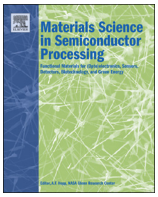
Materials Science in Semiconductor Processing 26 (2014) 130–136

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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



Room-temperature synthesis of nanocrystalline titanium dioxide via electrochemical anodization

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ARTICLE INFO

Available online 8 May 2014

Keywords:
Anodization
Crystal growth
Nanocrystalline titanium dioxide
Photoelectrochemical
Room temperature

ABSTRACT

This paper presents a study of the growth of nanoporous anatase and rutile phases of titanium dioxide (TiO_2) subjected to electrochemical anodization at room temperature without post-thermal treatment, using sulfuric acid as the electrolyte. Effects of the applied voltage on the morphological, structural, and photoelectrochemical (PEC) properties were examined. Images from field emission scanning electron microscopy reveal that pore size could be manipulated by changing the anodization voltage. In addition, X-ray diffraction (XRD) results indicate that anatase and rutile phases of TiO_2 appeared in samples subjected to minimum anodization voltages of 100 V and 150 V. The Scherrer method was used to calculate the mean crystallite size, and the interplanar *d*-spacing formula was used to obtain the in-plane and out-of-plane strains. XRD measurements reveal that the amount of anatase and rutile crystallinity and their mean crystallite sizes were affected significantly by the anodization voltage. Results of the PEC studies reveal that the photocurrent density and photoconversion efficiency increased with increasing anodization voltage. In addition, the synthesized nanoporous TiO_2 showed stable photoresponse where only a small decay of photocurrent density is observed in numerous on-to-off illumination cycles.

1. Introduction

Nanocrystalline titanium dioxide has received much attention recently from researchers because of its wide range of applications, including those in solar energy conversion, sensing, and photocatalysis [1–5]. TiO_2 occurs mainly as three well-known crystalline polymorphs namely, anatase, brookite, and rutile [6]. Both anatase and brookite are metastable phases of TiO_2, and anatase converts to rutile upon heating to >823 K [7].

Two methods are commonly used to fabricate anatase and rutile phases of TiO_2 at relatively low temperatures, namely, sol–gel process and hydrothermal treatment. However, preparation of anatase and rutile phases by sol–gel process may take days or even longer and is thus very time-consuming [8,9]. By contrast, preparing crystal-phase TiO_2 via hydrothermal treatment has several disadvantages. Hydrothermal treatment requires expensive and unstable precursors, some of which, such as TiCl and TiO_2 powder (P25), are difficult to prepare [10].

Normally, anatase and rutile are produced by annealing TiO_2 at high temperatures for a few hours. Many researchers reported that anatase and rutile could be obtained by calcination at around 400° and at 550 °C or higher, respectively [7]. However, Jaroenworaluck and coworkers [11] found that nanostructures of these phases collapsed partially after prolonged annealing at 550 °C, and that defects of the original structure increased with increasing temperature. In addition, high-temperature calcination also leads to agglomeration and coarsening of particles,

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http://dx.doi.org/10.1016/j.mssp.2014.03.023
1369-8001/

which adversely affect the applications of TiO_2 [10,12]. Hence, it is highly desirable to synthesize crystal-phase TiO_2 without post-thermal treatment so that the nanostructures could be preserved.

In this work, we demonstrated the synthesis of TiO_2 in rutile and anatase phases via electrochemical anodization at room temperature without post-thermal treatment. The voltage applied during fabrication was varied to study its effects on properties of the synthesized TiO_2.

2. Experimental details

Titanium foil (Strem Chemical, 99.7% purity and 0.127 mm thickness) was cut into a number of pieces. Prior to anodization, the foil pieces were polished, degreased with ethanol, rinsed in distilled water, and then dried. They were then anodized in a solution of 1.0 M sulfuric acid at room temperature.

During anodization, the foil sample served as the anode and copper wire was the cathode. The electrodes were placed 2 cm apart and the duration of anodization was maintained at 60 minutes. Various voltages (25 V, 50 V, 100 V, 150 V, and 200 V) were applied to the samples.

