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Photoelectrochemical Formation of Nano-Porous Structures on TiO_2 Film Electrode

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The photoelectrochemical etching (photoetching) of thick film electrodes of TiO_2 prepared by coating TiO_2 paste and sintering at various temperatures has been studied. We have found that photoetching of thick films sintered at temperatures higher than 900°C results in the formation of nano-porous structure depending upon the crystallographic orientation, while in the case of photoetching of thick films sintered at temperatures lower than 800°C, any change in surface morphology was not observed. We have concluded that grain growth of TiO_2 particles up to several micrometers by the sintering is required to create nano-porous layer of TiO_2 by photoetching.
Key words: photoetching, titanium dioxide, thick film, nano-porous structure

1. INTRODUCTION

TiO_2 is a very attractive material for photocatalysts, dye-sensitized solar cells and gas sensors by its favorable chemical, physical, optical and electrical properties [1-4]. As all the chemical events such as catalytic reactions, chemical adsorption and electrochemical charge transfer reaction take place at the surface, an enlargement of the active surface area must lead to the improvement of their performance. Therefore, electrodes for the above-mentioned applications have been usually prepared from their nano-crystalline powders. The control of the crystallographic orientation of the electrode materials is often important, especially when they are used as gas sensing devices, because the adsorption properties depend upon the crystallographic orientation [5].

Photoelectrochemical etching (photoetching) is a processing technique for tailoring a surface microstructure of various semiconductor materials. 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 [6-8]. 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 devices such as gas sensors etc. For example, the photoetching of TiO_2 improve its gas sensor characteristics in terms of both sensitivity and response time. The enlargement of the specific surface area in the grain bulk is responsible for the improved sensitivity. An improved response time is ascribed to relative increase in surface area of the (100) crystal face [6, 8] which allows fast adsorption of O_2 [5]. 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 paper we have used well-sintered TiO_2 thick film electrodes and made attempt to change them to highly crystallized nano-porous TiO_2.

2. EXPERIMENTAL

The TiO_2 paste was prepared from TiO_2 powder (JRC-TIO-4, The Catalysis Society of Japan) according to a method described in the literature [9]. The paste was coated on a titanium plate (10 mm × 5 mm × 0.2mm). After dried in air for half an hour it was sintered in air at various temperature (600°C - 1000°C). To obtain n-type semiconductivity the sintered film was reduced in 10% H_2/N_2 gas stream at various temperatures (600°C - 1000°C) for 1 hr. The TiO_2 film thickness was determined to be 10～20 μm by a surface profilometer.

The cupper lead wire was attached to top side of the TiO_2 electrode and insulated with silicone resin except the electrode surface. Three electrode cells were used, platinum counter electrode, SCE reference electrode, and TiO_2 film electrode for working electrode. Photoetching was carried out by illuminating the electrode with UV light (around 365 nm) using a 500W high pressure Hg arc lamp with band path filter (SIGMA UTVAF36U) in 1M H_2SO_4 solutions under potentiostatic condition at +1.0 V vs. SCE. The photoetching quantity was controlled with passed charges of photo current by digital coulomb meter (NIKKO KEISOKU NDCM-4) [7]. The carrier densities

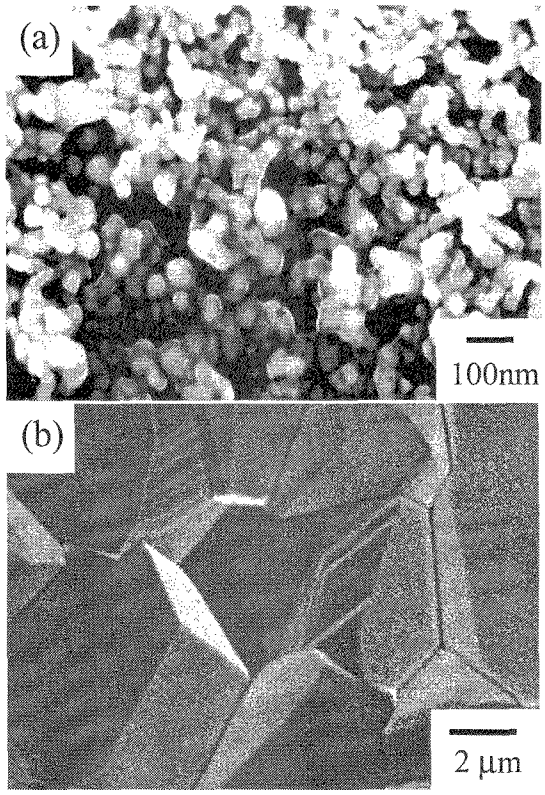

Fig. 1 SEM photographs of TiO_2 thick film surface after heat treatment.
Sintering Temperature : (a) 700℃ (b) 1,000℃

of the electrodes were estimated from Mott - Schottky analysis of the impedance measurement using frequency response analyzer (NF S-5720C) in 1 M H_2SO_4 solutions.

