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**Preparation of Non-annealed Anatase TiO₂ Film on ITO substrate by Anodizing in
Hot Phosphate/glycerol Electrolyte for Dye-sensitized Solar Cells**

Etsushi Tsuji^{a,b,*}, Naoto Hirata^b, Yoshitaka Aoki^{a,b}, Hiroki Habazaki^{a,b,c}

^aDivision of Materials Chemistry and ^cFrontier Chemistry Center, Faculty of
Engineering, Hokkaido University, Sapporo, Hokkaido, 060-8628, Japan

^bGraduate School of Chemical Sciences and Engineering, Hokkaido University,
Sapporo, Hokkaido 060-8628, Japan

Corresponding author: Phone & Fax: +81-11-706-6736, e-mail:

e-tsuji@eng.hokudai.ac.jp

ABSTRACT

In this study, mesoporous TiO₂ films were formed on ITO conductive glasses by anodizing of titanium thin films without post-annealing. The titanium thin films, ~200 nm thick, sputter-deposited on to the ITO substrates were anodized at 20 V in a phosphate/glycerol electrolyte at 433 K. A completely transparent TiO₂ specimen was obtained by anodizing for 60 s. The as-anodized mesoporous TiO₂ films consisted of anatase, even without post annealing. The transparent mesoporous TiO₂ film anodized for a suitable time showed much better photoelectrochemical performance than the post-annealed TiO₂ nanotubular film.

Keywords: non-annealed anatase TiO₂ film, anodizing, DSSC

1. Introduction

Dye-sensitized solar cell (DSSC) is one of the attractive solar cells and has been widely studied [1-10]. More recently, some researchers reported that the DSSC shows more than 11% energy conversion efficiency [1,2]. However, further higher energy efficiency is needed for practical application.

In general, TiO_2 thin films for DSSCs are formed on transparent conductive oxide (TCO) films such as F-doped tin oxide (FTO) and indium tin oxide (ITO) because of light irradiation from back side of the substrates. TiO_2 thin films have been formed on the TCO substrates by spin-coating [3,4], doctor-blading [5,6], sputtering [7,8] and anodizing [9,10] methods. The common process of these methods was post-annealing at ~ 723 K due to sintering of TiO_2 nanoparticles and crystallization of the deposited films. However, the TCO substrates are heat-labile materials, leading to an increase in the electric resistance [11,12].

Recently, we reported that anodizing of titanium at 20 V in a phosphate/glycerol electrolyte at 433 K formed anatase films, which had a mesoporous morphology with pore diameter as small as ~ 10 nm, even without post annealing [13,14]. In this communication, titanium thin films sputter-deposited on to an ITO substrate were anodized in the hot phosphate/glycerol electrolyte. The transparent TiO_2 specimens obtained revealed good photoelectrochemical performance without post annealing.

2. Experimental

The titanium films, ~ 200 nm thick, were prepared by DC magnetron sputtering on to ITO-coated glasses (ALDRICH, 576352-25PAK). The target used for the preparation

of the titanium films was 99.9% titanium disk. The deposition of the films was carried out with a current of 0.5 A and a voltage of 290 V under an argon pressure of 0.3 Pa. The deposition time was 15 min.

Then, the deposited titanium films were anodized at 20 V in a stirred glycerol electrolyte containing $0.6 \text{ mol dm}^{-3} \text{ K}_2\text{HPO}_4$ and $0.2 \text{ mol dm}^{-3} \text{ K}_3\text{PO}_4$ at 433 K under a nitrogen atmosphere. The water content in the electrolyte was $\sim 0.03 \text{ mass\%}$ determined by a volumetric Karl Fischer titrator (Hiranuma Sangyo Co. Ltd., AQVAQUACOUNTER AQV-7S). A platinum sheet was used as a counter electrode. The films anodized at 20 V are denoted as P-20V. For comparison, the deposited titanium film was also anodized in 0.25 wt% NH_4F and 1vol% water/ethylene glycol electrolyte at 293 K at 60 V. Then, the film was annealed at 723 K for 3 h in air (denoted as F-60V) [10].

