

**STUDIES ON PREPARATION AND APPLICATION OF  
HALOGEN-FREE AQUEOUS TITANATE SOLUTIONS**

**A THESIS  
SUBMITTED TO THE  
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## *Preface*

The studies presented in this thesis have been carried out under the direction of Professor Yasutaka Takahashi, Dr. Yutaka Ohya and Dr. Takayuki Ban at Department of Chemistry, Faculty of Engineering, Gifu University during 1998-2003.

The studies are concerned with Studies on Preparation and Application of Halogen-free Aqueous Titanate Solutions.

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# *Chapter 1*

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## **GENERAL INTRODUCTION**

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# *Chapter 1*

## GENERAL INTRODUCTION

### 1. 1. Introduction

In recent years, a topic of global environmental issues has been attracting much attention all over the world: destruction of the ozone layer, global warming, acid rain, and environmental endocrine disruptors. In order to check the spread of these environmental problems, we have to endeavor to prepare functional materials without using hazardous reagents and generating harmful substances.

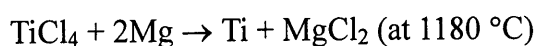
Titanium dioxide ( $\text{TiO}_2$ ), one of the useful functional materials, is a potential compound used as photocatalyst and electrode of dye-sensitized electrochemical cell in addition to classical use of light-scattering particles such as white paint. For many of these applications,  $\text{TiO}_2$  is used in the form of coating film. It is well known that a sol-gel processing is quite suitable for coating oxide films. The sol-gel technique is one of the conventional methods to prepare ceramics in various forms such as powders, fibers and films, and requires less equipment compared to other techniques such as vapor phase methods that need high vacuum condition. In particular, a film with nanometer thickness can be very easily prepared by dip and spin coating method. Metal alkoxides are commonly used as the important starting materials, and the quality of the films strongly depends on the stability of the alkoxides. Generally the alkoxides other than those of silicon are very reactive to water, and sometimes organic ligands must be applied to stabilize the alkoxide-derived sols. Titanium alkoxides as a famous starting material of  $\text{TiO}_2$  are the very case, so that they are used in organic solvents.

This study focuses on the development of concentrated, aqueous titanium solutions without containing halogens, alkaline cations and organic chelating ligands. As applications of these solutions, the preparation of  $\text{TiO}_2$  films by sol-gel method, and the effect of photoirradiation to the gel films are described. In this chapter, the outline of oxides of titanium, especially  $\text{TiO}_2$  and layered titanates, and the use of chelating

ligands as a stabilizer of titanium isopropoxide are described based mainly on our reported results. Aqueous titanium solutions that have been reported so far are also outlined and discussed in views of sol-gel technique.

## 1. 2. General Aspects of Titanium and Titanium Dioxide

Titanium is one of the relatively abundant elements in the earth's crust (0.44 %, the 9 th element in Clarke number), and is widely used in aerospace, industrial, marine and commercial applications. These days, titanium metal is produced by a series of chemical processes. The most popular production process for titanium is Kroll process, in which magnesium is the reducing agent:<sup>1, 2</sup>



The oxide  $\text{TiO}_2$  has two main crystal modifications, anatase (low temperature form, tetragonal) and rutile (high temperature form, tetragonal): the former transforms to the latter around 900 °C. Both anatase and rutile are chemically very stable and, hence, almost non-toxic, having the important and interesting properties, as shown in Table 1. 1.

Table 1. 1. Properties of important two forms of titanium dioxide.<sup>3</sup>

	Anatase	Rutile
Crystal form	Tetragonal (ccp oxide)	Tetragonal (hcp oxide)
Density	3.90	4.27
Refractive index	2.52 (2.5612, 2.4880)	2.71 (2.6124, 2.8993)
Mohs' hardness	5.5 to 6.0	7.0 to 7.5
Dielectric constant	48	110-117
Band gap	3.2 (380 nm)	3.0 (400 nm)

Rutile has the highest refractive index among the transparent materials and relatively higher hardness. Because of the high refractive index, the hardness and

chemical stability, it has various uses as coatings (paint), cosmetics, paper coatings, paper fillers, fillers of plastic and rubber, and ceramics. Thus, 269 thousand tons of  $\text{TiO}_2$  are produced in Japan in 1999 from ilmenite ( $\text{FeTiO}_3$ ) and rutile as raw materials. Titanium metal is not suitable for a raw material of  $\text{TiO}_2$ , because the production of titanium requires high energy as described above.

$\text{TiO}_2$  behaves as an n-type semiconductor and absorbs UV-light (with the wavelength shorter than about 400 nm) to generate electrons and energetic holes in the bulk of crystal, as shown in Fig. 1. 1. The latter can migrate to crystal surface and oxidize reductants adsorbed on the surface. Owing to this photoelectrochemical property,  $\text{TiO}_2$  is used as self-cleaning (soil-proof), anti-bacterial or air purifying materials.<sup>4</sup> Since the organic compounds, being adsorbed on the oxide surface and making it hydrophobic, can be effectively eliminated by UV light illumination, the hydrophilic property that the native oxide surface should have had can be quickly recovered by the UV illumination. Thus  $\text{TiO}_2$  coatings can be applied to the windows or door mirrors of automobiles, for example, as anti-fogging or hydrophilic coatings.<sup>4</sup>

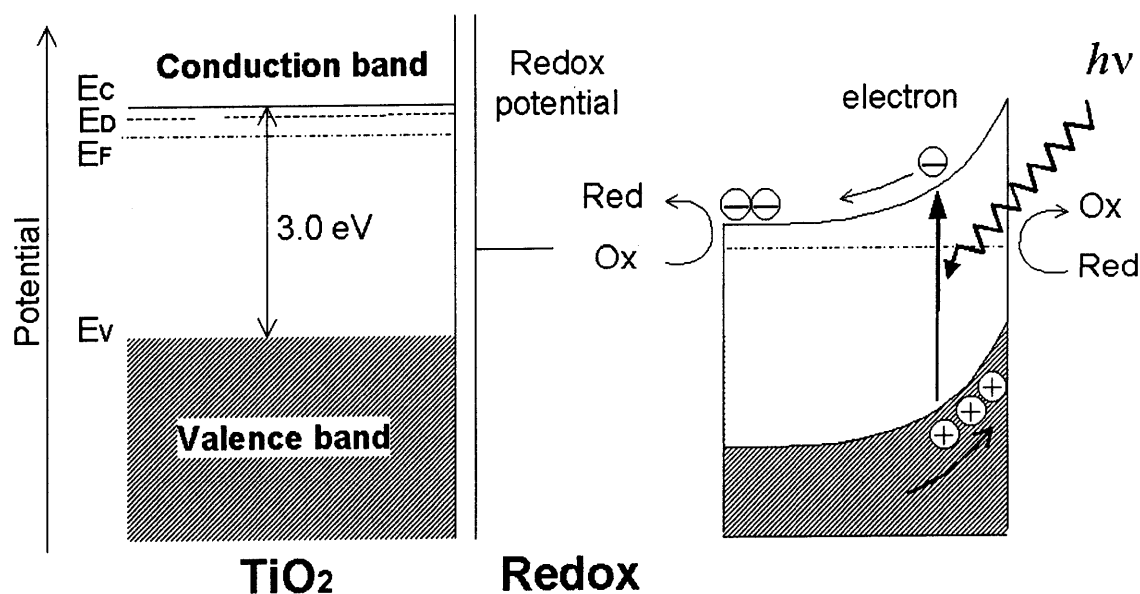


Fig. 1. 1. Energy diagrams of  $\text{TiO}_2$ .

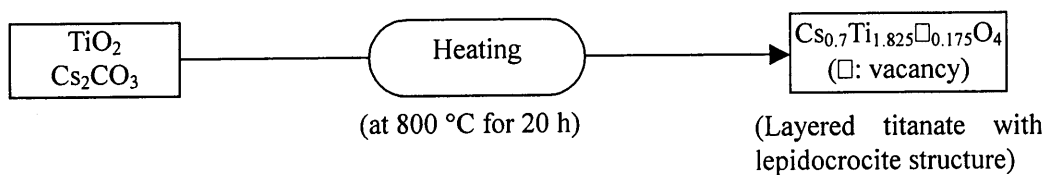
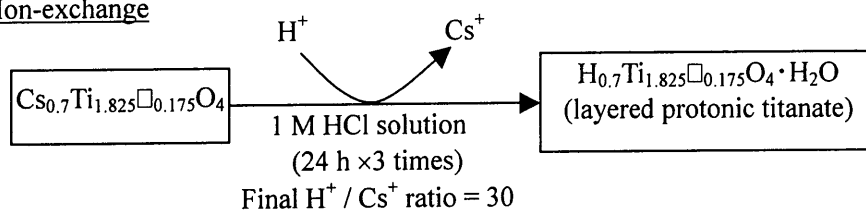
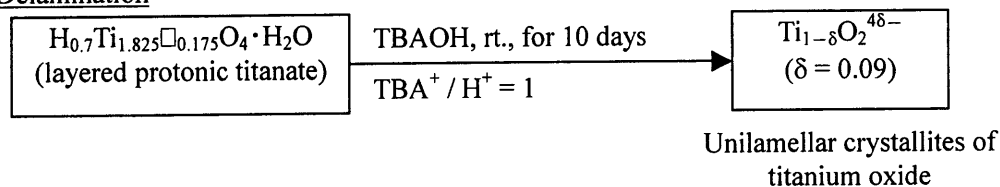
### 1.3. Layered Titanates

A number of layered materials have been found and synthesized in the system of silicates, titanate and niobates.<sup>5,6</sup> Since their interlayer spaces are available as a reaction site, these layered metallates can be applied to an ion-exchanger and photocatalyst. Layered titanates are of very attractive prospect due to the low cost, environmental acceptability, chemical stability, and photochemical properties.

Alkali-metal titanate compounds can be expressed such as  $M_2O \cdot TiO_2$  (M: alkali metal), and particularly  $K_2O \cdot nTiO_2$  is one of the most useful industrial materials, which are mainly used in the form of whisker and are applied to heat insulator, reinforcement of plastics, and friction materials in place of asbestos.

In 1981, Hervieu and Raveau reported a series of nonstoichiometric layered titanates,  $A_xTi_{2-x/4}\square_{x/4}O_4 \cdot H_2O$  ( $A = Li-Cs$  or  $H$ ,  $x = 0.67-0.73$ ,  $\square$  indicates vacant Ti sites) with a lepidocrocite-like structure.<sup>7</sup> In the past few years, Sasaki and co-workers prepared and characterized a protonated and exfoliated form of  $Cs_xTi_{(2-x/4)}\square_{x/4}O_4$ . The proton-exchanged form  $H_xTi_{(2-x/4)}\square_{x/4}O_4 \cdot H_2O$  swells and then delaminates in aqueous solution containing tetrabutylammonium hydroxide (TBAOH).<sup>8,9</sup> This can be regarded as a stable colloidal suspension of titania nanosheet or layered protonic titanate.

A typical preparation method of the titania nanosheet is illustrated in Fig. 1. 2.<sup>10</sup> Generally, colloidal layered titanates have been synthesized by a multistep process, that is, solid-phase reaction, ion-exchange, and delamination. First, layered  $Cs_xTi_{(2-x/4)}\square_{x/4}O_4$  ( $\square$ : vacancy) was synthesized by the solid-phase reaction of  $TiO_2$  with  $CsCO_3$ . Second, an ion-exchange reaction of  $Cs^+$  with  $H^+$  for a few days to give  $H_xTi_{(2-x/4)}\square_{x/4}O_4 \cdot H_2O$ , which was finally exfoliated by TBAOH. The resultant nanosheets are thought to have a composition of  $Ti_{1-\delta}O_2^{4\delta-}$ .

SynthesisIon-exchangeDelamination

TBAOH: tetrabutylammonium hydroxide

Fig. 1. 2. Typical preparation method of titania nanosheet.

It is known that a charge density of a layered compound relates to the ability of delamination. Table 1. 2 shows the several properties of layered protonic titanates,<sup>11</sup> and the structures are shown in Fig. 1. 3.<sup>12</sup> As clearly seen,  $\text{H}_x\text{Ti}_{2-x/4}\square_{x/4}\text{O}_4 \cdot \text{H}_2\text{O}$  ( $x=0.7$ ) has lowest negative charge density of the titanates, and layered zirconium phosphates and micas have values ranging from  $1/24$  to  $1/10 \text{ \AA}^{-2}$ . It is suggested that  $\text{H}_x\text{Ti}_{2-x/4}\square_{x/4}\text{O}_4 \cdot \text{H}_2\text{O}$  is easily delaminated by cations.

Table 1. 2. Protonic layered titanates.<sup>11</sup>

Layered protonic titanates	Interlayer spacing (Å)	Charge density <sup>#</sup> (Å <sup>-2</sup> )
$H_xTi_{2-x/4}\square_{x/4}O_4 \cdot H_2O$ (x=0.7)	9.4	1/32.2
$H_2Ti_3O_7$	7.9	1/17.2
$H_2Ti_4O_9 \cdot 1.2H_2O$	9.1	1/22.5
$H_2Ti_5O_{11} \cdot 3H_2O$	10.4	1/28.2

<sup>#</sup>Calculated as  $(2ac)/x$  for  $H_xTi_{2-x/4}\square_{x/4}O_4 \cdot H_2O$ , and  $(bc)/2$  for the others.

Sasaki, T et al, *Chem. Mater.* 1996, 8, 3, 777-782.

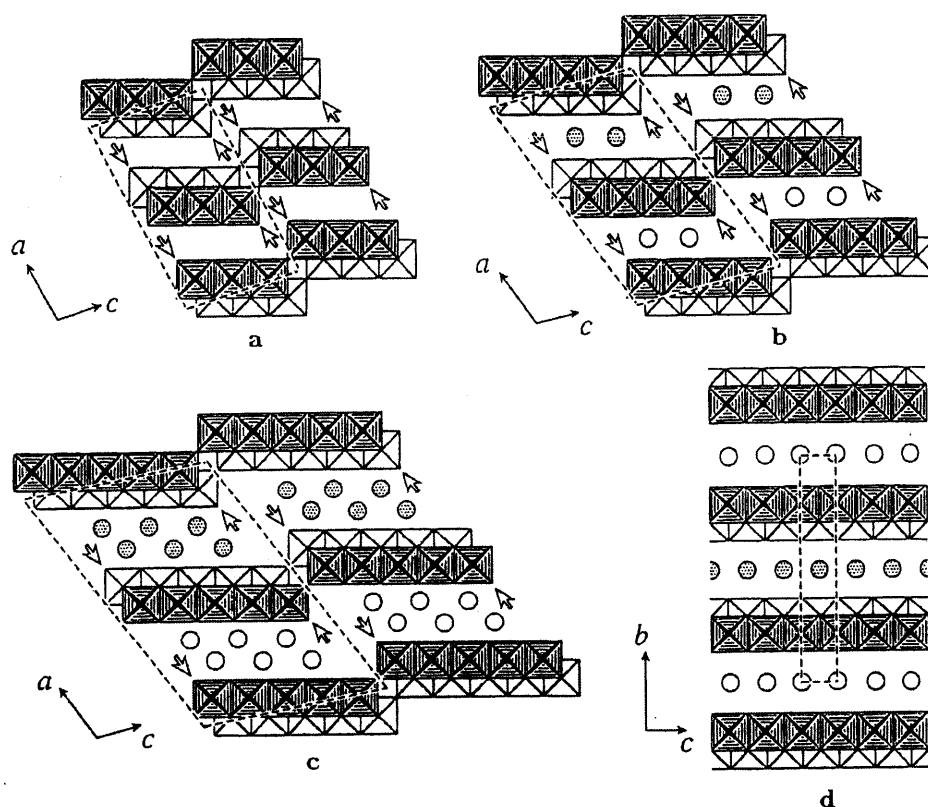


Figure 1. Schematic representation of crystal structures for the layered protonic oxides: (a, top left)  $H_2Ti_3O_7$  (trititanate), (b, top right)  $H_2Ti_4O_9 \cdot 1.2H_2O$  (tetratitanate), (c, bottom left)  $H_2Ti_5O_{11} \cdot 3H_2O$  (pentatitanate), (d, bottom right)  $H_xTi_{2-x/4}\square_{x/4}O_4 \cdot H_2O$  (lepidocrocite-related titanate). The unit cells (enclosed by broken lines) are C-base-centered monoclinic for  $H_2Ti_3O_7$ ,  $H_2Ti_4O_9 \cdot 1.2H_2O$  and  $H_2Ti_5O_{11} \cdot 3H_2O$ , and body-centered orthorhombic for  $H_xTi_{2-x/4}\square_{x/4}O_4 \cdot H_2O$ . Circles and arrows denote  $H_2O$  (or  $H_3O^+$ ) and position of hydroxylated proton, respectively. In  $H_2Ti_3O_7$ , another equivalent of protons besides indicated ones (terminal hydroxyls) is situated in the interlayer space.

Fig. 1. 3. Schematic illustration of layered protonic titanates.<sup>12</sup>

### 1.3.1. Ion-exchange of $H_xTi_{2-x/4}\square_{x/4}O_4 \cdot H_2O$

Various metal and organic cations were incorporated into the layered titanate by ion-exchange reaction. Since homogeneous colloidal suspension was obtained by treatment with TBAOH or ethylamine, ion exchange reaction can be carried out in the form of the film prepared by spin coating. Furthermore, the ion exchange of exfoliated layered titanate with larger cations is considered to be easier than that of the pristine layered titanate. The d value of the (020) diffraction of the powder, coated thin film and ion-exchange of  $H_{0.68}Ti_{1.83}\square_{0.17}O_4$  with various aqueous chloride solutions, and the extent of the ion-exchange is summarized in Table 1. 3.<sup>13</sup>

Thermal stability of the ion-exchanged thin film has been examined. Generally, the proton-exchanged forms of the layered compounds are not thermally stable. The layer structure of the  $Al^{3+}$ -exchanged thin film, for instance, was found to have collapsed on calcination because the  $Al^{3+}$  in the interlayer space is converted to aluminum oxide, and the layer was converted to amorphous  $TiO_2$ . The  $Cs^+$ -exchanged thin film had highest thermal stability in Table 1. 3.

Table 1. 3. The d value of the (020) diffraction of the powder, coated thin film and ion-exchange of  $H_{0.68}Ti_{1.83}\square_{0.17}O_4$  with various aqueous chloride solutions, and the extent of the ion-exchange.<sup>11, 13, 14</sup>

Interlayer cation	d value of (020) / nm	Thermal stability / °C	Interlayer cation	d value of (020) / nm	Thermal stability / °C
$H^+$ (68 %)	0.94	~ 200*	$Cr^{3+}$ (75 %)	1.05	< 300
$Li^+$ (70 %)	0.93	—	$Cu^{2+}$ (80 %)	0.92	< 300
$Na^+$ (70 %)	0.89	—	$Ni^{2+}$	1.15	400
$K^+$ (70 %)	0.90	—	$C_2H_5NH_3^+$	0.96	200
$Rb^+$ (70 %)	0.86	—	TBA <sup>+</sup>	1.75	200
$Cs^+$ (70 %)	0.88	600	C8-NH <sub>3</sub> <sup>+</sup>	2.31	—
$Al^{3+}$ (76 %)	1.25	< 300	C12-NH <sub>3</sub> <sup>+</sup>	2.47	—
$Co^{2+}$ (82 %)	1.13	< 300	C18-NH <sub>3</sub> <sup>+</sup>	3.59	—

\*in the form of powder

### 1.3.2. Organic-Inorganic Nanocomposites

Layered Nanocomposites are materials generally comprised of an organic polymer incorporated between sheets of an inorganic host. A wide range of polymers and hosts have been combined to form nanocomposite structures, and nanostructured materials have been shown to exhibit novel, and technologically useful, mechanical, optical, electrical, and barrier properties.<sup>15, 16</sup> So far, aluminosilicate smectite clays such as montmorillonite and hectorite,  $\text{MoO}_3$ ,  $\text{V}_2\text{O}_5$  have been used as a host, while poly(ethylene oxide), PEO, and poly(vinylpyrrolidone), PVP were incorporated as a organic polymer.<sup>17-25</sup> Sukpirom and Lerner reported that PEO and PVP could be incorporated between  $\text{H}_x\text{Ti}_{2-x/4}\square_{x/4}\text{O}_4$  titanate layers with interlayer distance of 1.49 and 2.88 nm, respectively.<sup>26</sup> These elemental analyses gave empirical formulas of  $\text{H}_{0.7}\text{Ti}_{1.83}\text{O}_4 (\text{C}_2\text{H}_4\text{O})_{1.54}(\text{H}_2\text{O})_{1.28}$  and  $\text{H}_{0.7}\text{Ti}_{1.83}\text{O}_4 (\text{C}_{16}\text{H}_{36}\text{N})_{0.05}(\text{C}_6\text{H}_9\text{NO})_{1.22} (\text{H}_2\text{O})_{0.92}$  for the PEO and PVP nanocomposites, respectively.

Moreover, Sasaki et al. reported layer-by-layer assembly of the titanate sheet / polydiallyldimethylammonium (PDDA) composite films.<sup>27, 28</sup> These films were obtained by alternately dipping a substrate in a colloidal suspension of the titania nanosheets and PDDA solution. Thermal or photocatalytic decomposition of polycations in the nanosheet gallery was achieved by heating to 400 °C or UV irradiation, respectively. The nanosheet architecture collapsed upon heating at 500 °C or higher, yielding ultrathin films of  $\text{TiO}_2$  (anatase and then rutile).

