

Effect of Photoelectrochemical Etching on Titanium Dioxide Gas Sensor

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This work reports the effect of photoelectrochemical etching (photoetching) of titanium dioxide (TiO_2) on its gas sensing properties. After photoetching, the regularly ordered sub micron porous structure consisting of thin walls of TiO_2 with (100) crystal faces appeared on the surface. The large specific surface area and high crystallinity of photoetched TiO_2 surface makes it an attractive material for sensor device. The sensor response properties were tested by monitoring electric resistance changes for the detection of hydrogen gas. The response time was improved due to the specific crystallographic faces, i.e., (100) surfaces of rutile, exposed after photoetching. The photoetching also improved the sensitivity by increasing a specific surface area of the sensor surface.

Key words: photoelectrochemical etching, gas sensor, titanium dioxide

1. INTRODUCTION

In recent years, studies on titanium dioxide (TiO_2) have come into renaissance because of its interesting properties, e.g., high photocatalytic activity, excellent chemical stability, suitable combination with dyes for the application to the dye-sensitized solar cells [1-4]. In addition, TiO_2 is a useful material as a gas sensor similarly to SnO_2 [5, 6]. As all the chemical events take place at the surface, its surface morphology is a crucial factor in those applications. Thereby, much attention has been paid to how to tailor its surface in nanometer order for improving the characteristics of these devices.

In semiconductor gas sensors, a reducing gas depletes the surface coverage of oxygen ions adsorbed on sensor surface and donates electrons to its conduction band, thereby resulting in a decrease in electric resistance [7, 8]. Most of the semiconductor gas sensors detect the various gas species in this principle [9]. Because chemical reaction between semiconductor and gases is the fundamental process, it is very important how to control the surface of the sensors. In general, high sensitivity can be achieved by increasing the specific surface area of the sensor materials [10]. As the quantity of O_2 gas on the surface during the gas sensing increases, the change of electric resistance will increase [11]. Thus, many of the previous studies aimed to increase specific surface area using nano porous materials [12]. On the other hand, selective response for various gases is expected by using the surface with a high crystallinity. However, highly crystallized materials such as sintered pellet with large grain size or single crystal inherently have small

surface area. It should be interesting for gas sensor application, if a porous surface can be made on highly crystallized materials, so that requests of the high surface area and the high crystallinity can be satisfied at the same time.

Photoelectrochemical etching (photoetching) is a unique technique for tailoring microstructure of semiconductors surfaces. Despite its high chemical stability, TiO_2 has been found to be photoanodically dissolved in aqueous sulfuric acid solution. This fact permits the material to be surface-designed in a "topdown" fashion. Actually, we have found that the photoetching creates unique porous surfaces, depending on the crystallographic orientation of each grain. One of the interesting features in thus obtained surface morphology is a selective exposure of the specific crystallographic faces, i.e., (100) surfaces of rutile, when photoetching is carried out under certain conditions [13, 14]. Such a surface processing of TiO_2 might be technologically applicable to some devices but no report has been found in this respect, although the microstructure of the photoetched TiO_2 has been analyzed in detail. In the present study, we have examined effects of the photoelectrochemical etching on gas sensing properties of TiO_2 .

2. EXPERIMENTAL

TiO_2 samples were prepared from high purity rutile type TiO_2 powder (99.99%, Rare Metallic Co. Ltd). This powder was ground by agate mortar and pestle for 1hr to get particles with uniform size. After dried at 120°C in an oven for 1hr, the powder was press molded in vacuo at 400kg/cm^2 for 15min to make a pellet. This pellet

was fired at 1300°C for 6hrs and slightly reduced at 1000°C for 1hr in a stream of 10% H₂/N₂ to obtain n-type semiconductivity. Single crystal TiO₂ (High Purity Chemicals Laboratory, o., Ltd.) polished for (100) and (001) faces were also used. They were reduced at above-mentioned condition before using.

