Effect of Reacting Temperature on the Microstructure and Electronic Property of Self-ordered TiO$_2$ Nanotube Arrays

Jiangyi Yan$^1$

$^1$Department of mechanical engineering, Tsinghua University, Beijing, 100084, China

2115731095@qq.com

Abstract. At present, with the rapid development of nanoscience, nanotubes have become an important part of nanomaterials. As a new type of multifunctional semiconductor nanotube material, the self-ordered TiO$_2$ nanotube arrays (TNTs) have excellent optical and electrical properties, and they have a very wide application prospects in modern industrial fields. By using the method of anodic oxidation, the specific influence of reaction temperature on the microstructure and electrochemical properties of TNTs under the condition of acid system was investigated by the way of controlling variables. The results show that the lengths of TNTs and the thickness of the barrier film decrease with increasing temperature, and which is opposite in the radius and tube wall thickness. Additionally, in electrochemical properties of TNTs, the equivalent electrochemical impedance and crystallinity usually decrease with increasing of the temperature.

1. Introduction

In many semiconductor nanomaterials, TNTs are very important multifunctional inorganic nanomaterials [1], they have extremely stable physical and chemical properties, and compared to TiO$_2$ nanoparticles [2], TNTs have high surface area, unique optical and electrical properties and they also have geometric features [17-19], which are more beneficial to the electronic transmission. Therefore, TNTs have a very wide range of applications in the field of modern industry [3]. First, because of its high photoelectric conversion efficiency [16], TNTs are used as an anode material for dye sensitized solar cells [19]. Second, TNTs are ideal materials for the photodissociation of hydrogen [8-10]. Third, as titanium has good biocompatibility and degeneracy, TNTs are also widely used as a raw material for some biological scaffolds [11-14]. In addition, by means of cyclic voltammetry and constant current measurement, some researchers studied the sensitivity of TiO$_2$ nanotube arrays with adsorption of horseradish peroxidase (HRP) and thionine chloride (TH) for hydrogen peroxide [4-7].

A detailed investigation on the microstructure and electrochemical properties of TNTs is beneficial to the application, so it is necessary to study the influences of fabrication temperature on the microstructure and electronic property of TNTs. Although a great deal of researchers paid attention to this issue [15],
there is no systematic researches and conclusion about the temperature influences on the formation parameters on the microstructure and characterization of TNTs, the purpose of this paper is mainly to investigate the concrete and comprehensive influences about the temperature on the microstructure and electronic property of TNTs by SEM, Roman spectrum, EIS and Mott-Schottky plot.

2. Experimental

2.1 Preparation of TiO₂ nanotube arrays
At present, the methods of preparing titanium dioxide nanotube arrays by anodic oxidation are mainly divided into two kinds: the acid system and the alcohol system: electrolyte solution is fluorine-containing inorganic acidic aqueous solution and electrolyte solution is fluorine-containing organic solution [3-5]. In this study, titanium nanotube arrays were fabricated in the acid system. The basic process of the experiment was as follows: Titanium sheets were deposited in the mixed solution of 0.15mol/LHF+1mol/LH2SO4 in electrolyte solution for 2 hours at the experimental temperature of 0, 30, 60 and 90℃ respectively, and the I-T curves of the film forming process were recorded. MS and EIS tests were carried out immediately in 0.5mol/L Na2SO4 solution, and then sintered and sintered. After completion, the SEM is observed on the side and the Raman spectrum is finally detected. For the temperature change and maintenance, DF-II collector magnetic heating mixer and DC-4015 energy-saving intelligent thermostat are needed.

2.2 Electrochemical measurement and microstructure observation
Electrochemical studies were conducted using the Solatron 1260+1287 Electrochemical Workstation. A conventional three-electrode glass cell was used to carry out the electrochemical studies, in which, Pt foil was the counter electrode and saturated calomel electrode (SCE) was used as the reference electrode.

EIS measurement was measured in the frequency range of 5 mHz to 100 kHz with the applied alternating sinusoidal potential of 10 mV. After each experiment, the impedance data were displayed as Nyquist and Bode in phase format plots.

Mott-Schottky plot was carried out in the potential range of -1.0V to 1.0V with a scanning rate of 20mV/S. In order to eliminate the frequency dispersion, the frequency of 1KHz was used as the applied frequency.

Micro-Raman spectra were obtained using the Horiba Jobin HR800 Raman spectrometer with 15mW of a 514 nm laser.

The surface and cross section morphologies of the TiO₂ NTs were examined by SUPRA55 Field Emission Scanning Electron Microscope.