### 1.3.3. Preparation and Optical Property of Thin Films of the Layered Titanate

The exfoliation of the layered titanate  $\text{H}_x\text{Ti}_{2-x/4}\square_{x/4}\text{O}_4 \cdot \text{H}_2\text{O}$  is also possible by the use of aqueous ethylamine solution instead of TBAOH. By using these suspensions, the exfoliated titanate sheets were easily oriented on glass plate by spin-coating and Langmuir-Blodgett (LB) technique.<sup>29</sup> Ethylammonium ion in the titanate film can be decomposed by UV-irradiation, because the host layer of titanate has the photocatalytic ability for the oxidation of organic materials.<sup>14</sup> The absorption of nanosheets of  $\text{Ti}_{1-\delta}\text{O}_2^{4\delta-}$  was blue shifted ( $>1.4$  eV) relative to the band edge for bulk  $\text{TiO}_2$ , which is attributed to size quantization effects.<sup>30</sup>

### 1.3.4. Pillared Layered Titanates

The pillaring of layered compounds by inorganic molecular clusters or nano-sols offers a promising means of fabricating porous materials with zeolitic properties.<sup>31-35</sup> By using the layered titanate  $H_xTi_{2-x/4}\square_{x/4}O_4 \cdot H_2O$  ( $x = 0.7$ ),  $SiO_2$ - and  $TiO_2$ -pillared layered titanate were successfully synthesized.<sup>36, 37</sup> Ion exchange of the H ions in the interlayer to  $TBA^+$  or  $n-C_nH_{2n+1}NH_3^+$  ( $n = 8, 12, 18$ ), expanded the interlayer space, and enabled intercalation of tetraethylorthosilicate (TEOS) or  $TiO_2$  nano-sol that was prepared from the TIP-acac- $HNO_3$  system (acacH: acetylacetone). The layered structure of  $SiO_2$ -pillared thin film was confirmed to stable up to 500 °C. On the other hand,  $TiO_2$ -pillared layered titanate showed a pillar height of ~2 nm with a high surface area of ~460 m<sup>2</sup>/g and a pore size of ~0.95 nm. Moreover, the pillared titanate had excellent photocatalytic activity, and an enhancement of in activity of ca. 170 % was obtained compared to that of the pristine layered cesium titanate,  $Cs_xTi_{2-x/4}\square_{x/4}O_4$ .

## 1. 4. Sol-Gel Processing

Sol-gel process defines as the production of inorganic oxides, either from colloidal dispersion or from metal alkoxides. However nitrides and sulfides that have been used recently in the synthesis of hybrid organic-inorganic materials are also included in the process. Metal salts such as acetates and nitrates are also used in the same manner as alkoxides. Sol-gel processing can provide a variety of forms: powders, fibers, monoliths, and coatings. Oxide films can be expected to have excellent properties different from bulk form. For instance, one of the interesting functions is considered to be optical ones, because oxides are transparent to visible light. They can also be used to protect a substrate against corrosion, abrasion, or scratch, and be used for chemical durability, alkali resistance, mechanical control, reflectivity control, coloring, and electrical conduction.<sup>38</sup> So far, there are many coating techniques, and the typical examples are illustrated in Fig. 1. 4. Compared to conventional thin film forming processes such as CVD, evaporation or sputtering, sol-gel film formation requires considerably less equipment and is potentially less expensive. The sol-gel method offers many other advantages:

1. Intimate mixing, at the molecular level, of the starting materials resulting in a

high degree of homogeneity even for multicomponent systems.

2. Low processing temperature that allows the use of volatile components and avoids the formation of undesired phases.
3. Dopants, even at trace level, can be introduced with relative ease.
4. Easy adjustment of the viscosity, and thereby the thickness per coating, by adequate choice of the solvent, chelating organic ligands, concentration, etc.
5. Large area coatings of desired thickness and composition can be obtained.
6. Inorganic-organic hybrids and/or composites can be prepared.

On the other hand, the greatest limitation to the synthesis of ceramics by sol-gel processing is cost of the precursors, and especially that of alkoxides. Residual carbon and hydroxyls in final materials sometimes causes problems that influenced their optical and electrical properties. Moreover, health hazards by organic solutions should be noted because organic solvents are mainly used in sol-gel processing.

#### 1.4.1. Dip Coating

Dip coating can be divided into five stages: immersion, start-up, deposition, drainage, and evaporation.<sup>39</sup> When the liquid viscosity ( $\eta$ ) and substrate speed ( $U$ ) are high enough to lower the curvature of the meniscus, then the deposited film thickness ( $h$ ) is the thickness that balances the viscous drag ( $\propto \eta U / h$ ) and gravity force ( $\rho g h$ ):

$$h = c (\eta U / \rho g)^{1/2}$$

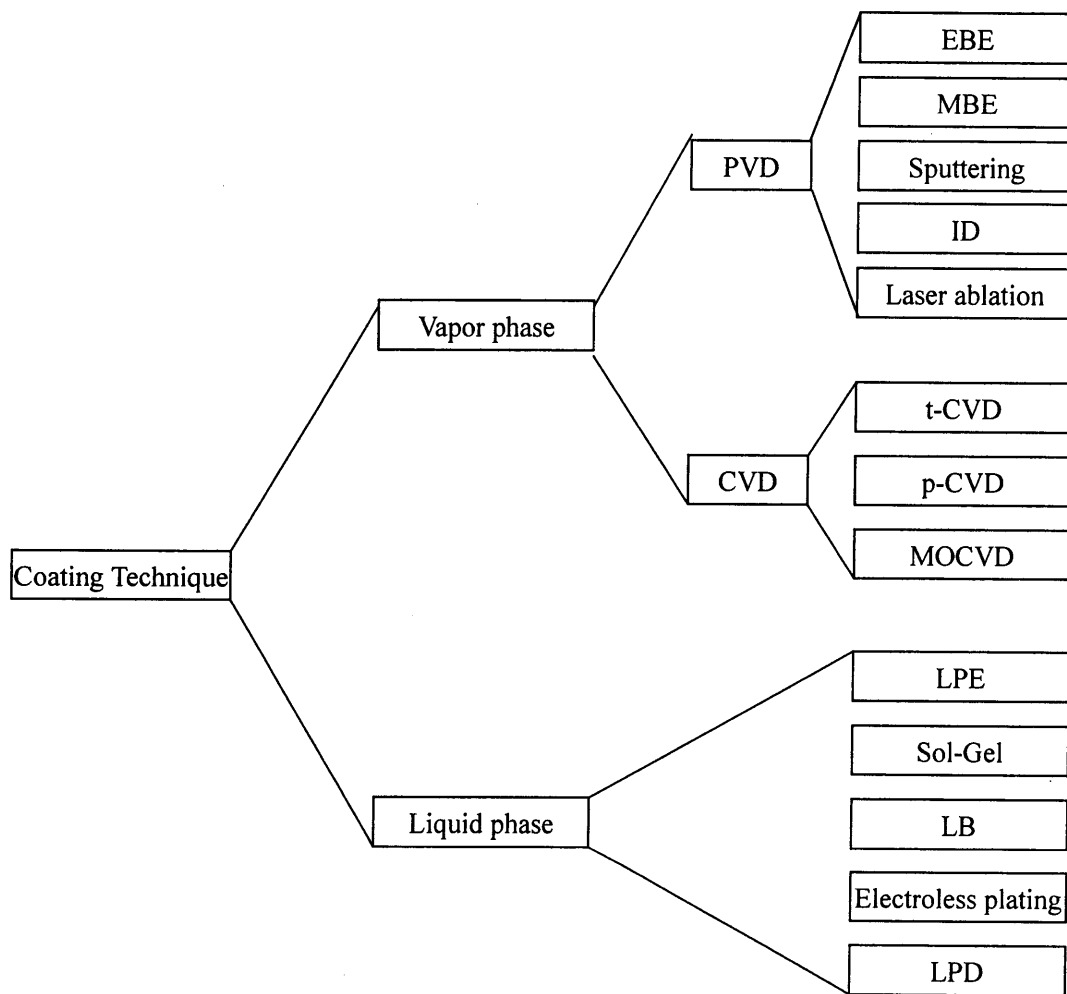
where the proportionality constant,  $c$  is about 0.8 for Newtonian liquids. As clearly seen, the film thickness is varied proportionally to the square root of the sol viscosity. In order to control the film thickness, therefore, the sol stability, especially in the viscosity, is significant. Volatility of the solvent in the sol is also important although it is not included in the equation. Special attention should be paid to volatile solvents such as alcohols because the sol concentration tends to change during coating operation. On the other hand, in the case of low volatility solvents such as water, the dip-coated liquid (gel) film becomes more fluid with increasing thickness. Therefore, in order to depress the fluidity, higher concentration of the sol and lower withdrawal speed are required.

### 1.4.2. Spin Coating

Spin coating is divided into four stages: deposition, spin-up, spin-off, and evaporation.<sup>39</sup> The thickness of an initially uniform film during spin-off is described by:

$$h(t) = h_0 / (1 + 4\rho\omega^2 h_0^2 t / 3\eta)^{1/2}$$

where  $h_0$  is the initial thickness,  $t$  is time, and  $\omega$  is the angular velocity:  $\rho$  and  $\eta$  assumed constant.



EBE: Electron Beam Evaporation  
 MBE: Molecular Beam Epitaxy  
 ID: Ionization Deposition  
 t-CVD: Thermal CVD  
 p-CVD: Plasma CVD

MOCVD: Metalorganic Chemical Vapor Deposition  
 LPE: Liquid Phase Epitaxy  
 LB: Langmuir Blodgett  
 LPD: Liquid Phase Deposition

Figure 1. 4. Coating techniques.

### 1.5. Use of Chelate Ligands as a Stabilizer of Metal Alkoxides in Views of Sol-Gel Technique

Sol-gel technique including dip or spin coating is one of the interesting and useful preparation methods to conventionally obtain uniform thin oxide films.<sup>39-42</sup> The metal alkoxides are commonly used as the important starting materials.<sup>43</sup> However, owing to their high reactivity, some modifiers or stabilizers have been used to stabilize the sols derived from the alkoxides. The stability of starting sols is one of key factors for the process to be useful especially for the industrial application. So far, some chelating agents such as  $\beta$ -diketones,<sup>44-50</sup> glycols,<sup>51-53</sup> alkanolamines<sup>54-66</sup> and so on<sup>67-71</sup> have been extensively used as the stabilizers, and the selection of chelating agents affects the sol stability, the photosensitization of the gel film and the crystallization temperature of the oxide film.

The chemical modifiers or chelates should satisfy the following conditions in order to be useful:

- (1) They have a suitable interaction with the alkoxides to control the number of the active alkoxy groups (functionality) and, if possible, their steric conformation,
- (2) They have a low boiling point and can be easily decomposed or oxidized at moderate temperatures, and
- (3) They are easily available with low price and non-toxic.

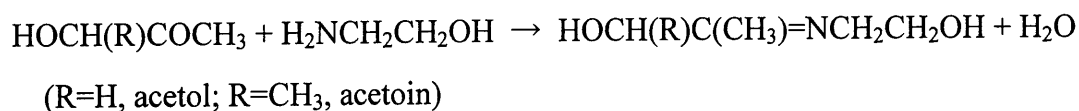
Lowering the firing temperatures is another important factors for the coating processes to be more useful. Therefore, it is a very important subject to develop more suitable modifiers generally applicable to various single and mixed alkoxide systems.

Some of organic ligands often used in sol-gel processing are shown in Fig. 1. 5. Acetylacetone (acacH) with a low boiling point reacts easily with alkoxides to give corresponding acetylacetonato complexes, and almost fulfils the above requirements. However, the complexes, in particular bis- or tris-(acetylacetonato) derivatives, are sometimes stable enough to be vaporized at higher temperatures,<sup>72</sup> leading to the stoichiometry deviations from the nominal starting composition on firing the gel films of mixed oxides.

Alkanolamines, especially diethanolamine (DEA) and triethanolamine (TEA) are useful, because they can effectively stabilize various alkoxides and yield uniform films of simple oxides such as  $\text{In}_2\text{O}_3$ ,<sup>56</sup>  $\text{SnO}_2$ ,<sup>57</sup>  $\text{TiO}_2$ <sup>58, 59</sup> and mixed oxides such as

$\text{Al}_2\text{MgO}_4$ ,<sup>61</sup> ITO,<sup>56</sup> PZT<sup>62</sup> and  $\text{LiTaO}_3$ <sup>63</sup> from the stabilized solutions. Moreover they promote the dissolution of metallic acetates into alcoholic solvents to enable the preparation of the films of  $\text{ZnO}$ ,<sup>64</sup> ITO<sup>65</sup> and PZT<sup>66</sup>. It is known that the alkanolamines can strongly interact with transition metal ions to form the corresponding chelate compounds in alcohols,<sup>67</sup> and also that the alcoholic exchange reaction with the alkoxides can yield the stable compounds with chelates through O-M-O and O-M-N bonds<sup>68, 69</sup>. The multifunctional structures (O-H bonds and strongly coordinating N atom) play a substantial role in their stabilization effect of the alkoxides. However, these alkanolamines has an unavoidable demerit of the boiling points around 250 °C or higher which may suppress the low temperature crystallization of coated oxide films and leave heavy carbonaceous impurity in the films on firing of the gel films.

Recently, we examined the effect of some imine compounds on the stabilization of 2-propanol solutions of  $\text{Ti}(\text{OPr}^i)_4$  (TIP). They can be derived by an *in-situ* reaction between an  $\alpha$ -hydroxyketone (acetol or acetoin) and monoethanolamine (MEA) in the presence of the alkoxide according to the following equation:



The organic products, namely imines, have a same chain unit as that of DEA. In contrast to the DEA, however, the derivatives contain a C=N bond that can hydrolytically dissociate at higher temperatures to regenerate MEA (bp. 170.8 °C), which is more volatile than DEA. Therefore, this imine type of ligands might be eliminated more effectively than DEA during the firing of gel films, suggesting that they have an ideal property as stabilizers for alkoxide-based dip-coating process. The results are summarized in Table 1. 4, which lists the molar ratios of the additives to TIP, the total molar ratios of water which can be added to the TIP solution stabilized by the additives of a given molar ratios to TIP without any gelation or precipitation, as well as the refractive index and rutile contents of the films prepared at 600 °C on glass plates from these solutions. The results for DEA and acetylacetone are added for comparison. Although MEA alone has no positive effect, the combinative use of MEA with the

$\alpha$ -hydroxyketones can very effectively stabilize the titanium alkoxide sols but crystallization temperature of the film remained about 500 °C, being almost comparable to DEA. This may be due to the fact that the imines have just the same main chain unit as that of DEA. Very interestingly acetol and acetoin are more effective than acetylacetone, comparable to that obtained in the case of DEA. These sol systems have a tendency to afford rutile-containing films with higher refractive index. The imines which have the C=N bond in the molecule can be photochemically excited with the irradiation of UV-light, leading to photo-patterning of the gel films formed from the imine-stabilized sols as described later.

Table 1. 4. The effects of a combinative use of the hydroxyketones with MEA on the stabilization of 0.5 M  $\text{Ti}(\text{OPr}^i)_4$  2-propanol solutions and the properties of  $\text{TiO}_2$  films dip-coated at 600 °C from each solution.

Hydroxyketone	Molar ratio to TTIP	Molar ratio of MEA to TTIP	Total $\text{H}_2\text{O}$ molar ratio to TTIP for gelation*	Refractive index of the $\text{TiO}_2$ film (for 600 nm light)	Rutile content / %
---	---	1	< 2 (ppt)	(Powdery film)	---
---	---	2	< 2 (ppt)	(Powdery film)	---
Acetol	1	1	~4	2.38	28
	2	2	> 30	2.40	29
Acetoin	1	1	~30	2.33	~0
	2	2	> 40	2.31	~2
Acetylacetone	1	1	~2	2.39	27
	2	2	> 2	2.36	25
DEA <sup>#</sup>	1	---	~5	~2.3	15

\* The water generated by the *in-situ* reaction between the carbonyl compounds with the amines is not included in the molar ratio.

<sup>#</sup> Diethanolamine: this run is added for comparison with other systems.

<sup>§</sup> Gelation takes place before  $\text{H}_2\text{O}$  addition.

It was of our great interest that we found that the  $\alpha$ -hydroxyketones themselves, namely without MEA, already could strongly stabilize the 2-propanol solutions of TIP, as shown in Table 1. 5. When acetoin was added to the alkoxide solution in the molar ratio of acetoin/TIP=2, a large excess amount of water can be added to the solution without any gelation or precipitation. Its sol-stabilization effect is much more remarkable than acetylacetone that has been used as an excellent stabilizer so far.

Table 1. 5. The effects of the hydroxyketones on the stabilization of 0.5M  $\text{Ti}(\text{OPr}^i)_4$  2-propanol solutions and the properties of  $\text{TiO}_2$  films dip-coated at 600 °C from each solution.

Hydroxyketone	Molar ratio to TTIP	Total $\text{H}_2\text{O}$ molar ratio to TTIP for gelation	Refractive index of the $\text{TiO}_2$ film (for 600 nm light)	Rutile Content (%)
Acetol	1	$\leq 2$	2.19	0
	2	$\leq 4$	2.24	0
Acetoin	1	$\leq 4$	2.16	0
	2	$> 40$	2.12	0
Acetylacetone*	1	$\leq 2$	2.06	0
	2	$\geq 2$	2.08	0

\*Since the enol form can be regarded as  $\beta$ -hydroxyketone, it was included in this table.

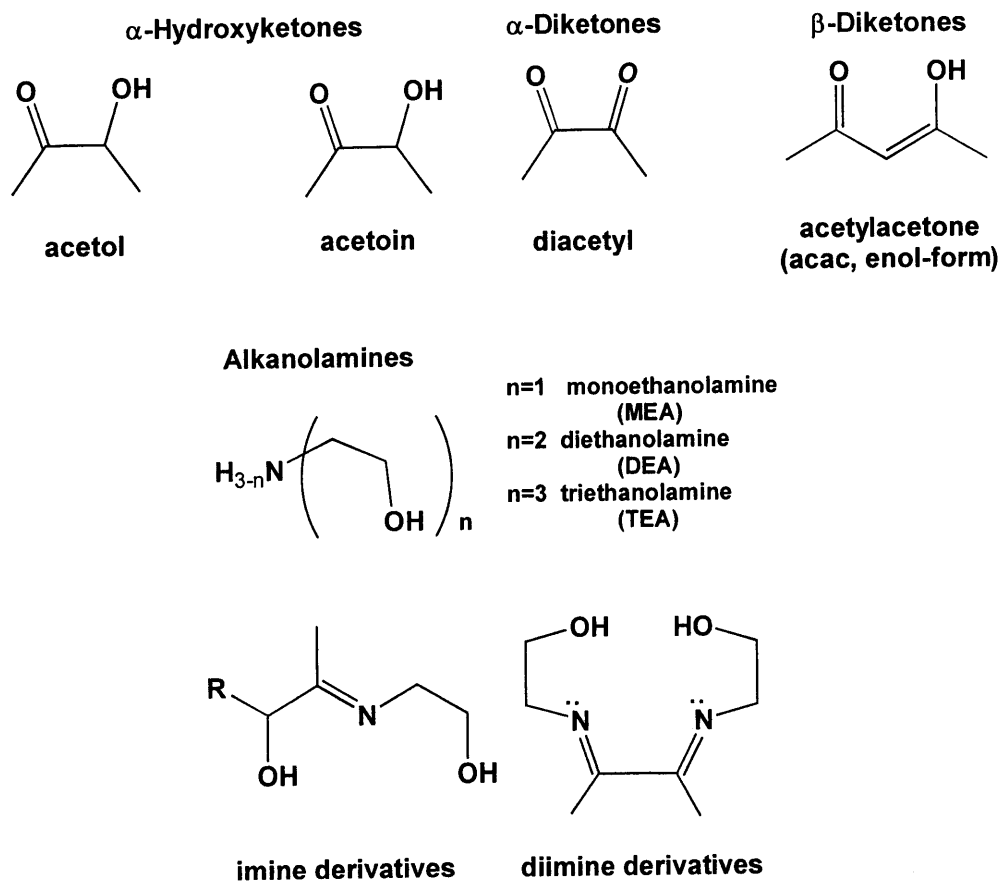


Figure 1. 5. Structures of the chelating ligands used in this study.

### 1.5.1. Properties of TiO<sub>2</sub> Thin Films Prepared by Sol-Gel Technique

So far, many sol systems for TiO<sub>2</sub> coating have been reported. Typical examples are listed in Table 1. 6, together with the rutile formation temperatures that are very important to control the physical properties of the coated films. It is clearly seen from Table 1. 6 that a wide range of starting materials from simple inorganic salts to the alkoxides have been selected, and that the alkoxides are modified by some chelating compounds such as carboxylic acids, diols, acetylacetone and ethanolamines. These compounds are extensively used as the stabilizers for other alkoxides, too. Here it is noteworthy that which the crystal form of deposited TiO<sub>2</sub> strongly depends on the sol system or modifiers. Among the organic modifiers, diethanolamine yields rutile at the lowest temperature.

Table 1. 6. Typical examples of the sols used for the dip- or spin-coating of TiO<sub>2</sub> films.

Sol composition	Rutile formation temp. (°C)	Ref.
Hydrosol from TiO(SO <sub>4</sub> )	r. t.	78
Hydrosol from Alkoxide + Acid	Around 350	87
TiCl <sub>4</sub> + HCl + H <sub>2</sub> O	250	80, 81
Ti(OEt) <sub>4</sub> + H <sub>2</sub> O in air	---	82
Ti(OEt) <sub>4</sub> + HCl + H <sub>2</sub> O	Around 800	84
Ti(OPr <sup>i</sup> ) <sub>4</sub> + H <sub>2</sub> O (Spin-coating)	---	83
Ti(OPr <sup>i</sup> ) <sub>4</sub> + HCl + H <sub>2</sub> O	> 800	84, 85
Ti(Obu <sup>n</sup> ) <sub>4</sub> + HCl + H <sub>2</sub> O	>= 800	77
Ti(OPr <sup>i</sup> ) <sub>4</sub> + CH <sub>3</sub> COOH + H <sub>2</sub> O (Spin-Coating)	---	76
Ti(OPr <sup>i</sup> ) <sub>4</sub> + Diols etc. + H <sub>2</sub> O	> 800-900	53
Ti(acac) <sub>2</sub> (OR) <sub>2</sub> + H <sub>2</sub> O	> 800	86
Ti(OPr <sup>i</sup> ) <sub>4</sub> + (HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> NH (DEA) + H <sub>2</sub> O	Around 600	79
Ti(OPr <sup>i</sup> ) <sub>4</sub> + acetoin + HOCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> (MEA)	650	71

These findings strongly suggest that the rutile formation was due to the ligands with much carbon content. This type of ligands leaves carbonaceous impurities in the films or powders on the thermal decomposition. The impurities may retard the crystallization and subsequent crystal growth. And, the small crystallite size of the formed  $\text{TiO}_2$  may accelerate the transformation to rutile.

