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Time dependence of growth and crystallization of anodic titanium oxide films in potentiostatic mode

Junheng Xing, Zhengbin Xia *, Jianfeng Hu, Yanhong Zhang, Li Zhong

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, Guangdong 510640, China

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ABSTRACT

The influence of anodizing time on formation and crystallization of potentiostatically formed titanium oxide films is studied both at "low" (10 V) and "high" (30 V) applied potentials. It is revealed that prolonging the anodizing time is beneficial for the growth and crystallization of titania anodic films, especially at low applied voltages. The titanium anodization process follows two distinct stages. In the film formation stage, the film thickness and crystallinity increase fast. While in the film aging stage, the thickness and crystallinity of titanium oxide films only slightly change with anodizing time due to the enhancement of film dissolution rate.

1. Introduction

As an important method for preparation of functional TiO_2 thin films, anodization of titanium (or its alloy) has found its applications in many areas, such as corrosion protection [1–8], sensors [9], solar cells [10], batteries [11], photocatalytic engineering [12,13] and biomedical engineering [14–16]. It is revealed that the application performances of thin anodic oxide films on titanium depend on their structure (crystalline or amorphous) and surface features (smooth or porous) [17], and the structure and properties of titanium oxide films are determined by their preparation conditions [18–23]. In general, the anodic films on titanium grow with crystalline structure at high potentials and with amorphous structure at low potentials [24]. Mantzila and Prodromidis for instance, revealed that the anodic oxide film was amorphous at low applied potential (10 V), while anatase was the predominant phase for high voltage anodization (45 V) [25]. However, some other authors reported that the thin titania anodic films formed at very low potentials had crystalline structure [26]. By using scanning tunneling microscopy (STM), Nanjo et al. revealed that the anodic titanium oxide films formed at very low potentials (as low as −50 mV vs. Ag/AgCl) contained TiO_2 nanocrystals [27].

The anodizing time also plays an important role in the crystallization behavior of titanium oxide films, especially under potentiostatic anodization mode. The crystallization of titanium oxide films is usually enhanced by prolonging the oxidation time [28–30]. Nevertheless, the structure and composition of titania anodic films are very complex, making it difficult to estimate the crystallization degree of those titanium oxide films. Hence, the time evolution of the crystallinity of anodic oxide films during titanium anodization has been seldom reported. In addition, as reported by Arsov et al., the crystalline form of titanium oxides (anatase or rutile) is only determined by the applied potentials. In other words, at a given voltage, prolonging the oxidation time can only change the film crystallinity, rather than its crystalline form [29].

As reported in the literature, the thickness of anodic titanium oxide films also changes with the oxidation time. By prolonging the anodizing time, the oxide films on titanium usually get thicker [31]. While in some other works, the time evolution of the film thickness shows a declining tendency, probably due to the dehydration of anodic films on titanium [32]. Moreover, the chemical composition of anodic titanium oxide films can be also influenced by the oxidation time [33]. However, until now, few works have put their attention on this subject. In fact, although the effect of anodizing time on the growth and crystallization of titanium oxide films has been studied by some researchers, a long-time anodization of titanium is rarely performed, and the mechanisms of the influence of time on the growth and crystallization of the anodic oxide films are still not well understood yet [31]. In our present work, the high purity titanium samples are potentiostatically treated with different anodizing time both at "low" (10 V) and "high" potentials (30 V). The crystallinity, surface topography and chemical composition of titanium oxide films as a function of anodizing time are studied, and the formation and crystallization process of anodic oxide films on titanium under potentiostatic condition are discussed.

* Corresponding author. Tel.: +86 20 8711 2047; fax: +86 20 8711 2093.
E-mail address: cezhbxia@scut.edu.cn (Z. Xia).

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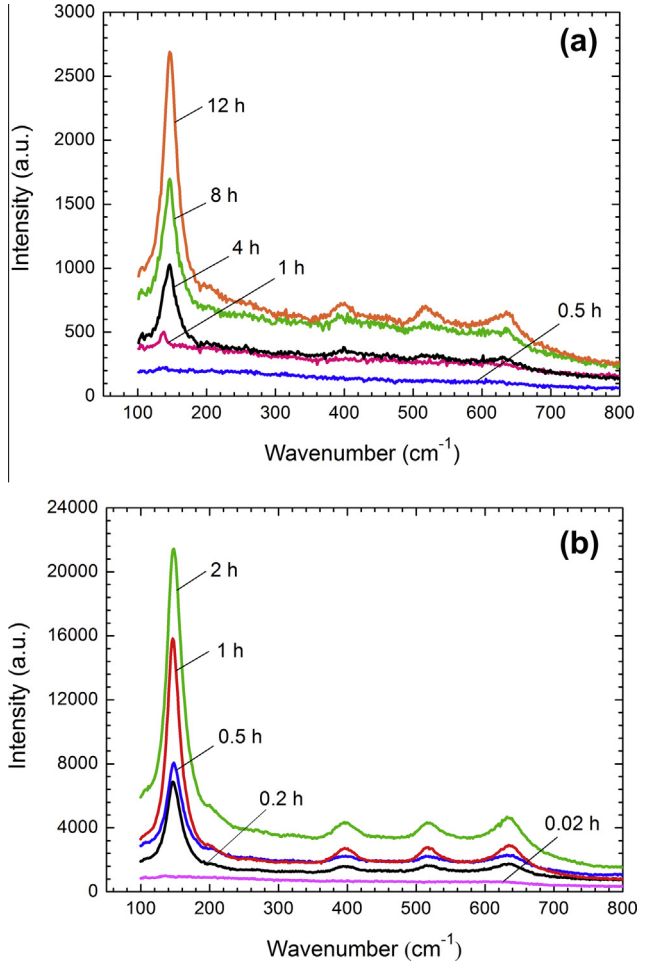

Fig. 1. Raman spectra of anodic titanium oxide films formed under potentiostatic mode at (a) 10 V and (b) 30 V for different time.

