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Crystal structure and optical property of TiO_2 gels and films prepared from Ti-edta complexes as titania precursors

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Titania gel and films were prepared from Ti-edta complex solutions as new ceramic precursors, and their crystal structures and optical properties were investigated. Anatase appeared in the gel at firing temperatures between 450 and 500 °C, and was transformed to rutile at temperatures between 550 and 600 °C. This low transformation temperature is presumed to be due to the small crystalline size and micro pores in the gel. Refractive indices of the films were higher than those of the films prepared by a sol-gel process at firing temperatures above 700 °C. These high values were caused by the rutile phase in the TiO_2 films. © *2000 Kluwer Academic Publishers*

1. Introduction

Preparation of ceramic gels and thin films by wet processes such as a sol-gel method has attracted a great deal of interest [1, 2]. More advanced processes such as complexing agent-assisted sol-gel methods have also been proposed recently [3–6]. These processes are designed to tailor the structures or properties of the gels and films using an organic ligand as a modulator.

TiO_2 films are attractive materials for many applications because of their optical, electrical and photoelectrochemical properties [1, 2]. Several studies on TiO_2 films formed by conventional and advanced sol-gel processes have been reported [4–11]. Yoldas [7] reported that the refractive index of TiO_2 films varied depending on the type of substrate used or the film thickness. One of the authors has studied the effect of ligands on the crystal phase and refractive index of TiO_2 films prepared by a complexing agent-assisted sol-gel process, and reported that an organic ligand can be used to control the crystal structures and optical properties of the films [4]. Takahashi and Matsuoka [6] prepared a titania sol solution and TiO_2 films using diethanolamine as an organic ligand in the sol-gel process. In TiO_2 films, transformation from the anatase to the rutile phase occurs between 550 and 600 °C, which is a low transformation temperature. These studies indicate that the properties of TiO_2 films appear to depend on the process conditions and the materials used in the processes.

In our recent studies [11, 12], we have investigated a new wet process for preparing metal oxide films using metal complexes coordinated organic ligands. In this process, ethanol solutions of Co(III)- or Ti(IV)-ethylenediamine-N,N,N',N'-tetraacetic acid (H_4edta) complex anion and tri- or dialkylammonium cations were used as precursors of the Co_3O_4 and TiO_2 films, respectively. The solutions were coated on soda-lime glass substrates, followed by firing at temperatures from 450 to 550 °C to form Co_3O_4 and anatase TiO_2. In TiO_2 films, anatase appears between 450 and 500 °C, and the optical properties of the films are similar to those formed by conventional sol-gel processes.

This paper describes the crystalline structures and optical properties of TiO_2 gel and films which were prepared from titanium(IV)-edta complexes as their precursors and fired at temperature from 400 to 900 °C.

2. Experimental

2.1. Preparation of gels and films

2.1.1. Ti-edta complex process

The titanium(IV)-edta complex and ethanol solutions for the gel and the coating were prepared by a process similar to that mentioned in ref. [12]. The molar amount of diethylamine used for the gel was one and half times greater than that of the $[Ti(H_2O)(edta)]$ complex, then the solution containing diethylamine-Ti(IV)-edta complex, whose structure is still unknown, was prepared. A gel was obtained by evaporation of the solvent using a rotary evaporator at 80 °C, and was heated at 200 °C for 30 min before undergoing firing or X-ray diffraction (XRD) analysis.

The solution for the coating was prepared by a similar process, using twice the molar amount of dipropylamine to that of the $[Ti(H_2O)(edta)]$ complex. TiO_2 films were formed on quartz glass substrates by spin coating of the solution, heated at 200 °C for 30 min, and then fired at temperatures from 400 to 900 °C.

2.1.2. Conventional sol-gel process

A titania sol was prepared at ambient temperature by adding H_2O (0.2 mol) and 70% HNO_3 (0.02 mol) to a solution of titanium tetra-isopropoxide ($Ti(O\text{-}i\text{-}Pr)_4$) (0.2 mol) in ethanol (200 ml), and letting the solution stand for over 1 h. The gel and films were obtained by a similar process as described above.

The film thickness was controlled to approximately 300 nm for XRD measurement and approximately 100 nm for other measurements.