The carbonaceous impurity can also work as a strong reducing agent for titanium species at higher temperatures. The reducing property of organic species would induce the oxygen deficiency in titanium dioxide, through which the transformation to rutile would be enhanced. It has been reported that oxygen vacancies introduced to  $\text{TiO}_2$  lattice by a heat treatment under a reducing atmosphere, say hydrogen, accelerate the crystal growth<sup>88</sup> and the transformation from anatase to rutile.<sup>88, 89</sup>

### **1.5.2. Effect of UV-irradiation on the Gel Films Prepared from Chelate-stabilized Metal Alkoxide Sols**

UV-irradiation of gel films before heat-treatment causes some interesting effects. The main role of photo-irradiation is thought to break metal-chelate bonds in the gel films, and to accelerate the condensation to develop M-O-M (M: metal) networks, which might make the film insoluble in the parent solvent. By using this difference in solubility, patterned films can be obtained. Furthermore, as a result of the decomposition of organic chelates, the crystallization can easily occur at lower temperatures. Here, effect of photoirradiation to the gel films prepared from TIP and zirconium *n*-tetrabutoxide (ZNB) sols stabilized some chelating ligands was outlined.

The effect of the UV-light irradiation to the gel film prepared from acetol-MEA-TTIP system on the  $\text{TiO}_2$  crystallization is shown in Fig. 1. 6 as typical examples. This Figure comparatively shows XRD profiles of the  $\text{TiO}_2$  films fired at different temperatures after only drying or the additional exposure to UV-light, clearly indicating that the UV-irradiated film is composed of crystalline  $\text{TiO}_2$  film even at a temperature as low as 400 °C, while non-irradiated one was crystallized around 500 °C. Therefore, the crystallization temperature can be lowered by about 100 °C by the UV-irradiation. Very similar UV-effects were generally observed for the gel films prepared not only from other imine systems but also even from DEA-stabilized solution.

Moreover, it is notable that with the photoirradiation pure anatase films were obtained from chelate-stabilized solution at a temperature as high as 600 to 650 °C, while rutile was formed in the case without photoirradiation.

The UV irradiation effect was further confirmed by the observation of crystallite size of  $\text{TiO}_2$  as shown in Table 1. 7, where the crystallite sizes of  $\text{TiO}_2$  films prepared from acetoin-MEA-TTIP (1:1:1) solution are listed. The Table clearly indicates that UV-irradiation effectively assists the crystal growth of  $\text{TiO}_2$ .

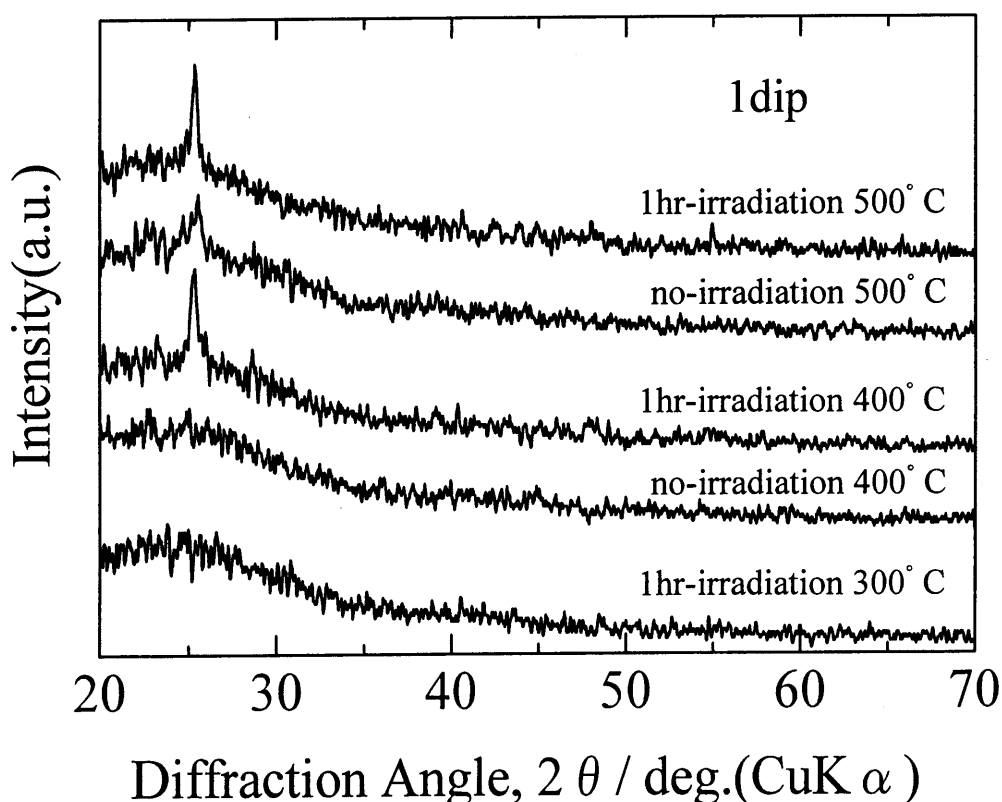


Figure 1. 6. Firing temperature dependence of XRD patterns of the singly coated gel films from acetoin-MEA-TTIP (1:1:1) solution and with and without subsequent photoirradiation treatment.

Table 1. 7. Firing temperature dependence of the crystallite sizes of  $\text{TiO}_2$  films prepared with and without photoirradiation to the gel films derived from acetoin-MEA-TTIP (1:1:1) solution.

Firing temperature / °C	Anatase crystallite size / nm*	
	No irradiation	Photoirradiated
400	---	20
500	12	37
600	21	52
650	27	33
	(15.5)	

\* The value in the parentheses denotes the crystallite size of rutile phase.

#### 1.5.2.1. Absorption Spectra of Chelate-stabilized $\text{TiO}_2$ and $\text{ZrO}_2$ Gel Films

The absorption spectra of the  $\text{TiO}_2$  (Fig. 1. 7(a)) and  $\text{ZrO}_2$  (Fig. 1. 7(b)) gel films prepared from various sols on  $\text{SiO}_2$  glass before photo-irradiation are shown in Fig. 1. 7. The  $\text{TiO}_2$  gel films absorbed light with the wavelength shorter than 500 nm regardless of the chelating ligands used, whereas the  $\text{ZrO}_2$  gel films absorbed light with the wavelength shorter than 250 nm for the alkanolamine system, and wavelength below 500 nm for the imine systems.

The alkoxide 2-propanol solution has a strong UV absorption band ( $\lambda_{\text{max}} = \text{ca. } 300 \text{ nm}$ ,  $\epsilon = 1.2 \times 10^3$ ), assignable to a charge transfer (CT) from a ligand orbital to a d-orbital of titanium atom.<sup>90, 91</sup> The charge transfer excitation is considered to commonly play a fundamental role for the photo-effects, but not the excitation including  $\pi$ -bond system, because DEA-stabilized systems without  $\pi$ -bond system also receive very similar photo-effects. Its charge transfer may weaken the ligand-metal bonds and help their dissociation. However, the latter, namely the excitation by light of a longer wavelength region, sometimes can not be ignored. The fact that the films derived from acetoin-MEA-ZNB (2:2:1) were sensitized by light with the wavelength longer than 350 nm, as described above, may be attributed this excitation.

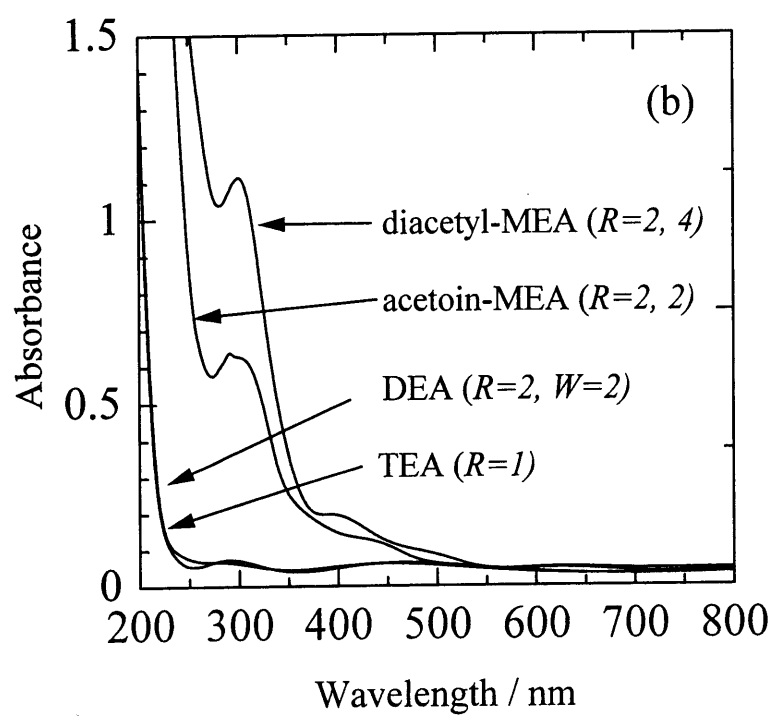
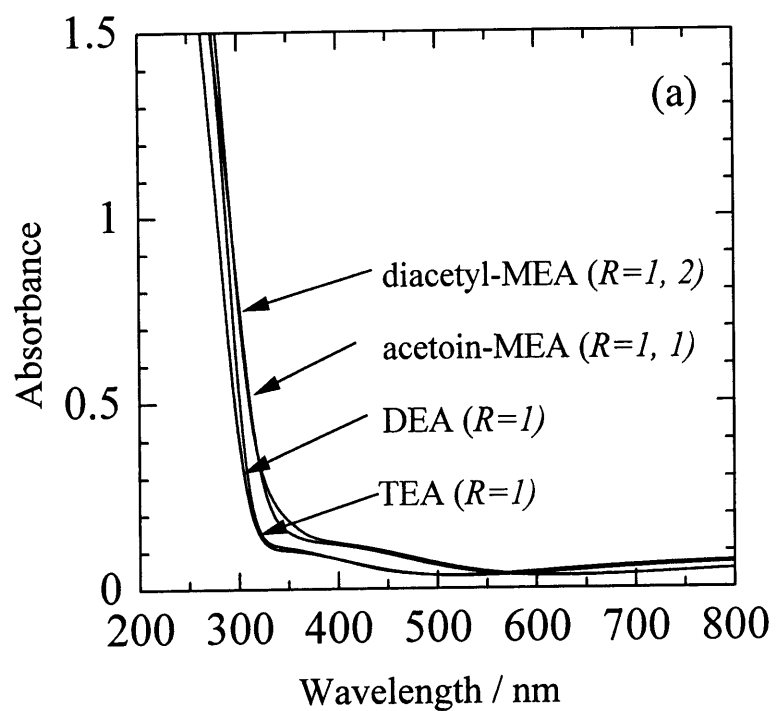


Figure 1. 7. Absorption spectra of (a) the TiO<sub>2</sub> gel films and (b) the ZrO<sub>2</sub> thin films prepared on SiO<sub>2</sub> glass after drying at 110 °C for 10 min.

### 1.5.2.2. Patterning of $\text{TiO}_2$ and $\text{ZrO}_2$ Thin Films

Many studies on the patterning of metal oxide films using organic chelates such as  $\beta$ -diketones and alkanolamines<sup>92-97</sup> were reported.

First, the gel film was dip-coated on the glass substrate (corning, #7059) at 2 cm/min, dried at 110 °C for 10 min, and then irradiated by UV light through a filter and a photo mask as shown in Fig. 1. 8. The irradiation power density through the filter was 0.4 W/cm<sup>2</sup>. A 500 W super high-pressure mercury lamp was used as a UV light source. After irradiation for 60 min, the unirradiated region was removed by leaching in 2-propanol. Finally, the film was fired at 600 °C in air for 30 min.

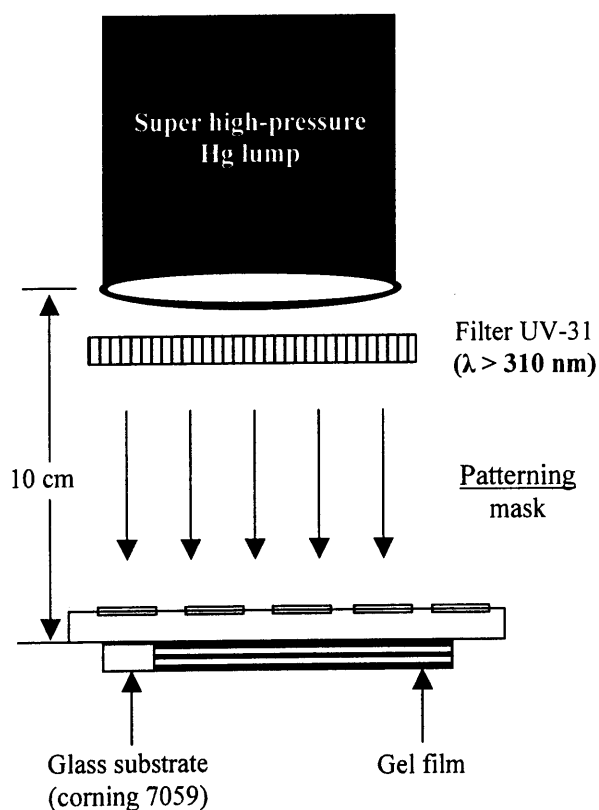


Fig. 1. 8. Schematic diagram of experimental apparatus used for patterning in this study.

It was found that alkanolamines such as DEA and TEA were effective only for  $\text{TiO}_2$  films, while the imine derivatives such as diacetyl-MEA and acetoin-MEA were effective for both  $\text{TiO}_2$  and  $\text{ZrO}_2$  films, comparable to the results of the absorption spectra of the gel films.

Figure 1. 9 shows a typical example of an SEM image for a patterned  $\text{ZrO}_2$  thin film, indicative of a precise pattern. Figure 1. 10 shows EDX spectra of the UV-irradiated ( $\text{ZrO}_2$ ) and the UV-unirradiated (glass) part, suggesting that the unirradiated part of the  $\text{ZrO}_2$  gel film was completely removed by leaching. The surface profile (Fig. 1. 11) indicated that the width between patterned areas in  $\text{ZrO}_2$  films was  $20\text{ }\mu\text{m}$ , and the thickness of the patterned film was  $50\text{ nm}$ , comparable to that of the film without leaching.

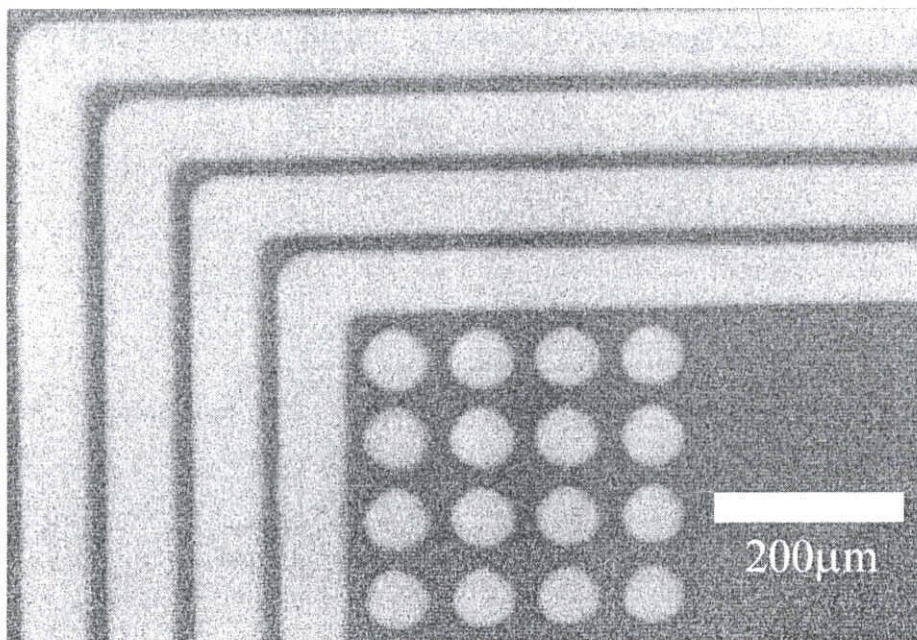


Figure 1. 9. SEM image the patterned  $\text{ZrO}_2$  thin film from the ZNB-diacetyl-MEA ( $R=2, 4$ ) system.

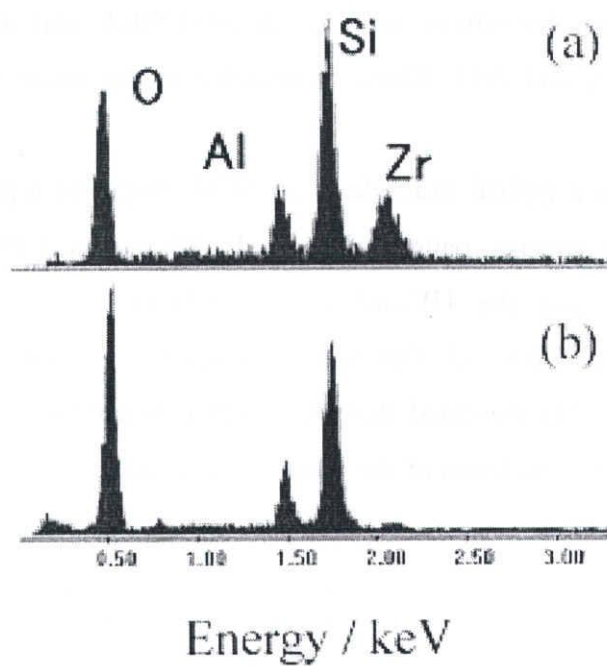


Figure 1. 10. EDX spectra of (a) irradiated- and (b) unirradiated parts in Fig. 7.

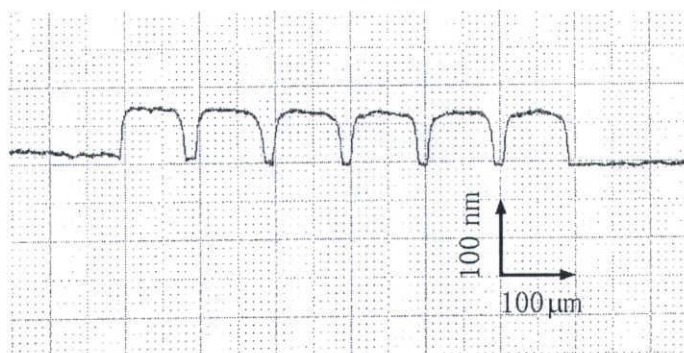
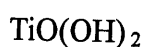
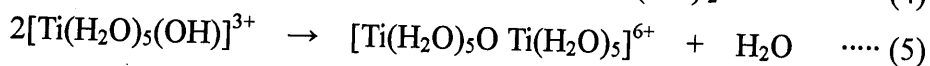
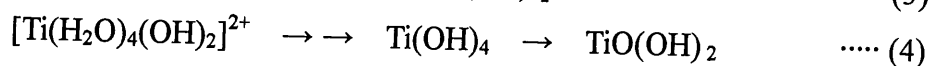
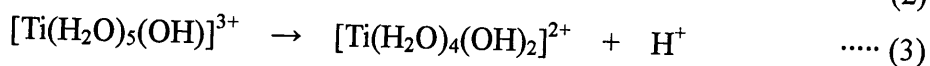
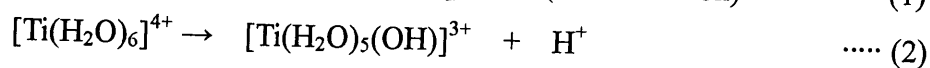
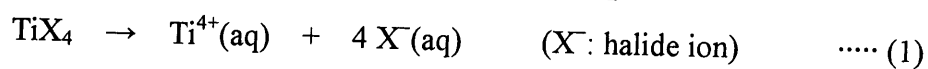


Figure 1. 11. Surface profile of the patterned  $\text{ZrO}_2$  thin film prepared from ZNB-diacetyl-MEA ( $R=2, 4$ ) system.

## 1. 6. Water-soluble Titanium Compounds

Aqueous solutions must be more benign for the environment and can be more safely handled than organic solutions. However, many transition metals with higher formal oxidation states such as elements in Groups 4 and 5 are readily hydrolyzed to give insoluble metallic acids. In the case of  $Ti^{4+}$ , for instance, the hydrolysis and condensation reaction readily occurs in the presence of trace amount of water.

### *Hydrolysis and Condensation of Aqueous $Ti^{4+}$ Ions*



Titanium ion in water commonly exists as the aqua complex  $[Ti(H_2O)_6]^{4+}$ , which is strongly hydrolyzed to yield titanic acid  $TiO(OH)_2$  owing to high positive charge density of  $Ti^{4+}$  to give a hydroxo complex or the insoluble polymer of titanyl ion ( $TiO^+$ ) that is insoluble in any solvent. To keep the solution stable, highly acidic condition is required to retard proton dissociation steps ((2)-(4)), on the notion of equilibrium. This behavior is common to the transition metals with higher formal oxidation states, especially the elements in Groups 4 and 5. The use of chelating ligands is also applicable to reduce the hydrolysis rate due to its chelate effect. Therefore, in order to obtain stable solutions of the elements in Groups 4 and 5, only highly acidic condition or the use of chelating ligands seems to be effective.

