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TiO_2 Thin Films Synthesized by the Spray Pyrolysis Deposition (SPD) Technique

Masayuki Okuya,* Nina A. Prokudina, Katsuya Mushika and Shoji Kaneko

Department of Materials Science and Technology, Shizuoka University 3-5-1 Johoku, Hamamatsu 432-8561, Japan

Abstract

*Anatase-type TiO_2 thin films with high transmittance (> 70%) in the visible region were successfully synthesized on glass substrates by the spray pyrolysis deposition (SPD) technique. Two kinds of starting solutions; $TiCl_4$ ethanol solution and Ti(*i*-OC_3H_7)$_4$ 2-propanol solution with $TiCl_4$ as an additive were prepared separately. The TiO_2 thin film obtained from the former solution showed the preferred orientation along the [101] direction. However, a 1·5 μm thick film from the latter solution revealed almost the same transmittance as a 200 nm thick film from the former. The result indicates that the complexes produced by adding $TiCl_4$ in Ti(*i*-OC_3H_7)$_4$ 2-propanol solution plays an important role in the mechanism of the crystallization of TiO_2.* *© 1999 Elsevier Science Limited. All rights reserved*

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1 Introduction

Titanium dioxide (TiO_2) has been one of the most attractive materials in the experimental investigation during the last decades due to its scientific and technological importance. For example, the electrochemical photolysis of water with TiO_2 was intensively studied as a candidate for a new energy source.[1] Sterilization[2] and sewage disposal[3] using TiO_2 as an electrochemical catalyst were also investigated. A current topic is a new electrochemical solar cell with high conversion efficiency.[4] Anatase-type TiO_2 thin film was employed for the cell as a working electrode, and then the improvement of the film preparation technique is required. Among many processing techniques, the spray pyrolysis deposition (SPD) technique is one of the most promising ones, since the structure of the apparatus is quite simple and the technique is applicable to produce thin films on a large scale. We have already succeeded in the syntheses of SnO_2,[5] Sn_2OS[6] and Cu_2 O[7] thin films by this technique. In the present work, we have developed this technique to TiO_2 thin film preparation.

In this paper, we report anatase-type TiO_2 thin film synthesis by the SPD technique using titanium tetrachroride ($TiCl_4$) and titanium tetraisopropoxide [Ti(*i*-OC_3H_7)$_4$] as starting solutions. We found that the surface morphology of the film thus obtained strongly depends on the starting solutions.

2 Experimental

Two kinds of starting solutions; 0·5 wt% of $TiCl_4$ (99%, Wako Pure Chemical Industries Ltd.) ethanol solution and 0·5 wt% of Ti(*i*-OC_3H_7)$_4$ (95%, Wako Pure Chemical Industries Ltd.) 2-propanol solution with an additive of $TiCl_4$ with a molar ratio of Ti(*i*-OC_3H_7)$_4$/$TiCl_4$ = 1 to prevent the hydrolysis with moisture from the air were prepared.

The apparatus used for the spray pyrolysis was described elsewhere.[5–7] After setting up the spray gun (Lumina STA-6R-1 mmϕ, Fuso Seiki Co. Ltd.) approximately 30 cm above the glass substrate ($25\times25\times1\ mm^3$ in size; Corning 7059) on the holder, the substrate was heated up between 300 and 450°C, and then the pyrolysis procedure was initiated using 2·3 kg/cm^2 of compressed air or pure oxygen gas as a carrier gas. Since the sprayed mist cooled down the substrate, the period and the volume of the solution for each spraying was fixed at 1·0 s and 1·0 ml, respectively. After recovering the substrate temperature, the same pyrolysis procedure was carried out again. Each procedure was then repeated 200 times for one substrate.

The crystal structure of the film was determined by XRD using CuK_α radiation (Rigaku Rint-2000).

*To whom correspondence should be addressed. Fax: +81-53-478-1199; e-mail: tcmokuy@eng.shizuoka.ac.jp

The transmittance in the visible region was measured by the spectrophotometer (Jasco V-570). The surface morphology was observed by FE-SEM (JSM-6320F, JEOL). The film porosity was evaluated from the water adsorption.