2.2. Measurements

The crystal structure of the gels was determined by XRD using a MAC Science MXP3 to measure the X-ray intensity as the temperature of the sample was increased at 10 °C/min under an air flow rate of 200 ml/min. The analysis was carried out from ambient temperature to 900 °C. After measurement at 900 °C, the XRD spectra of the samples were also measured at ambient temperature. The crystal phase of the films was also determined by the same equipment at ambient temperature after the films were fired at temperatures from 400 to 900 °C. Crystalline sizes in TiO_2 films were determined using half line width of the anatase (101) or rutile (110) peaks. The X-ray photoelectron spectra were measured from 0 to 1100 eV using a Perkin-Elmer Phi model 5600 X-ray photoelectron spectrometer. The refractive index of the films was measured with a Mizojiri DHA-OLX ellipsometer employing a He-Ne laser (632.8 nm). The film thickness was measured with a DEKTAK 3030 stylus profilometer. Thermal gravimetry (TG) and differential thermal analysis (DTA) were performed using a MAC Science TG-DTA 2000.

3. Results and discussion

3.1. Crystal structure of TiO_2 gels and films

Fig. 1 shows the XRD spectra of the gel prepared from Ti-edta complex (spectra below 400 °C and over 800 °C are not shown and × denotes the peaks from the Pt pan in the equipment). No peaks are observed in the region measured here ($2\theta = 20$–$50°$) for the gel fired below 450 °C. Peaks ascribed to anatase begin to appear at a firing temperature of 500 °C (○ in figure) and those ascribed to rutile (△ in figure) at 600 °C.

The intensity of the anatase (101) ($2\theta = 25.0°$) and rutile (110) ($2\theta = 27.1°$) peaks is shown as a function of the firing temperature in Fig. 2. The relative intensity of the anatase and rutile peaks is normalized to their maximum intensities, respectively. The intensity of the anatase peaks increases up to a firing temperature of

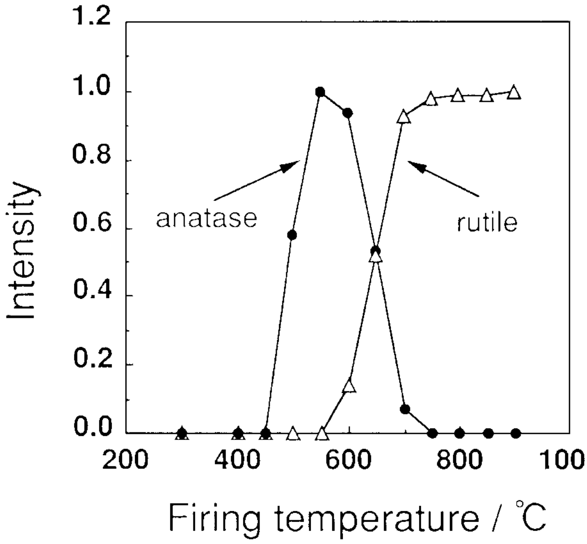

Figure 2 Peak intensity of anatase (101) and rutile (110) of titania gel prepared from Ti-edta complex as a function of the firing temperature.

