deposition, the target was prior sputtered for 10 min to remove the oxide layer or other impurities on the titanium target surface. During the deposition process, the argon gas (99.999% purity) pressure (p_{Ar}) was 0.5 Pa with gas flowing at $10 \text{ mL} \cdot \text{min}^{-1}$ and the sputtering power (P_s) was 150 W at room temperature. After deposition for 0.5 h, the samples were kept in vacuum for 6 h.

1.2 Preparation of TiO₂ nanotubes on FTO glass using an anodization method

Anodization was carried out using a two-electrode configuration. Titanium film/FTO with an exposed surface area of 1.0 cm^2 was used as the working electrode. A platinum sheet ($2 \text{ cm} \times 1.5 \text{ cm}$) with a copper wire was used as the counter-electrode.

The distance between the working and counter-electrodes was kept at 3 cm. A DC power source (WYK-1502, Eksi Electronic Co., Ltd., Jiangsu, China) supplied the required anodization potential (10–40 V) in a single step (without ramping). Anodization was conducted in 0.5% (w) NH₄F/glycerol at room temperature using a digital multimeter interfaced with a computer. After anodization, the samples were immediately washed with distilled water and subsequently dried in air. Some samples were heat treated for 3 h at different temperatures ranging from 300 to 550 $^{\circ}\text{C}$ in air at a heating rate of $5 \text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$, and then the samples were cooled in the furnace.

2 Results and discussion

2.1 Characterization of titanium films deposited at room temperature

The atom deposition process can be divided into three steps, namely the gas phase atom's deposition or adsorption, the surface diffusion, and the bulk self-diffusion. The morphological features of metal films are given on the basis of the relative substrate temperature T_s/T_m (T_s is substrate temperature, T_m is melting point of the deposited material) and the energy of deposition atoms. The morphological features were named as zone 1, zone T, zone 2, and zone 3 for high melting point metal film by taking into account the T_s/T_m and the pressure^[1–4]. Based on the titanium film ($T_{\text{m(Ti)}}=1660 \text{ }^{\circ}\text{C}$) deposited at room temperature ($T_{\text{s(FTO)}} < 150 \text{ }^{\circ}\text{C}$) in this experiment and hence $T_{\text{s(FTO)}}/T_{\text{m(Ti)}} < 0.3$, the Ti film structure depended on the sputtering pressure and power will be formed between zone 1 and zone T. Compared with zone 1, the critical nucleus size of Ti grains is still small and the structure is also consisted of an array of fibrous grains in the zone T, however, the surface diffusion of the atom is significant, causing the relatively compact structure at grain boundaries without holes and tapered crystals. Apparently, it is necessary to choose the appropriate sputtering parameters to promote the appearance of zone T structure. At suitable low sputtering pressure and high sputtering power, the Ti atom will obtain higher energy. Therefore, the surface diffusion is improved and the substrate temperature increases, yielding a movement of the structure to zone T region.

FESEM images, XRD pattern, and EDX spectrum of Ti film deposited under the conditions of $p_{\text{Ar}}=0.5 \text{ Pa}$, $P_s=150 \text{ W}$, and $t=0.5 \text{ h}$ at room temperature are shown in Fig.1. In Fig.1(a–c), it is found that a close-packed hexagonal structure of α -Ti film with (002) preferred orientation appears when 150 W power is applied. The microstructure of the film is uniform with the grain size of 100 nm, and a banding distribution of columnar structure belonged to the typical zone T structure with high density is seen from the cross-section of the film. The Ti atom has high energy to migrate and occupy the equilibrium sites of titanium crystal lattice when the Ti

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