Copper lead wire was attached to the backside of the pellet and insulated with silicone resin. Photoetching treatment of the electrode surface was carried out in a 1 M sulfuric acid solution under potentiostatic condition (1.0 V vs. SCE). The electrode was illuminated using a 500W high pressure Hg arc lamp with band path filter (SIGMA UTVAF36U). The photoetching quantity was controlled with passed charges of photo current by a digital coulomb meter (NIKKO KEISOKU NDCM-4).

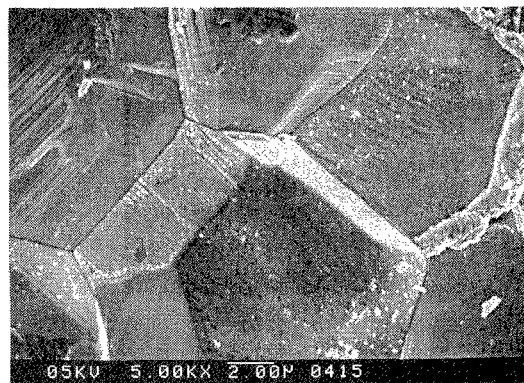
The surface morphologies after photoetching were observed with a scanning electron microscope (SEM, TOPCON ABT-150FS).

In order to make a sensor devices, two strips of conductive silver paste, separated by approximately 4mm were painted on the sample surface for providing the electrical contact and it was placed on an alumina substrate. A surface of 4mm × 5mm was exposed for a 0.3mm thick TiO₂ sample in the sensor device prepared in such a way. The electric resistance of the sensor was calculated from a dc current measured using a DC current voltage source monitor (ADVANTEST TR6143) under a constant voltage (0.5 V) and recorded on a personal computer feeding the data through a GPIB interface. Most of the measurements were carried out at 400°C. Concentration of H₂ was varied from 0% to 10% in a mixture with air used as a background gas. Flow rate of the gas was maintained at 380 ml/min. After the resistance had reached a steady value in the stream of air, H₂ was introduced.

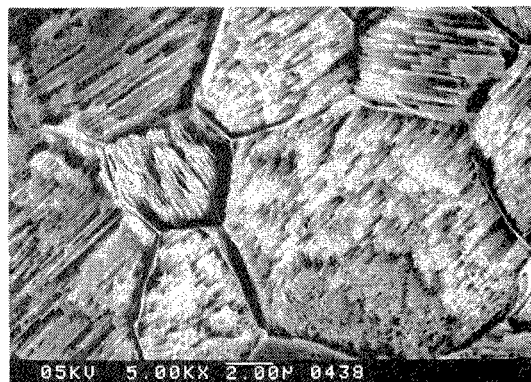
3. RESULTS AND DISCUSSION

TiO₂ is a stable material against photocorrosion but it is photoetched in aqueous sulfuric acid solution under illumination with UV light. Fig. 1 shows a set of SEM pictures of a sintered TiO₂ pellet before and after photoetching at 1 V vs. SCE in 1 M H₂SO₄. The passed charge of photocurrent was adjusted to 100 C/cm². The grain size is in the range from 3μm to 10μm. After photoetching, the grain boundaries are selectively dissolved and in each grain a unique nano-porous pattern appeared. The porous structure is created by flat platelets of TiO₂ which are aligned in a single direction in each grain. We have previously identified that the photoetching of TiO₂ proceeds along the c-axis of rutile and that the interior surfaces of the etch pits have (100) crystal faces [13]. The photoetching therefore increases the surface area in a controlled manner, so that the remaining surfaces are of (100) planes of highly crystallized TiO₂.

Fig. 2 shows the dynamic response of the electric resistance of polycrystalline TiO₂ sensor



(a) before photoetching



(b) after photoetching

Fig. 1 SEM photographs before and after photoetching under 1 V/SCE in H₂SO₄ solution.