The surface microstructure was investigated by scanning electron microscope (SEM, TOPCON ABT-150FS) and transmission electron microscope (TEM, HITACHI H-8100).

3. RESULTS ANS DISCUSSION

Prior to the photoetching experiments, the effect of sintering temperature on the morphology of TiO_2 thick film electrode was examined. Fig. 1 shows clear difference in surface morphology between TiO_2 films sintered at 700°C and 1,000°C. At low temperatures (600°C - 800°C), the grains are spherical in shape and interconnected with each other, as seen in Fig. 1(a). When sintered at higher temperatures (900°C – 1,000°C), on the other hand, the grain shape changes from spherical to polyhedral, and continuous grain boundary network has been formed as is shown in Fig. 1(b). The XRD analyses have shown that TiO_2 thick films sintered at lower temperatures (600°C - 800°C) are composed of rutile and anatase phases, whereas higher temperature sintering up to 900°C results in the formation of only rutile phase.

The average grain size of the film is plotted against

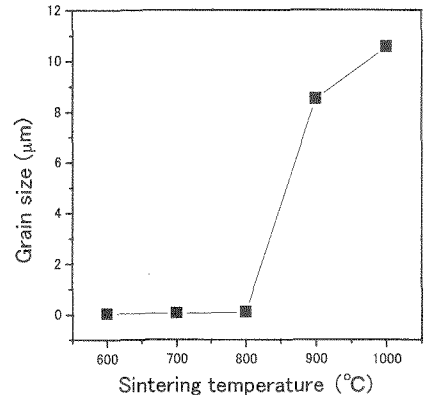

Fig. 2 Grain size of the TiO_2 thick films after sintering at various temperatures.

the sintering temperature in Fig. 2. It is apparent that a remarkable change in grain size of TiO_2 thick film takes place at temperature between 800°C and 900°C. At temperatures lower than 800°C, the grain size is less than 100 nm, while at temperatures higher than 900°C, the grain size increases up to about 8 μm.

For the TiO_2 samples sintered at low temperatures (600°C - 800°C), any change in surface morphology was not observed by photoetching. On sintering at higher temperatures (900°C - 1,000°C), on the other hand, the nano-porous surface structure is created. Typical etch pit size of the photoetching patterns reported previously for the sintered pellet electrode are larger than 100nm [6, 10]. As is seen in Fig. 2, the grain size of TiO_2 film sintered at low temperature was very small compared to the etch pit size to be expected.

The surface SEM photographs for TiO_2 thick films sintered at 1,000°C after photoetching with various etching quantities are shown in Fig. 3. By the photoetching of 10 C/cm^2 (a), nano-porous patterns were created on some grains but most of the grains are unphotoetched. Further photoetching up to 20 C/cm^2 (b) brings about the nano-porous structure on all of the grains and its surface has a unique pattern depending upon the crystallographic orientation of each grain. The pit size of nano-porous structures is a few tens of nanometer and the remaining thin walls of TiO_2 are interconnected with each other. We have reported similar nano-porous structures (nano-honeycomb structure) consisting of (100) plane in the case of sintered pellet and single crystal electrode [6, 8]. But the size of the etch pit for the photoetched thick film electrode is smaller than that of the sintered pellet or single crystal electrode which is usually more than 100 nm. By increasing photoetching quantity, the wall of nano-porous structure gradually changed to be narrower and thinner by the dissolution of wall faces. As a result the surface structure changed to nano-rod structure as is clearly seen in (c). In the case of photoetching of