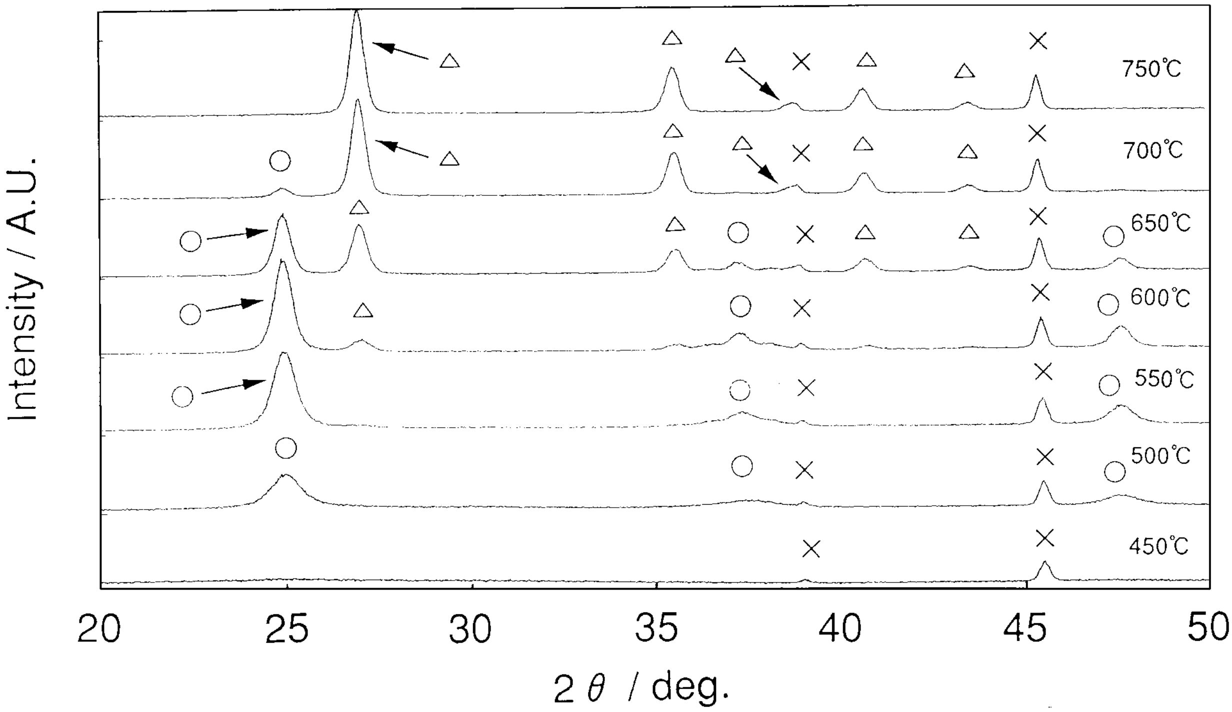

Figure 1 X-ray diffraction patterns of TiO_2 gel prepared from Ti-edta complex precursor.

550 °C but decreases after that point, and the peaks disappear at 750 °C. The intensity of the rutile peaks appears at 600 °C, increases to 750 °C and is constant at higher temperatures. These results indicate that anatase crystals are formed in the TiO_2 gel between 450 and 500 °C, begin to transform to rutile ones between 550 and 600 °C and are completely transformed at 750 °C.

The intensity of the anatase (101) and rutile (110) forms of the conventional sol-gel-derived TiO_2 gel is also shown as a function of the firing temperature in Fig. 3. The anatase (101) peak appears at 450 °C, shows almost constant intensities from 500 to 650 °C, lower intensities after 650 °C, and disappears at 850 °C. The rutile peak appears at 650 °C, and the intensity increases with increasing firing temperature up to 850 °C, after which it is almost constant.

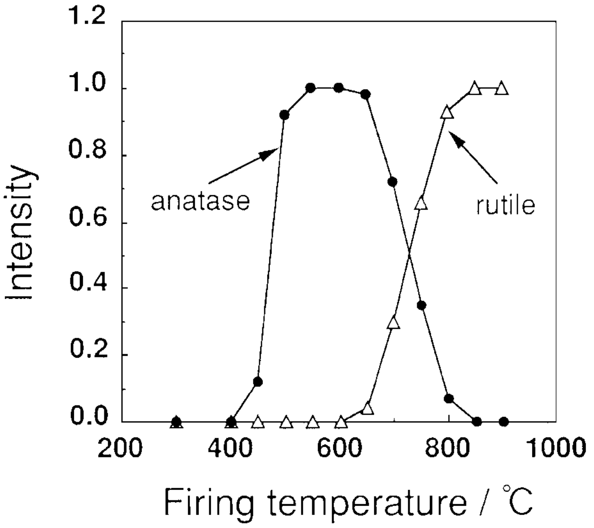

Figure 3 Peak intensity of anatase (101) and rutile (110) of titania gel prepared by sol-gel process as a function of the firing temperature.

These results indicate that the rutile is transformed at lower temperature in the TiO_2 gel prepared from the Ti-edta complex precursor than in that prepared by the conventional sol-gel process.

The sizes of the rutile crystals from the Ti-edta and the sol-gel processes were measured at ambient temperature after firing at 900 °C. The crystals were found to be similar in size, measuring 46 and 49 nm, respectively.

Fig. 4 shows the XRD patterns of TiO_2 films formed using the Ti-edta complex and fired at temperatures from 500 to 900 °C. Below 400 °C, no peaks were observed in the region measured here ($2\theta = 20$–$50°$) (not shown in Fig. 4), indicating that the titania is amorphous. An anatase (101) peak (○ in figure) is observed when the film was fired at 500 °C. Only rutile peaks (△ in figure), however, appear and the anatase one disappears when fired at 700 °C. The intensity of the rutile peaks increases at 900 °C.

These results indicate that the anatase phase appears between 400 and 500 °C and is transformed to rutile between 500 and 700 °C, which is similar to the behavior observed for the gel.