3 Results and Discussion

3.1 $TiCl_4$ ethanol solution

Figure 1 shows the XRD patterns of TiO_2 thin films deposited at various substrate temperatures from $TiCl_4$ ethanol solution using compressed air (a) or pure oxygen gas (b) as a carrier gas. In both cases, the TiO_2 thin films thus obtained revealed several crystalline structures from amorphous to anatase and then to rutile with increasing substrate temperature. Anatase single phase was obtained between 350 and 380°C with air, while the anatase single phase region was spread between 350 and 430°C with pure oxygen gas. The result contradicts the observation that rutile is more stable than anatase in an oxygen atmosphere. However, the fluorescent X-ray analysis detected a slight trace of residual chlorine in all anatase structure films. We suppose the residual chlorine is related to the stability of anatase structure in an oxygen atmosphere, although the detail of the mechanism is not clarified.

Figure 2(a) shows the SEM image of the surface morphology of anatase-type TiO_2 thin film with the thickness of 200 nm deposited at 380°C with air. The film surface consists of many platelets, being 300 nm in length and 20–30 nm in width, arranged in a porous microstructure. According to the XRD patterns shown in Fig. 1, the platelets are believed to be oriented along the [101] direction. In case of SnO_2 thin film deposited by SPD technique, the orientation along the [200] direction was explained by the molecular association between the solvent, ethanol and the raw material, di-n-butyltin diacetate (DBTDA).[5] We suppose our result is related to the association between ethanol and $TiCl_4$. However, since $TiCl_4$ shows much smaller polarity due to its symmetrical molecular structure

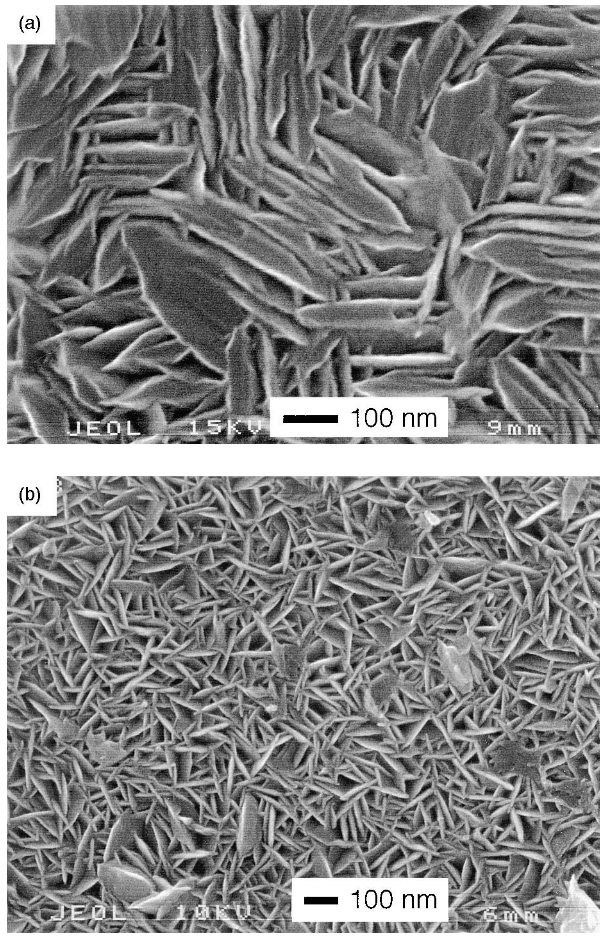

Fig. 2. SEM image of the surface morphology of TiO_2 thin film deposited with compressed air (a) from $TiCl_4$ ethanol solution at the substrate temperature of 380°C and (b) from $Ti(i\text{-}OC_3H_7)_4$ 2-propanol solution with the additive of $TiCl_4$ at 430°C.

