Effect of Photoetching on Photoinduced Hydrophilicity of Titanium Dioxide Film

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The effect of photoetching (photoelectrochemical etching) on photoinduced hydrophilic conversion of titanium dioxide (TiO_2) film electrodes prepared by thermal oxidation of Ti plate has been studied. We have found that photoetching of TiO_2 film results in the formation of nano-porous structure depending upon preparation condition (oxidation temperature), photoetching condition (electrode potential) and crystallographic orientation of the TiO_2 grain. Photoetching of the film oxidized at temperature higher than 900°C makes nano-porous structure consisting of (100) plane of rutile structure of TiO_2 and improves the photoinduced hydrophilic conversion property. Photoetching under anodic polarization increases the rate of photoinduced hydrophilic conversion, while the film photoetched under weak anodic polarization does not show the photoinduced hydrophilic conversion property.

Key Words : Photoetching, Photoinduced Hydrophilicity, Titanium Dioxide

1 Introduction

TiO_2 is a very attractive material for photocatalyst, dye-sensitized solar cell and gas sensor due to its favorable chemical, physical, optical and electrical properties.¹⁻³⁾ Recently, photoinduced hydrophilic conversion property of TiO_2 has been discovered.⁴⁻⁷⁾ Although a TiO_2 surface is originally less hydrophilic, it becomes highly hydrophilic by its band gap excitation. This property gives new application of TiO_2 such as anti-fogging and self-cleaning coatings. For example, TiO_2 -coated rearview mirrors of a car give clear view even on a rainy day and stain on TiO_2 coated wall can be easily washed off by rain water. Experimental results suggest that this hydrophilicity is mainly due to the reconstruction of surface structure such as an increase of hydroxyl groups formed by the photogenerated holes.⁷⁾ Strong dependence of the crystal face of rutile single crystal TiO_2 was reported by T. Watanabe *et al.*⁸⁾ By comparing the reactivity of photoinduced hydrophilic conversion of (110), (100) and (001) surfaces, they concluded that the oxygen bridging sites played an important role.

Photoelectrochemical etching (photoetching) is a unique processing technique for tailoring a surface microstructure of various semiconductor materials. We have already reported that the photoetching of titanium dioxide in sulfuric acid solution leads to a unique nano-porous structure to be related to the crystallographic orientation of each grain on the single crystal, the sintered pellet and the film sintered of TiO_2 paste electrodes.⁹⁻¹²⁾ During the photoetching, the regularly ordered sub micron porous structure (named “nano-honeycomb” structure) consisting of thin wall with (100) crystal face is formed on the TiO_2 surface. This surface has both high crystallinity and large specific surface area. T. Shibata *et al.* reported¹³⁾ that the exposing of (100) crystal

face by photoetching of single crystal TiO_2 improves the hydrophilic conversion rate and the sensitivity for weak excitation.

In the present paper, the effect of photoetching on photoinduced hydrophilic conversion of TiO_2 film electrodes prepared by thermal oxidation of Ti plate will be described.

2 Experimental

TiO_2 film electrodes were prepared by thermal oxidation of Ti plates (99.5%, Nilaco Co.). Ti plates ($8 \times 8 \times 0.2$ mm) were chemically etched by immersing in an etchant solution (HNO_3 43 ml, HF 2.8 ml, H_2O 50 ml) for 60 sec. After dried in air they were oxidized in O_2/N_2 gas stream (O_2 : 0.5 ml min^{-1} , N_2 : 300 ml min^{-1}) at various temperatures (800°C - 1000°C) for 10 min. During heating-up and cooling-down period, only N_2 gas (300 ml min^{-1}) was flowed to avoid excess oxidation. To obtain n-type semiconductivity the sintered film was reduced in 10% H_2/N_2 gas stream at 800°C for 30 min.

The copper lead wire was attached to the top side of TiO_2 electrode and insulated with silicone resin. Three electrode cells were used for photoetching experiments, with a platinum counter electrode, an SCE reference electrode, and TiO_2 film electrodes for working electrodes. Photoetching was carried out in 1 M H_2SO_4 solutions under potentiostatic condition. The TiO_2 film electrode was irradiated using a 500 W high pressure Hg arc lamp with band path filter (SIGMA UTVAF36U). The photoetching quantity was controlled with passed charges of photocurrent by digital coulomb meter (NIKKO KEISOKU NDCM-4).

The surface microstructure was investigated by scanning electron microscope (SEM, KEYENCE VE-7800).

The hydrophilicity of the surface was evaluated by the

contact angle measurement by taking photographs of droplet of water on the surface in ambient atmosphere. A cylindrical black-light lamp was employed as an excitation source. Light intensity was adjusted at $810 \mu\text{W cm}^{-2}$.

3 Results and Discussion

Figure 1 shows SEM photographs of TiO_2 surface before and after photoetching. As is seen from (a), before photoetching, the grain sizes of TiO_2 film oxidized at 900°C were 5 to $10 \mu\text{m}$ and its thickness was about $3 \mu\text{m}$ from cross sectional observation (not shown here). The sample oxidized at 800°C (b) consists of relatively small

Fig. 1 SEM photographs for TiO_2 surface before (a) and after (b), (c) photoetching at $+1.0 \text{ V}$, 100 C cm^{-2} . Oxidizing temperature : (a), (c) 900°C , (b) 800°C .

grains and some parts of grains were dissolved and its grain boundary were left undissolved after the photoetching. In the case of sample oxidized at 900°C (c), surface of TiO_2 film was selectively dissolved and unique etching patterns appeared depending upon its crystallographic orientations. The surface was covered with the plate-like crystallite of TiO_2 and its thickness was about several tens of nano-meter and its length was several micrometer. We have reported similar etching patterns consisting of (100) crystal plane in the case of single crystal and polycrystalline TiO_2 electrodes.⁹⁾