3. Results and discussions

3.1 Effect on the micromorphology of TiO₂ nanotube arrays
TNTs fabricated at different temperatures were enlarged 100 thousand times under an electron microscope for observation, and the micro-morphologies of the side and front were obtained in SEM images as shown in figure 1 and figure 2 and the characteristic size of TNTs at different temperatures is calculated as Table 1 shows. It is obviously seen that the length of nanotubes and the thickness of barrier
layer decrease with the increasing temperature and the rate of change decreases. And, the diameter and wall thickness of nanotubes increase with the increasing temperature, and the rate of change decreases too. In addition, it can be seen that the change rate of the characteristic sizes of nanotubes with temperature changes from large to small is length > barrier thickness > diameter > wall thickness, that is to say, temperature has the greatest influence on the length and the smallest influence on wall thickness.

![Figure 1](image1.png)

**Figure 1.** The side-section SEM images of TiO$_2$ nanotube arrays fabricated by anodization at different temperatures for 2h in 0.15M HF+1.0M H$_2$SO$_4$ solution, (a)0°C, (b)30°C, (c)60°C, (d)90°C.

![Figure 2](image2.png)

**Figure 2.** The front-section SEM images of TiO$_2$ nanotube arrays fabricated by anodization at different temperatures for 2h in 0.15M HF+1.0M H$_2$SO$_4$ solution, (a)0°C, (b)30°C, (c)60°C, (d)90°C.

**Table 1.** The characteristic size of TNTs fabricated at various temperatures for 2h in 0.15M HF+1.0M H$_2$SO$_4$ solution.

| Temperatures/°C | Diameter/nm | Wall thickness /nm | Length/nm | Barrier thickness /nm |
|-----------------|-------------|--------------------|-----------|----------------------|
| 0               | 61.41       | 13.40              | 466.7     | 106.1                |
| 30              | 79.27       | 14.89              | 275.8     | 69.22                |
3.2 Effect on the electronic property of TiO$_2$ nanotube arrays

In order to detect the influence of temperature on the electronic properties of TNTs, the EIS and MS curves of TNTs are measured in 0.5M Na$_2$SO$_4$ solution. The EIS and Mott-Schottky curves of TNTs obtained at different temperatures are shown in figure 3. The EIS curve shows that the radius of different curves decreases with the increased temperature, which indicates equivalent electrochemical impedance decreases continuously with the increased temperature. And, from the MS curve, reversed sigmoidal plots can be observed with an overall shape consistent with that typical for n-type semiconductors, and the slope of the linear region sharply decreases with the increased temperature, that is to say, the flat-band voltage of TNTs is increasing, which means conductivity of TNTs is getting stronger and stronger according to the carrier density formula of semiconductors. Also, it indicates the increased donor density for the TNTs electrode when the temperature is increasing, and a higher donor density is an indicator of the enhanced pitting corrosion susceptibility.

![Figure 3. EIS (a) and MS (b) curves of TNTs at different temperatures for 2h in 0.15M HF+1.0M H$_2$SO$_4$ solution.](image)

In addition, the phase composition of TNTs is tested by micro-Raman spectroscopy utilizing variable excitation wavelengths, and Figure 4 shows four micro-Raman spectra of TNTs fabricated at different temperatures. Four Raman bands are clearly seen at 143, 393, 512, and 632 cm$^{-1}$, respectively [20]. And, the characteristic peaks of Raman spectra of the TNTs prepared at different temperatures are basically the same, and there is no change, which indicates that temperature has little effect on the microstructure of the TNTs.

In addition, with the increase of temperature, the overall intensity of Raman spectroscopy is decreasing, which shows that the temperature is negatively related to the crystallinity of TNTs. In other words, it means that the crystallinity of TNTs decreases with the increased temperature.
4. Conclusion
Temperature has a great influence on the microstructure and electronic properties of TNTs fabricated by anodic oxidation in the acid environment, conclusions can be drawn as following:

1) the length and the thickness of barrier layer of TNTs decrease with the increasing temperature and the diameter and wall thickness increase with the increasing temperature. And, it can be seen that the change rates of four characteristic sizes are length > barrier thickness > diameter > wall thickness with temperature changing from large to small;
2) the stability of TNTs is decreasing and the conductivity is increasing with the increase of temperature.
3) the crystallinity of TNTs is decreasing with the increase of the temperature.

