Characterization of Some Properties of TiO_2 on Ti surface by Anodization in Acid Solution

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Phosphorus ions doped titanium oxide films were prepared by anodic oxidation of Ti metal in phosphoric acid solution. The microstructure and/or electric state of phosphorus ions in the oxide film were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The surface of the oxide film obtained by anodic oxidation in 0.25 M phosphoric acid at 50V was flat without pores. On the other hand, the oxide film obtained at 350V had porous structure with the open pore of about 1 μ m in diameter. The oxide film was consisted of fine particles of 20-50nm in diameter. From XPS profiles of the oxide film prepared by the anodic oxidation in phosphoric acid solution, it was revealed that phosphorus ions were doped in the oxidation film. In addition, the phosphorus ions at the surface of the oxide film would exist as P^{5+} state, while phosphorus ions at inside of the film was P^{3+} state. These results suggest that anodic oxidation techniques have the potentials for preparation of novel photocatalyst, that will lead to the properties with responding visible light.

1. Introduction

Photocatalytic reaction is much expected to environmental repair technique that can use inexhaustible solar energy. Titanium dioxide (TiO_2) has been widely used for photocatalyst.

Recently, novel photocatalysts are developing which can respond with visible light[1]-[4]. It is considered that the ion doping is one of effective technique for preparation of photocatalyst reacting with visible light. For example, Asahi et al reported that N_2 doped to titanium dioxide obtained by gas process reaction method(4) have possibility of photocatalytic reaction under visible light. The reason of the responding visible light is because N_2 doped titanium dioxide can produce new band gap state between valence band and conduction band by O ion was replaced to N ion. The photo catalytic reaction was occurred by electron excitation. As a result, ion doped titanium dioxide will be able to react under visible light.

Anodic oxidation is one of the surface treatment techniques. According to previous paper, electrolyte cation would be included in the anodic oxide film during anodic oxidation(5). Therefore, anodic oxidation is expected to development of active photocatalyst that can react with visible light. However, electron state of doping ions in oxidation film was not clearly elucidated. In this study, phosphorus ions doped titanium oxide films were prepared by anodic oxidation of Ti metal in phosphoric acid solution.

2. Experimental Methods

Ti metal (10 mm × 10 mm × 0.4 mm, Nilaco. Co. Ltd) was used as an anode and carbon block (diameter 5 mm ×10 mm, Toyo carbon) was used as a cathode. The distance between electrodes was approximately 3 cm. Ti substrate was polished using abrasive paper.

After polishing, the substrate was soaked in HNO_3/HF=3:1 mixing solution to order to remove oxide film resulting from natural oxidation. Finally it was washed with dionized water and dried in atmosphere before it was used as an electrode.

Anodic oxidation was carried out under a 50mA /cm^2 of current density supplied a direct current power (TP0650-01, Takasago Seisakusyo). Then electrolyte was mixed with a magnetic stirrer during an anodic oxidation treatment. Here, 0.25M

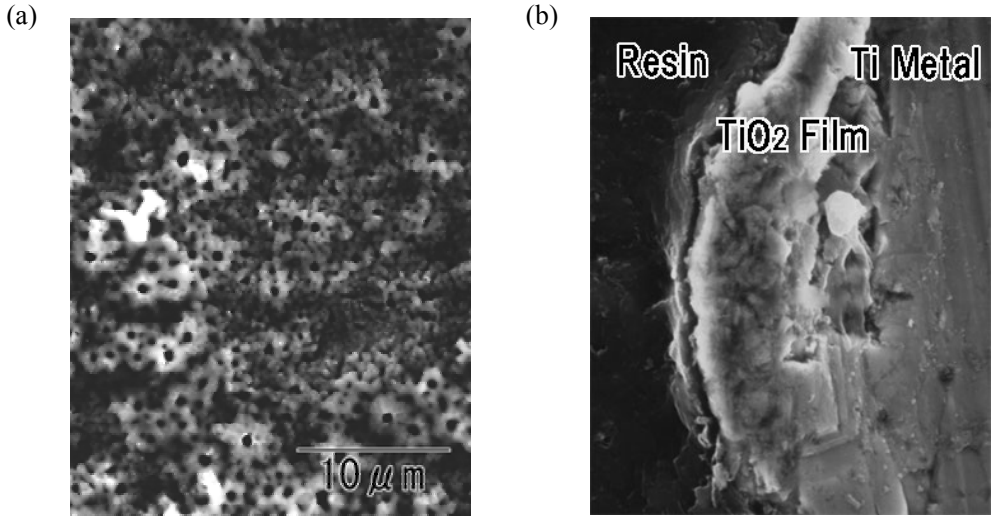

Fig.1 .SEM image of anodic titanium oxide titanium films.
(a) surface image of anodic titanium oxide titanium.
(b) cross section image of anodic titanium oxide titaniu.m

phosphoric acid was used as electrolyte. Applied voltages were held for 2 min when reached at set voltage.