Figure 2 shows the changes of contact angle of water for TiO_2 thin film surface with the UV light irradiation time. Each electrode was photoetched at $+1.0 \text{ V}$, 100 C cm^{-2} . Data for an unphotoetched sample are also shown in this figure as the reference (■). The contact angle of water on all of the samples decreased with UV irradiation time, but the hydrophilic conversion rates were different from each other. The unphotoetched sample shows very slow hydrophilic conversion rate and the contact angle does not decrease below 60° even by long time irradiation. The photoetched samples oxidized at equal or lower than 800°C show high hydrophilicity with the contact angle less than several degrees, but it needs to irradiate for more than 1000 min. In this case some of the grain selectively dissolved and the grain boundaries partially covered the surface. The grain boundary play a negative role for photoinduced hydrophilic conversion as described later. On the other hand, the photoetched samples oxidized at the temperature higher than 900°C show that the contact angle of water rapidly decreases down to several degrees within 100 min. In the case of lower sintering temperature such as 800°C , the grains of TiO_2 were less than $1 \mu\text{m}$ and the characteristic photoetching pattern does not evolve. The photocurrent of TiO_2 electrode in H_2SO_4 aqueous solution decreased after photoetching in all cases whereas the hydrophilic conversion rates increased after formation of photoetching patterns. This result reveals that the surface structures

Fig. 2 Changes of the contact angle of water for photoetched TiO_2 thin film surface with the UV light irradiation time. Photoetching condition : $+1.0 \text{ V}$, 100 C cm^{-2} . Inset shows oxidizing temperatures.

Fig. 3 SEM photographs for TiO_2 thin film surface after photoetching. (a) : photoetching at +0.1 V, 100 C cm^2 , (b) : photoetching at +1.0 V, 100 C cm^2 , Oxidizing temperature : 1000 $^\circ\text{C}$.

such as a crystallographic orientation of surface and a surface roughness are more important for photoinduced hydrophilic conversion than the photoelectrochemical activities such as the photocurrent. As mentioned above T. Watanabe *et al.* reported that the existence of bridging site oxygen on (100) crystal faces accelerate photoinduced hydrophilic conversion.^{8,13} In addition H. Irie *et al.* reported that both the hydrophilic and hydrophobic properties are enhanced by increasing the surface roughness by photoetching (accordance with Wenzel's equation).¹⁴ In this case the surface crystal orientation and the surface roughness created by photoetching speed up the photoinduced hydrophilic conversion.

Figure 3 shows SEM photographs for TiO_2 thin film surface after photoetching at different etching potentials. In the case of the sample photoetched at +0.1 V (a), weak anodic polarization, which is close to the flat band potential, the bulk of each grains were selectively dissolved and the grain boundaries were left undissolved. Similar etching site selectivity was observed for the sintered pellet electrodes photoetched at weak anodic polarization and this phenomenon was explained by using energy band model of polycrystalline semiconductor with grain boundaries in contact with electrolyte.¹⁰ At the grain boundary, many lattice defects exist and act as recombination centers for photogenerated holes and elec-

Fig. 4 Effect of the photoetching potential on the changes of the contact angle of water for TiO_2 thin film surface with the UV light irradiation time. Inset shows photoetching conditions. Oxidizing temperature : 1000 $^\circ\text{C}$.

trons. Resultingly it suppresses the photoanodic dissolution. The sample photoetched at +1.0 V (b) shows the typical etching pattern similar to Fig. 1 (c) consisting of plate-like crystals, although its size was smaller than that of Fig. 1 (c). Higher oxidation temperatures accelerate the grain growth of the TiO_2 film which results in fine etching pattern.

Figure 4 shows the effect of photoetching potential on the changes of contact angle of water for TiO_2 thin film surface with the UV light irradiation time. Symbols ($\blacktriangle$) and ($\square$) in this figure are the same as those in Fig. 3 (a) and (b) respectively. The initial contact angles for photoetched samples ($\blacktriangle$) and ($\square$) before UV irradiation are larger than 100 $^\circ$. According to H. Irie *et al.*, these relatively high hydrophobicity on the photoetched samples were caused by intrusion of air among roughness structures in accordance with Cassie's equation.¹⁴ The hydrophobicity of the sample photoetched at +0.1 V was not changed by UV irradiation. It is well known that the photogenerated holes play an important role for the hydrophilic conversion.^{6,7} The surface photoetched at +0.1 V is covered with skeleton structure of grain boundaries, so photogenerated holes recombine with electrons and does not lead hydrophilic surface. The contact angle of water for the sample photoetched at +1.0 V decreases down to several degrees after UV irradiation for several tens of minutes. In this case, the surface roughness of the fine etching pattern and the exposed surface consisting of plate-like crystals with (100) crystal face effectively worked for photoinduced hydrophilic conversion.

4 Conclusion

The effect of photoetching on photoinduced hydrophilic conversion of TiO_2 film electrodes prepared by thermal oxidation of Ti plate has been studied. Photoetching of TiO_2 film electrode oxidized at temperatures higher than 900 $^\circ\text{C}$ leads to nano-porous structure consisting of (100) crystal face of rutile TiO_2 and in turn exhibits high photoinduced hydrophilicity. By contrast,

photoetching under weak anodic polarization results in the formation of skeleton structure consisting of grain boundaries and its surface shows relatively high hydrophobicity and no photoinduced hydrophilic property.

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