Table 1. 8 shows some aqueous titanium compounds that are commercially available, and other water-soluble titanium compounds that have been reported are listed in Table 1. 9. As described above, chelating ligands and/or acidic condition seem to be essential for stable titanium compounds that are soluble in water. Compounds containing halogens and sulfur are not suitable as the starting materials for sol-gel

method because of generating corrosive hydrogen halides and  $\text{SO}_x$  gas during heat treatment. Ammonium salts are also preferable to alkali ion derivatives, because the latter would introduce the alkali ions when they were used for the preparation of titanium based mixed oxides, for example. The chelates would sometimes retard the crystallization because they tend to remain in the film at higher temperatures due to their strongly coordination to the titanium ion. Accordingly, free titanium compounds, namely those without chelate modifications, are more useful. In these respects, “peroxotitanic acid” is the best example of such free titanium compounds. However, its solubility to water seems to be somewhat limited (0.2 to 0.4 M, almost neutral solutions),<sup>98, 99</sup> although the compound seems to be further stabilized by a suitable chelating agent<sup>100-102</sup> as shown in Table 1. 8. An interesting compound with the composition  $\text{Ti}_4\text{O}_{15}[\text{N}(\text{CH}_3)_4]_2\text{H}_{12}$  has been reported<sup>103</sup>, but its structure and properties including the solubility to water is unclear. A homogeneous concentrated colloidal suspension containing very fine, crystalline  $\text{TiO}_2$  (anatase) is also commercially available.<sup>104</sup>

Table 1. 8. Commercially available aqueous titanium compounds and  $\text{TiO}_2$  sol.

Compounds	pH of Solution	Remarks	Ref.
$\text{TiCl}_4$	Strongly acidic	Contains halogen	105
$(\text{NH}_4)_2[\text{TiF}_6]$	Strongly acidic	Contains halogen	105
$\text{Ti}(\text{SO}_4)_2, \text{TiOSO}_4$	Strongly acidic	Contains sulfur	105
$(\text{NH}_4)_2[\text{TiO}(\text{Ox})_2] \cdot \text{H}_2\text{O}$	Acidic		106
$\text{K}_2[\text{TiO}(\text{Ox})_2] \cdot 2\text{H}_2\text{O}$	Slightly acidic		105
$(\text{NH}_4)_2[\text{Ti}(\text{LA})_2(\text{OH})_2]$	Neutral		102
$([\text{Ti}(\text{OPr}')_2(\text{C}_6\text{H}_{14}\text{O}_3\text{N})_2])$	Slightly basic	Triethanolaminate complex	108
$(\text{NH}_4)_8[\text{Ti}_4(\text{CA})_4(\text{O}_2)_4]$		Peroxo derivatives	100
$\text{TiO}_2$	Acidic - neutral	Anatase-dispersed suspension	104

$\text{Ox}^{2-}$ : oxalate ion,  $\text{LA}^{2-}$ : lactate ion,  $\text{CA}^{4-}$ : citrate ion

Table 1. 9. Halogen-free and water-soluble titanium compounds.

Compounds	Chelating Agent Used	Reference
$K_2[Ti_2O(H_3NC_7O_4)_2(O_2)_2] \cdot 5H_2O$	Dipicolinate ion ( $H_3NC_7O_4$ )	101
$K_2[Ti(O_2)(EDTA)] \cdot H_2O$	EDTA ion	101
$K_2[Ti(O_2)OH(NTA)] \cdot 3H_2O$	Nitrilotriactate ion	101
$Ti_4O_{15}[N(CH_3)_4]_2H_{12}$	(None)	103
$Ti(OBu)_4$ -choline	(None)	107
“Peroxititanic acid”	(None, but $O_2^{2-}$ ion )	98, 99

Choline: (2-hydroxyethyl)trimethylammonium hydroxide

### 1. 7. Objective and Organization of the Thesis

The organization of this thesis is shown in Fig. 1. 12. This thesis aims at developing of a stable aqueous titanate solution or sol without halogens and alkaline cations, because it can be expected to become an important starting material for  $TiO_2$  and other mixed oxides containing titanium. Furthermore, in order to suppress  $CO_2$  generation due to combustion of organic chelating ligands during heating, this work mainly deals with aqueous solutions without chelating ligands. Preparation and characterization of concentrated, halogen-free aqueous titanium solutions is first discussed in Chapter 2, then their applications in Chapters 3 and 4. The photoirradiation effect of the layered titanate film before heat treatment is described under consideration of low temperature deposition of  $TiO_2$  films. Several aqueous titanate solutions stabilized by chelates were prepared and characterized for a comparison (Chapter 5). Concluding remarks and future perspectives are finally described in Chapter 6.

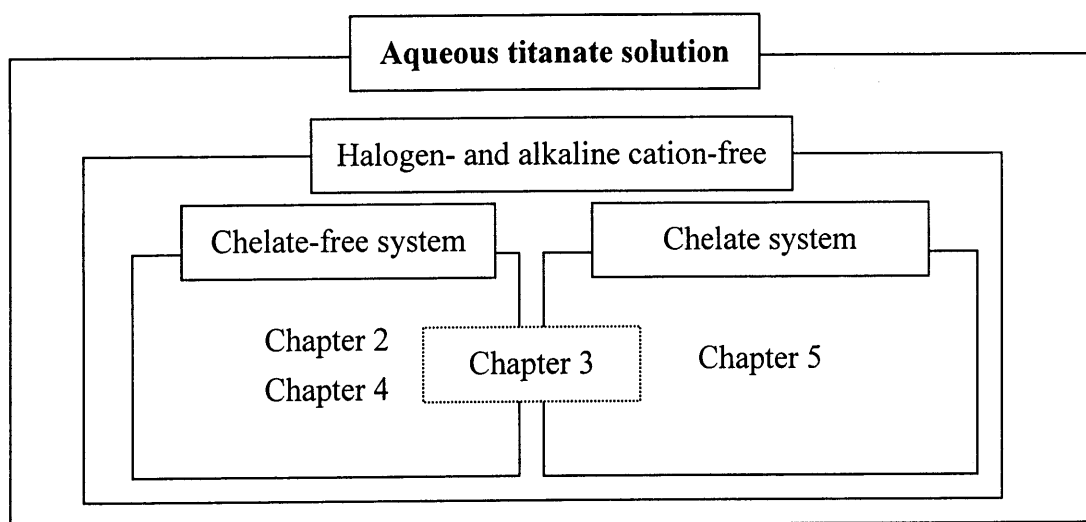


Figure 1. 12. Organization of this thesis.

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## *Chapter 2*

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### **PREPARATION OF CONCENTRATED, HALOGEN-FREE AQUEOUS TITANIUM SOLUTIONS**

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## ***Chapter 2***

### **SYNTHESIS AND CHARACTERIZATION OF HALOGEN-FREE, TRANSPARENT, AQUEOUS COLLOIDAL TITANATE SOLUTIONS FROM TITANIUM ALKOXIDE**

#### **ABSTRACT**

Transparent, aqueous colloidal titanate solutions were prepared by a reaction between titanium tetraisopropoxide and alkylamines or tetraalkylammonium hydroxides. The chemical species containing titanium atoms were found to be a colloidal particle (15 nm) with a layered structure. The formation reaction can be explained as an acid-base reaction between the amines and titanate acid derived from the alkoxide to yield ammonium titanates. Both the basicity of the amines and the sizes of the conjugate acid (ammonium cations) are crucial factors to determine whether the aqueous solutions can be prepared. Similarly, aqueous oxo metallate solutions of V, Nb, Ta, Al, Si and Sn are easily prepared from corresponding alkoxides.

#### **2.1. INTRODUCTION**

In recent years "aqueous" solution chemistry is attracting increasing interest as a way to synthesize compounds and/or materials without organic solvents in both inorganic<sup>1</sup> and organic<sup>2</sup> fields. Water is more economical, less toxic and easier to handle compared with other solvents. Groups 4 and 5 metal ions play a significant role in ceramics<sup>3</sup>, electrode devices<sup>4</sup> and catalysts<sup>5</sup>. However, it is very difficult to obtain the aqua complexes in water because they are strongly hydrolyzed to insoluble oxo species due to their high charge density. Therefore, a highly acidic condition or chelation to the metal<sup>1,6-9</sup> is required to keep the solution stable, so that few papers related to aqueous solutions free of halogen and chelating ligands are

reported.<sup>10, 11</sup> There are two patents which reported the preparation of colloidal solutions, using a reaction of hydrate metal oxide or metal alkoxides with quaternary ammonium hydroxides or amines as peptizers.<sup>12, 13</sup> The chemical species were written as a colloidal hydrous metal oxide (e.g. hydrous stannic oxide). These patents, however, did not report on the colloidal solutions containing titanium with amines as peptizers, since these inventions were focused on tin.

On the other hand, as already described in Chapter 1,  $\alpha$ -hydroxyketones and their imine derivatives so effectively stabilized titanium isopropoxide that excess water, in the molar ratio more than 30, could be added into the alcoholic solution without any occurrence of precipitation or gelation. This observation prompted us to try to prepare aqueous titanium solutions stabilized by such type of modifiers.

In this chapter, the preparation of concentrated, halogen-free aqueous titanium solutions is investigated, and the factors to control the formation of aqueous solutions and the structure of chemical species in the solution are discussed. Furthermore, preparation of aqueous solutions derived from metal alkoxides (V, Nb, Ta, Al, Si and Sn) is similarly examined.

## 2.2. EXPERIMENTAL SECTION

### 2.2.1. Chemical Reagents

Commercial extrapure reagents, aqueous solutions of ammonia (28 %,  $\text{NH}_3$ ), methylamine (40 %,  $\text{MeNH}_2$ ), ethylamine (70 %,  $\text{EtNH}_2$ ), dimethylamine (50 %,  $\text{Me}_2\text{NH}$ ), trimethylamine (30 %,  $\text{Me}_3\text{N}$ ), and tetramethylammonium hydroxide (15 %, TMAOH) were used as received from Wako Pure Chemical Industries, Ltd., Osaka, Japan. *t*-Butylamine (*t*- $\text{BuNH}_2$ ), diethylamine ( $\text{Et}_2\text{NH}$ ), triethylamine ( $\text{Et}_3\text{N}$ ), pyridine ( $\text{C}_5\text{H}_5\text{N}$ ), tetrapropylammonium bromide (TPABr) and NaOH were also used as received from Wako Pure Chemical Industries, Ltd., Osaka, Japan. Commercial extrapure reagents, acetoin and acetol (Tokyo Kasei Kogyo, Tokyo, Japan) and alkanolamines such as monoethanolamine (Wako Pure Chemical Industries, Ltd., Osaka, Japan) were also used as received. Titanium tetraisopropoxide ( $\text{Ti}(\text{OPr}^i)_4$ : TIP, Wako Pure Chemical Industries, Ltd., Osaka, Japan) was used after distillation under reduced pressure. Aluminum isopropoxide ( $\text{Al}(\text{OPr}^i)_3$ ), tetraethylorthosilicate ( $\text{Si}(\text{OEt})_4$ , Wako Pure Chemical Industries, Ltd.,

Osaka, Japan), zirconium tetra-*n*-butoxide in *n*-butanol ( $\text{Zr}(\text{O}i\text{Bu})_4$ , Mitsuwa Pure Chemical Co., Osaka, Japan), vanadium(V) triethoxideoxide ( $\text{VO}(\text{OEt})_3$ , 5N), niobium pentaethoxide ( $\text{Nb}(\text{OEt})_5$ , 3N), tantalum pentaethoxide ( $\text{Ta}(\text{OEt})_5$ , 5N, High Purity Chemical Co., Saitama, Japan) were used as received. Stannic acid, which was obtained by a reaction of  $\text{SnCl}_4$  with aqueous  $\text{NH}_3$ , was used as a tin source. A layered titanate,  $\text{H}_2\text{Ti}_4\text{O}_9$  was prepared through an ion-exchange reaction of  $\text{K}_2\text{Ti}_4\text{O}_9$  (Otsuka Chemical Co. Ltd., Osaka, Japan) by  $\text{HCl}$ .

### 2.2.2. Characterizations

The chemical species in the solutions or precipitates were examined by elemental analysis (CHN CORDER MT-6, Yanako Analytical Instruments Co., Kyoto, Japan), and thermogravimetric and differential thermal analysis (TG-DTA, Models DTA 50 and TGA 50, Shimadzu, Kyoto, Japan) at a heating rate of 5 °C/min from room temperature to 800 °C under flowing dry air.

Aqueous titanate solutions were examined also by electrical conductivity (Twin Cond B-173, Horiba Ltd., Kyoto, Japan), pH, dynamic light scattering (DLS-700, Otsuka Electronics Co. Ltd., Osaka, Japan), and Raman spectroscopy (NR-1800, JASCO Co., Tokyo, Japan).

For the thin films prepared from the titanate solutions at room temperature, XRD patterns (Model Geigerflex, Rigaku Co., Tokyo, Japan) were recorded using graphite monochromated  $\text{CuK}\alpha$  radiation with a scanning speed of 2° /min over the  $2\theta$  range of 2°-70°.

### 2.2.3. Reaction of TIP with $\alpha$ -Hydroxyketones, Amines or Alkylammonium Hydroxides and Examination of the Chemical Species Separated from the Solutions

The reaction of TIP with  $\alpha$ -hydroxyketones and amines in the presence of  $\text{H}_2\text{O}$  was conducted at room temperature in air. The molar ratio of the amine or ammonium hydroxide to titanium in the reaction mixtures was denoted as *R*. The detail experimental procedure and the results of elemental analysis are described as follows. All the products used for elemental analysis were highly hygroscopic.

### 2.2.3.1. Reaction of TIP with MeNH<sub>2</sub>

When 3.0 ml of TIP (10 mmol) was mixed with 0.8 g of 40 % aqueous solution of MeNH<sub>2</sub> (10 mmol), exothermic reaction instantly occurred to give a white precipitate. They were separated by centrifugal separation, and then washed by deionized water. This separation-washing process was repeated three times, and finally dried *in vacuo* at room temperature. The elemental analysis of the powder gave the results: H: 2.89, C: 3.16, N: 3.30, Ti: 44.4%, suggesting the composition [CH<sub>3</sub>NH<sub>3</sub>][HTi<sub>4</sub>O<sub>9</sub>] $\cdot$ 3H<sub>2</sub>O (H: 3.10, C: 2.84, N: 3.31, Ti: 45.3%). The yield of dried powder was 0.8 g (76 %).

NH<sub>3</sub> and EtNH<sub>2</sub> were found to behave similarly to MeNH<sub>2</sub> and gave the following results: for NH<sub>3</sub> system: H: 2.69, C: 0.00, N: 2.82, Ti: 44.7%, suggesting the composition [NH<sub>4</sub>][HTi<sub>5</sub>O<sub>11</sub>] $\cdot$ 5H<sub>2</sub>O (H: 2.88, C: 0.00, N: 2.67, Ti: 45.6%). For EtNH<sub>2</sub> system: H: 3.57, C: 5.99, N: 3.27, Ti: 44.4%, corresponding to the composition [C<sub>2</sub>H<sub>5</sub>NH<sub>3</sub>][HTi<sub>4</sub>O<sub>9</sub>] $\cdot$ 3H<sub>2</sub>O (H: 3.46, C: 5.50, N: 3.21, Ti: 43.9%).

### 2.2.3.2. Reaction of TIP with Et<sub>2</sub>NH

When 3.0 ml of TIP (10 mmol) was mixed with 1.0 ml of Et<sub>2</sub>NH (10 mmol), followed by adding pure water, exothermic reaction instantly occurred to give a solid mass. However, the solid product was gradually dissolved under stirring and yellow clear solution with the concentration of 0.5 M was obtained within one day. The solution was very stable for more than one year. The yellow powder was obtained by evaporation of the solvent and unreacted amine *in vacuo* at room temperature. The powder was not dissolved in water but re-dissolved by adding the amine. The elemental analysis of the powder gave the results: H: 3.46, C: 10.4, N: 2.83, Ti: 40.9%, suggesting the composition [(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH<sub>2</sub>][HTi<sub>4</sub>O<sub>9</sub>] $\cdot$ 3H<sub>2</sub>O (H: 4.12, C: 10.3, N: 3.01, Ti: 41.2%). The yield of dried powder was 1.4 g (86 %).

*t*-BuNH<sub>2</sub> and Et<sub>3</sub>N showed the same reaction tendency as Et<sub>2</sub>NH. The colors of the solutions from *t*-BuNH<sub>2</sub> and Et<sub>3</sub>N were colorless and yellow, respectively. For Et<sub>2</sub>NH system: H: 3.51, C: 10.6, N: 2.77, Ti: 41.4%, suggesting the composition [(CH<sub>3</sub>)<sub>3</sub>CNH<sub>3</sub>][HTi<sub>4</sub>O<sub>9</sub>] $\cdot$ 3H<sub>2</sub>O (H: 4.12, C: 10.3, N: 3.01, Ti: 41.2%). For Et<sub>3</sub>N system: H: 3.45, C: 9.31, N: 1.84, Ti: 43.9%, suggesting the composition [(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NH][HTi<sub>7</sub>O<sub>15</sub>] $\cdot$ 4H<sub>2</sub>O (H: 3.54, C: 9.38, N: 1.82, Ti: 43.6%).

### 2.2.3.3. Reaction of TIP with TMAOH

3.0 ml of TIP (10 mmol) was directly added into 2.4 g aqueous solution of 15% tetramethylammonium hydroxide (TMAOH: 4 mmol), almost exothermically affording an opaque colloidal solution under stirring. Then, the degree of transparency of the solution increased with time, and finally a clear solution (1 M) was obtained within a few hours. A precipitate was obtained by an addition of excess amount of 2-propanol to the solution, separated by filtration, washed several times by 2-propanol to remove unreacted ammonium species, and finally dried *in vacuo*. The elemental analysis of the powder gave the result: H: 5.60, C: 11.4, N: 3.30, Ti: 34.8%, suggesting the composition  $[(\text{CH}_3)_4\text{N}][\text{HTi}_3\text{O}_7] \cdot 5\text{H}_2\text{O}$  (H: 5.51, C: 11.4, N: 3.33, Ti: 34.1%). The white powder was readily dissolved in water, and the total yield of dried powder was 1.3 g (99 %).

### 2.2.3.4. Synthesis of Water-soluble Titanium Alkylammonium Oxalate from Aqueous Titanate Solutions

2.5 g of oxalic acid dihydrate ( $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , 20 mmol) was added to the 20 ml of 0.5 M aqueous solution of TIP-TMAOH ( $R=2$ ). The acid was quickly and completely dissolved with some heat evolution, yielding colorless clear solution. After stirring for 24 h, the addition of large quantity of 2-propanol to the solution caused a precipitate. The precipitate was separated by filtration, washed by 2-propanol, and finally dried under vacuum at room temperature. The elemental analysis of the powder gave the results: H: 7.19, C: 33.7, N: 6.57, Ti: 11.2%, which are consistent with the calculated data (H: 6.84, C: 32.6, N: 6.33, Ti: 10.8%) for tetramethylammonium dioxalato oxotitanate (IV) trihydrate  $[(\text{CH}_3)_4\text{N}]_2[\text{TiO}(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$ . The white powder was readily redissolved in water, and the yield was 4.0 g (90 %).

### 2.2.3.5. Reaction of Aqueous Titanate Solutions with Aqueous KCl Solution

0.5 M TIP- $\text{Et}_2\text{NH}$  ( $R=2$ ) (8 ml, 4 mmol) solution was mixed with 12 ml of 1.0 M KCl aqueous solution (12 mmol), yielding a white precipitate. The precipitate was separated by centrifugal separation, and then washed by deionized water. This separation-washing process was repeated five times, and finally dried at 110 °C in

air. The resultant powder was found to be amorphous by XRD, and did not contain both carbon and nitrogen components from elemental analysis. XRD and Raman spectra of the powder heat-treated at 800°C were the same as those of authentic sample of  $\text{K}_2\text{Ti}_6\text{O}_{13}$  (TISMO-N, Otsuka Chemical Co., Ltd., Osaka, Japan). The amorphous powder before heat treatment can be formulated as  $\text{K}_2\text{Ti}_6\text{O}_{13} \cdot 4\text{H}_2\text{O}$  from TG-DTA and elemental analysis. The yield of the powder was 0.42 g (98 %). The  $\text{K}_2\text{Ti}_6\text{O}_{13}$  powder was similarly prepared from the aqueous solutions of TIP- $\text{Et}_3\text{N}$  ( $R=1$ ) and TIP-TMAOH ( $R=0.4$ ).

#### 2.2.3.6 Preparation of KTP ( $\text{KTiOPO}_4$ ) Powder

Equi-volumes of 0.5 M TIP-acetoin-MEA (1:1:1) and 0.5 M  $\text{KH}_2\text{PO}_4$  aqueous solutions were mixed at room temperature to form KTP ( $\text{KTiOPO}_4$ ). The viscosity of the mixed solution increased with time, and after several hours brownish gel was obtained. The resulting gel was dried at 80°C for 20 h in air on a hot plate, and then the formed powder was heat-treated in air to yield well-crystallized pure KTP.

### 2.3. RESULTS

#### 2.3.1. Preparation of Aqueous Titanium Solutions from TIP

In Chapter 1, it has been reported that  $\alpha$ -hydroxyketones themselves and much more the combinative use of the  $\alpha$ -hydroxyketones and monoethanolamine (MEA) exhibited an excellent stabilization effect for 2-propanol solutions of TIP. Therefore, first the effect of those systems on the preparation of aqueous titanium solutions was examined. In order to clarify the effect of the amines that coexist with the  $\alpha$ -hydroxyketones, various amines and ammonia were also examined in this study. The results are shown in Table 2. 1, which indicates that the combinative systems are very effective to prepare the concentrated aqueous solutions almost irrespective of the structure of the amines used. Even the combination of ammonia with acetol could yield the solution, while single use of the  $\alpha$ -hydroxyketones that were useful for the stabilization of alcoholic solutions of TIP, was useless for the preparation of the aqueous solutions. The molar ratios of the additive to the alkoxide had no strong effect. Acetylacetone, which is not shown in Table 2. 1, was ineffective even when used with the combinative use of some amines.

Table 2. 1. Effect of a hydroxyketone or a combinative use of the hydroxyketone with amine on the formation of 0.5 M titanium aqueous solutions.

Amine	Molar ratio to TIP	Molar ratio of the additive to TIP		State
		Acetol	Acetoin	
---	---	1 or 2	---	Dark brown precipitates
---	---	---	1 or 2	Dark brown precipitates
H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> OH	1 or 2	1 or 2	---	<b>Dark brown clear solution</b>
		---	1 or 2	<b>Dark brown clear solution*</b>
Me <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> OH	1 or 2	---	1 or 2	<b>Dark brown clear solution</b>
NH <sub>3</sub>	2	2	-	<b>Dark brown clear solution</b>
	2	-	2	White precipitates
H <sub>2</sub> NNH <sub>2</sub>	2	2	-	<b>Light yellow clear solution</b>
	1	-	1	<b>Light yellow clear solution</b>
Trien	1	2	-	Brown clear gel
	1	-	2	<b>Brown clear solution</b>

\*1 M aqueous solution can be prepared.

