Photoelectrochemical Preparation of Nano-Porous Structure on Thermally-Oxidized TiO_2 film

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The photoelectrochemical etching (photoetching) is a unique technique for tailoring surface microstructure of semiconductors. We have already reported that the photoetching of TiO_2 in H_2SO_4 solution creates a unique nano-porous structure on its surface, depending upon the crystallographic orientation, which has been analyzed for single crystal and sintered pellet electrodes [1]. Remarkable experimental results we have found are that a layer with "nano-honeycomb" structure is created on the surface of TiO_2 electrodes and this layer satisfies both high crystallinity and high specific surface area, which seems favorable for the application to various optical and electrical devices such as solar cells, gas sensors etc. For example, the photoetching of TiO_2 improve its gas sensor characteristics in terms of both sensitivity and response time [2]. However, the thickness of such a unique layer thus formed is limited only to several μm from the top surface. It is desirable for the above-mentioned applications to get TiO_2 samples in which nano-honeycomb structure is formed throughout the electrodes from the top surface to the bottom, because existence of the bulk part can decrease the sensitivity. In the present study we have used thermally oxidized TiO_2 film electrode and made attempt to change them to highly crystallized nano-porous TiO_2.

TiO_2 film electrode was prepared by the thermally oxidizing the Ti plate. The Ti plate (10 mm X 5 mm X 0.2mm) was sintered in nitrogen gas stream at 1000°C for 10min to 10 hr. To obtain n-type semiconductivity the sintered film was reduced in 10% H_2/N_2 gas stream at various temperatures (700°C - 1000°C) for 30 min to 1 hr. The TiO_2 film thickness was determined from SEM observation to be 2 to 20 μm. The photoetching was carried out by illuminating the electrodes with a high pressure Hg arc lamp in a sulfuric acid aqueous solution at potentiostatic condition. The etching quantity was controlled by monitoring the passed charges of the photocurrent.

Fig. 1 shows SEM photographs of thermally-oxidized TiO_2 film electrode surface (A,C) and cross section (B, D) before (A,B) and after photoetching (C,D) in 1.0 M H_2SO_4 aqueous solution at +1.0 V vs. SCE. After sintering of Ti plate (A, B), dense TiO_2 film formed on the Ti surface and its thickness is about 2.5 μm. After photoetching (C, D), the regularly ordered sub-micron porous structure (named "nano - honeycomb" structure) consisting of thin wall with (100) crystal face appeared on the TiO_2 surface. We have reported similar nano-porous structures in the case of sintered pellet and single crystal electrode [1]. Thickness of the photoetching pattern is about 1 μm. After photoetching of 80 C/cm^2, The whole film were changed to nano-porous structure. In the cross-sectional view (D), the etch pit with deep square hollows observed. This suggests that the c-axis of rutile structure of TiO_2 is parallel to the surface.

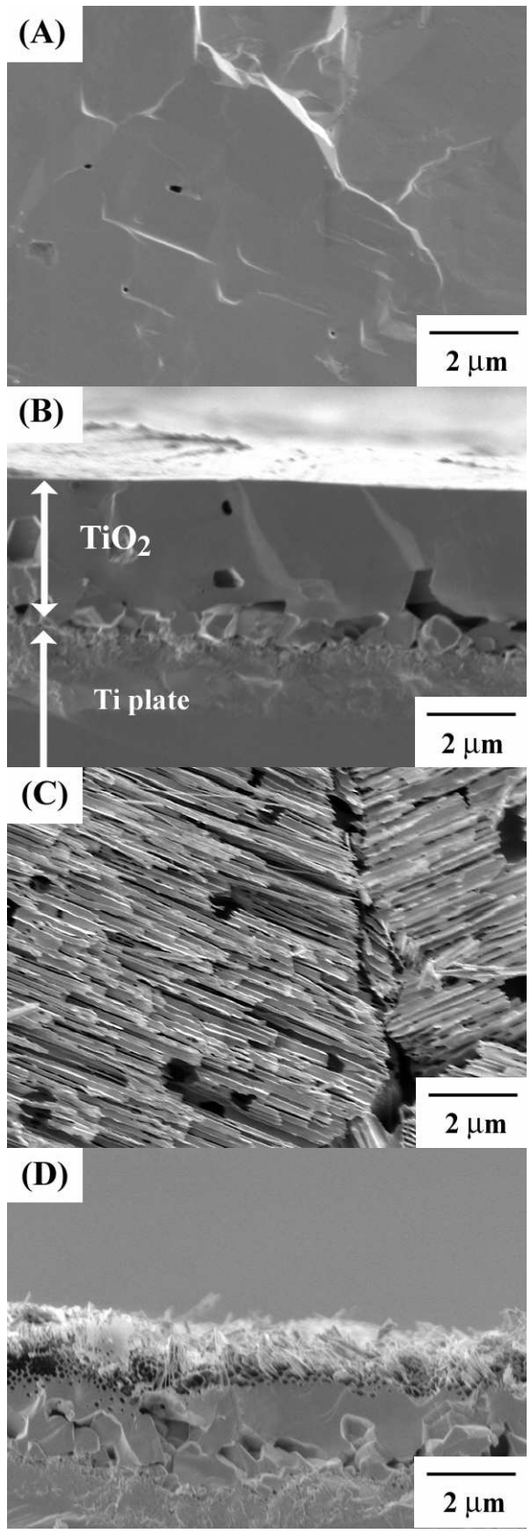

Fig. 1 SEM photographs of thermally-oxidized TiO_2 film electrode surface (A,C) and cross section (B, D) before (A,B) and after photoetching (C,D) in 1.0 M H_2SO_4 aqueous solution at +1.0 V vs. SCE.
Sintering condition : 1000°C, 10 min
Reducing condition : 700°C, 30 min
Etching quantity (passed charges of photocurrent) in C, D : 40 C/cm^2

REFERENCES

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[2] H.J. Ryu, T. Sugiura, T. Yoshida and H. Minoura, *Trans. Mater. Res. Soc. Jpn*, **27**, 695 (2002).

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