After the electrochemical process, the morphological and structural properties of samples were analyzed by field emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD) measurements, respectively. The photocatalytic activity of the samples was also studied in this experiment.

The photocurrent activity of the samples was characterized by using a two-electrode PEC cell with platinum wire as counter electrode and TiO_2 samples as working photoelectrode. The supporting electrolyte was 1.0 M potassium hydroxide with 1.0 wt% ethylene glycol solution. The electrodes were connected to a Gamry potentiostat. A 0.28 cm^2 exposed area of the photoelectrodes was illuminated by a solar simulator with light intensity of 100 mW/cm^2. A linear sweep potential (LSP) was scanned from -0.2 V to 1.0 V at a rate of 10 mV/s. During the voltage sweep, the corresponding photocurrent was measured. Next, differential-pulse voltammetry was performed to examine the responsiveness of the samples. Measurements for the photocurrent density–time curve at a fixed bias voltage of 0.6 V were obtained by on–off switching of the simulator at regular intervals. The duration of each sweep was set at 3 minutes.

3. Results and discussions

3.1. Morphological properties

FE-SEM images in Fig. 1 show the top view of the anodized samples. Porous structures were not observed in the samples anodized at 25 V and 50 V. Samples anodized at higher voltages show evolution of morphology to spongelike nanopores. This result indicates that anodization voltage could significantly affect the morphological properties of samples. Nanopores of the 100 V, 150 V, and 200 V samples were inhomogeneous in distribution, shape, and size. Such inhomogeneity could be closely related to the unstable current density at high voltages [13].

We also found that with the increase in applied voltage, the pore size of samples increased as well. This trend suggests that rate of reaction in the experiment increased with voltage as the latter supplied more energy compared with that in low-voltage anodization. As the rate of reaction increases, it might cause faster nucleation of adjacent pores, and hence larger size of pores [14].

3.2. Structural properties

Fig. 2A illustrates XRD patterns of the samples anodized at various applied voltages. Fig. 2B shows XRD patterns of a sample anodized at 100 V under expansion. XRD patterns indicate that the porous structure of the sample anodized at 100 V consisted of anatase and that a mixture of anatase and rutile TiO_2 phases could be obtained at higher voltages.

No anatase or rutile peaks were detected in samples anodized at applied voltages of 50 V and below. Diffraction peaks of anatase appeared in samples anodized at 100 V and at higher voltages. Meanwhile, peaks of the rutile phase appeared at 150 V and above. These results could be explained by the greater requirement of rutile for energy for its formation, that is, when higher anodization voltage is applied, more energy is provided.

We believe that H_2SO_4 functioned as a chemical catalyst during our experiment. It provides an alternative route for crystal formation with a lower activation energy, resulting in the formation of crystal phases of titanium dioxide at room temperature without post-thermal treatment.

Peaks typically located at 25.4°, 37.8°, 48.0°, 54.5°, and 54.9° were assigned to the (1 0 1), (0 0 4), (2 0 0), (1 0 5), and (2 1 1) planes of the anatase phase. The growth orientation of the (1 0 1) plane is favored among planes for all nanostructures, as evidenced by its dominant intensity compared with that of the other anatase peaks. Furthermore, the peaks located at 27.5° and 36.1° correspond to the (1 1 0) and (1 0 1) planes of rutile, respectively.

The amount of anatase and rutile crystals formed could be determined by calculating the area under the peaks of the XRD patterns. Table 1 summarizes the amounts of both crystal phases in the samples. The amount of rutile formed increased when the applied voltage increased from 100 V to 200 V because of the greater amount of energy provided at higher voltage. We believe that conversion of anatase to rutile phase occurred when there is excess energy during synthesis, thereby increasing the rutile-to-anatase ratio at higher applied voltage.

The mean crystallite size may be calculated through the Scherrer equation using data collected from XRD measurements [15], $D = K\lambda/(\beta \cos \theta)$, where D is the mean crystallite size, K is a dimensionless constant (typically equal to 0.9), λ is the K-alpha1 wavelength (0.15406 nm), and β is the full width at half maximum of the diffraction peak. θ is the diffraction angle, which can also be taken as the value of the maximum point of the diffraction peak.