Identification of TiO_2 Films Prepared by Sol-Gel and Dip-Coating Methods by Ti K-Edge XANES Spectra

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1. Introduction

Titanium oxide (TiO_2) has superior photocatalytic activity, and the photocatalytic ability increases in the order of amorphous-, rutile-, and anatase-TiO_2. TiO_2 coated materials have been used as the photocatalyst to purify water and atmospheric pollution. However, it is difficult to identify the crystal phase of TiO_2 coating film by X-ray diffraction and electron diffraction because the film is thin and damaged by the electron beam. In this study, the identification of amorphous-, anatase-, and rutile-TiO_2 films that were prepared by sol-gel and dip-coating methods, was carried out by Ti K-edge X-ray absorption spectroscopy.

2. Experimental

A TiO_2 gel film was made on an SiO_2 substrate (9×70×1 mm) from a sol solution consisting of $Ti(O\text{-}i\text{-}C_3H_7)_4$: distilled water : ethanol : $NH(C_2H_4OH)_2$ = 1 : 1 : 40 : 1 (molar ratio) by dip-coating technique. Amorphous-, anatase-, and rutile-TiO_2 films were obtained by heating the gel films at 400, 500, and 900 ℃ for 3h, respectively. Ti K-edge X-ray absorption near-edge structure (XANES) spectra of the films were measured in the fluorescence yield (FY) mode using a 3-elements solid-state detector (SSD) at the BL-3 beamline with an Si(220) monochromator in the SR Center, Ritsumeikan University.

3. Results and Discussion

Ti K-edge XANES spectra of the amorphous, anatase, and rutile films are shown in Fig. 1. In the pre-edge region of the amorphous film, three features A, B, and C appeared at 4967.8, 4971.6, and 4978.6 eV, respectively. In addition, for the anatase film, the features A_1 and A_2, due to the splitting of A, appeared at 4966.4 and 4969.6 eV, respectively. It is considered that the feature A appeared in the pre-edge region, since the structure of the grain boundary in

anatase is similar to that of the amorphous film. For the rutile film, the features A_1 and A_2 appeared at energies lower than those of the anatase film, and the features B and C appeared at the same energy as the amorphous and anatase films. In the post-edge region of the amorphous film, the feature D and E appeared at 4986.7 and 4999.3 eV, respectively. For the anatase film, two features D_1 and D_2, due to the splitting of D, appeared at 4985.0 and 4988.5 eV, respectively. A feature E appeared at energy higher than that of the amorphous film. For the rutile film, as compared with the anatase one, the feature D_1 appeared at low energy, while D_2 and E appeared at high energies. The energies and assignments of the features are shown in Table 1. The amorphous film has the intense and broad A, broad D and E, and the anatase and rutile films have the features A_1, A_2, D_1, and D_2. In addition, the anatase film has a greater intensity ratio of A_1 to A_2 than the rutile film, and the rutile film has the intense D_2. In this manner the crystal phases of the TiO_2 films can be identified by the features of the Ti K-edge XAFS spectra.

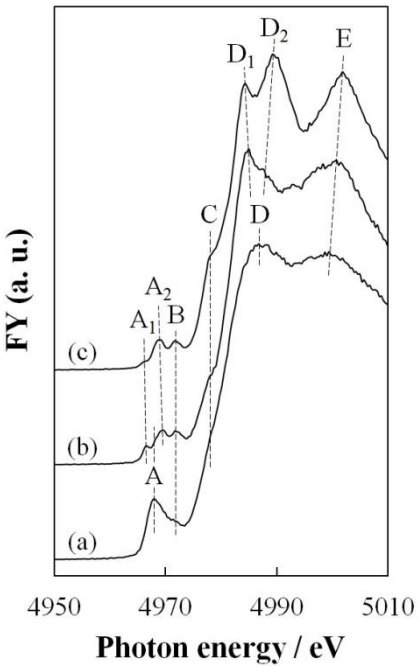

Fig. 1 Ti K-edge XANES spectra of (a) amorphous, (b) anatase, and (c) rutile films.

Table 1 Energies and assignments of features in Ti K-edge XANES spectra.

Amorphous		Anatase		Rutile		Assignments
Feature	Energy / eV	Feature	Energy / eV	Feature	Energy / eV	
A	4967.8	A_1	4966.4	A_1	4966.1	Quadrupolar transition of $1s\rightarrow3d(t_{2g})$ [1]
		A_2	4969.6	A_2	4968.9	Dipolar transition of $1s\rightarrow3d(t_{2g})$-4p hybridized states including a little $1s\rightarrow3d(e_g)$ quadrupolar component [1]
B	4971.6	B	4971.7	B	4971.7	Pure dipolar transition of $1s\rightarrow3d(e_g)$-4p hybridized states [1]
C	4978.6	C	4978.3	C	4978.7	1s-4p transition [2]
D	4986.7	D_1	4985.0	D_1	4984.3	1s-*n*p dipole-allowed transitions [3]
		D_2	4988.5	D_2	4989.2	
E	4999.3	E	5000.7	E	5001.8	

References

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