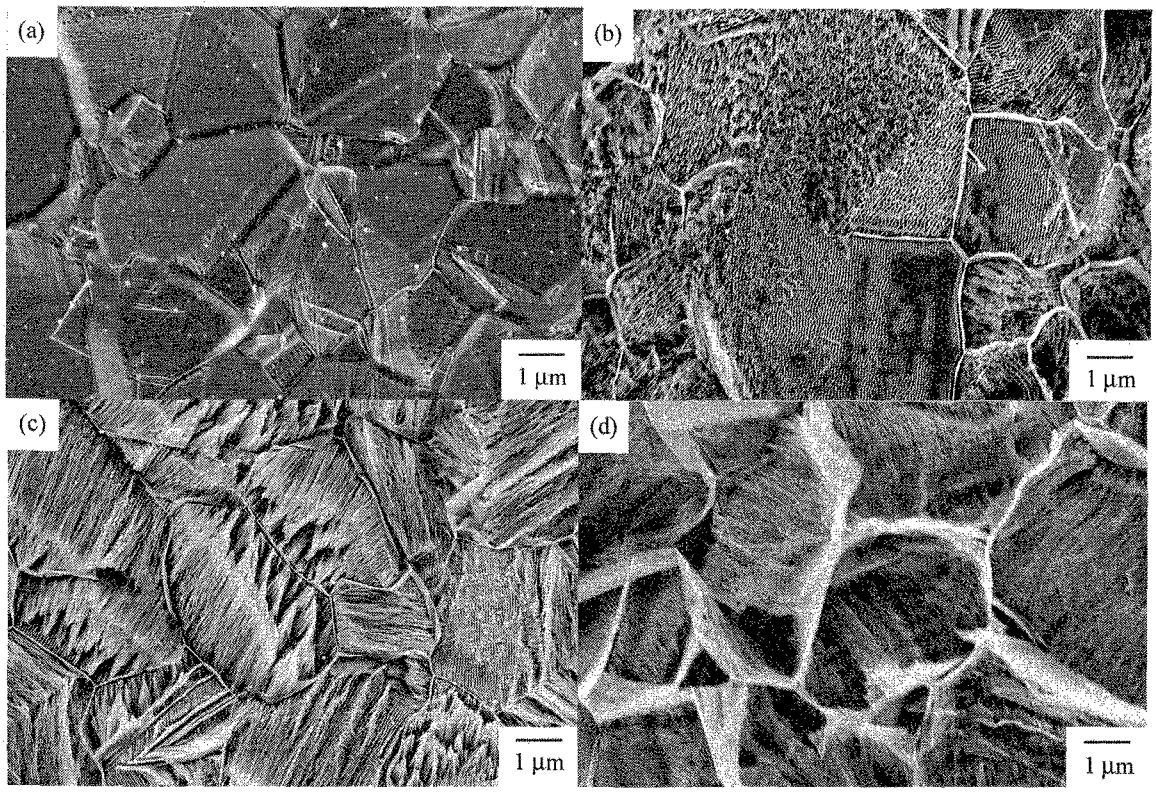

Fig. 3 SEM photographs for the TiO_2 thick film electrode after photoetching with various etching quantities.

Sintering condition : 1,000℃, 5 hrs in air, Reduction condition : 1,000℃, 1 hrs in 10 % H_2/N_2 gas stream
Passed charges of photocurrent : (a) 10 C/cm^2 (b) 20 C/cm^2 (c) 40 C/cm^2 (d) 100 C/cm^2

sintered pellet electrode reported in our previous paper, more than several hundred C/cm^2 is needed to change nano-honeycomb structure to nano-rod structure [10]. The change to nano-rod structure takes place with less photoetching quantity (40 C/cm^2) in the thick film electrode. This is probably due to thinner etch pit wall thickness for the thick film electrode, where the sintering temperature is lower than that for sintered pellet electrode. The wall of the etch pit for thick film electrode thus disappear faster than the case of sintered pellet and the surface morphology changes to nano-rod structure with less etching quantity than 100 C/cm^2. As shown in Fig. 3(d), the bulk of each grain was selectively dissolved and the grain boundaries were left undissolved by the photoetching of 100 C/cm^2. 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 the polycrystalline n-type semiconductor with grain boundaries in contact with an electrolyte [11]. It is interesting to note that for a thick film electrode the grain boundaries are left undissolved even at strong anodic bias, e.g., +1.0 V. It is explained as follows. For the thick film electrode, nano-rod structure is formed on the surface at the early stage of photoetching and it results in increase in the resistivity of the film. As a result, the potential slope in the space charge layer of TiO_2/elecrolyte interface becomes smaller. This situation is quite similar to the case of weak anodic polarization in the sintered pellet electrode. As mentioned above, an increase of photoetching quantity results in the formation of nano-rod structure or grain boundary skelton structure so that the etch pit depth is limited to several μm which corresponds to the garin sizes.