XRD analysis of the films prepared by the conventional sol-gel process showed that the anatase phase appeared between 400 and 500 °C, but was not transformed to rutile even when fired at 900 °C. Hashimoto *et al.* [13] have reported that the crystal phase of TiO_2 films is still anatase when the films are formed by a sol-gel process and fired at 600 and 800 °C. Our results coincide with their finding.

Some researchers have reported that the rutile is obtained at a low transformation temperature [6, 14]. Takahashi and Matsuoka [6] indicated that anatase is transformed to rutile between 550 and 600 °C when TiO_2 films are formed using a sol prepared from a

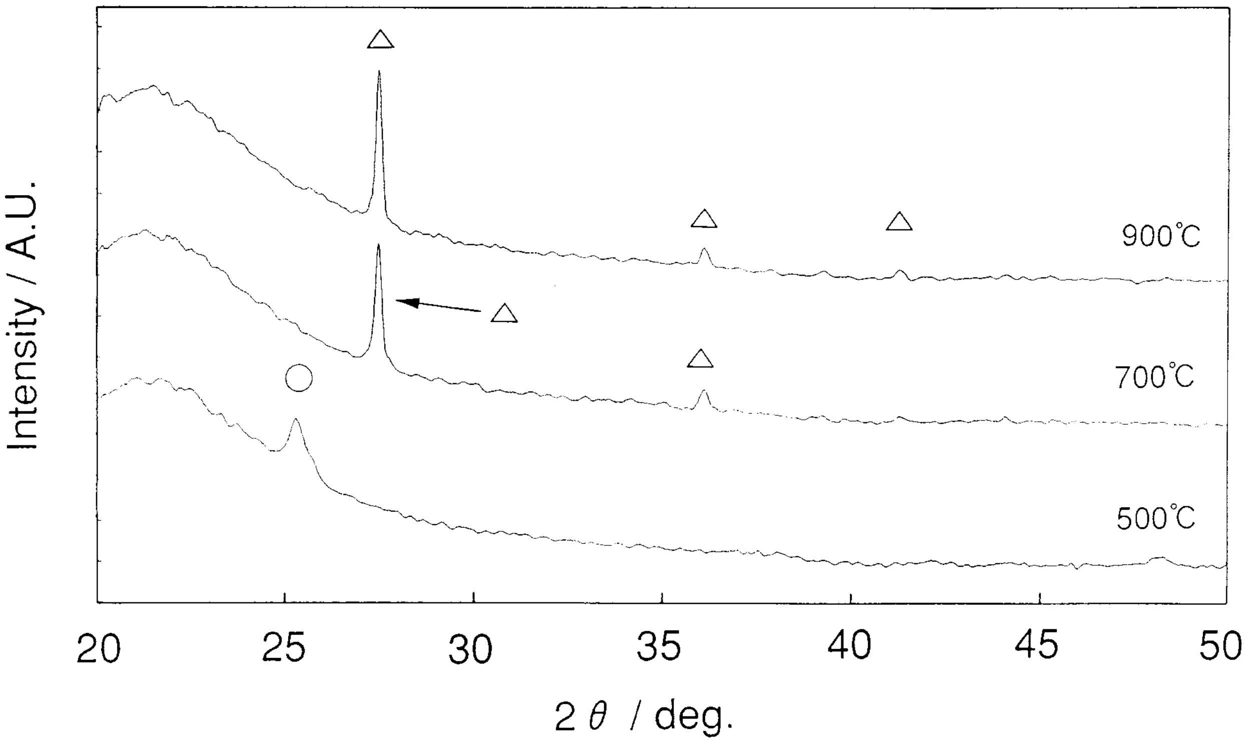

Figure 4 X-ray diffraction patterns of TiO_2 films prepared from Ti-edta complex precursor.

solution of Ti (O-*i*-Pr)$_4$ and diethanolamine as an organic ligand. Our result is similar to their observation. In the TiO_2-B_2O_3 film formed by a sol containing titania sol and boric acid, some of the anatase crystals are reported to transform to rutile below 500 °C but the amount of anatase crystals increase to 700 °C [14]. The reason for this transformation at low temperature is thought to be that the smaller size of the anatase crystals generated by the presence of B_2O_3 or $B(OH)_3$ promotes the transformation to rutile.

Both of the TiO_2 gels in this work and ref. [6] contained nitrogen element. XPS analysis of the TiO_2 gel derived from the Ti-edta complex indicates that the gel contained nitrogen elements at ambient temperature but no N after fired at 500 °C. This indicates that nitrogen elements is removed from the gel by firing and plays no role in the transformation process.