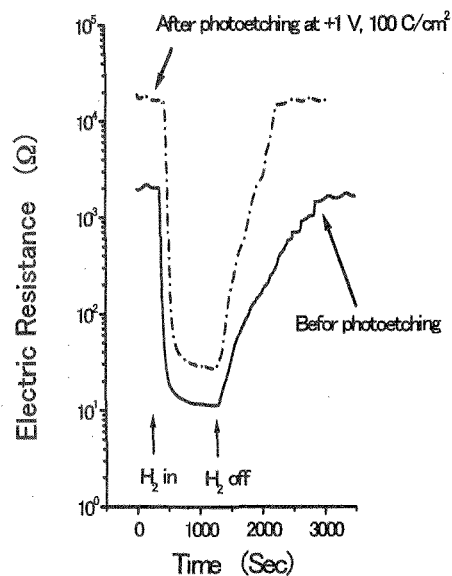


Fig. 2 Dynamic response changes in the electric resistance of titanium dioxide sensor before and after photoetching in the stream of 2.5% hydrogen gas at 400 °C.

Table 1. The response time and sensitivity in the stream of 2.5% hydrogen gas at 400°C

	Response time (Sec)	Reverse response time (Sec)
Before photoetching	186	2033
After photoetching (1 V/SCE, 100C/cm ²)	207	980

before and after photoetching upon introduction of 2.5% H₂ at 400°C. Table 1 summarizes the forward and reverse response times defined as the times needed for the electric resistance to change from the highest value to the lowest for 90% and vice versa. When H₂ gas is introduced, the electric resistance decreased about two orders of magnitude within a few minute by removal of the chemisorbed oxygen from the surface. On closing the flow of H₂, the electric resistance rises back to its original value due to chemisorption of O₂ molecules onto the surface. After photoetching, the electric resistance under air was increased and the reverse response time was quickened. However the response time was not changed significantly by photoetching. The increase of the

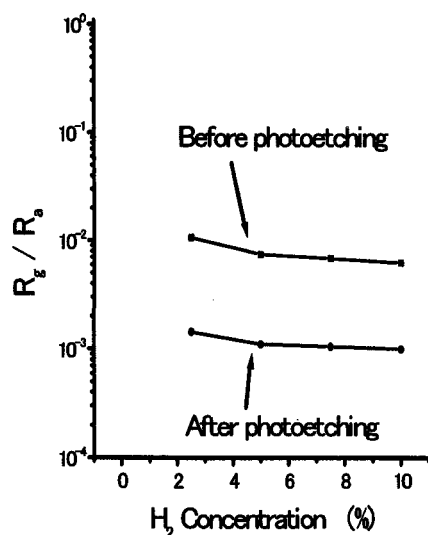


Fig.3 Relative resistance changes of titanium dioxide gas sensor exposed to the various concentration of hydrogen gas stream at 400°C.

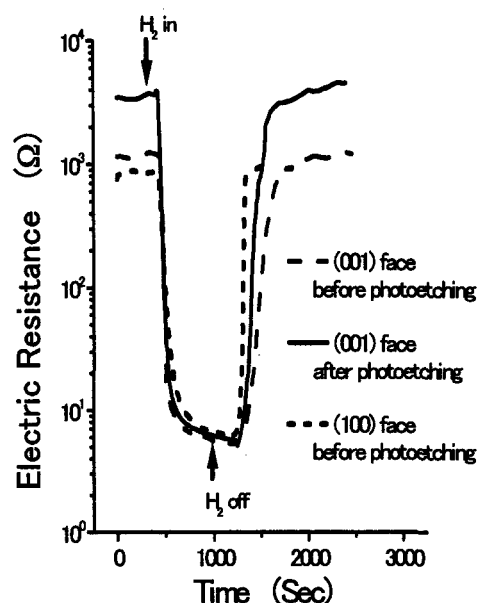


Fig. 4 Dynamic response changes in the electric resistance of single crystal titanium dioxide in the stream of 2.5% hydrogen gas at 400 °C.

electric resistance by photoetching is attributed to the increase of the surface area, as it leads to an increase of chemisorbed O₂ gas. The reason for the improved reverse response time is to be discussed later.