Acknowledgment
1. This work is supported by the State Key Laboratory of Tribology in Tsinghua university of China.
2. This work is supported by the National Science and Technology Major Project 2017ZX04010001 of China.
3. This work is supported by Research Room of Intelligent CNC System of Department of mechanical engineering in Tsinghua university of China.

5. References
[1] Wu P and Xu Z 2005 Silanation of nanostructured mesoporous magnetic particles for heavy metal recovery Industry and Engineering Chemistry Research. 44(2005)816-825.
[2] Hiroaki T, Jan M, Andrei G, Arlindo S, Luciano T and Patrik S 2007 Characterization of electronic properties of TiO$_2$ nanotube films Corrosion Science. 49 (2007) 203–210.
[3] Fujishima A and Honda K 1972 Electrochemical photolysis of water at a semiconductor electrode Nature. 238(1972)37-39.
[4] Shankar K, Mor G K, Prakasam H E, Yoriya S, Paulose M, Varghese O K and Grimes C A 2007 Highly-ordered TiO$_2$ nanotube arrays up to 220μm in length: use in water photo electrolysis and dye-sensitized solar cells Nanotechnology 8(2007)065707.
[5] Varghese O K, Gong D, Paulose M and Grimes 2003 Extreme changes in the electrical resistance of

![Figure 4. Raman spectrum of TNTs fabricated at different potentials for 2h in 0.15M HF+1.0M H$_2$SO$_4$.](image-url)
titania nanotubes with hydrogen exposure Adv. Mater. 15(2003)624-627.

[6] Guan D S, Paul J, Hymel and Wang Y. Growth 2012 mechanism and morphology control of double-layer and bamboo-type TiO$_2$ nanotube arrays by anodic oxidation Electrochemical Acta. 83(2012) 420-429.

[7] Regonini A, Schmidt C Aneziris T and Graule F J 2015 Clemens Impact of the Anodizing Potential on the Electron Transport Properties of Nb-doped TiO$_2$ Nanotubes Electrochemical Acta. 169(2015) 210-218.

[8] Paulose M, Shankar K, Varghese O K, Mor G K and Grimes C A 2006 Application of highly-ordered TiO$_2$ nanotube-arrays in heterojunction dye-sensitized solar cells Corros. Sci 39(2006)2498.

[9] Lu X H, Wang G M, Zhai T, Yu M H, Gan J Y, Tong Y X and Li Y 2012 Hydrogenated TiO$_2$ Nanotube Arrays for Supercapacitors Nano Lett. 12(2012)1690.

[10] Ohtsuka T, M. Masuda M and Sato N 1985 Ellipsometric Study of Anodic Oxide Films on Titanium in Hydrochloric Acid, Sulfuric Acid, and Phosphate Solution. 132(1985)787.

[11] Lu H F and Li Feng 2008 Amorphous TiO$_2$ nanotube arrays for low-temperature oxygen sensors Nanotechnology 19 405504.

[12] Nelson J C and Oriani R A 1993 Stress generation during anodic oxidation of titanium and aluminum. 34(1993)307.

[13] Regan B O, Moser J, Anderson M, and Graetzel M 1990 Vectorial electron injection into transparent semiconductor membranes and electric field effects on the dynamics of light-induced charge separation J. Phys. Chem. 84(1990)8720.

[14] Leach J S L and Pearson B R 1988 Crystallization in anodic oxide films Corros. Sci. 28(1988)43.

[15] Armstrong N R and Quinn R K 1977 Auger and X-ray photoelectron spectroscopic and electrochemical characterization of titanium thin film electrodes Surf. Sci. 67(1977)451.

[16] Shibata T and Zhu Y C 1995 The effect of film formation conditions on the structure and composition of anodic oxide films on titanium Corros. Sci. 37(1995)253.

[17] Krishnamurthy B, White R E and Ploehn H J 2005 Electric field strength effects on time-dependent passivation of metal surfaces Electrochemical Acta. 47(2002)2505.

[18] Prakasam H E, Paulose M and Varghese O K 2007 TiO$_2$ nanotube arrays of 1000μm length by anodic oxidation of titanium foil Journal of Physical Chemistry C. 111:14993-14996.

[19] Schmidt A M, Azambuja D S and Martini E M A 2006 Semiconductive properties of titanium anodic oxide films in McIlvaine buffer solution Corros. Sci. 48(2006)2901.

[20] Paulose M, Shankar K and Yoriya S 2006 Anodic growth of highly-ordered TiO$_2$ nanotube arrays up to 134 μm in length Journal of Physical Chemistry B. 110 (2006): 16179-16184.