Proceedings of Symposium on Ultrasonic Electronics, Vol. 31 (2010) pp. 25-26
6-8 December, 2010

Photoacoustic Spectra of Self-Assembled TiO_2 Nanotube Electrodes by Anodic Oxidation

陽極化成法による自己組織化 TiO_2 ナノチューブ電極の光音響スペクトル

Akari Yamada[1†], Tomoka Ota[1], Qing Shen[1,2], and Taro Toyoda[1] ([1]Dept. Appl. Phys. & Chem., Univ. Electro-Commun. [2]PRESTO, JST)
山田 灯 [1‡], 太田 朋佳 [1], 沈 青 [1,2], 豊田 太郎 [1] ([1]電通大 量子・物質工; [2]JST さきがけ)

1. Introduction

Nanostructured TiO_2 film have attracted much interest for the application of photocatalyst and dye sensitized solar cells (DSSCs).[1] Conventional DSSCs are composed of working electrode with TiO_2 nanoparticles, counter elctrode and electrolyte. TiO_2 electrodes with a higher degree of order than those made from disordered assembly of nanoparticles are desirable for the improvement of the electron transfer rate and DSSC efficiency. Recently, highly ordered TiO_2 nanotube (NT) electrodes have been reported as a candidate of new electrodes for DSSCs.[2] TiO_2 NT film was prepared on Ti foil using an electrochemical anodizing method. One-demensional tubular structure of TiO_2 NT is useful for separating and transporting electrons to the Ti substrates. In this study, we characterize the dependence of anodization temperature on the optical absorption of TiO_2 NT by using photoacoustic (PA) technique. PA technique is a photothermal methods and has advantages as follows:[3]

(1) available for light absorption mesurment for opaque or strong scattering samples.
(2) nondestructive and noncontact method.
(3) useful for the simultaneous characterization of thermal property, optical property and carrier relaxation process.
(4) possible for depth profile analysis of a sample by changing incident light modulation.

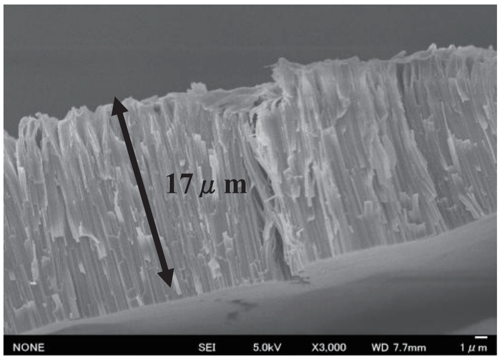

Fig. 1 SEM images of TiO_2 NTs prepared with 40 ℃ (cross section).

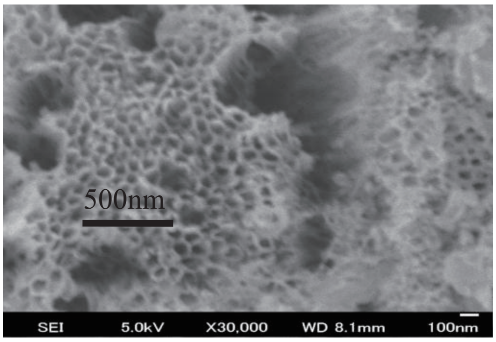

Fig. 2 SEM image of TiO_2 NTs prepared with 40 ℃ (surface).

Experiments

2.1 Sample preparation

TiO_2 NT electrodes were prepared by electrochemical anodization of Ti foils in ethylene glycol containing 0.25wt% NH_4F with an applied voltage of 50 V for 1 hour.[4] The anodization temperature was controlled from 10 to 40 ℃ and we prepared 4 different samples. After anodization, the electrodes were annealed at 480 ℃ for 3 hours in air.