The structure of the anodic films was identified by X-ray diffraction (XRD) (Rigaku, RINT-2000) using $\text{Cu K}\alpha$ radiation. Depth profiles of the anodic films were obtained by a glow discharge optical emission spectroscopy (GDOES) (Jobin-Yvon 5000 RF) in an argon atmosphere of 600 Pa with application of RF of 13.56 MHz and power of 50 W.

The current density (j) vs potential (E) curves of the anodic films for oxygen photoevolution were measured by using a normal three-electrode system. The anodic film, a platinum sheet and an Ag/AgCl/KCl(satd) electrode were used as a working electrode, a counter electrode and a reference electrode, respectively. The electrodes were mounted in an electrochemical cell having a quartz window, and UV irradiation was carried out by the 365 nm band from a 500 W high-pressure xenon lamp(WACOM, HX-504), obtained by using of the band-pass filter (ASAHI SPECTRA,UTVAF 50S-33U). The intensity of the UV light was 60 mW/cm². 0.1 M deoxygenated Na₂SO₄ aqueous solution was used as an electrolyte. The applied potential was swept from -0.85 to 1.15 V vs Ag/AgCl/KCl(satd) with a potential-sweep rate of 50 mV s⁻¹. In all of the experiments, special-grade chemicals were used without further purification. Pure water was obtained by purifying deionized water with a Milli-Q water purification system.

3. Results and discussion

Fig. 1 shows the current transient of titanium thin film sputter-deposited on to the ITO substrate during anodizing at 20 V in the hot phosphate/glycerol electrolytes containing 0.03% water (P-20V). At the commencement of anodizing, the current increases to ~1 kA m⁻², followed by a rapid decrease to less than 400 A m⁻². Then, the

current density gradually decreases with anodizing time until ~60 s. Such gradual current decrease is typical in anodizing of metals in the hot phosphate/glycerol electrolyte [15-17]. During this period, the specimen gradually became transparent from the edges of the specimen (Fig. 1a, b) and completely transparent after anodizing for ~60 s (Fig. 1c). Then, the current density steeply decreased. The details of this behavior are described later. By SEM observation, a rough and nano-granular surface was developed after anodizing and the thickness of the film was ~195 nm.

Fig. 2 shows XRD patterns of the P-20V anodized for 80 s and F-60V. The peaks corresponding to anatase appeared in both patterns, even though the P-20V was not annealed after anodizing. In addition, the 004 peak of anatase TiO_2 is the strongest in the XRD pattern of P-20V, whereas the 101 peak is the strongest in that of F-60V as in the randomly oriented anatase. A similar result was reported at TiO_2 mesoporous films formed on titanium specimen in our previous study [13,14].

Fig. 3 shows j - E curves of the P-20V anodized for the various periods ((a) to (d) indicated in Fig. 1) and the F-60V annealed at 723 K. From the comparison of the current densities of the F-60V under the UV irradiation and dark condition, it is observed that the photocurrent is dominant in the anodic current under the UV irradiation. Since the dark anodic current densities for the P-20V specimens were

similar to that of F-60V, the anodic current densities of all the specimens under the UV irradiation condition correspond to the photocurrent densities. The P-20V specimens anodized up to 60 s (Fig. 3c) show much higher photocurrent in comparison with the F-60V, although photocurrent is markedly reduced by anodizing for 80 s (Fig. 3d). Since the specimens became transparent after anodizing for 60 s, the film (c) in Fig. 3 was the best transparent electrode for DSSCs.