Various microstructural analysis were performed by scanning electron microscopy (SEM; S-800, Hitachi) and transmission electron microscopy (TEM; JEM2010/SP, JEOL). The acceleration voltage was 20 kV for SEM and 200 kV for TEM observation. Especially, in order to obtain the cross section images, the sample of anodic titanium oxide film for SEM observation was buried in epoxy resin. And then it was groung and polished for obserbation.

The samples obtained by various anodic oxidations were identified by powder X-ray diffraction analysis (XRD: CuK_α radiation, 40 kV, 50 mA: RINT 2000 / Rigaku Co.,Ltd), The XRD profiles were collected between 20-60° of 2 θ angles with a step interval of 0.01° and scanning rate of 4° /min.

Electronic state of Ti2p and P2p were investigated by X-ray photoelectron spectroscopy (XPS; JPS9010MC, JEOL). XPS analysis condition was X-ray source Mg-K α 10 mA-10 kV. The XPS depth profile measurement was performed after Ar ion etcing. Ar ion etching was performed with rapid etching ion gun (XP-HSIG, JEOL). Ar ion bombardment angle was 90° , while current and voltage was 19 mA and 800 V. XPS spectra were measured after Ar bombardment each time. Quantitative analysis of various anodic titanium oxide films was evaluated with each XPS spectra from P, O, and Ti ions.

3. Results and Discussion

Titanium oxide film obtained by anodic oxidation at 50 and 350 V showed metallic yellow and gray colors, respectively. From SEM observation, the surface of the oxide film obtained by anodic oxidation in 0.25 M phosphoric acid at 50 V was flat without pores. On the other hand, the oxide film obtained at 350 V had a porous structure having open pores of about 1 μ m in diameter (Fig.1 (a)). The oxide film consisted of fine particles of 20-50 nm in diameter. From cross section SEM
image, the thickness of oxidation film was about 10 μ m. (Fig. 1 (b))

XRD patterns of oxidation film are shown in Fig. 2. As shown in Fig. 2, both XRD patterns of oxide film obtained by anodic oxidation at 50 and 350 V showed a broad titanium oxide peak between

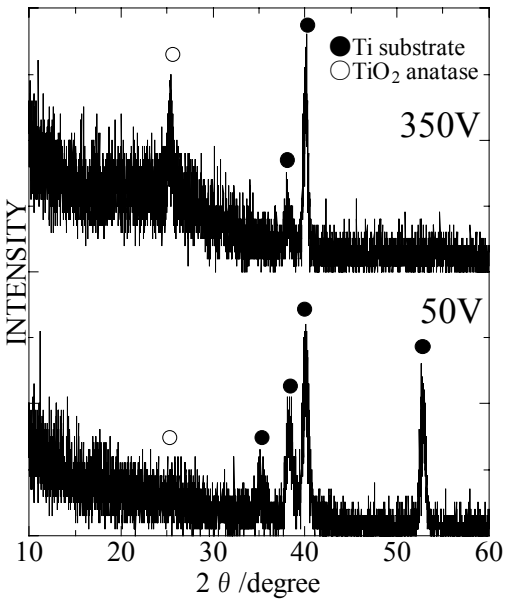

Fig. 2. XRD patterns of anodic oxide film of titanium prepared by anodic oxidation in 0.25 M phosphoric acid at 50 and 350 V.

2θ=20-30°. Sharp peaks at about 40°and 52° could be identified as Ti substrate.

TEM observation (not shown here) revealed that the oxide film was consisted of fine particles of 20-50 nm in diameter. According to result of TEM observations, the broad peak was though to be caused by the microstrucutres composed of fine crystals of titanium oxide.