Trien: triethylenetetramine

It was initially assumed that the remarkable effect of the combinative systems was due to the formation of the imine products having a structure like diethanolamine (DEA), which can act as a multidentate chelating ligand. However, ammonia and *N,N*-dimethylmonoethanolamine (DMEA) can not form such compounds but they were very effective combination. In particular, the latter is *N,N*-dimethyl derivative of MEA and hence can not form the imines with ketones. These results strongly suggest that the amines used must have some unexpected effect. Therefore, the effect of single use of various amines was examined. The results of this investigation are summarized in Table 2. 2.

Table 2. 2. The effect of various amines on the formation of 0.5 M aqueous titanium solutions.

Classification	Amine	Molar ratio to TIP	State
Ammonia	---	1 or 2	White precipitates
Primary Amines	Methylamine	1 or 2	White precipitates
	Ethylamine	1 or 2	White precipitates
	<i>t</i> -Butylamine	1 or 2	<b>Clear solution</b>
Secondary Amines	Dimethylamine	2	<b>Clear solution</b>
	Diethylamine	1	<b>Clear solution</b>
	Dioctylamine	1 or 2	White precipitates
	Dicyclohexylamine	1 or 2	White precipitates
Tertiary Amines	Trimethylamine	2	<b>Clear solution</b>
	Triethylamine	1	<b>Clear solution</b>
Polyamines	Hydrazine	1 or 2	White precipitates
	En	1 or 2	White precipitates
	Dien	1	White precipitates
	Trien	1	White precipitates
Alkanolamines	MEA	1 or 2	White precipitates
	DMEA	1 or 2	White precipitates
	DEA	1 or 2	Colorless clear gel
	MDEA	1	<b>Clear solution</b>
	EDEA	1	<b>Clear solution</b>
	DIPA	1	<b>Clear solution</b>
	TEA	1	<b>Clear solution</b>

En: ethylenediamine, Dien: diethylenetriamine, MEA: monoethanolamine,  
DMEA: *N,N*-dimethylmonoethanolamine, DEA: diethanolamine,  
MDEA: *N*-methyldiethanolamine, EDEA: *N*-ethyladiethanolamine,  
DIPA: diisopropanolamine, TEA: triethanolamine

As clearly seen from Table 2. 2, amines with bulky structure, and special alkanolamines, namely substituted DEA's such as MDEA, EDEA, TEA, DIPA effectively yield clear solutions. In contrast, the primary amines including monoethanolamine and hydrazine and secondary amines containing longer alkyl groups resulted in precipitation or gelation. Even in the case without forming chelates, amines with bulky structure were found to give clear solutions.

In order to examine whether the amines act as a base or a ligand, 2,2,6,6-Tetramethylpiperidine was reacted with Ti, Nb and Ta alkoxides. It is a strong base but a lone pair on nitrogen atom can hardly coordinate to  $\text{Ti}^{\text{IV}}$  because of steric hindrance of four methyl groups. Table 2.3 shows the effect of amines with different coordination ability on the formation of aqueous solutions of Ti, Nb and Ta, together with  $\text{pK}_a$  of the conjugate acids of the amines. The structures of the amines used are shown in Fig. 2. 1.

Table 2. 3. Effect of amines with different coordination ability and basicity on the formation of aqueous solutions of Ti, Nb and Ta.

Amine	$\text{pK}_a$	Group 4	Group 5	
		$\text{Ti}(\text{OPr}^t)_4$	$\text{Nb}(\text{OEt})_5$	$\text{Ta}(\text{OEt})_5$
Pyridine	5.2		Precipitates	
Triethylamine	10.7		Clear solution	
Piperidine	11.2		Clear solution	
2,2,6,6-Tetramethylpiperidine	—		Clear solution	

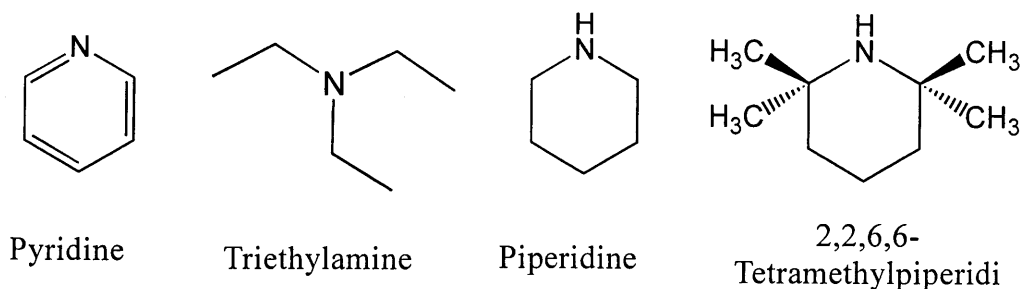


Fig. 2. 1. Structures of the amines listed in Table 2.3.

It is clear from the table that the amines acted as a base not but a ligand. The effect of quaternary ammonium hydroxides such as TMAOH and TPAOH was further examined, and the results are shown in Table 2. 4. These compounds are strongly basic, can not datively bond to Ti, and have bulky cation structures. The neutral corresponding bromide salt and NaOH also were examined to compare with the hydroxides. As a result, it was found that direct reaction between TIP and an aqueous solution of TMAOH or TPAOH in the ratio of  $R=1$  could afford a clear solution with the high concentration of 1 M. Interestingly, even at smaller modifier ratio of  $R=0.4$ , similar aqueous solutions could be obtained. In place of TIP, titanilic acid, which was obtained by hydrolysis of TIP, could be used to yield similar clear solutions. On the other hand, the ammonium bromide and NaOH did not show any positive effect. These results strongly support that the existence of both  $\text{OH}^-$  and bulky cation is necessary for the preparation of aqueous titanium solutions.

Table 2. 4. Effect of the tetraalkylammonium compounds on the formation of 1.0 M aqueous titanium solutions.

Tetraalkylammonium compound	Molar ratio to TIP	State
TMAOH	0.5	Colorless clear solution
TPAOH	1	Colorless clear solution
(NaOH)	1	White precipitates
TPABr	1	White precipitates

### 2.3.2. Factors Controlling the Formation of Chelate-free Aqueous Metallate Solutions

The representative titanate solution is shown in Fig. 2. 2, along with distilled water and crystalline  $\text{TiO}_2$  (anatase) suspension (STS-01, Ishihara Sangyo Kaisha, Ltd., Osaka, Japan) for comparison. The titanate solution was not suspension because it had a transparency comparable to water. When a He-Ne laser light was illuminated to them, the trace of the light passage through the titanate solution was clearly recognized, indicative of the colloidal nature of the solutions.

The addition of large amount of 2-propanol to these clear solutions caused precipitates, which redissolved in water, indicating that the solutions contain ionic species or colloids. As described in the experimental section, the elemental analysis showed that all of the powders obtained from the clear solutions could be formulated as  $[\text{R}_n\text{H}_{4-n}\text{N}^+][\text{HTi}_m\text{O}_{2m+1}^-]$  (R: alkyl group, n, m: integer, n=1–4, m=4–7). Namely, the powders are not a simple colloidal mixture (e.g.  $\text{TiO}_2$ ) but the compounds with some stoichiometry. The molar ratio of nitrogen to titanium (N/Ti) in the compounds changed a little bit with the basicity or the size of ammonium ions, and almost independent of the ratios amine/TIP in the starting mixtures.

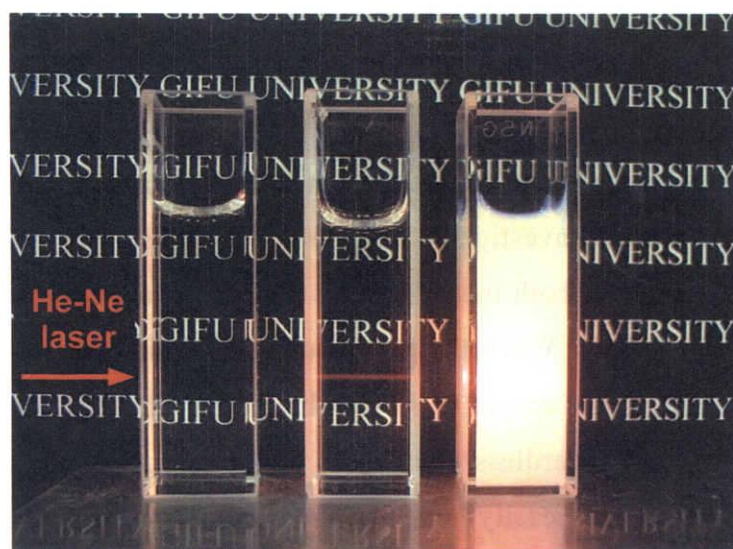


Fig. 2. 2. Photograph of the solutions of (a) distilled water, (a) 1 M TIP-TMAOH ( $R=0.4$ ) and (c) 0.5 M crystalline anatase suspension (STS-01).

On the other hand, the reaction of TIP with aqueous solutions of primary amines  $\text{MeNH}_2$  and  $\text{EtNH}_2$  exothermically occurred to give white precipitates, but it had never been dissolved even in the presence of excess amount of the amines or when refluxed for more than a week. However,  $t\text{-BuNH}_2$  was interestingly effective to prepare the similar clear solutions. In the case of pyridine and ammonia only precipitates were obtained. It is very interesting to note that except for pyridine, all precipitates formed contained corresponding amines in some stoichiometric amounts, and could be formulated again as  $[\text{R}_n\text{H}_{4-n}\text{N}^+][\text{HTi}_m\text{O}_{2m+1}^-]$  ( $n=0$  or  $1$ ,  $m=4$  or  $5$ ), while pyridine afforded simple titanate acid or hydrous titanate oxide ( $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ ).

All of the results found for the preparation of the solutions are summarized in Table 2. 5. The composition of the isolated solution species or the precipitates, which were evaluated from the elemental analysis, was recited. The  $\text{p}K_a$  values of the conjugate acids of the corresponding amines are also included in this table.<sup>14</sup> This table indicates that amines which were relatively large in molecular size and strong bases with the  $\text{p}K_a$  values more than 9 tended to yield clear titanate solutions. Tetraalkylammonium hydroxides are the typical ones. In addition, strongly basic and bulky cobaltocenium hydroxide,  $[\text{Co}^{\text{III}}(\text{C}_5\text{H}_5)_2(\text{OH})]$ , which is prepared from the oxidation of cobaltcene  $[\text{Co}^{\text{II}}(\text{C}_5\text{H}_5)_2]$  with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in water, yielded the yellowish clear solution. These observations also indicate that both basicity and size of the bases play an important role for the formation of clear solutions.

The reactions of some metal alkoxides other than titanium with alkylamines and TMAOH were similarly investigated and the results are summarized in Table 2. 6. Here again,  $\text{p}K_a$  values of both metallic acids and conjugate acids of the amines are also shown in this table.<sup>14</sup> When the  $\text{p}K_a$  value of an amine was larger than that of a metallic acid, that is, the amine was more basic than the acid, clear metallate solutions can be prepared regardless of the size of the amines used. Vanadic acid, the most acidic in this study, easily gave the clear solutions by the reaction with amines, and the metallic acids with almost the same  $\text{p}K_a$  values such as  $\text{Ta}(\text{OH})_5$ ,  $\text{H}_2\text{SiO}_3$  and  $\text{H}_2\text{SnO}_3$  showed similar tendencies. Aluminic acid was soluble only in the presence of strongly basic TMAOH because of its weak acidity ( $\text{p}K_a$  11.2).

Zirconic acid is thought to be much more basic than aluminic acid, and was difficult to dissolve by the reaction with amines.

Table 2. 5. Influence of the basicity of the amines on the formation of aqueous solution derived from TIP.

Amine	$pK_a^a$	State	Estimated chemical composition <sup>b</sup>
C <sub>5</sub> H <sub>5</sub> N	5.2	White precipitates	TiO <sub>2</sub> · 0.75H <sub>2</sub> O
(NH <sub>3</sub> )	9.24	White precipitates	[NH <sub>4</sub> ][HTi <sub>5</sub> O <sub>11</sub> ] · 5H <sub>2</sub> O
MeNH <sub>2</sub>	10.64	White precipitates	[CH <sub>3</sub> NH <sub>3</sub> ][HTi <sub>4</sub> O <sub>9</sub> ] · 3H <sub>2</sub> O
EtNH <sub>2</sub>	10.63	White precipitates	[C <sub>2</sub> H <sub>5</sub> NH <sub>3</sub> ][HTi <sub>4</sub> O <sub>9</sub> ] · 3H <sub>2</sub> O
<i>t</i> -BuNH <sub>2</sub>	10.69	Colorless clear solution	[ <i>t</i> -C <sub>4</sub> H <sub>9</sub> NH <sub>3</sub> ][HTi <sub>4</sub> O <sub>9</sub> ] · 3H <sub>2</sub> O
Me <sub>2</sub> NH	10.77	Pale yellow clear solution	—
Et <sub>2</sub> NH	10.93	Yellow clear solution	[(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH <sub>2</sub> ][HTi <sub>4</sub> O <sub>9</sub> ] · 3H <sub>2</sub> O
Me <sub>3</sub> N	9.8	Pale yellow clear solution	—
Et <sub>3</sub> N	10.72	Yellow clear solution	[(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH][HTi <sub>7</sub> O <sub>15</sub> ] · 4H <sub>2</sub> O
(TMAOH)		Colorless clear solution	[(CH <sub>3</sub> ) <sub>4</sub> N][HTi <sub>3</sub> O <sub>7</sub> ] · 5H <sub>2</sub> O
(TPAOH)	Strong	Colorless clear solution	—
(TBAOH)	base	Colorless clear solution	—
(NaOH)		White precipitates	—

<sup>a</sup>conjugate acid of corresponding amines

<sup>b</sup>based on elemental analysis

Table 2. 6. The relationship between the  $pK_a$  values of metallic acids and the conjugate acids of alkylamines and tetraalkylammonium hydroxide on the formation of the aqueous solutions of metallate ions (sol = clear solution, ppt = precipitates).

Metallic acids	$pK_a$	EtNH <sub>2</sub>	Et <sub>3</sub> N	Et <sub>2</sub> NH	(TMAOH)
		10.63	10.72	10.93	Strong base
H <sub>3</sub> VO <sub>4</sub>	3.78	sol	sol	sol	sol
H <sub>2</sub> SnO <sub>3</sub>	9.4	sol	sol	sol	sol
Nb(OH) <sub>5</sub>	–	sol	sol	sol	sol
Ta(OH) <sub>5</sub>	9.6	ppt	sol	sol	sol
H <sub>2</sub> SiO <sub>3</sub>	9.7	sol	sol	sol	sol
TiO(OH) <sub>2</sub>	–	ppt	sol	sol	sol
H <sub>3</sub> AlO <sub>3</sub>	11.2	ppt	ppt	ppt	sol
Zr(OH) <sub>4</sub>	–	ppt	ppt	ppt	ppt

The addition of pyridine ( $pK_a = 5.2$ ) and ammonia ( $pK_a = 9.24$ ) to the metallic acids in this table resulted in precipitates.

### 2.3.3. Measurements of Electric Conductivity, pH Values and Dynamic Light Scattering (DLS) of the TIP-TMAOH Solution

All of the titanate solutions prepared in this study were highly transparent and looked like common aqueous solutions. However, colloidal nature was recognized as shown in Fig. 2. 2, and hence, the size distribution of colloidal particles in the TIP-TMAOH (0.5 M,  $R=1$ ) solution was measured by DLS. The results are shown in Fig. 2. 3. The average size was estimated to be 15 nm. The solution species is expected to contain a kind of ammonium titanates that may be dissociated to free ions, and hence the solution may be highly electrically conductive. If the equivalent ionic conductance were obtained, a rough measure of anion size and hence the structure would be evaluated. Figure 2. 4 shows the electric conductivities and the pH values for various TIP-TMAOH solutions at 20 °C. The measurement was made under conditions that the titanium concentration was varied in the range of  $[Ti] = 0$  to 0.5 M with keeping the  $TMA^+$  concentration at  $[TMA^+] = 0.1$  M. The clear

solutions were obtained from  $[\text{Ti}] = 0$  to  $0.25$ , while colloidal suspension or precipitates at the concentration higher than  $0.25$  M, indicating that  $\text{N/Ti}$  ratio of more than  $0.4$  is necessary to yield clear solutions. This ratio is roughly the same as the composition of the isolated solution species ( $\text{N/Ti} = 0.33$ ) that was assumed from the elemental analysis. In Fig. 2. 4, as the  $[\text{Ti}]$  concentration was increased, both electric conductivity and pH decreased. These results will be discussed later.

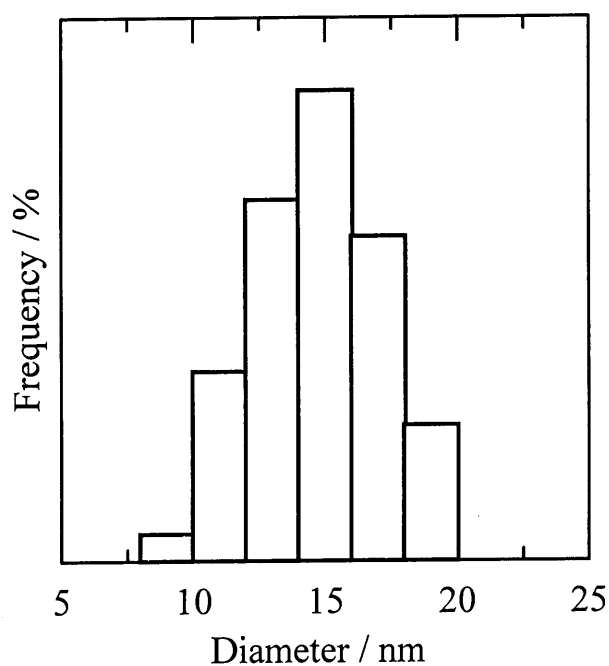


Fig. 2. 3. Size distribution of the particles in the aqueous colloidal solution of TIP-TMAOH ( $0.5$  M,  $R=1$ ).

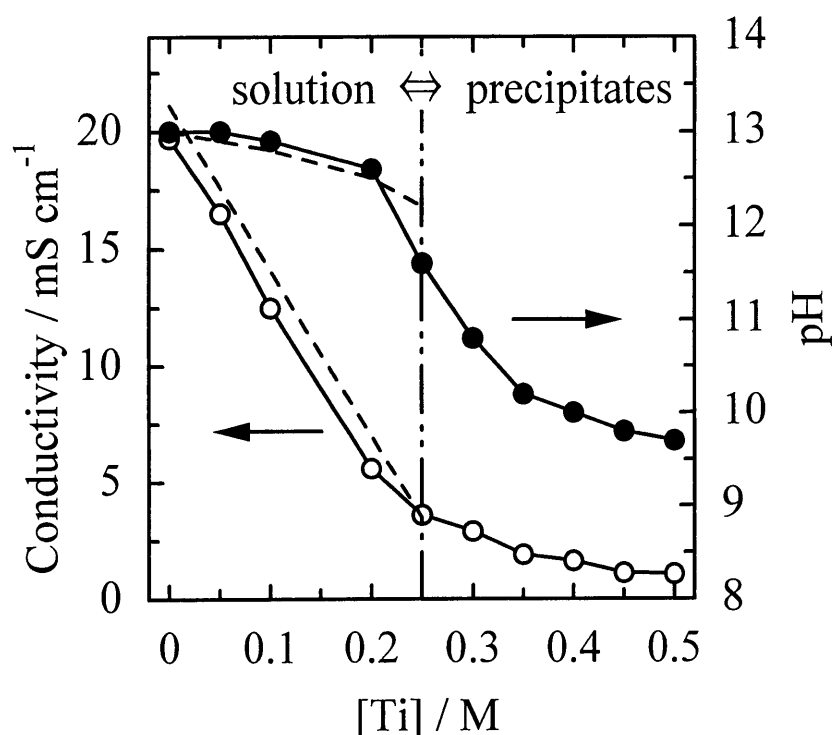


Fig. 2. 4. Electric conductivity and pH change of the TIP-TMAOH solution.

#### 2.3.4. Raman Spectra

Figure 2. 5 shows the Raman spectra of the tetramethylammonium titanate solution and the powder isolated from the solution, along with those of  $\text{TiO}_2$  (anatase and rutile). A layered titanate, tetratitanic acid ( $\text{H}_2\text{Ti}_4\text{O}_9$ ) is also recorded for comparison. The tetramethylammonium titanate solution (Fig. 2. 5(a)) had four peaks at 279, 376, 449, 662  $\text{cm}^{-1}$  in addition to the peaks assignable to 2-propanol and  $\text{TMA}^+$ . No peak shifts were observed when Ti or TMAOH concentration was varied, and even after the solution was refluxed for 6 h. The powder obtained from the solution after evaporating water gave the fundamentally same spectrum as shown in Fig. 2. 5(b). In the case of  $\text{Et}_2\text{NH}$ , no distinct spectra were observed. However, the same pattern as TMAOH was recognized after refluxing for a week as

shown in Fig. 2. 5(c). The spectra of the titanates powder (Figs. 2. 5(a) and 5(b)) were rather similar to that of the tetratitanic acid ( $\text{H}_2\text{Ti}_4\text{O}_9$ , Fig. 2. 5(d)), and completely different from those of anatase and rutile (Figs. 2. 5(e) and 5(f)), strongly suggesting that the titanate solution is not a simple colloidal dispersion of  $\text{TiO}_2$  (anatase or rutile) but contain a layered structure.