Fig. 4 (a) and (b) shows the GDOES depth profiles of the P-20V anodized for 60 s and 80 s. Both the anodic films are oxide-based, since the intensity ratio of oxygen to titanium was similar to TiO_2 film formed in an aqueous electrolyte. The most important feature of the P-20V is that the phosphorus increased at not only the bottom of the TiO_2 film, but also the surface of ITO substrate after more than 60 s. This result indicates that the excess anodizing such as the case of Fig 4b induced the phosphorus doping at ITO surface. In addition, when only the ITO substrate was applied 20 V in the same electrolyte, the phosphorus also doped in ITO surface, leading to quite high electric resistance. Therefore, the excess anodic TiO_2 /ITO shows little anodic current (Fig. 1) and photocurrent (Fig. 3).

4. Conclusions

The TiO₂ thin film can be formed on the ITO conductive glass by anodizing at 20 V in the hot phosphate/glycerol electrolyte. The obtained film without post-annealing showed anatase phase. The TiO₂/ITO prepared by anodizing for optimized time showed much better performance than the nanotubular TiO₂/ITO formed in NH₄F/ethylene glycol with post-annealing. However, the excess anodizing induced doping of phosphorus at ITO surfaces, leading to high electronic resistance of the ITO.

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FIGURE CAPTIONS

Fig. 1 The current transient of titanium films during anodizing at 20V (P-20V) in 0.6 mol dm⁻³ K₂HPO₄ + 0.2 mol dm⁻³ K₃PO₄ glycerol electrolytes containing 0.03 mass% water at 433 K and the photographs of the specimens after anodizing for (a) 30 s, (b) 50 s, (c) 60 s and (d) 80 s.

Fig. 2 X-ray diffraction patterns of (a) the P-20V films formed by anodizing for 80 s, together with (b) that of the NT film annealed at 723 K in air for 3 h (F-60V).

Fig. 3 *j*-*E* curves of the P-20V films formed by anodizing for (a) 30 s, (b) 50 s, (c) 60 s and (d) 80 s, together with that of the F-60V film. The curves were measured in

0.1 M Na₂SO₄ under UV light irradiation and also under dark condition for the F-60V film.

Fig. 4 GDOES depth profiles of the P-20V films formed by anodizing for (a) 60 s and (b) 80 s.