In order to investigate the electric state for Ti and P ion in oxide film, XPS depth profile analysis was performed. Fig. 3(a) and (b) show XPS depth profiles of titanium oxide film obtained by anodic oxidation at 50 V. Before etching of anodic titanium oxide film, Ti2p XPS peak at 458.4 eV was observed, which could be identified as that of Ti^{4+} from TiO_2. Intensity of the peak due to Ti^{4+} decreased with an increase of etching time. In contrast, the XPS peak due to Ti^{2+} (455.1eV) or Ti^{3+} (457.8 eV) appeared in the sample etched for 1-5 min. Finally, those peaks due to Ti^{2+}or Ti^{3+} disappeared and XPS peak due to Ti metal (454 eV) from the substrate appeared. On the other hand, P2p XPS spectra of anodic titanium oxide film before etching could be observed at 133 eV, which was identified as P^{5+} state resulting from PO_4^{3-}atom group. The peak caused by P^{5+} disappeared in the sample etched for 1 min. In contrast, the peak at

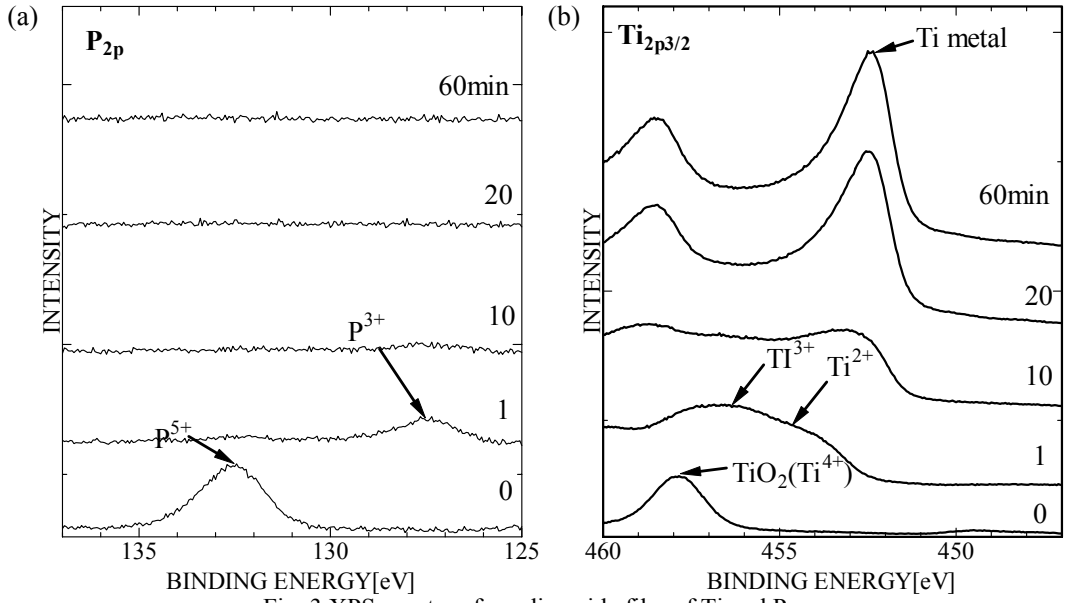

Fig. 3 XPS spectra of anodic oxide film of Ti and P. anodic oxidation at 50V (a) P2p (b) Ti2p3/2

128.4 eV due to P^{3+} appeared. The XPS peak disappeared in the sample etched for 10 min. Therefore, it is considered that P ions are taken into anodic oxidation film. In addition, the XPS depth profiles revealed that the phosphorus ions at the surface of the oxide film would exist as P^{5+} state, while phosphorus ions at inside of the film was P^{3+} state.

According to these results, various ions can be taken into anodic titanium oxide film during anodic oxidation process, and anodic titanium oxide film is expected to be useful for photocatalyst reacting with visible light.

4. Conclusions

In this study, phosphorus ions doped titanium oxide films were prepared by an anodic oxidation treatment of Ti metal in phosphoric acid solution and the microstructures of the obtained thin films are investigated. In addition, electric state of phosphorus ions in the oxide film was evaluated by XPS measurements.

The oxide film consisted of fine particles of 20-50 nm in diameter. From cross section SEM image, the thickness of oxidation film was about 10 μ m. From XPS profiles of the oxide film prepared by the anodic oxidation in phosphoric acid solution, it was revealed that phosphorus ions was doped in the oxidation film. Furthermore, phosphorus ions at the surface of the oxide film would exist as P^{5+} state, while phosphorus ions at inside of the film was P^{3+} state.

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