Superlattices and Microstructures 64 (2013) 37–43

Contents lists available at ScienceDirect

Superlattices and Microstructures

journal homepage: www.elsevier.com/locate/superlattices

X-ray analysis of nanoporous TiO_2 synthesized by electrochemical anodization

Y.L. Cheong *, F.K. Yam, I.K. Chin, Z. Hassan

Nano-Optoelectronics Research and Technology Laboratory, School of Physics, Universiti Sains Malaysia, 11800 Penang, Malaysia

ARTICLE INFO

Article history:
Received 10 June 2013
Accepted 6 September 2013
Available online 14 September 2013

Keywords:
Nanoporous titanium dioxide
Anodization
Characterizations
Williamson–Hall method
Scherrer method

ABSTRACT

This paper presents the study of the growth of nanoporous titanium dioxide (TiO_2) via electrochemical anodization method. The effects of electrolyte with different ratios of ethanol to distilled water (i.e. from 1:9 to 5:5) on the morphological and structural properties were studied. X-ray diffraction (XRD) results revealed that crystalline structure (anatase) was obtained after being annealed at 600 °C for 30 min. Scherrer and Williamson–Hall methods were employed to calculate the crystallite size and lattice strain of the TiO_2. It is found that similar trend was shared for both graphs of crystallite size versus ratio of ethanol to distilled water by both methods. The lattice strain is assumed to be compressive and it is inversely proportional with crystallite size. Results show that electrochemical anodization with ratio 3:7 ethanol to distilled water electrolyte produced lowest crystallite size and highest compressive strain.

1. Introduction

Titanium dioxide occurs in nature as a mineral in three well-known multi-crystal forms, rutile, anatase, and brookite [1]. The most common crystal form of titanium dioxide is rutile. However, titanium dioxide has an undesirable property – it is a photosemiconductor. The band gap energy of titanium dioxide is around 3.02 eV for rutile and 3.2 eV for anatase, and is only activated under ultraviolet (UV) light where the wavelength is smaller than 380 nm [2,3]. Titanium dioxide has been widely used as a pigment [4], water splitters [5,6], dye sensitized solar cells [7,8], anti-reflective coatings and as a sensors [9,10]. Various methods have been used and reported by researchers to fabricate titanium

---

* Corresponding author.
E-mail address: cheong.y.ling@gmail.com (Y.L. Cheong).

0749-6036/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.spmi.2013.09.016

dioxide nanostructures which include electrochemical anodization [11–13], sol–gel [14], hydrothermal [15], microwave-hydrothermal [16], metal organic chemical vapor deposition (MOCVD) [17] and direct current (DC) magnetron sputtering methods [18]. Despite many studies of the various properties of titanium dioxide, the availability of research literature on crystallite size and strain of nanoporous titanium dioxide is still scarce.

It is well known that crystallite size and lattice strain are the two key factors which lead to the observed broadening of the diffraction peaks of XRD [19,20]. The former depends on the mean size of a coherent scattering domain [21]. Crystallite size was first introduced by Scherrer in 1918 [19], which is referred to the size of a single crystal inside the particles or grains, it is different from particle or grain size where the single particle or grain can be comprised of several crystal aggregates. On the other hand, lattice strain is caused by crystal imperfection such as dislocations and point defects [21]. There are two types of lattice strains in a crystal, namely, uniform and non-uniform strain. However, only the non-uniform strain will cause the peak broadening [22]. Apart from that, lattice strain can either be elongation or compression [22].

There are a few analysis methods for calculating size-strain in materials which includes Scherrer [19,23], Williamson–Hall [24,25] and Warren–Averbach methods [26,27]. Scherrer and Williamson–Hall methods are both based on the full width half maximum (FWHM) values and the integral breadths, while Warren–Averbach method is based on the Fourier coefficient of the profile [28]. Since the Warren–Averbach method is time consuming and mathematically cumbersome [26,29], only Scherrer method and Williamson–Hall method are employed in this study for size-strain analysis.

In this paper, titanium dioxide nanostructured synthesized via electrochemical anodization under different ethanol and distilled water ratios. TiO_2 nanostructured samples were then characterized by XRD. The crystallite size an d strain subsequently were derived and determined using Scherrer and Williamson–Hall methods.

2. Experimental details

Titanium foils (Strem Chemical, 99.7% purity and 0.127 mm thickness) with dimensions of 4.0 cm length and 1.0 cm width were cut into a number of pieces. Prior to anodization, the titanium foil was cleaned by washing with ethanol and alkalized solution, rinsing in distilled water a few times and then dried. After drying, the samples were anodized under in electrolytes with different ethanol and distilled water ratios.

The electrolyte of this experiment contains 0.4198 g 1.0 M of NaF, 0.7102 g 1.0 M of Na_2SO_4, 5 ml 0.05 M of H_3PO_4, ethanol and distilled water. The ethanol to distilled water ratio of the electrolytes were 1:9; 2:8; 3:7; 4:6; 5:5 and were denoted as S1A, S2A, S3A, S4A and S5A respectively.

The electrolyte was then stirred until the powder of NaF and Na_2SO_4 completely dissolved. During the anodizing process, the initial titanium foil was acted as the anode while the cathode for this electrochemical anodization process was a copper wire. The electrodes were placed 2 cm apart from each other. The bias voltage was 60 V and the electrolyte solution was maintained at room temperature. The duration of the anodization process was 60 min.

The samples after anodization process were then rinsed with distilled water, cleaned ultrasonically for 10 min and dried. The sample was segmented and some segments were then annealed (thermal treatment) in the furnace at 600 °C for 30 min. The samples were subsequently characterized and analyzed using FE-SEM and XRD.

3. Results and discussions

3.1. FE-SEM

The morphological properties of the samples can be revealed by employing FE-SEM method.

The FE-SEM image in Fig. 1 shows the top view of as-anodized sample formed. It can be observed that the formation of sponge-like porous TiO_2 occurred after the anodization process.