The low transformation temperature of the TiO_2 gel and films prepared from Ti-edta complexes is presumed to be due to their small crystalline size and micro porosity. The sizes of the anatase crystals in the gels prepared from the Ti-edta complex and by the sol-gel process, measured after firing at 530 °C, were 13 and 19 nm, respectively. Refractive indices of anatase TiO_2 films depend on their crystalline size and the densities of the films. The smaller crystalline size and more densified film show higher refractive indices. Both TiO_2 films formed from the Ti-edta complex and from the sol-gel process show the same refractive index (Fig. 5). Because the crystalline size of the former (13 nm) is smaller than that of the latter (19 nm), the former is more porous than the latter. Thermal analysis of the gel prepared from the Ti-edta complex showed that organic compounds burned out below 520 °C. The gel contained organic compounds below 520 °C and many micro pores at that temperature and even at higher temperatures. These suggest that the small size of the crystals and the presence of micro pores in the gel and the films cause the low-temperature transformation.

3.2. Refractive index of films

The refractive index of the TiO_2 films is shown in Fig. 5. The refractive indices of the films prepared by the sol-gel process increase linearly as the firing temperature increases. Those of the films prepared from the Ti-edta complex increase in the same manner up to a firing temperature of 500 °C, but show a sharper increase to high values at firing temperatures above 700 °C (2.49 at 700 °C and 2.54 at 900 °C).

The refractive index of TiO_2 films is related to the crystal phase (anatase or rutile), the crystalline size and the densities of the films [15]. Generally speaking, the rutile phase shows a higher refractive index than anatase, and phases of higher density and smaller crystal size also show higher refractive indices. Brinker *et al.* [15] reported a reciprocal relationship between the refractive index and the cluster size in silica sol prior to film deposition. They also reported that the higher refractive index of SiO_2 films stems from a smaller degree of porosity. In these factors, transformation from anatase to rutile causes the largest increase of refractive index of TiO_2 films.

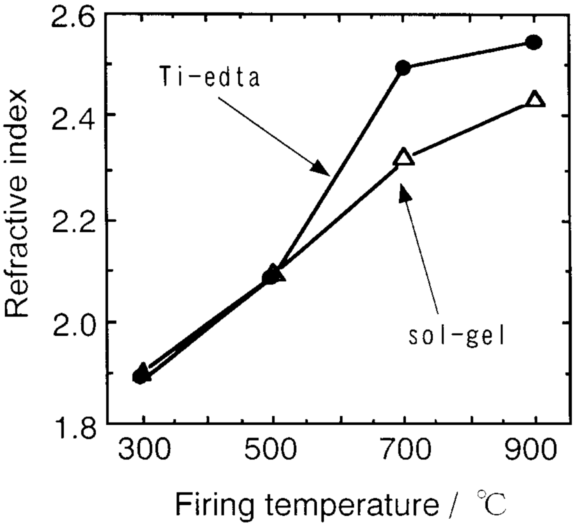

Figure 5 Refractive indices of TiO_2 films formed from Ti-edta complex precursor and by sol-gel process on quartz glass substrates and fired between 500 and 900 °C.

The crystal phases of the films prepared by the sol-gel process are amorphous when fired below 400 °C and anatase when fired from 500 to 900 °C. On the other hand, the crystal phases of the films prepared from the Ti-edta complex are amorphous when fired below 400 °C, anatase at 500 °C and rutile at 700 and 900 °C (Fig. 4). The rutile phase causes the higher refractive index of the film.

The refractive index of anatase TiO_2 film deposited by a reactive ionized cluster beam deposition (RICB) method is reported to be 2.3 [16]. The data of these refractive indices indicates that the anatase TiO_2 films prepared from Ti-edta complex are more porous than that obtained by the RICB method.

The refractive index of the rutile phase has been reported to be about 2.4 when the TiO_2 film was formed by a sol obtained from Ti- (O-*i*-Pr)$_4$ and diethanolamine [13]. This value is lower than that of the rutile one in this work (2.49–2.54), indicating that the rutile TiO_2 films in this work are more densified than the former because the crystalline sizes of both the films are similar.

4. Conclusion

Titania gel and films were prepared from Ti-edta complexes as new precursors. Anatase appeared in the gel when fired between 450 and 500 °C, and was transformed to rutile between 550 and 600 °C, which is a low transformation temperature. The reason for this is presumed to be due to the small crystalline size and porosity of the gel and films. Refractive indices of the films were higher at higher firing temperatures (700–900 °C) than those of the films prepared by the sol-gel process. The presence of the rutile phase caused the high values.

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