

Photoetching of Cr, Sb Doped Visible - Light Sensitive TiO₂

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Titanium dioxide (TiO₂) is a very attractive material for photocatalysts, dye-sensitized solar cells, etc. by its favorable chemical, physical, optical and electrical properties. It is important to increase visible - light sensitivity of TiO₂ from a viewpoint of solar energy utilization. One of the possible method for increasing the visible-light response of TiO₂ is obtained by the formation of donor levels by the doped Cr³⁺ of transition metal cation in the wide gap of TiO₂ host material. The co-doping Cr³⁺ with high valent ions (Sb⁵⁺) played an important role for suppression between photogenerated electrons and holes [1]. The photoetching is a unique technique for tailoring surface microstructure of semiconductors [2]. We have already reported that after photoetching of TiO₂ under certain condition, the photoresponse of the electrode is improved. In this study we have examined the photoelectrochemical properties of photoetched Cr, Sb doped TiO₂ electrode.

Sintered pellets of Cr, Sb doped TiO₂ were used in this study. Initially, TiO₂, Cr₂O₃ and Sb₂O₃ powders were mixed and press molded in vacuo to get the pellets. The pellets were fired at 1300 °C, 10 hr in the air. 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 wavelength of the light for photoetching was selected by the use of band path filter (365nm) for ultraviolet (UV) light and sharp cut filter (>420nm) for visible (VS) light illumination. The etching quantity was controlled by monitoring the passed charges of the photocurrent.

Fig. 1 shows SEM photographs for Cr, Sb doped TiO₂ electrode surface before (A) and after (B, C) photoetching in 1.0 M H₂SO₄ aqueous solution at +3.0 V vs. SCE. Before photetching (A), step - terrace structures were observed on the grain surface. This structure was made during sintering process. After UV light photoetching, roughness of the surface increases and convexo-concave structures with several tens of nanometer size were observed. Whereas after photoetching of VS light illumination, the steps are selectively undissolved and convexo-concave structures with about one hundred nanometer size were observed on its terrace surface. The photoetching reaction competitively takes place to the oxygen evolution reaction by photodecomposition of water. It suggests that at the step site oxygen evolution reaction effectively occurs and photoetching reaction was suppressed. Fig. 2 shows photocurrent action spectra for Cr, Sb doped TiO₂ electrode before and after photoetching. After photetching with UV and VS light, the photoresponse for VS light region increases up to 4 % of IPCE (incident photon to current conversion efficiency). On the contrary the photoresponses for UV region decrease in both cases.

REFERENCES

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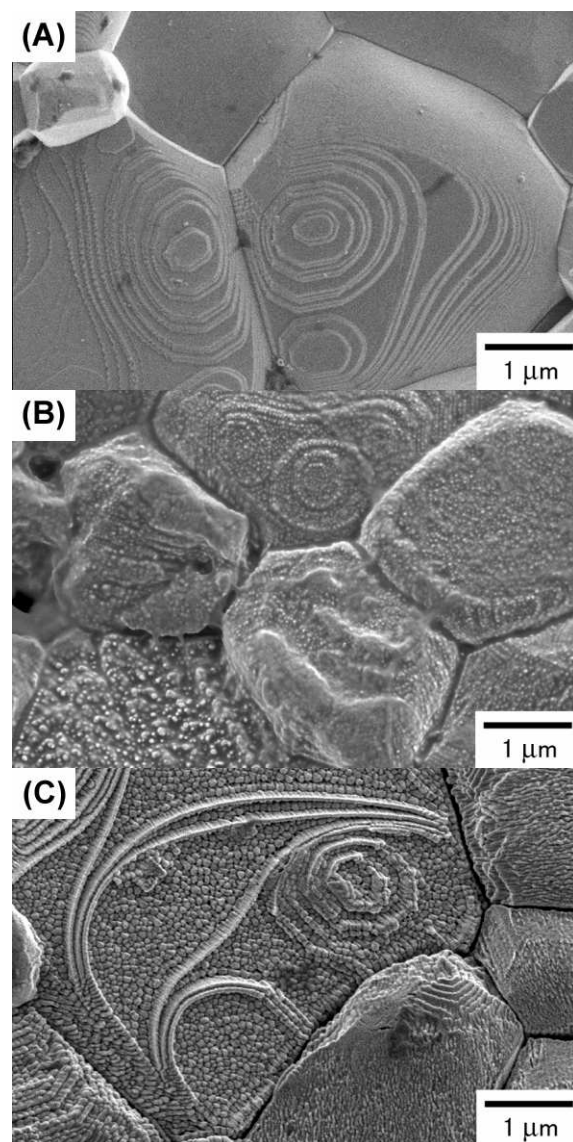


Fig. 1 SEM photographs of Cr, Sb doped TiO₂ electrode surface before and after photoetching in 1.0 M H₂SO₄ aqueous solution at +3.0 V vs. SCE.

Etching quantity (passed charges of photocurrent) :
400 C/cm²

(A) before photoetching, (B) after photoetching under ultraviolet-light illumination, (C) after photoetching under visible-light illumination

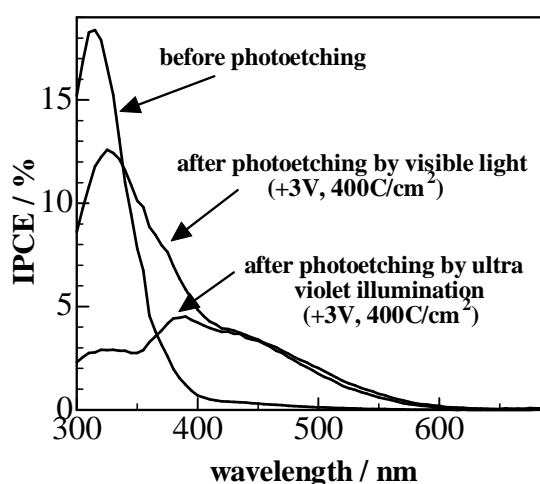


Fig. 2 Photocurrent action spectra for Cr, Sb doped TiO₂ electrode before and after photoetching.

Electrolyte : 1.0 M H₂SO₄ aqueous solution
Electrode Potential : +1.0 V vs.SCE