2. Experimental method

2.1. Sample preparation

Highly pure titanium plates (>99.99%) with a thickness of 1 mm were firstly cut into small sheets with a size of 10 × 10 mm, and then mechanically abraded by using 600, 1000, 1500 and 3000 emery papers. Subsequently, the titanium sheets were chemically polished by etching in a solution of 1% HF and 3% HNO_3 for 3–4 s. Before anodization, all samples were ultrasonically cleaned with acetone for 20 min and later with deionized water for 20 min.

2.2. Anodization procedure

The titanium samples were anodically treated in a two-electrode electrochemical cell. The titanium samples were used as the working electrode, a Pt plate, parallel to the working electrode, was used as the counter electrode, and 0.1 M H_2SO_4 solution (800 mL in volume) was used as the electrolyte. The anodization process was carried out using an electrochemical workstation (Metrohm Autolab PGSTAT100, Switzerland), which was equipped with a Voltage Multiplier module. The titania anodic films were formed under potentiostatic control at 10 V and 30 V with the oxidation time ranging from 0.02 h to 24 h. The solution was stirred with purified nitrogen gas before and during anodization process, and all experiments were carried out at a constant temperature of 25 °C.

2.3. Film characterization

The structure of titanium oxide films was detected with Raman spectroscopy by using a HORIBA Jobin Yvon LabRAM Aramis instrument (France) with the incident power of 10.4 mW and the excitation wavelength of 532 nm. Spectroscopic ellipsometer (SE, HORIBA Jobin Yvon Auto SE, France), which was carried out at an incidence angel of 70° with the wavelength range of 439–842 nm, was used to determine the thickness of titanium oxide films. A single layer model (Ti substrate and TiO_2 layer) was used in modeling procedure. The surface topography of the anodized samples was observed by using scanning electron microscopy (SEM, LEO 1530 Vp, Germany) with the electron beam of 5 kV. The chemical composition of the formed films was detected by X-ray photoelectron spectrometry (XPS), which was performed on a Kratos Axis Ultra DLD spectrometer (UK). Al Kα (1486.6 eV) was used as the X-ray source and operated at 15 kV and 150 W. A Shirley background was used for the peak fitting procedure, and all spectral positions were corrected by normalizing the C 1s spectrum at 284.6 eV.

2.4. Solution analysis

The concentration of the dissolved titanium ions in the solution was detected by graphite furnace atomic absorption spectroscopy (GFAAS). The measurements were carried out by a SHIMADZU AA-6800 atomic absorption spectrophotometer (Japan), which was equipped with an ASC-6100 autosampler, a pyrolytic coated graphite tube and a Ti hollow cathode lamp. In order to study the dissolution behavior of titanium oxide films, 2 mL solution samples were intermittently removed from the electrochemical cell every 2 h (at 10 V) or 0.5 h (at 30 V) during titanium anodization.

3. Results

3.1. Crystallization

Fig. 1 displays the Raman spectra of titanium oxide films formed under potentiostatic control at 10 V and 30 V with different anodizing time. The Raman band at about 144 cm^{-1}, assigned to E_g mode of anatase phase, indicates the long-range order of crystalline titanium oxide films, while the bands at about 399 cm^{-1}, 516 cm^{-1} and 639 cm^{-1}, belong to B_{1g}, A_{1g} or B_{1g}, and E_g modes of anatase, respectively, give indication of the short-range order of anatase phase [34,35].

For the applied voltage of 10 V, as shown in Fig. 1a, when the anodizing time is short (0.5 h), no Raman peaks can be found for the formed titanium oxide film. While the low-frequency E_g mode is observed in the anodized titanium sample with the anodizing time of 1 h, and the Raman band is weak and has a clear shift towards lower wavenumber, which may mean that the formed film is composed of nanometer-scale titanium oxide crystals [35]. With the anodizing time of 4 h, four Raman bands, attributed to anatase type of TiO_2, can be detected for anodic titanium oxide films. Subsequently, the Raman peaks become sharper and more intensive when the oxidation time is prolonged to 8 h and 12 h. By contrast, for the titanium oxide films formed at 30 V (Fig. 1b), four Raman bands of anatase TiO_2 can be clearly found even though the oxidation time is very short (0.2 h). To sum up, Fig. 1 clearly shows that the crystallization of anodic titanium oxide films is promoted by prolonging the oxidation time or by enhancing the potentials.

In order to well understand the effect of anodizing time on the crystalline behavior of titania anodic films, the intensity of the strongest Raman peak at 144 cm^{-1} (which indicates the long-range order of titanium oxides) and the thickness of anodic titanium

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