The carrier density of TiO_2 electrode is a crucial factor to determine the etch pit size of nano-porous structure for the photoetching of sintered pellet or single crystal electrodes [7]. Fig. 4 shows SEM photographs for nano-porous structure evolved on the TiO_2 thick films having different carrier density. The carrier densities were controlled by changing the reduction conditions. The etch pit sizes are changed by varying the carrier density as has been reported for a sintered pellet and a single crystal electrode [12]. For the electrode (a) with the carrier density, 4.5×10^{19} cm^{-3}, etch pit size was estimated to be about 100 to 200 nm. On the other hand for the heavily reduced electrode (b), 4.5×10^{20} cm^{-3}, the etch pit size was estimated to be less than 50 nm. The detailed study of the etch pit size control will be reported in the future.

Fig. 5 shows TEM photograph (a) and its complementary selected area electron diffraction (SAD) pattern (b) of the specimens picked up from the

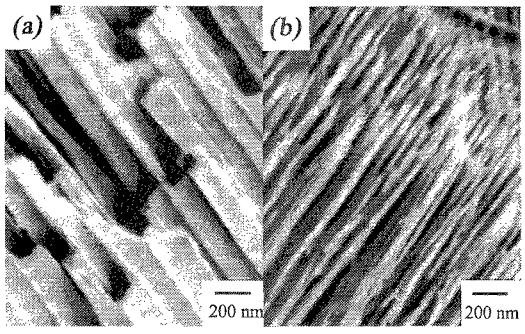

Fig. 4 SEM photographs for nano-porous structure evolved on TiO_2 thick film surface having different carrier densities.
Passed charges of photocurrent : 80 C/cm^2
Carrier density : (a) 4.5×10^{19} cm^{-3}, (b) 4.5×10^{20} cm^{-3}
Reducing condition : (a) 700 ℃, 1hr (b)1,000℃, 1hr in 10% H_2/N_2 gas stream

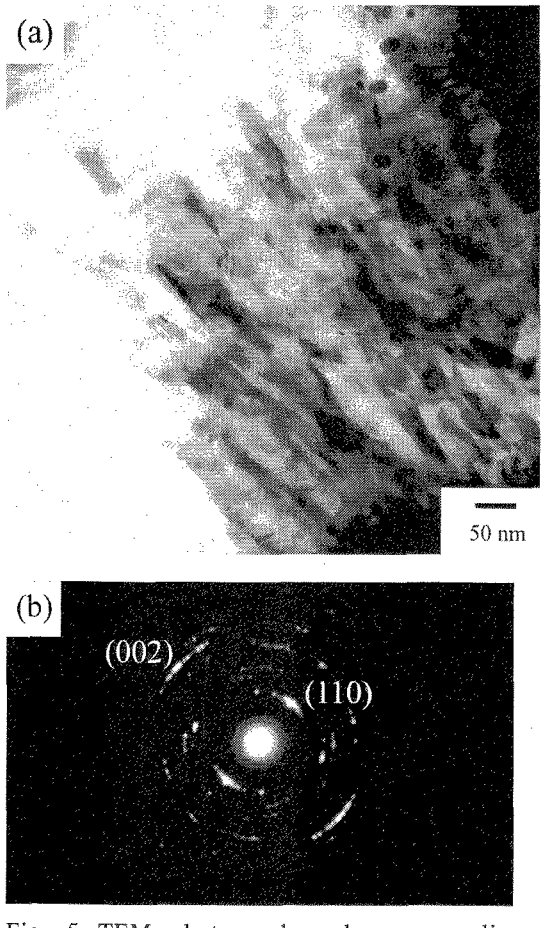

Fig. 5 TEM photograph and corresponding selected area electron diffraction pattern for the nano-rod TiO_2 specimen picked up from photoetched surface.
Photoetching quantity : 100 C/cm^2

photoetched thick film surface with nano-rod structure in Fig. 3(c). Nano-rod samples are clearly seen. Each nano-rod has a diameter of several tens of nanometer and its length is several μm. The SAD pattern produced from the same part of the specimen has a [110] zone axis of TiO_2 with a rutile structure and its long axis agreed with the c-axis.

4. CONCLUSION

We have concluded that grain growth of TiO_2 particles up to several micrometers by the sintering at high temperature is required to create nano-porous layer of TiO_2 by the photoetching. Photoetching of thick films sintered at temperatures higher than 900°C results in the formation of nano-porous structure depending upon the crystallographic orientation, while sintering at temperatures lower than 800°C does not cause any change in surface morphology. The surface morphology changes of photoetched thick film electrode sintered at high temperature are similar to that of photoetching for sintered pellet and single crystal electrode.

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