Evolution of Nano-Rod Structure of TiO_2 by Photoelectrochemical Etching Technique

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The photoelectrochemical etching (photoetching) is a unique technique for tailoring surface microstructure of semiconductors. We have reported that the photoetching of TiO_2 in sulfuric acid aqueous solution lead to unique surface structure depending upon the grain structure such as crystallographic orientations of the electrode and etching condition.[1–3] TiO_2 is known to be highly resistive against the photocorrosion. Normally photogenerated holes at the TiO_2 surface oxidize the water and lead to evolve oxygen. But in sulfuric acid solution, TiO_2 itself react with the holes in competition with the oxygen evolution reaction and it dissolve. After photoetching, 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. The large specific surface area and high crystallinity of the photoetched TiO_2 surface makes it an attractive material for photoelectronic devices.

Sintered pellets of TiO_2 were used in the present study. Initially, TiO_2 powder was press molded in vacuo to get the pellets. The pellets were fired at 1300 °C under a stream of N_2 gas and then slightly reduced by heating in the range of 1,000 °C from 700 °C for several hours under a stream of 10 % H_2 / N_2 gas to obtain an n-type semiconductivity. 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 that SEM photograph of polycrystalline TiO_2 surface after photoetching. SEM and TEM examination of this surface revealed that this structure consists of thin and long plate-like crystals having (100) crystal face of rutile structure which are interconnected vertically to create deep square hollows. This suggests that the etching reaction proceeds along a specific crystallographic orientation (c-axis). Fig. 2 shows that SEM photographs of TiO_2 surface after photoetching for different etching quantity ((A) 100 C/cm^2, (B) 1,000 C/cm^2). (A) shows the nano-honeycomb structure consists of thin and long plate-like crystals. Increasing an etching quantity, very thin and long rod-like structure (named "nano - rod" structure) was evolved at the surface as shown in (B). Its diameter is several tens of nanometer and its length was several tens of micrometer. Detailed crystallographic properties of these samples have been analyzed, which will be discussed in the presentation.

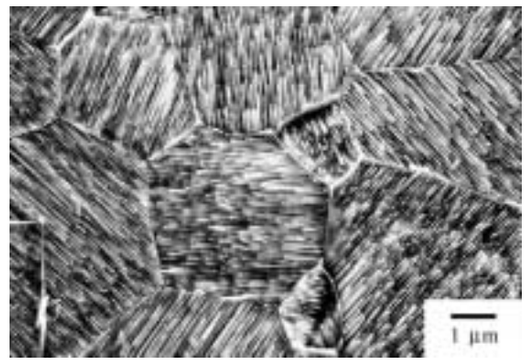

Fig. 1 SEM photograph of of polycrystalline TiO_2 surface (nano-honeycomb structure) after photoetching. Passed charges of photocurrent : 100 C/cm^2

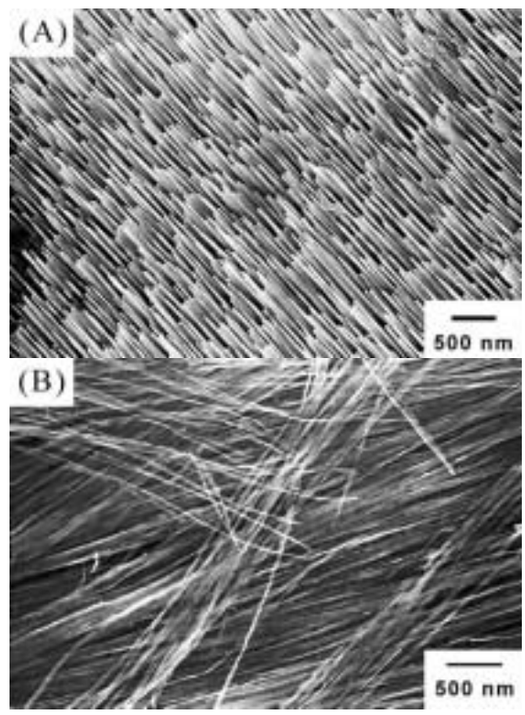

Fig. 2 SEM photographs of TiO_2 surface after photoetching.
Passed charges of photocurrent :
(A) 100 C/cm^2, (B) 1,000 C/cm^2

References

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