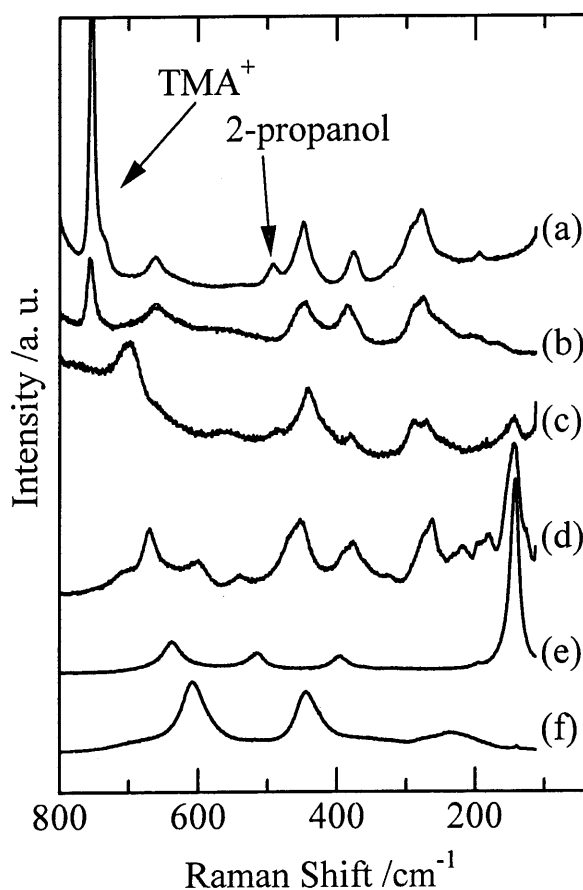


Fig. 2. 5. Raman spectra of various titanium compounds: (a) 1 M TIP-TMAOH ( $R=1$ ) solution, (b) powder obtained from 1 M TIP-TMAOH ( $R=0.4$ ) solution, (c) 0.5 M TIP- $\text{Et}_2\text{NH}$  ( $R=1$ ) solution, (d)  $\text{H}_2\text{Ti}_4\text{O}_9$ , (e) anatase powder, and (f) rutile powder.

### 2.3.5. XRD

Figure 2. 6 shows XRD patterns of the films prepared from the TIP-TMAOH solution refluxed for a period within 6 h. The films were dip-coated on glass (Corning Inc, #7059) and dried *in vacuo* at room temperature.

From the as-prepared solutions, only a very broad peak was found at about  $6^\circ$  ( $2\theta$ ). However, as the solution was refluxed for a longer time, the peak became sharper with shifting slightly to a lower angle. After refluxing for 6 h, three diffraction peaks with regular interplanar spacing were clearly observed, indicating that refluxing helped crystallization to a layered compound.<sup>15</sup> Similar tendencies were observed in the case of TBAOH and alkylamine systems as shown in Fig. 2. 7.

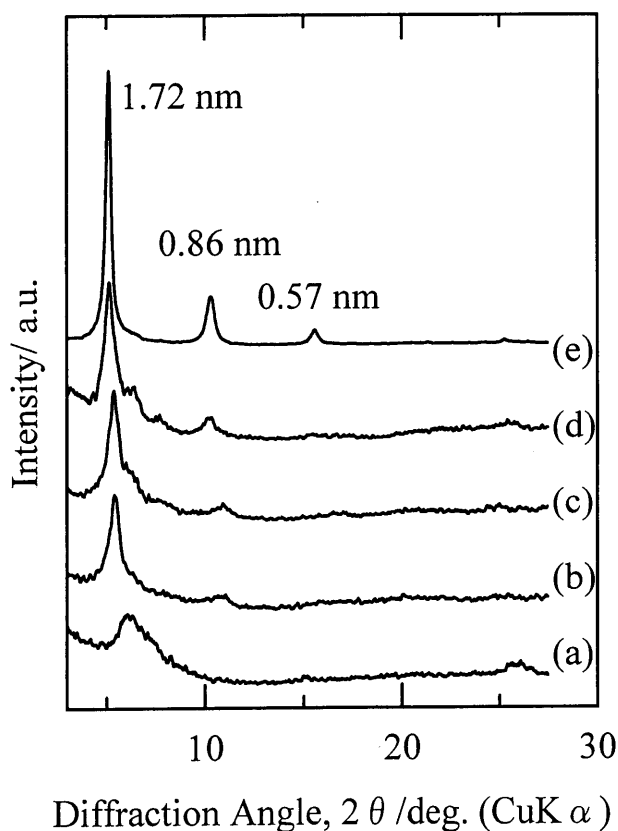


Fig. 2. 6. Reflux time dependence of XRD patterns of thin films prepared on glass plate at room temperature from 0.5 M TIP-TMAOH ( $R=1$ ) solution: (a) as-prepared, (b) 1 h, (c) 2 h, (d) 3 h and (e) 6 h.

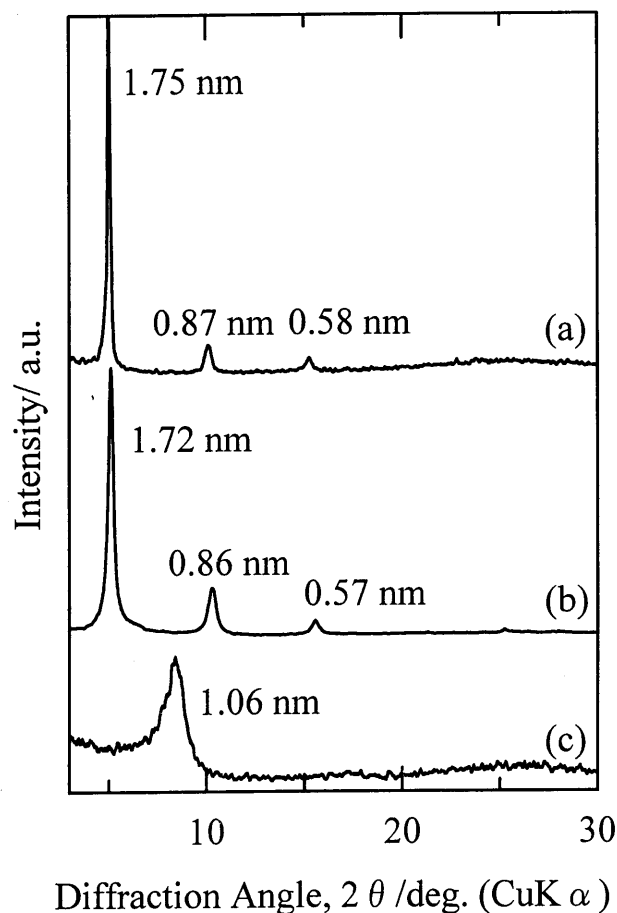


Fig. 2. 7. XRD patterns of thin films prepared from (a) 0.3 M TIP-TBAOH ( $R=1$ ) refluxed for 6 h, (b) 0.5 M TIP-TMAOH ( $R=1$ ) refluxed for 6 h, and (c) 0.5 M TIP-Et<sub>2</sub>NH ( $R=1$ ) refluxed for 7 d.

### 2.3.6. TG-DTA

Figure 2. 8 shows TG-DTA curves of the powders prepared from the solutions of the TIP-TMAOH ( $R=0.4$ , Fig. 2. 8(a)) and TIP-Et<sub>3</sub>N ( $R=0.5$ , Fig. 2. 8(b)). The Ti content (wt%) in the powder was calculated from the final mass loss in the TG curves, which was shown in the Experimental Section. As clearly seen, the final decomposition temperature for the TIP-TMAOH (460 °C) was much lower than that of the TIP-Et<sub>3</sub>N (530 °C), suggesting that TMA<sup>+</sup> in the titanate powder is more easily removed than Et<sub>3</sub>NH<sup>+</sup>.

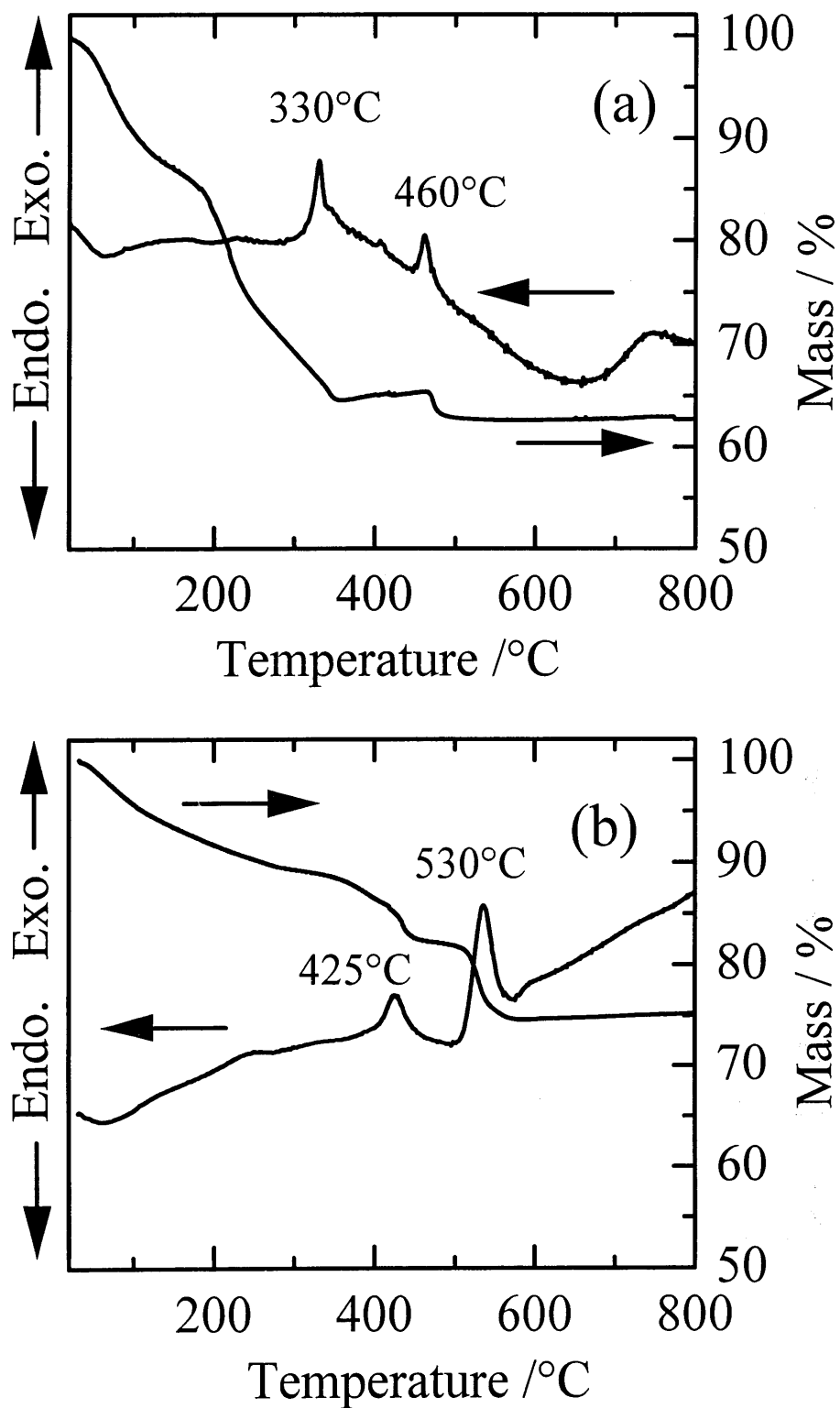
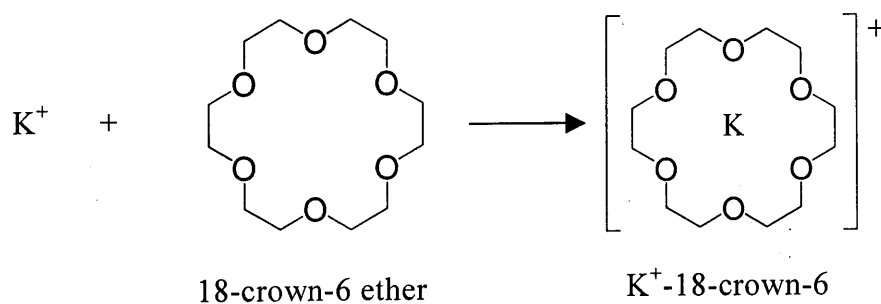


Fig. 2. 8. TG-DTA of the powder prepared from the solutions of (a) TIP-TMAOH ( $R=0.4$ ) and (b) TIP-Et<sub>3</sub>N ( $R=0.5$ ).

### 2.3.7. Effect of Cation Size on the Stability of Aqueous Titanate Solutions

The influence of cation size on the stability of the aqueous titanate solution was examined through observing the change that occurred on the addition of several alkaline salts to the TIP-TMAOH solution. Here, chloride salts were used as a cation supplier. Tetraphenylphosphonium chloride  $[(C_6H_5)_4PCl]$  and the complex of  $K^+$  with 18-crown-6 ether (denoted as  $K^+$ -18-crown-6) were also employed as examples of bulky cation.  $K^+$  and 18-crown-6 are known to form a very stable complex with stability constant of 6.08.



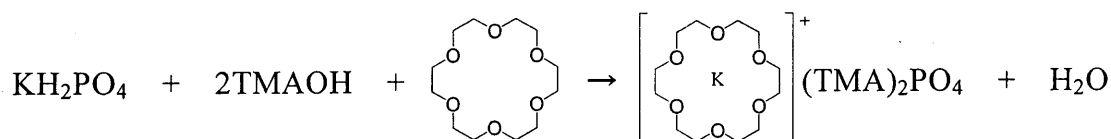
The addition of proton ( $H^+$ ) and alkaline metal ions ( $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Rb^+$  and  $Cs^+$ ) to the TIP-TMAOH sol resulted in the formation of amorphous precipitates, which can be supposed to be protonic and alkaline metal titanates, respectively, while the cations of tetramethylammonium, tetraphenylphosphonium and  $K^+$ -18-crown-6 to the solution remained unchanged. Irrespective of the type of the TIP-amines or ammonium hydroxides used, the precipitates derived on KCl addition were crystallized as potassium hexatitanate ( $K_2Ti_6O_{13}$ ) when heated to 600 °C even after washing thoroughly with water.

### 2.3.8. Preparation of Mixed Oxides

Simple water-soluble compounds can almost freely be added to the aqueous titanium solution. Therefore, a starting material for some ternary titanium oxide can be very easily prepared using the titanium solution. KTP ( $\text{KTiOPO}_4$ ) is one of the typical examples, so here its preparation was tested. KTP is a useful material with non-linear optical effect. In sol-gel processing, however, it is difficult to prepare precursor solution of KTP because the potassium phosphate, one of starting materials, is usually insoluble in alcoholic solvents.

Figure 2. 9 shows the XRD patterns of KTP powder prepared by mixing the titanate sol and aqueous  $\text{KH}_2\text{PO}_4$ . It was seen that crystallization started at about  $500^\circ\text{C}$ , and well-crystallized one was obtained at  $700^\circ\text{C}$ . All of the observed peaks were assigned to KTP. No peaks assignable to  $\text{TiO}_2$  were detected, indicative of the usefulness of the aqueous titanium solution for the preparation of mixed oxides containing Ti.

As already described, the titanate solution is destabilized by the addition of small cation and/or acidic proton ( $\text{H}^+$ ). When  $\text{KH}_2\text{PO}_4$  is added to the titanate sol, as a matter of course, the mixture resulted in precipitates. However, a stable precursor solution of KTP is obtained when  $\text{K}^+$  and  $\text{H}^+$  of  $\text{KH}_2\text{PO}_4$  is modified with 18-crown-6 ether and neutralized with TMAOH as follows:



Using the solution thus resulted, KTP films on glass plate were successfully spin-coated.

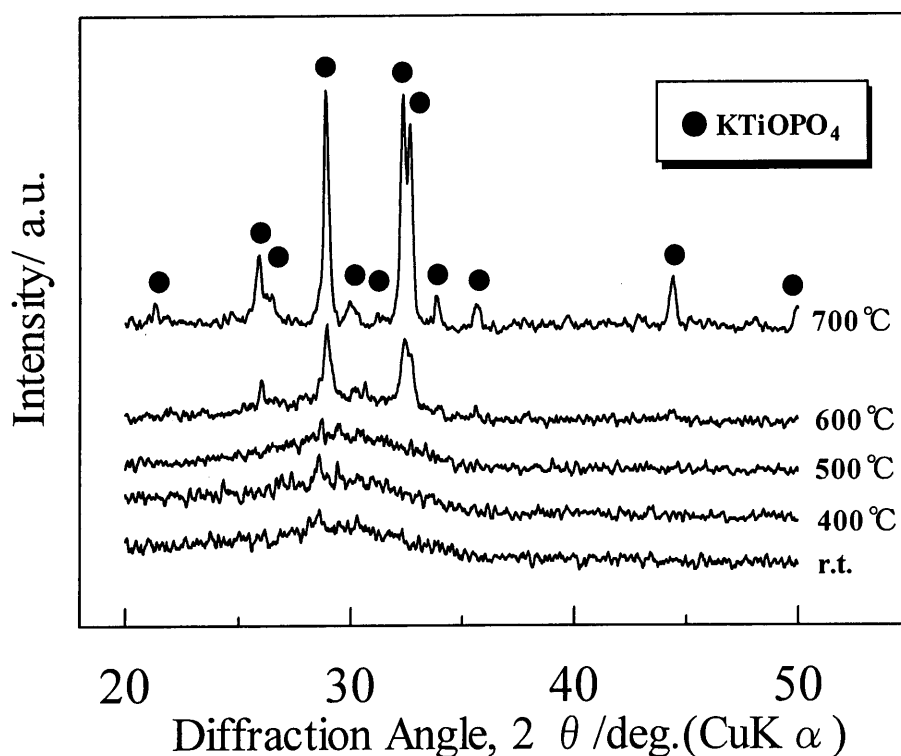


Figure 2. 9. XRD patterns of KTP powder fired at various temperatures.

## 2.4. DISCUSSION

### 2.4.1. Interaction between TIP and Alkylamines or Alkylammonium Hydroxides and Factors to Yield Clear Aqueous Titanate Solutions

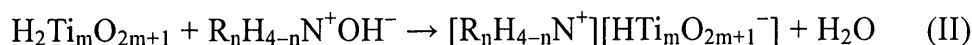
The results of elemental analysis (Table 2. 5) suggest that an acid-base reaction between amines and titanate acid derived from the hydrolysis of TIP occurred to yield the alkylammonium titanates. For example, the following reaction schemes can be written.

Hydrolysis reaction:

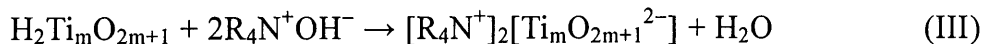


Acid-base reaction:

For weak bases (alkylamines),



For strong bases (tetraalkylammonium hydroxides),

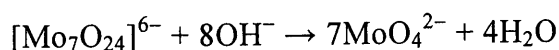


The first reaction is a simple hydrolysis reaction to afford polymeric titanic acid or hydrous titanium dioxide (I), and the others are the acid-base reactions of the titanic acid with the alkylamines or alkylammonium hydroxides, yielding alkylammonium hydrogen titanates (II) and alkylammonium titanates (III), respectively. The acid-base reactions take place when the alkylamines or alkylammonium hydroxides are more basic than titanate ion. Otherwise only hydrolysis reaction may occur and pure hydrous oxides would be obtained. Pyridine is the very case, and neutral ammonium compounds such as bromide also have no interaction with titanic acid. The facts that the reaction time required to form the final clear solution depended on the basicity and the aqueous titanate solutions also could be prepared directly even from titanic acid, strongly support the idea of acid-base interaction. On the other hand, in the case of the strong base like TMAOH, it is possible to lead the second acid-base reaction, yielding neutral salts (III).

The  $\text{p}K_a$  ( $\text{p}K_1$ : primary dissociation exponent) value of titanic acid, which is not available in literature, can be estimated to be around 9 because stoichiometric amounts of ammonium ion  $\text{NH}_4^+$  was found in the precipitates derived from the reaction of TIP with ammonia ( $\text{p}K_a = 9.24$ ). According to Pauling's rule on the acidity of oxo acids<sup>16</sup>, it can be assumed that the  $\text{p}K_2$  value for the titanic acid is around 15, and thus second proton dissociation is impossible by the amines, but possible by the strong bases such as TMAOH. This can well account for the difference in the N/Ti ratios between the products obtained from the alkylamines and TMAOH. In the case of the alkylamines, only the first acid-base reaction may take place, to give acidic salts (II). The composition, namely the number of  $m$  in the formula (II) varies in the range from 4 to 7 depending on the kind of the amines. It is inferred that the variation is probably due to the formation of mixture containing tetratitanate, hexatitanate and so on. At any rate, dissociable protons still remain in the titanates (II) derived from the alkylamines. As described later, the titanates are

considered to have a layered structure, and the interaction between the titanate layers through proton (including hydrogen bonding) would be enhanced, since the charge density of proton ( $H^+$ ) is much higher than that of  $TMA^+$  or alkylammonium cations ( $R_nH_{4-n}N^+$ ). This may be the reason why the decomposition temperature of the powder derived from the TIP- $Et_3N$  (type (II)) was higher than that of the powder from the TIP-TMAOH (type (III)) shown in Fig. 2. 8.

It can be thought also that titanate acid is depolymerized in basic condition to yield soluble oligomeric species. Actually, isopoly oxometallates are well known to be depolymerized or decomposed to lower condensed species in basic conditions. Isopolymolybdate (VI), for example, undergoes the reaction<sup>17</sup>:



Furthermore, the fact that water-soluble complexes such as  $[(CH_3)_4N]_2[TiO(C_2O_4)_2]$  could be synthesized from the addition of oxalic acid to the basic titanate solution clearly indicates that the depolymerization of tetramethylammonium titanate by organic chelates readily occurs to transform a monomer-like structure. Accordingly, the chemical species in the titanate solutions seems to have a soft, flexible structure easily changeable by a reaction with bases or chelate ligands.

By the way, it has been reported that water-soluble complexes of niobium and tantalum were formed with alkylamines<sup>18, 19</sup>. Fairbrother et al. suggested that the amines coordinated to the central metals, forming amine-coordinated metal complexes through dative bonds. However, as shown in Table 2. 3, clear solutions of titanates, niobates and tantalates were quickly and easily obtained from the corresponding alkoxides by the reaction with basic 2,2,6,6-tetramethylpiperidine that is hardly coordinated to metals due to steric hindrance of four methyl groups near to nitrogen atom. This fact suggests that the coordination to metals was not necessarily required to obtain the clear metallate solutions.

