Applied Surface Science 254 (2008) 6619–6622

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

# Synthesis and characterization of brookite/anatase complex thin film

Chiaki Ohara, Teruhisa Hongo *, Atsushi Yamazaki, Toshio Nagoya

*Department of Resources and Environmental Engineering, School of Creative Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo 169-8555, Japan*

ARTICLE INFO

*Article history:*
Received 25 October 2007
Received in revised form 9 April 2008
Accepted 11 April 2008
Available online 27 May 2008

*Keywords:*
Brookite
Anatase
$TiO_2$
Thin film

ABSTRACT

$TiO_2$ films were prepared on a silicon or soda-glass substrate using a sol suspension. The $TiO_2$ film on the silicon substrate was composed of pure anatase phase and showed almost no contaminations. In contrast, the $TiO_2$ film on the soda-glass substrate was composed of anatase and brookite phases. The diffusion of Na into the $TiO_2$ film on the soda-glass substrate was observed by XPS, and Na was concentrated on the surface of the film. The yield of the brookite phase increased with decreasing distance from the surface of the film on the soda-glass substrate. Na promoted the formation of the brookite phase, although the preparative procedure was used for anatase synthesis.



## 1. Introduction

Titanium dioxide ($TiO_2$) has been investigated extensively for many years because of its various applications as a low-cost material in photocatalysis [1–3], in photovoltaics [4,5], in electronchromic [6] or as gas sensor [7,8]. The use of $TiO_2$ as a catalyst during photochemical oxidation aimed at decomposing organic compounds is well known [9]. $TiO_2$ exists in three different crystalline phases: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). In nature, rutile is the most common, while brookite is scarce. Among these phases, anatase and rutile can be obtained by several synthetic methods and their various properties have been widely studied. Recent reports on the preparation of pure brookite and the study of its characteristics are limited [10–12]. Some reports indicated that brookite-type $TiO_2$ shows high photoinduced hydrophilicity and high photocatalytic activity compared with rutile and anatase [13,14]; thus, brookite is a good candidate material for solar-energy conversion devices.

Brookite is the metastable phase of $TiO_2$; thus, it is difficult to prepare pure brookite under laboratory conditions. Many researchers reported that it is typically obtained as an accessory second phase when rutile or anatase is synthesized [15–17]. It has been shown that the titania phase, which is the most difficult phase to prepare in thin-film form, is brookite [18,19]. Brookite/anatase complex films have been obtained by various techniques, such as pulsed laser deposition [20] and the electrochemical oxidation of titanium electrodes [21]. Djaoued et al. [22] have prepared brookite-rich films by a sol–gel method using diethanolamine and polyethylene glycol as modulators. Recently, Kuznetsova et al. [23] have prepared a spin-coated film of pure brookite with a preferred orientation.

We prepared $TiO_2$ films on silicon and soda-glass substrates using a sol suspension. This suspension was coated onto the substrates by dip coating. The $TiO_2$ film on the silicon substrate was found to be composed of pure anatase phase by grazing incident asymmetric X-ray diffraction (GIAXRD) analysis. However, the $TiO_2$ film on the soda-glass substrate was composed of anatase and brookite phases. In this work, we characterized these $TiO_2$ films by GIAXRD analysis and X-ray photoelectron spectroscopy (XPS). These measurements revealed the difference between the film on the silicon substrate and that on the soda-glass substrate. We also discussed the mechanism of brookite phase generation on the soda-glass substrate.

## 2. Experimental

### 2.1. Preparation of $TiO_2$ films

$TiO_2$ thin films were prepared by dip coating using a sol suspension on soda-glass and silicon substrates. Titanium tetraisopropoxide (TTIP) (90.6 ml) was used as the starting material. The required amount of ethanol (93.8 ml) was divided into two parts: the first part was added to the stirred TTIP. The second part was mixed with 5.2 ml of hydrochloric acid solution (38 wt.%) and then added dropwise (1.5 cm/min) into the solution with stirring

* Corresponding author.
*E-mail address:* hongo@aoni.waseda.jp (T. Hongo).

0169-4332/$ – see front matter 
doi:10.1016/j.apsusc.2008.04.030

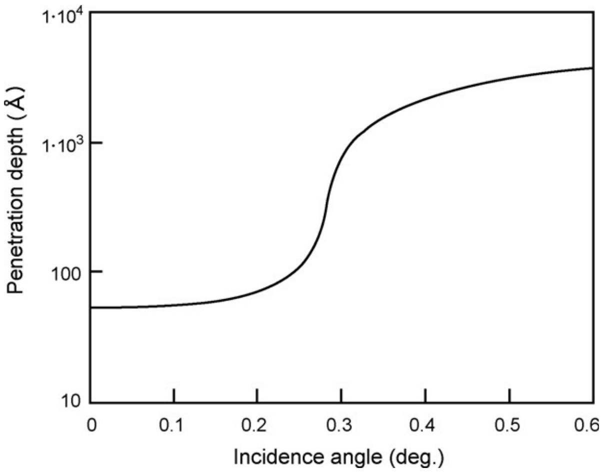


**Fig. 1.** X-ray penetration depth for $TiO_2$ as function of incidence angle.

to promote hydrolysis. This homogenous solution was continuously stirred for 24 h at room temperature.

The soda-glass and silicon substrates were first cleaned carefully in an ultrasonic bath. Using this prepared solution, the $TiO_2$ thin films coated onto the substrates (soda glass or quartz) by dip coating. The films were then dried in a desiccator for 10 min and subsequently calcined at 500 °C in air for 2 h. After cooling to room temperature, the dip coating and calcination process were repeated. The $TiO_2$ film thickness was about 150 nm.