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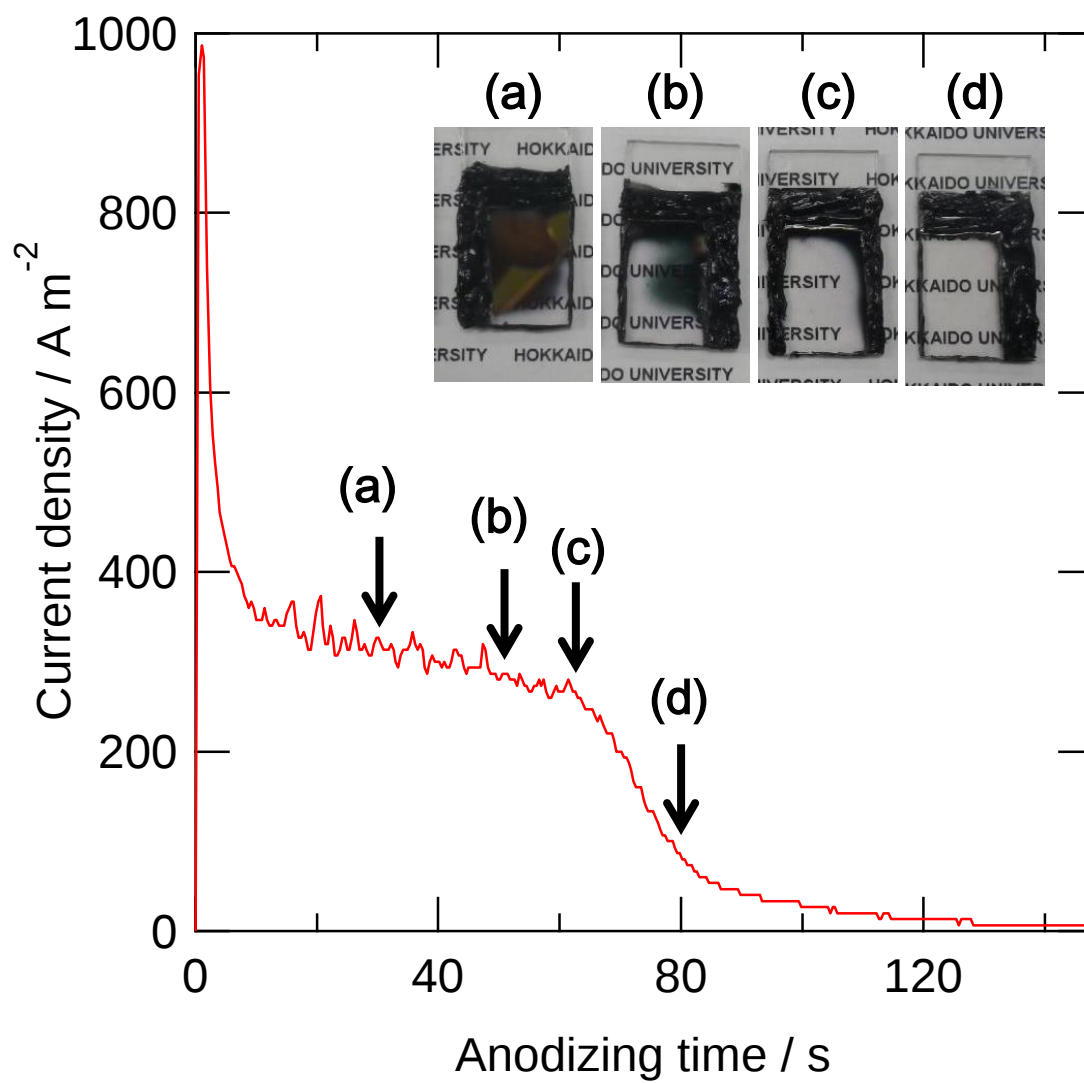


Fig. 1. E. Tsuji, et. al.