The size of ammonium ion also seems to be a crucial factor to obtain the clear titanate solutions. According to the results of Raman spectra, XRD and electrical conductivity, the chemical species in the solutions can be thought to contain layered titanate anions and the counter ions, alkylammonium ions. The latter may locate

between the titanate sheets without dissociation as the conductivity measurements showed. In the case of larger ammonium ions, the sheets would be partially exfoliated to yield colloidal solutions containing particles around 15 nm in diameter (by DLS). However, when small amines were employed, the layered structure too strongly tightened due to larger charge density to be exfoliated, leading to the coagulation or precipitates.

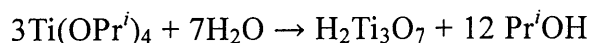
In the case of the TIP-Et<sub>2</sub>NH system, for instance, in Table 2. 5, the amorphous powder from the solution had the composition corresponding to tetratitanate, and the Raman spectrum was almost the same as that of tetratitanic acid as shown in Fig. 2. 5. Nevertheless, hexatitanate (K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>) was obtained by ion-exchange and subsequent heat-treatment at 600 °C. These results seem to be somewhat contradictory, but can be understood by assuming that the structure in the solution is so flexible as to change the composition by the kind of the ion used or heat-treatment, and that crystalline K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> is most stable in the K<sub>2</sub>O-xTiO<sub>2</sub> compounds.<sup>20</sup>

In the case of other metallates shown in Table 2. 6, cation size is not as important as the basicity, indicating that the structure and nature of metallates may be different from that of titanates. The formation of clear titanate solution can be explained by a synergic effect between the acid-base reaction and the size of ammonium ion. At the same time, titanate polymers such as titanic acid would be depolymerized by the base, and delaminated by the existence of large ammonium ion.<sup>21-22</sup> The chemical species in the solutions does not exist as simple colloidal dispersions but as a compound “layered alkylammonium titanate”.

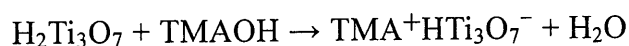
#### 2.4.2. Electric Conductivities, pH Values of the TIP-TMAOH Solutions

As shown in Table 2. 5, the clear solutions derived from the mixture of TIP and TMAOH may contain [TMA<sup>+</sup>][HTi<sub>3</sub>O<sub>7</sub><sup>-</sup>], which was formed through the following reactions.

Hydrolysis reaction:



Acid-base interaction:



In the solution containing  $x$  M concentration of titanium [Ti] and 0.1 M of TMAOH, following relationships hold true:

$$[\text{Ti}] = x \text{ (M)} \quad (x = 0 \text{ to } 0.25),$$

$$[\text{TMAOH}] = [\text{TMA}^+] = [\text{OH}^-] = 0.1 \text{ (M)} \text{ (complete dissociation)}$$

If the resultant  $[\text{TMA}^+][\text{HTi}_3\text{O}_7^-]$  is NOT dissociated to  $\text{TMA}^+$  and  $\text{HTi}_3\text{O}_7^-$  in the solution, the conductivity of  $[\text{TMA}^+][\text{HTi}_3\text{O}_7^-]$  would become zero and the conductivity of the solution comes to depend only on that of unreacted, free  $\text{TMA}^+\text{OH}^-$ , that is,

$$[\text{TMA}^+] = [\text{OH}^-] = 0.1 - x/3$$

using the reported equivalent ionic conductivity of  $\text{TMA}^+$  and  $\text{OH}^-$  ( $\lambda^\circ(\text{TMA}^+\text{OH}^-) = 211 \text{ (S}\cdot\text{cm}^2\cdot\text{eq}^{-1})$ , at  $18^\circ\text{C}$ )<sup>23</sup>, the dependence of the solution conductivity and pH value on Ti concentration  $x$  can be designated as follows:

$$\lambda = 211 (0.1 - x/3) \text{ (mS}\cdot\text{cm}^{-1})$$

$$\text{pH} = 14 + \log (0.1 - x/3)$$

Those curves derived from the equations are plotted in Fig. 2. 4 as dash lines and agree approximately with the experimental results (solid lines) in the range of  $x$  from 0 to 0.3. The slight deviation might be attributed to that from the assumed composition, and to the influence of the concentration of the solution species because the conductivity is generally decreased as increasing concentration. On the other hand, in the range of  $x$  higher than 0.3, it is difficult to estimate the behaviors because of the precipitation. This result indicates that the tetramethylammonium titanate is not dissociated and the  $\text{TMA}^+$  was trapped or constrained by the counter anions, namely layered titanates.

### 2.4.3. Layered Titanates

As shown in Figs. 2. 6, 7, the reaction of TIP with tetraalkylammonium hydroxides was more likely to form the layered titanates than that with alkylamines. And the diffraction patterns showed regularly d-spacings, and are in good agreement with those of the layered titanates previously reported by several researchers.<sup>21-22</sup> Raman spectra (Fig. 2. 5) also support the presence of layered titanates comparable to layered  $\text{H}_2\text{Ti}_4\text{O}_9$ .

Generally, colloidal layered titanates have been synthesized by a multistep process, that is, solid-phase reaction, ion-exchange, and delamination. As a typical example, first,  $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$  ( $\square$ : vacancy) was synthesized by the solid-phase reaction of  $\text{TiO}_2$  with  $\text{CsCO}_3$ . Second, an ion-exchange reaction of  $\text{Cs}^+$  with  $\text{H}^+$  for a few days to give  $\text{H}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ , which was finally exfoliated by quaternary ammonium ion. This process requires high temperature and a large amount of ammonium ions, and moreover takes long time. On the other hand, our process consists of simple reactions at room temperature, and is advantageous for time and material saving. In addition, our solutions are completely free of halogen and alkaline ions, being the most suitable as the starting materials for other titanium compounds. Using these solutions, not only layered titanates but also  $\text{TiO}_2$  thin films can be prepared at low temperatures as will be reported in Chapter 3. Our process and the chemical species formed by each step in this study can be illustrated as in Fig. 2. 10. Alkylammonium titanates can be prepared by the acid-base reaction of TIP with water and alkylamines or tetraalkylammonium hydroxides. Transparent titanate solutions are prepared when basic and bulky amines or ammonium hydroxides are used. Otherwise, amorphous precipitates are obtained. Starting from the titanate solution, many kinds of compounds or precursor of ceramics can be prepared in aqueous medium. Titanium chelate compounds are synthesized through depolymerization. Potassium hexatitanate ( $\text{K}_2\text{Ti}_6\text{O}_{13}$ ) is prepared by ion-exchange, followed by heat treatment at 600 °C. Potassium titanyl phosphate (KTP,  $\text{KTiOPO}_4$ ) is easily prepared by mixing with potassium dihydrogenphosphate ( $\text{KH}_2\text{PO}_4$ ), and then heated at 600 °C. The layered titanate film is dip-coated on glass, and anatase film can be obtained as low as 350 °C. The details of the preparation and characterization will be reported in the next chapter.

The formation of these compounds described above demonstrates the availability, and at the same time, the properties of our titanate solutions.

## 2.5. CONCLUSIONS

It is concluded that very stable, clear titanate colloidal solutions were obtained by the reactions of metal alkoxides with bulky amines or quaternary ammonium hydroxides, and that the reaction can be generalized as the acid-base reactions between metallic acids and amines based on  $pK_a$  values. The chemical species in the solutions exist not as simple colloidal dispersions of  $TiO_2$  (anatase or rutile) but as compounds “layered alkylammonium titanates”. To our knowledge, this study is the first report on the preparation of layered alkylammonium titanates by the solution method.

These aqueous metallate solutions are completely free from halogens, alkaline metal ions and chelates, and can be used as a source material to prepare various titanium compounds including sol-gel technique and will realize a novel, environmentally-friendly synthetic process of ceramic films, which can be applied to photocatalysts, zeolites, optical and electronic devices.

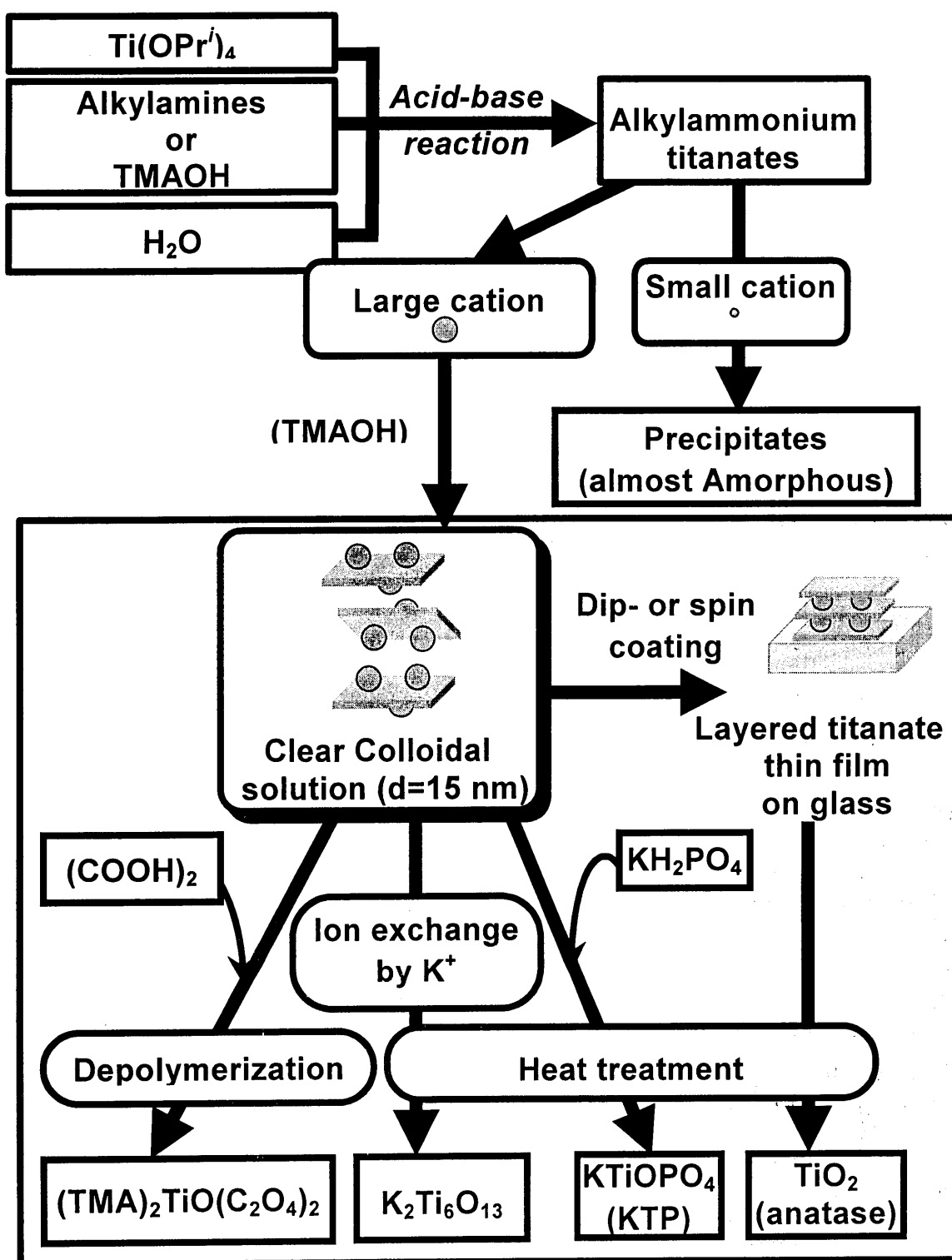


Fig. 2. 10. Schematic illustration for the reaction investigated in this study, and for the usefulness of aqueous titanate solution as a starting material.

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## *Chapter 3*

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### **PREPARATION AND CHARACTERIZATION OF TITANIA THIN FILMS FROM AQUEOUS SOLUTIONS**

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## *Chapter 3*

### **PREPARATION AND CHARACTERIZATION OF TITANIA THIN FILMS FROM AQUEOUS SOLUTIONS**

#### **ABSTRACT**

Dip- or spin-coating and characterization of titania ( $\text{TiO}_2$ ) thin films from various aqueous solutions have been studied. The aqueous titanium solutions mainly used in this study were halogen- and chelate-free solutions with the concentrations up to 1.4 M derived from titanium isopropoxide (TIP) with tetramethylammonium hydroxide (TMAOH) or some alkylamines, while aqueous and alcoholic solutions containing titanium atoms stabilized chelating ligands were examined for comparison. The  $\text{TiO}_2$  films prepared from the TIP-TMAOH solution were already crystallized at 350 °C to anatase form and those formed at 600 °C had high transparency and refractive indices of 2.40. No carbon residue in the film prepared at 400 °C was detected by XPS. The pure anatase form was sustained up to 850 °C. Interestingly, it was found that the (004) preferentially oriented anatase films were obtained from TIP-lactic acid (LA) system until 700 °C. The solutions containing citric acid (CA) or alkanolamines yielded anatase and rutile form fired at the temperatures equal to or higher than 600 °C. Carbon residue was detected in the film fired at 400 °C. The film thickness monotonically decreased from the upper to the bottom ends of the substrate. However, it was found that the thickness uniformity was drastically improved by an addition of sucrose to the aqueous solutions. The effects of the solution composition and polyhydroxy compounds on the crystal modifications of formed films and the film uniformity are discussed.

#### **3.1. INTRODUCTION**

Titanium dioxide ( $\text{TiO}_2$ ) is attracting much attention to new applications such as the self-cleaning, anti-fogging and/or hydrophilic films. Preparation of useful materials like  $\text{TiO}_2$  at lower temperature without using toxic substances is one of the most

important subjects to be achieved. A solution method including sol-gel processing is more useful for such purposes than other techniques, and the precursor solutions are well known to have a significant factor to determine the property of the final products. Water may be the most desirable solvent of the precursor solution in the processing.

So far, there are some reports regarding water-soluble titanium compounds.<sup>1-6</sup> As described in Chapter 2, it has been found that transparent, halogen- and chelate-free aqueous solutions could be prepared.<sup>7,8</sup> In this chapter, preparation of TiO<sub>2</sub> thin films from aqueous titanate solutions was investigated, focusing on the influence of starting precursor solutions on crystal form, crystallinity and orientation of TiO<sub>2</sub> thin films. Effect of various additives such as polyhydroxy compounds on the uniformity of TiO<sub>2</sub> thin films was also studied.

### 3.2. EXPERIMENTAL

Titanium tetraisopropoxide (Ti(OPr<sup>i</sup>)<sub>4</sub>: TIP) was used after distillation *in vacuo*. The other chemicals were used as received. The solutions were prepared by directly mixing TIP with tetramethylammonium hydroxide (TMAOH) in air at room temperature, followed by adding suitable amount of water. Triethylamine (Et<sub>3</sub>N), diethylamine (Et<sub>2</sub>NH), lactic acid (LA), citric acid (CA) and triethanolamine (TEA) were similarly used as TMAOH. The molar ratio of these additives to TIP is abbreviated as *R* henceforce. In the case of TIP-LA-NH<sub>3</sub>, ammonia was added to the TIP-LA solution.

The TiO<sub>2</sub> thin films were prepared by a dip- or spin-coating method onto a glass substrate (#7059, Corning Inc.). For dip-coating, the plate was immersed for 30 sec, followed by withdrawing at 1 cm/min. For spin-coating, the substrate on which the precursor solution (50-200 μl) was dropped and held for 30 sec, was rotated at 6000 rpm for 30 sec. After dried at 110 °C for 10 min, both films were heat-treated at various temperatures for 30 min in air. The resultant films were characterized by XRD, XPS, UV-VIS and AFM. The thickness and refractive index of the films were measured by ellipsometer (He-Ne laser).

### 3.3. RESULTS AND DISCUSSION

#### 3.3.1. Selection of Starting Solution: Usefulness of Aqueous Solution of TIP-TMAOH

All of the aqueous solutions examined and properties of TiO<sub>2</sub> thin films obtained from them are summarized in Table 3. 1. The results of the films prepared from the 2-propanol solutions<sup>9</sup> are also shown for comparison.

Table 3. 1. Properties of the TiO<sub>2</sub> thin films prepared from aqueous and alcoholic solutions.

Solvent	Stabilizer (Additive)	$R^a$	Crystallization temp. (°C)	Crystal phase <sup>b</sup>	Refractive index <sup>b</sup>	Orientation of anatase <sup>b</sup>	Film uniformity
Water	TMAOH	0.4	350	A	2.40	(101)	Excellent <sup>c</sup>
	Et <sub>2</sub> NH	0.4	600	A	2.33	(101)	Fair
	Et <sub>3</sub> N	0.5	600	A	2.34	(101)	Fair
	LA	1	(400) <sup>d</sup>	A	2.21	(004)	Poor
	LA-NH <sub>3</sub>	1:1	(400) <sup>d</sup>	A	2.30	(004)	Good
	CA-NH <sub>3</sub>	1:1	500	A+R	2.33	(101)	Good
	TEA	1	500	A+R	2.33	(101)	Fair
<hr/>							
	HNO <sub>3</sub> (STS-01)	---	---	A	(1.65)	---	Poor
<hr/>							
2-propanol	DEA	1	500	A+R	2.30	(101)	Excellent
	TEA	1	500	A+R	2.33	(101)	Excellent
	Acetoin	2	400	A	2.12	(101)	Good
	acac	2	400	A	2.08	(101)	Good

<sup>a</sup> $R = [\text{stabilizer}]/[\text{Ti}]$ , molar ratio

<sup>b</sup>for the films heat-treated at 600 °C, A: anatase, R: rutile

<sup>c</sup>in the presence of sugar (see text)

<sup>d</sup>brown-colored film

Table 3. 1 clearly indicates that the TIP-TMAOH solution is the best from the point of view of low crystallization temperature (350 °C), high refractive index (2.40), and film uniformity. The films were found to be superior to those from commercial anatase colloidal suspension (STS-01, Ishihara Sangyo Kaisha, Ltd.). Except for TMAOH and the alkylamines, the clear solutions were obtained at  $R=1$  or higher, indicating chelate formation. Rutile formation was recognized in the case from the solution containing CA, diethanolamine (DEA) and TEA. The properties of the  $\text{TiO}_2$  films will be discussed later.

The decomposition behavior of the chemical species in the aqueous solutions was investigated by TG-DTA, showing that the powder obtained from TMAOH system was almost fully decomposed at 330 °C. The powder from the TIP-alkylamines was not crystallized until about 600 °C in spite of less organic content. On the other hand, the powder from the TIP-TEA contains much larger amount of organics than that from the formers, and the TG curve indicated that below 500 °C much carbonaceous residues remained in the powder.

### 3.3.2. Characterization of $\text{TiO}_2$ Thin Films Prepared from Aqueous Titanate Solutions

Figure 3. 1 shows the XRD patterns of the  $\text{TiO}_2$  thin films prepared from (a) the 1.2 M TIP-TMAOH ( $R=0.4$ ) and (b) the TIP-LA- $\text{NH}_3$  ( $R=1:1$ ) solutions. The numbers of coating were 1 and 5, respectively. In Fig. 3. 1(a), pure anatase with only (101) peak appeared already at 350 °C, and carbon residue in the film prepared at 400 °C was not detected by XPS. The anatase form was sustained up to 830 °C on  $\text{Al}_2\text{O}_3$  plate without yielding rutile. Crystallite size was almost constant to be 15 to 20 nm in the temperature range examined. The refractive index of the film fired at 600 °C was 2.40 in spite that it is composed of pure anatase. In the case of 0.8 M TIP- $\text{Et}_3\text{N}$  ( $R=0.5$ ) and 0.7 M TIP- $\text{Et}_2\text{NH}$  ( $R=0.4$ ), the anatase films were similarly obtained, but not crystallized until 600 °C. In Fig. 3. 1(b), pure anatase films were obtained at 400 to 700 °C, but the films prepared at 400 °C were brownish, indicative of carbonaceous residue. Interestingly, the films preferentially oriented to (004). This orientation was also observed in the case of TIP-LA ( $R=1$ ) system.

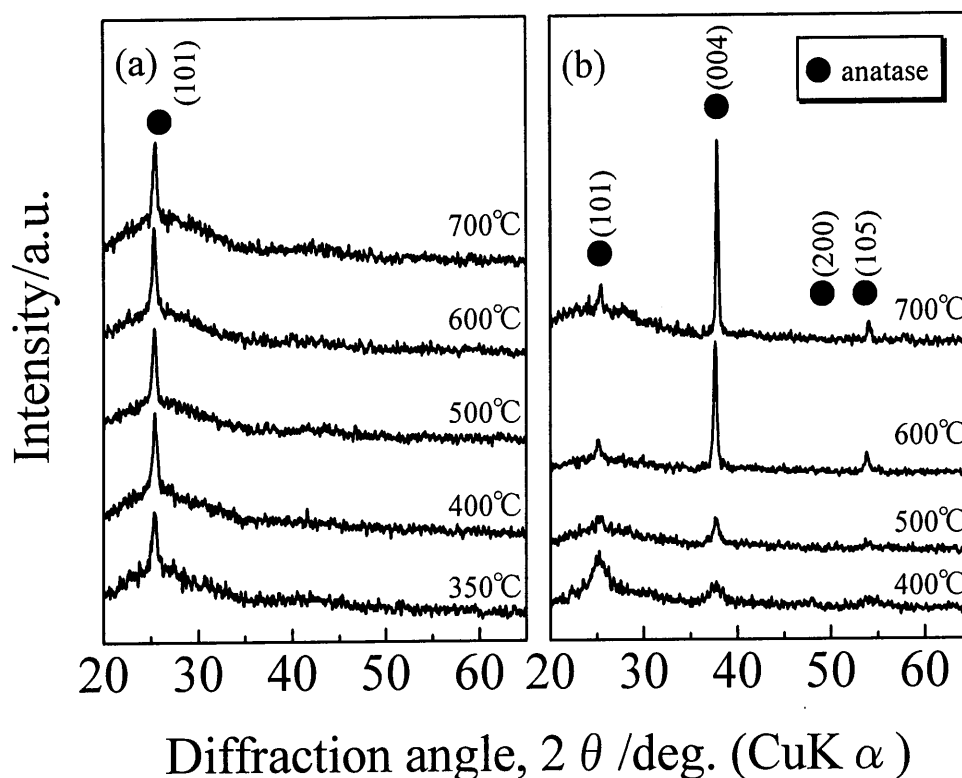


Fig. 3. 1. XRD patterns of the TiO<sub>2</sub> thin films prepared from the aqueous solution of (a) 1.2 M TIP-TMAOH ( $R=0.4$ ) and (b) 1 M TIP-LA-NH<sub>3</sub> ( $R=1:1$ ).