### *2.2. Characterization*

The crystallographic properties of the $TiO_2$ films were determined by GIAXRD analysis using a monochromatic Cu K$\alpha$ radiation. Incidence angle was used to determine the change in the crystal phase along the film depth. The variation in the penetration depth of $TiO_2$ as a function of incidence angle is shown in Fig. 1. Diffraction patterns were obtained in an $2\theta$ angular range from 24.0° to 32.0°.

The surface chemical compositions of the $TiO_2$ films were determined by XPS. Spectra were collected using a monochromatic Mg K$\alpha$ source with an energy of 1253.6 eV operated at 10 kV. For the $TiO_2$ film on the soda-glass substrate, elemental depth profiling was carried out using $Ar^+$ sputtering beams under the applied conditions (3 keV, 8 mA).

## 3. Results and discussion

The GIAXRD patterns of the $TiO_2$ films are shown in Fig. 2. The GIAXRD patterns of the $TiO_2$ film on the silicon substrate (Fig. 2(a)) were obtained at grazing incidence angles from 0.2° to 0.5°. The diffraction line at about 25.5° was the 101 line of the anatase phase, and the sample was confirmed to be single-phase anatase from the upper layer to the lower layer. The diffraction patterns of the $TiO_2$ film on the soda-glass substrate (Fig. 2(b)) were obtained at grazing angles of incidence from 0.2° to 0.6°. The diffraction line at about 30.9°, which was assigned to the 121 line of the brookite phase, was observed in addition to those from the anatase phase. The intensity of this line relative to the strongest 120 line of the brookite phase at 25.4° was about 90%. However, this relative intensity in Fig. 2(b) was clearly low. This result shows that the anatase and brookite phases coexist in the $TiO_2$ film on the soda-glass substrate. Therefore, the strongest diffraction line at about 25.4° overlaps the 120 line of the brookite phase ($2\theta$ (Cu K$\alpha_1$) = 25.339° from JCPDS 29-1360) and the 101 line of the anatase phase ($2\theta$ (Cu K$\alpha_1$) = 25.281° from JCPDS 21-1272), and the diffraction shoulder at about 25.8° is the 111 line of the brookite phase.

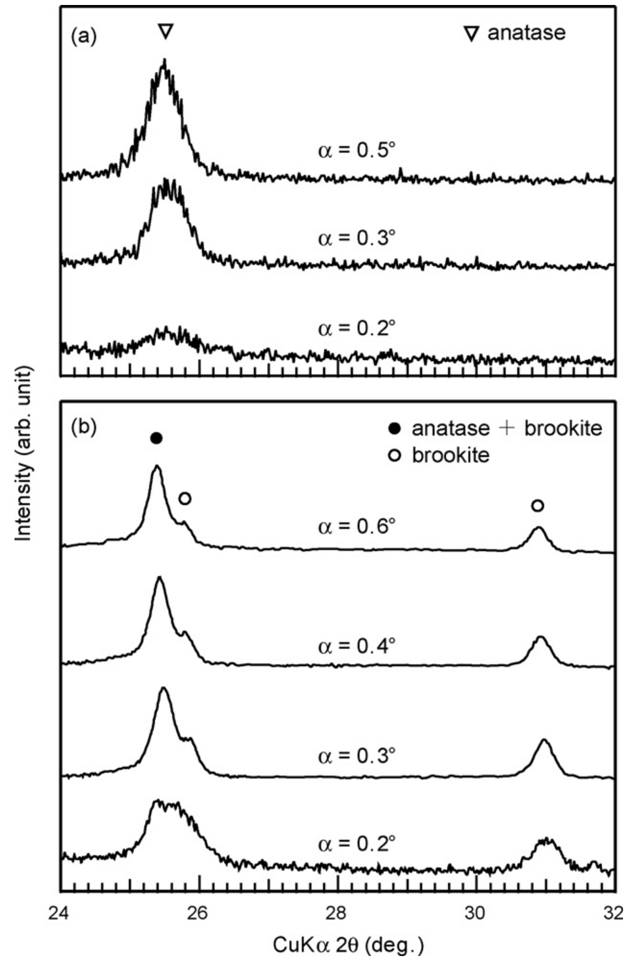


**Fig. 2.** GIAXRD patterns of $TiO_2$ films on (a) silicon and (b) soda-glass substrates.

Fig. 3 shows the intensity of the 121 diffraction line of the brookite phase relative to that of multiple lines at around 25.0–

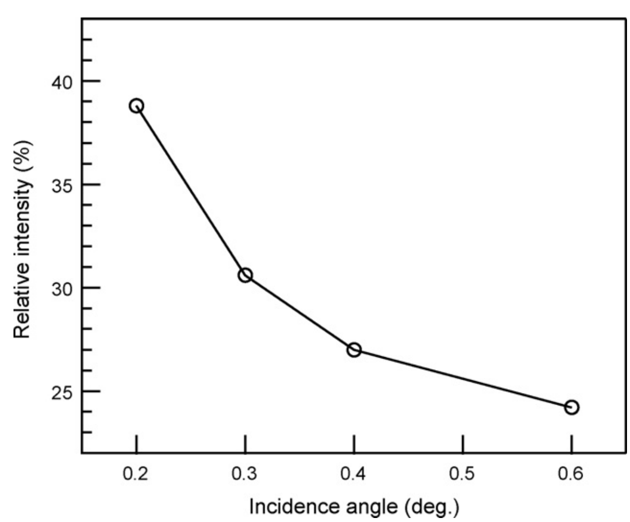


**Fig. 3.** Intensity of diffraction line 121 of brookite phase relative to multiple lines at around 25.0–26.0° in diffraction patterns of $TiO_2$ film on soda-glass substrate as function of incidence angle.