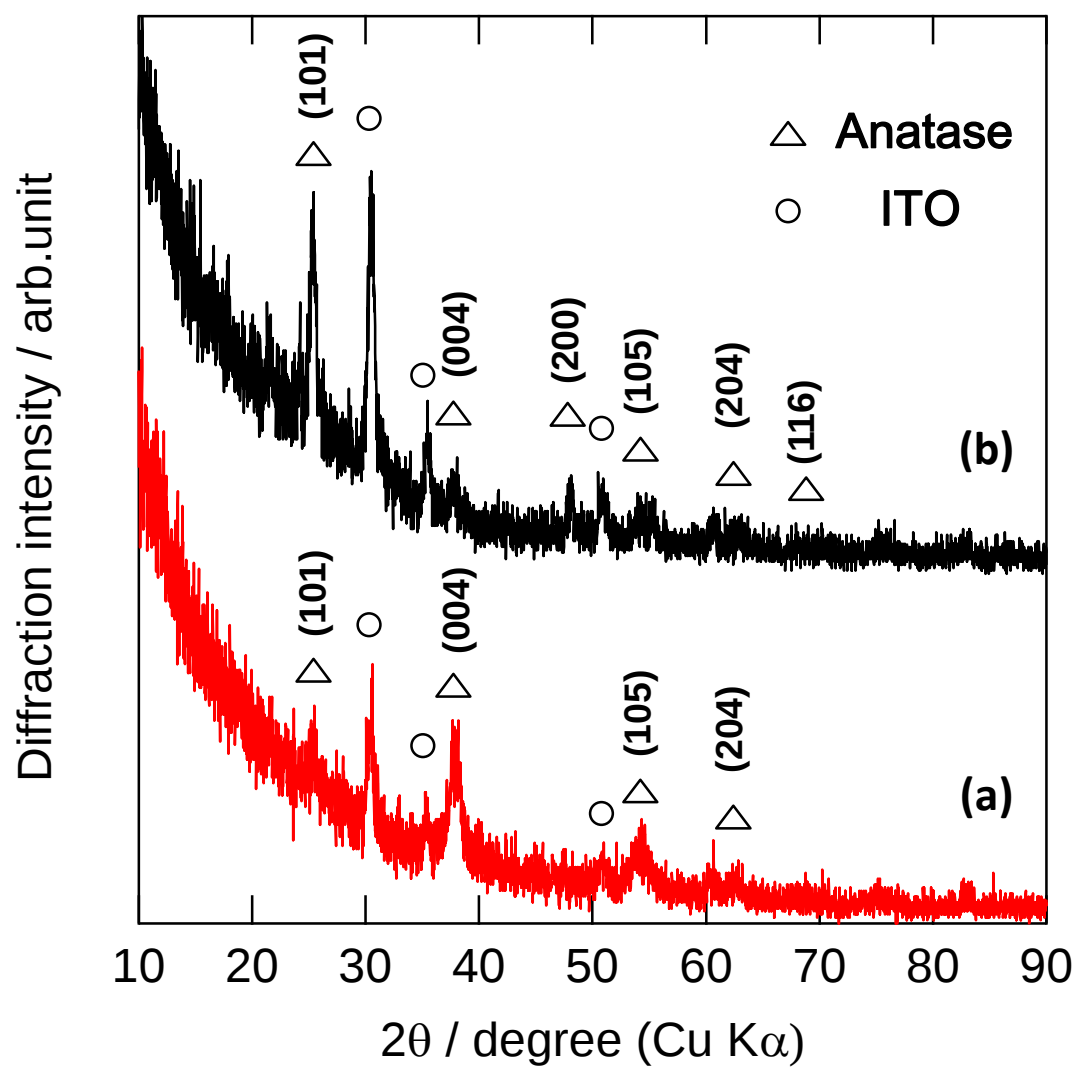


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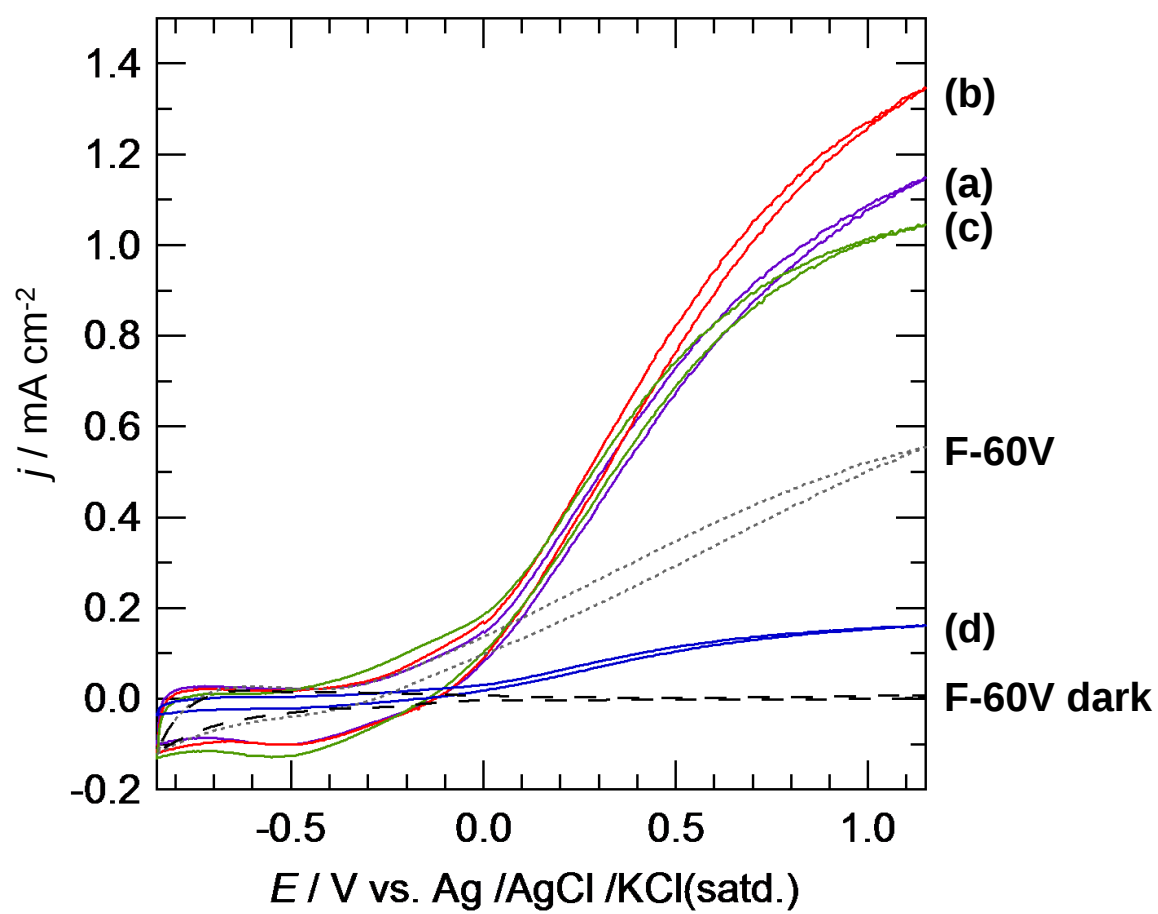