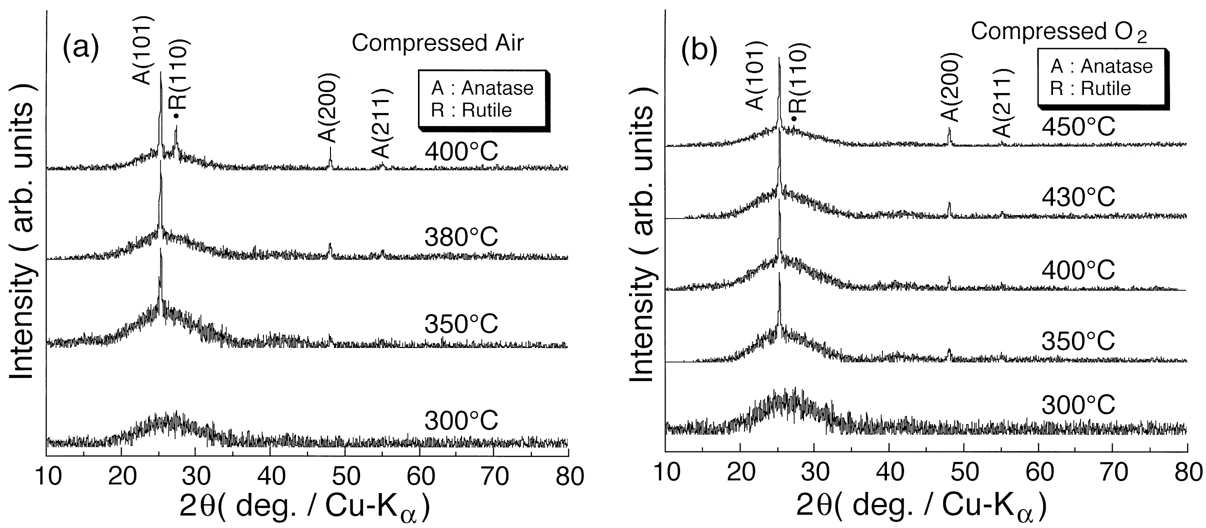

Fig. 1. XRD patterns of TiO_2 thin films deposited at various substrate temperature from $TiCl_4$ ethanol solution: (a) compressed air and (b) pure oxygen gas was used as a carrier gas. A and R corresponds to anatase and rutile, respectively.

comparing with DBTDA, the association between $TiCl_4$ and ethanol is not so strong as that between DBTDA and ethanol. This is the reason why the TiO_2 thin film obtained here is not so highly oriented as SnO_2.

Figure 3 shows the transmittance spectra of the 200 nm thick TiO_2 thin films deposited with compressed air at 380°C (sample A) and pure oxygen gas at 430°C (sample B). The transmittance spectrum of the glass substrate is also shown as a reference. The average transmittance in the visible region (400–800 nm) was evaluated to be 73, 77 and 89% for samples A, B and the glass substrate, respectively. Both samples A and B show enough transmittance for their practical applications, while there are only a few interference fringes, indicating the relatively rough surface structure. This result corresponds to the SEM image in Fig. 2(a).

3.2 $Ti(i\text{-}OC_3H_7)_4$ 2-propanol solution with $TiCl_4$ additive

There are two merits in dissolving $TiCl_4$ in $Ti(i\text{-}OC_3H_7)_4$ 2-propanol solution. One is that $Ti(i\text{-}OC_3H_7)_4$ and $TiCl_4$ are known to form $[Ti(i\text{-}OC_3H_7)_{4-x}Cl_x]_n$ complexes, which exhibit a lower sensitivity towards hydrolysis and show high solubility in organic solvent.[8] Another is that both $Ti(i\text{-}OC_3H_7)_4$ and $TiCl_4$ contain titanium ion, corresponding to the higher titanium ion concentration than the nominal one. The solution is then more favorable to deposit a thick film than the $TiCl_4$ ethanol solution discussed in the previous section.

Figure 4 shows the XRD patterns of TiO_2 thin films deposited at various substrate temperatures from $Ti(i\text{-}OC_3H_7)_4$ 2-propanol solution with $TiCl_4$ stabilizer using compressed air as a carrier gas. Anatase single phase was obtained at substrate temperatures between 350 and 430°C. Many peaks corresponding to the anatase structure appeared with increasing temperature without any preferred orientation.

Figure 2(b) shows the SEM image of the surface morphology of TiO_2 thin film with the thickness of 1·5 μm deposited at 430°C with compressed air. This film is made up of platelets, approximately 100 nm in length and 10 nm in width. The volume in the film is calculated to be approximately 0·15 $cm^3\,g^{-1}$, thus the film porosity is about 37%. The surface morphology of the film is similar to that obtained from $TiCl_4$ ethanol solution, while the size of platelets is smaller than that in Fig. 2(a). The platelet structure observed here is supposed to be relevant to $TiCl_4$ derived from the decomposition of $[Ti(i\text{-}OC_3H_7)_{4-x}Cl_x]_n$ complexes on the substrate. This is explained by the fact that the morphology of the TiO_2 particles in the film changes from platelet to granular when 2-octanol is used as a solvent. Since 2-octanol has a much higher boiling temperature than ethanol or 2-propanol, the reaction rate of $[Ti(i\text{-}OC_3H_7)_{4-x}Cl_x]_n$ to $TiCl_4$ reduces in 2-octanol.