Figures 1 and 2 show the cross section and surface of TiO_2 NTs prepared with 40 ℃, respectively. Average inner and outer diameters of the TiO_2 NTs were around 50 nm and 70 nm, respectively. The length of the NTs was about 17 μm. The NTs grew from 3 to 17 μm, and also inner and outer diameters changed from 20 to 70nm between 10 to 40 ℃.
.

ota@jupiter.pc.uec.ac.jp

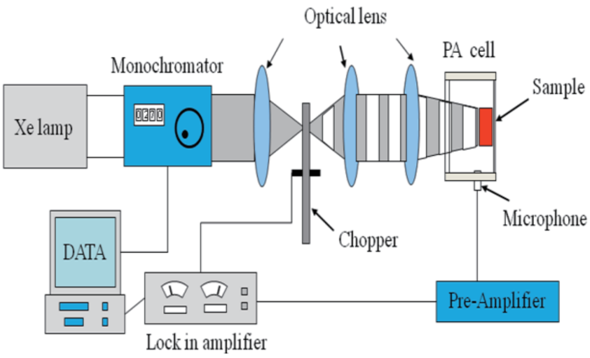

Fig. 3 Schematic diagram of PA spectrometer, in which light is incident directly on electrode surface.

2.2 PA measurement

PA measurements were carried out by using a gas-microphone PA technique. A 300 W xenon arc lamp was used as the light source. A monochromatic light is obtained through a monochromater and its intensity is modulated using a mechanical chopper. The modulated light is irradiated on the sample placed inside the PA cell. The light absorbed by the sample is converted into heat by nonradiative relaxation process, which results in a pressure fluctuation of the air inside the cell. The pressure fluctuation is detected as the PA signal by a microphone. In this study, PA measurements were carried out in the wavelength range between 273-700 nm with a modulation frequency of 133 Hz at room temperature.

3. Result and Discussion

Figure 4 shows the PA spectra of TiO_2 NTs prepared with 10 and 40℃. The exponential slope of spectrum increases with the increase of anodization temperature. PA signal intensity (P) is

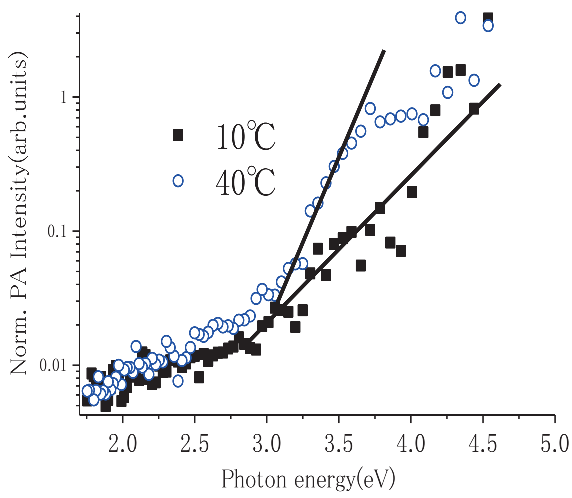

Fig. 4 PA spectra of TiO_2 NTs.

Anodization Temp.(℃)	σ
10	0.031
20	0.068
30	0.078
40	0.107

Table 1 σ of TiO_2 NTs prepared by different anodization temperature.

expressed with the following eq. (1) because P is proportional to optical absorption coefficient.

$$\mathbf{P = P_o exp[-\sigma(E_o - E)/k_B T]} \quad (1)$$

P: PA signal intensity
σ : steepness factor
E: photon energy
k_B: Boltzmann constant
T: temperatures
P_o, E_o: constant

Steepness factor, σ reflects the crystal quality of the material (defects, impurities, etc).[5] The value of σ increases with the increase of anodization temperature (Table 1), indicating the improvement of crystal quality. From the SEM images, we confirmed that the anodization temperature influenced on the structure and length of TiO_2 NTs. We have measured photocurrent characteristics and there is a correlation between σ factor and photocurrent, suggesting the improvement of crystal quality.

References

1. B. O'Regan, M. Grätzel; Naturea **353**, 737 (1991).
2. D. Gong, C. A. Grimes, O.K. Varghese, W. Hu, R.S. Singh, Z. Chen, E. C. Dickey, J. Mater. Res. **16**, 3331 (2001).
3. A. Rosencwaig: Photoacoustic and Photoacoustic Spectroscopy (Wiley Interscience, New York 1980).
4. J. M. Macak, P. Schmuki, Electro. Acta **52,** 1258 (2006).
5. F. Orbach: Phys. Rev. **92**. (1953) 1424.