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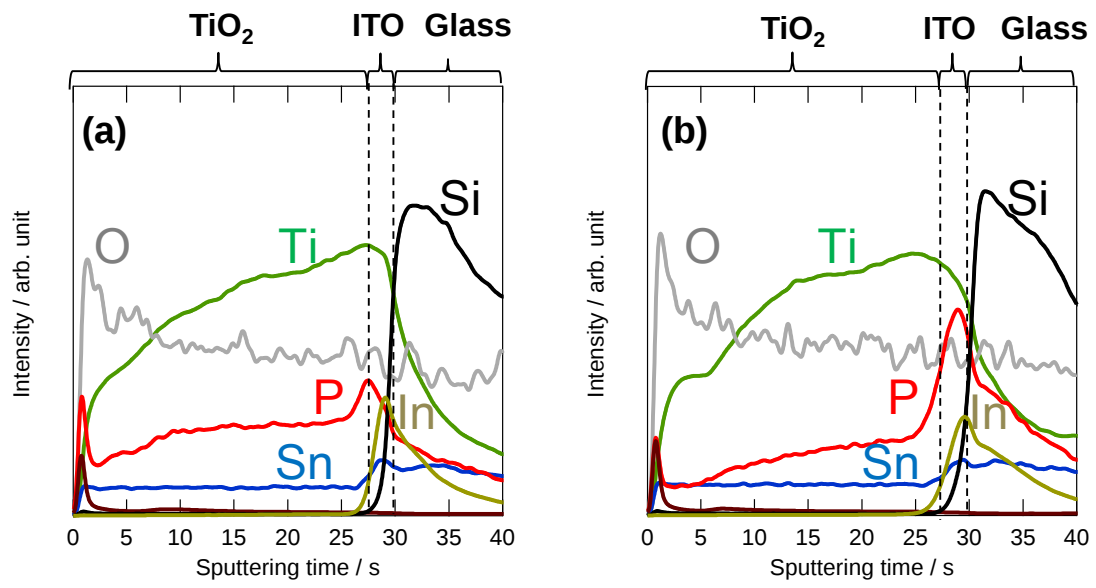


Fig. 4. E. Tsuji, et. al.