The dotted curve in Fig. 3 shows the transmittance spectrum of the 1·5 mm thick TiO_2 thin film. The average transmittance of the film is 71% in the range between 400 and 800 nm. The value is almost same as that deposited from $TiCl_4$ ethanol solution, although the film from $Ti(i\text{-}OC_3H_7)_4$ is approximately 8 times thicker than that from $TiCl_4$. However, the thicker film from $Ti(i\text{-}OC_3H_7)_4$ does not show many more interference fringes than the thinner films from $TiCl_4$. This is because of the low average index due to the porosity.

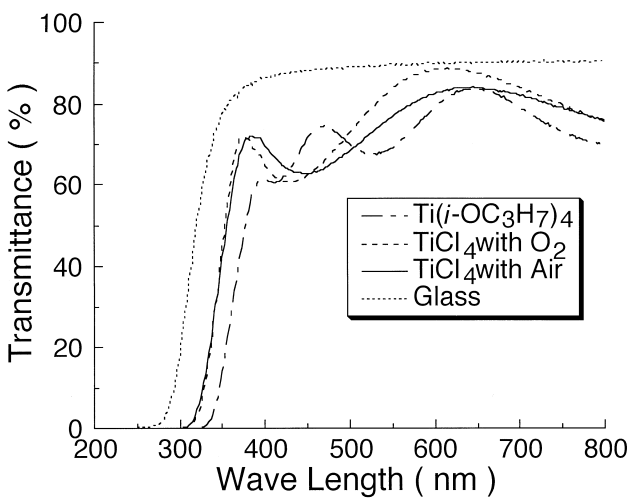

Fig. 3. Transmittance spectra of TiO_2 thin films as a function of wave length. The films were deposited from $TiCl_4$ ethanol solution at the substrate temperature of 380°C by compressed air (200 nm in thickness), at 430°C by compressed pure oxygen gas (200 nm in thickness), and from $Ti(i\text{-}OC_3H_7)_4$ 2-propanol solution with the additive of $TiCl_4$ at 430°C by compressed air (1·5 μm in thickness), respectively. The data of a glass substrate are shown as a reference.

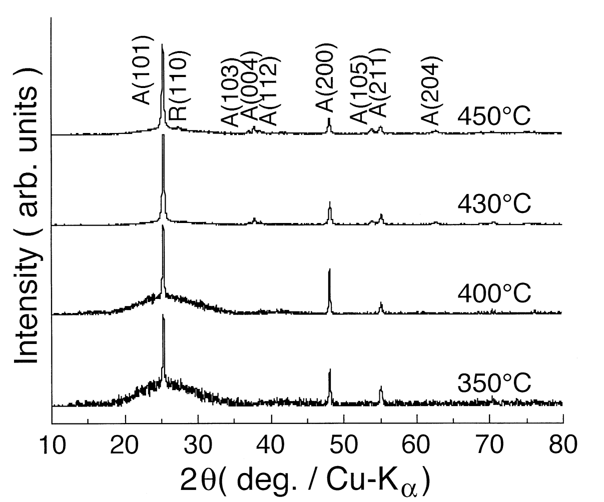

Fig. 4. XRD patterns of TiO_2 thin films deposited at various substrate temperature by compressed air from $Ti(i\text{-}OC_3H_7)_4$ 2-propanol solution with the additive of $TiCl_4$. A and R corresponds to anatase and rutile, respectively.

4 Conclusion

We have succeeded in synthesizing anatase-type TiO_2 thin films with high transmittance ($>70\%$) in the visible region on the glass substrate by the SPD technique. The film from $TiCl_4$ ethanol solution was consisted of platelets and showed the preferred orientation along the [101] direction, which is related to the molecular association between $TiCl_4$ and ethanol. On the other hand, the film from $Ti(i\text{-}OC_3H_7)_4$ together with $TiCl_4$ as a stabilizing agent showed scarcely the preferred orientation. However, the film with the thickness of $1{\cdot}5\,\mu m$ had the transmittance as high as 71% in the visible region, while the film did not show many more interference fringes than the thinner ones (200 nm) from $TiCl_4$ due to the porosity.

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