Fig. 3 shows variation of the gas sensitivity at different H₂ concentrations. The sensitivity (S) has been defined as the ratio of the electric resistance in the stream of the test gas (R_g) to that in the air (R_a), i.e., $S = R_g/R_a$. The sensitivities do not change significantly in the range of 2 to 10% of H₂ concentrations both before and after photoetching. On the other hand, the sensitivity is increased about one order of magnitude after photoetching under the same H₂ concentration. The increased specific surface area leads to an increase of the electric resistance in the air, but does not affect the resistance in the H₂ atmosphere so much. As the consequence, the higher the sensitivity towards H₂ detection has been improved after photoetching.

Low temperature sintered porous materials are generally used in gas sensors, for which the density of the grain boundaries is made to be high as the grain boundaries serve as the main pathways for electrical conduction and the change of the resistance at the grain boundary by gas adsorption is supposed to be the principal mechanism of gas detection in such devices [15]. As the TiO₂ pellet used in this study is sintered at a high temperature and thus is made of compactly packed large grains, there are not so many grain boundaries so that the grain boundary may not

Table 2 The response time of (100) and (001) single crystal TiO₂ in the stream of 2.5% hydrogen gas at 400°C

	Response time (Sec)	Reverse response time (Sec)
(100) face before photoetching	278	148
(001) face before photoetching	255	669
(001) face after photoetching	235	484

play a major role in the electrical conduction in the present material. From Fig. 1, we found selective dissolution of the grain boundaries, but the increase of the specific surface area should mainly arise from the creation of the porous structure in the bulk of the grains. It is therefore supposed that the contribution of the electric conduction in the bulk of the grains becomes significant in the present material and the improvement of the gas sensitivity mainly arises from the increase of the surface area of the bulk grains.

It has been reported that, the electric resistance of the TiO₂ based gas sensors towards H₂ is highly dependent on the oxygen partial pressure [16]. Thus, the forward and reverse response times depend on the desorption and adsorption rate of oxygen at the surface of the sensor, respectively. The fact that the reverse response time is improved by photoetching suggests that the rate of oxygen adsorption depends on the crystallographic orientation of TiO₂ surface, because the surfaces of TiO₂ remaining after photoetching become mainly those of (100) faces. Fig. 4 shows the electric resistance changes measured for single crystals of TiO₂ with different crystal faces upon exposure to a stream of 2.5% H₂ at 400°C. The response times determined for Fig. 4 are summarized in table 2. The forward response time is not much different between (100) and (001), indicating that the rate of O₂ desorption is almost the same for these two faces, whereas the reverse response time is much faster for (100) than (001), proving the fast adsorption of O₂ on the (100) face. After photoetching of the (001) sample, the reverse response time is clearly decreased. Since the photoetching of the (001) sample proceeds perpendicularly to create straight pores

surrounded by the (100) faces, the reverse response time is improved owing to the formation of (100) faces which allow fast adsorption of O₂. The same arguments should be valid also for the improved reverse response time for the photoetched sintered TiO₂ pellet electrode.

4. CONCLUSION

The photoetching of TiO₂ improve its gas sensor characteristics in terms of the reverse response time and sensitivity. The enlargement of the specific surface area in the grain bulk seems to be responsible to the higher sensitivity. The photoetching increases the resistance in air due to the adsorption of O₂ at a higher amount, which, however, can be efficiently desorbed to reduce resistance to the same level to that of the untreated material. As the photoetching not just increases the surface area but leads to a relative increase of the (100) faces which allow fast adsorption of O₂, the reverse response time has been shortened, due to their increased share in the gas sensing process.

5. REFERENCE

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