Figure 3. 2 shows the influence of the starting solutions on the crystal phase of TiO<sub>2</sub> films heat-treated at 600 °C for 3-5 coatings. The TMAOH and LA-NH<sub>3</sub> systems yielded only anatase, especially (004) orientation was observed in the LA-NH<sub>3</sub> system. For CA and TEA systems, crystallization occurred at 500 °C, and a small amount of rutile was detected at 600 °C regardless of the solvent used. These results indicates that the chemical species in the precursor solutions control the crystal form, and hence the properties of the resultant TiO<sub>2</sub> films. Organic chelates are well known to control the hydrolysis but tend to reside in the films until higher temperatures, which is thought to cause both the formation of rutile around 600 °C and the increase of crystallization temperature. As already reported, the rutile formation seems to be accelerated by reducing property of organic species, the increase of the film thickness and firing time.<sup>9</sup>

<sup>10</sup> Moreover, rutile films are obtained from the sol containing reducing chelating agents with hydrazine unit.<sup>11</sup> TIP is readily hydrolyzed in the presence of strongly basic TMAOH to give the colloid particles ( $d = 15$  nm) with layered structure similar to tetratitanic acid ( $H_2Ti_4O_9$ ).<sup>8</sup> The  $H_2Ti_4O_9$  can be readily transformed topotaxially to anatase<sup>12</sup>, so that the films could be crystallized at a temperature as low as 350 °C. In the case of alkylamines, however, the films are not crystallized below 600 °C because they do not have such layered structure as TMAOH. For LA system, the orientation of  $TiO_2$  seems to be related to the structure of solution species although the details remain unclear at present.

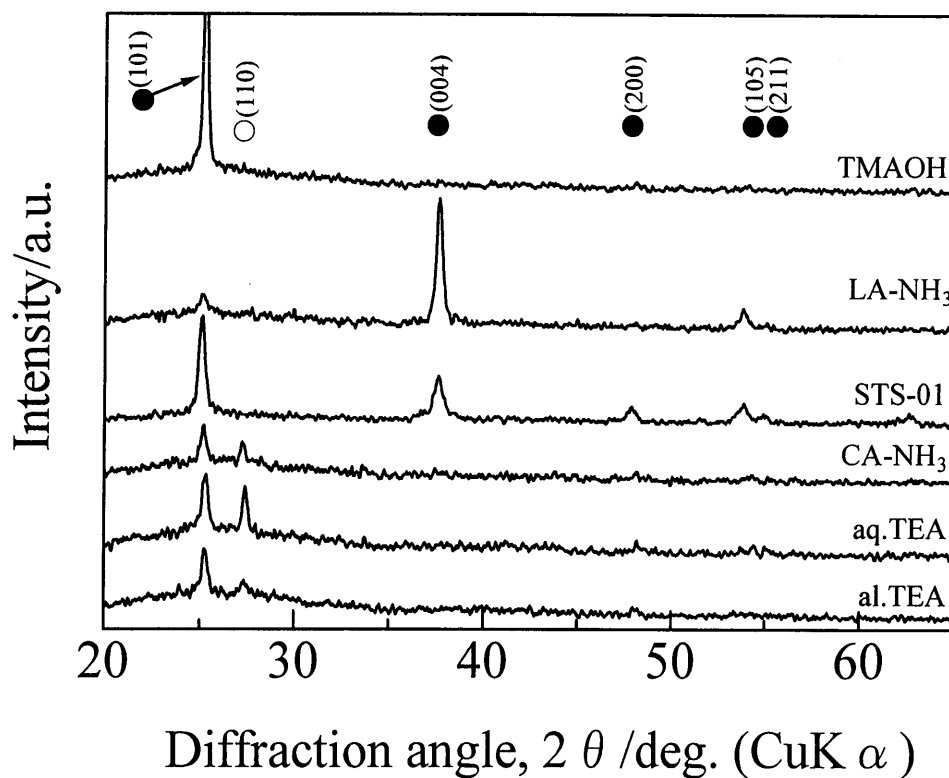


Fig. 3. 2. XRD patterns of the  $TiO_2$  thin films prepared from various aqueous titanate solutions.

### 3.3.3. Improvement of the Uniformity of the Film Prepared from TIP-based Aqueous Solutions

In this study, the precursor solutions normally contain 30-40 vol% of 2-propanol generated by hydrolysis of TIP. In the process of dip coating, the liquid film was observed to climb up the substrate, then to gather into drops, and to move down. As a result, the upper side of the film was thicker than the bottom side. This phenomenon is caused by the difference of evaporation rate of 2-propanol and water, called “*Tears of Wine*”.<sup>13</sup>

To restrain the movement of the liquid film on glass plate, it is important to increase the viscosity of the liquid. An addition of various water-soluble polymers (PEG and PVA) or polyhydroxy compounds to the TIP-TMAOH solution was examined to improve the uniformity. As shown in Fig. 3. 3, the addition of sucrose showed the best uniformity with high refractive index of 2.40. AFM observation indicated that the film was not porous but smooth although the grain size was slightly smaller than the case

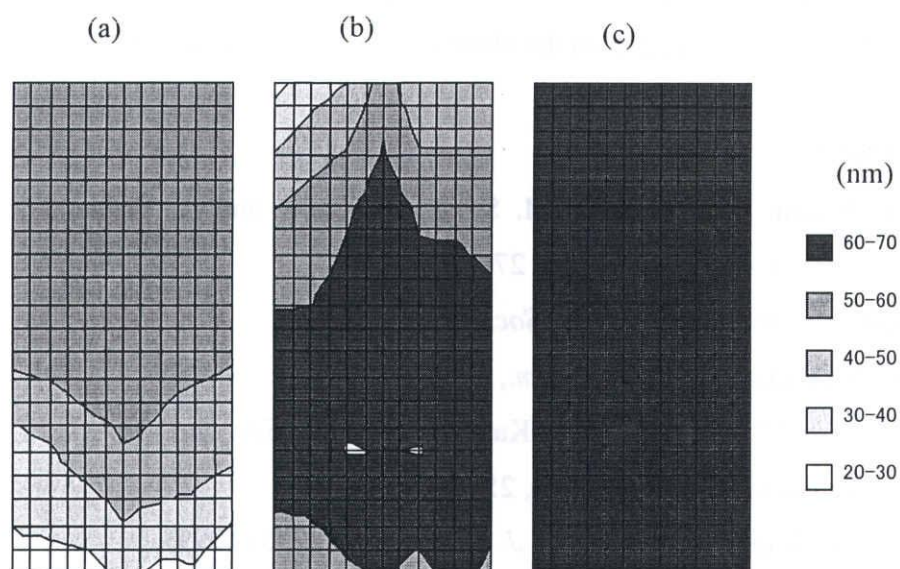


Fig. 3. 3. Thickness distribution of the  $\text{TiO}_2$  thin films prepared from the aqueous solution of 1.2 M TIP-TMAOH ( $R=0.4$ ) added (a) none, (b) 3 mol% PVA and (c) 3 mol% sucrose. The films were heat-treated at 600 °C for 30min.

without sucrose. Small amount of sucrose less than 3 mol% was also effective, and surprisingly, the dense, smooth TiO<sub>2</sub> films with high refractive index could be obtained even in the presence of excess sucrose up to 30 mol%. One of the typical functions of the saccharides is thought to increase the viscosity in the liquid. As the evaporation of alcohol in the liquid film on the glass proceeds, the viscosity becomes high. As a result, the liquid film loses its fluidity, leading to form smooth film. When polymers such as PEG were employed, porous films are obtained.<sup>14</sup> In contrast, the non-polymeric saccharides may be easily decomposed without changing the film morphology during the heat-treatment.

### 3.4. CONCLUSION

It is concluded that the TIP-TMAOH aqueous solution was the best precursor, to give TiO<sub>2</sub> films with high transparency and refractive index at lower temperatures. The uniformity of the film from the TIP-TMAOH solution was drastically improved by the addition of sugar. The crystal form, orientation and crystallization of the TiO<sub>2</sub> films were found to depend strongly on the chemical species of the starting solutions.

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## *Chapter 4*

### **EFFECT OF PHOTOIRRADIATION ON THE PROPERTIES OF LAYERED TITANATE THIN FILMS FROM TRANSPARENT AQUEOUS TITANATE SOLS**

## **Chapter 4**

### **EFFECT OF PHOTOIRRADIATION ON THE PROPERTIES OF LAYERED TITANATE THIN FILMS FROM TRANSPARENT AQUEOUS TITANATE SOLS**

#### **ABSTRACT**

UV irradiation on films prepared by a spin-coating method using aqueous titanate sols was investigated. The transparent sols used in this study were prepared by a reaction of titanium tetraisopropoxide (TIP) with tetramethylammonium hydroxide (TMAOH) or alkylamines, and consisted of a layered compound. The refractive indices and hardening of the films increased with the irradiation time, indicating that photoirradiation accelerated densification of the films. It was found that these phenomena were caused by the photocatalytic decomposition of alkylammonium ions located between the titanate sheets to contract the interlayer distance. Interestingly, when the film prepared from the TIP-TMAOH sol containing 30 mol% of sucrose to Ti was irradiated through a patterning mask and subsequently heated in air at 500 °C, the irradiated part of the film selectively turned dark brown due to residual carbon. It was thought that sucrose molecules were confined within the host titanate layers densified by UV irradiation and that the oxidation of the sucrose by oxygen in air was difficult under heating because the densified titanates might suppress the diffusion of oxygen.

On the other hand, such coloring of the films by sucrose was not found for films prepared from an aqueous suspension of crystalline  $\text{TiO}_2$  (anatase), an aqueous solution of TIP-lactic acid (LA)- $\text{NH}_3$ , and alcoholic sols such as the TIP-diethanolamine (DEA) system.

#### **4.1. INTRODUCTION**

Recently, the low-cost, low-energy fabrication of functional materials has been

attracting attention from industrial and environmental points of view. A sol-gel technique, which is one of the promising solution processes, is widely used to prepare oxide films and oxide gel films.<sup>1</sup> Using water as a solvent is the most favorable, but many transition metals with higher formal oxidation states are readily hydrolyzed to give insoluble metallic acids. Therefore, chelate compounds are often used to form a stable aqueous solution of them.

Photoirradiation to the gel films consisting of chelate compounds makes it possible to decompose organic chelates to promote densification of the gel films. Light corresponding to ligand-to-metal charge transfer (LMCT) is especially effective because metal-chelate bonds would be weakened. As a result, the irradiated part of films became insoluble into the solvent. Utilizing this difference in solubility, fine patterning of the oxide films has been prepared.<sup>2-5</sup>

In Chapter 2, it has been reported that halogen-free, transparent, aqueous colloidal metallate solutions were prepared by a reaction of metal alkoxide (Ti, V, Nb, Ta, Al, and Si) with tetramethylammonium hydroxide (TMAOH) or bulky alkylamines in water.<sup>6,7</sup> In particular, titanate solutions, in which the solute had the same structure as a titanate sheet obtained by the delamination of a layered titanate,  $H_xTi_{(2-x/4)}\square_{x/4}O_4$  ( $\square$ : vacancy),<sup>8</sup> are very stable over many years and are free of halogens, alkaline cations and organic chelates. Titanate solutions can be prepared much more easily than by the conventional method, which comprises multiple steps, such as a solid-state reaction of  $TiO_2$  with  $CsCO_3$ , the ion exchange of  $Cs^+$  with  $H^+$  and the delamination of  $H_xTi_{(2-x/4)}\square_{x/4}O_4$  using tetrabutylammonium hydroxide (TBAOH) or ethylamine.<sup>9</sup> In the near future, these pure aqueous titanate solutions will become much important not only for environmental considerations, but also for the fabrication of functional ceramics requiring high purity. A film prepared from the TIP-TMAOH sol was found to crystallize to anatase at temperatures as low as 350 °C with a refractive index of 2.40 at 600 °C; it was also found that a small amount of sucrose (3 mol% to Ti) added to the sol made the resultant film drastically uniform.<sup>10</sup> Furthermore, when a film prepared from the sol containing 30 mol% of sucrose to Ti was irradiated through a patterning mask and subsequently heated in air at 500 °C, it was found that the irradiated part of the film selectively turned dark brown.

There are many reports regarding the preparation and characterization of a delaminated titanate suspension: synthesis,<sup>11-13</sup> ion-exchange property of the film,<sup>14</sup> intercalation of polymer,<sup>15,16</sup> swelling of the layered film,<sup>12,17,18</sup> photocatalytic property,<sup>19,20</sup> and fabrication of Langmuir-Blodgett (LB) films.<sup>21,22</sup> To our knowledge, there is no report relating to any change in the properties of the layered titanate films themselves by photoirradiation, although the densification of TiO<sub>2</sub> gel films derived from the hydrolysis of TIP was published.<sup>23</sup> In this chapter, the effect of photoirradiation on the change in the hardness, thickness and refractive indices of the titanate film, and the behavior of coloring by sucrose was investigated.

## 4.2. EXPERIMENTAL

### 4.2.1. Chemical Reagents

Titanium tetraisopropoxide (Ti(OPr)<sup>i</sup><sub>4</sub>: TIP, Wako Pure Chemical Industries, Ltd., Osaka, Japan) was used after distillation under reduced pressure. Commercial extrapure reagents, tetraethyl orthosilicate (Si(OEt)<sub>4</sub>: TEOS), diethylamine (Et<sub>2</sub>NH), triethylamine (Et<sub>3</sub>N), aqueous solution of tetramethylammonium hydroxide (15 %, TMAOH), were used as received from Wako Pure Chemical Industries, Ltd., Osaka, Japan. An aqueous solution of choline ((2-hydroxyethyl)trimethylammonium hydroxide, 48-50 %, Tokyo Kasei Kogyo Co. Ltd.) was also used instead of TMAOH.

### 4.2.2. Preparation of Layered Titanate Films

The preparation of aqueous titanate solutions from TIP was performed as reported previously.<sup>6-7</sup> The molar ratios of TMAOH, choline, alkylamines or chelating ligands to Ti are denoted by *R* henceforth. Thus, 1.2 M TIP-TMAOH (*R*=0.4), 1.0 M TIP-choline (*R*=0.4), 0.7 M TIP-Et<sub>2</sub>NH (*R*=0.5), 0.8 M TIP-Et<sub>3</sub>N (*R*=0.5) and 1.0 M TEOS-TMAOH (*R*=0.5) were prepared. A small amount of sucrose (3 mol% to Ti) was added to the solution in order to improve the film uniformity.<sup>10</sup> It was confirmed that its addition up to 30 mol% did not affect the interlayer distance of titanate layer compounds and the crystallization temperature of anatase.

The films were prepared on either borosilicate glass (Corning Inc, #7059) or

SiO<sub>2</sub> glass (Nippon Silica Glass) by a spin-coating method (6000 rpm, 30 sec). The film was irradiated by a 500-W super high-pressure mercury lamp (Ushio Denki Co., Ltd.) through water as an IR-cut filter. The irradiation power density through the filter was 0.4 W·cm<sup>-2</sup>. In a heat treatment of the coated titanate films, the films were directly introduced into a horizontal furnace electrically heated at a given temperature, and then heated for 30 min in air.

#### 4.2.3. Characterizations

All characterizations were performed for single-coated films. XRD patterns (Model Geigerflex, Rigaku Co., Tokyo, Japan) were recorded using graphite monochromated CuK $\alpha$  radiation with a scanning speed of 2°/min over the 2 $\theta$  range of 2°-70°. The thickness and the refractive index of films were measured by an ellipsometer (DVA-36VMW, Mizojiri Optical Co., Ltd.) equipped with a He-Ne laser (632.8 nm), and a UV-Vis spectrometer (Hitachi U-3500). The carbon content of the film was analyzed by Electron Spectroscopy for Chemical Analysis (ESCA, Shimadzu ESCA-850). Infrared (IR) spectra of the powder scraped away from the photoirradiated films on a glass plate were recorded with a spectrophotometer (PERKIN-ELMER System 2000 FT-IR) in the 4000-400 cm<sup>-1</sup> wavenumber range (KBr method). Liquid-state <sup>1</sup>H-NMR spectra (Model FT-NMR alpha-400, JOEL, Tokyo, Japan) were measured at room temperature under an external magnetic field of  $H_0 = 9.4$  T with an internal standard of sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS). The specimens were mixed with D<sub>2</sub>O in a sample tube with a diameter of 5 mm.

#### 4.2.4. Determination of Film Hardness

The film hardness was measured by a pencil method,<sup>24</sup> in which Mitsubishi Hi uni pencils (hardness: 6B-6H) were used.

#### 4.2.5. Patterning of Films Prepared from Titanate Sols

The gel film prepared from the titanate sols was irradiated through a patterning mask for 30 min, leached in water and finally fired at 500 °C for 30 min in air. Similarly, a film prepared without leaching process was also examined.

### 4.3. RESULTS

#### 4.3.1. Properties of the 1.2 M TIP-TMAOH ( $R=0.4$ ) Sol and the Films

##### Prepared from the Sol

The aqueous sol of 1.2 M TIP-TMAOH ( $R=0.4$ , sucrose 3 mol%) contains about 37 vol% 2-propanol resulted from the hydrolysis of TIP. The sol remained stable even after evaporating the alcohol. The presence of 2-propanol did not affect the results obtained in this study. Therefore, in this study, the sol was used as it was prepared without the evaporation of 2-propanol.

Fig. 4. 1(a) shows the XRD patterns of films prepared from the TIP-TMAOH sol. The film dried at 100 °C had a broad diffraction peak below 5 °. The peak became slightly sharp at 200 °C, but again broad at 300 °C. Finally, the film crystallized to anatase at 350 °C. The crystallite size of the anatase film fired at 400 °C was estimated to be 14 nm from the peak width of the (101) reflection of anatase using Scherrer's equation. A film prepared at 100 °C seemed to be almost amorphous by XRD. However, as described in Chapter 2, Raman spectra revealed that the solute (or colloid) was a layered titanate,<sup>7</sup> indicating that the species consisted of a short-range order. Actually, when titanate films were coated using the clear sol refluxed for 3 h, a distinct diffraction pattern of the layered structure was found, as shown in Fig. 4. 1(b). Three sharp peaks located at 5.16 ° (1.71 nm), 10.36 ° (0.85 nm) and 14.90 ° (0.59 nm) were clearly observed at 100 °C. The pattern is similar to that reported for delamination of the layered titanate,  $H_xTi_{(2-x/4)}\square_{x/4}O_4$  ( $\square$ : vacancy).<sup>8</sup> However, in the case of titanate films prepared from refluxed sols, crystallization to anatase was observed at 550 °C, which was higher than that of the film from the sol without reflux. It was inferred that the crystallization to anatase was difficult, since the framework of the layered structure might be built by reflux.

A decrease in solubility toward water was observed for a film fired at 200 °C, but the film was soluble in aqueous TMAOH (15 %). However, films heated above 350 °C, which was composed of anatase, were insoluble in both water and aqueous TMAOH.

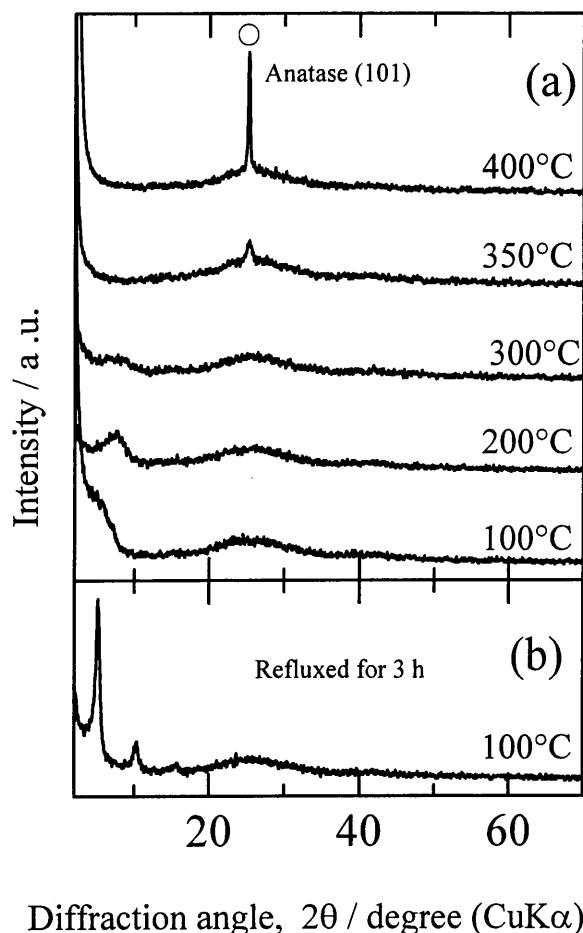


Figure 4. 1. XRD patterns of the thin films prepared from (a) 1.2 M TIP-TMAOH ( $R=0.4$ , sucrose 3 mol%) and (b) 1.2 M TIP-TMAOH ( $R=0.4$ , sucrose 3 mol%) refluxed for 3 h.

#### 4.3.2. Effect of Photoirradiation to the Films

Fig. 4. 2 shows the variations in the XRD patterns of the films for various UV irradiation time durations. The films were prepared from the refluxed TIP-TMAOH sol. Since the films were prepared from the refluxed sol, as described above, the unirradiated film exhibited distinct diffraction peaks. After photoirradiation for 20 min, the clear diffraction patterns was broadened and shifted to higher angles,

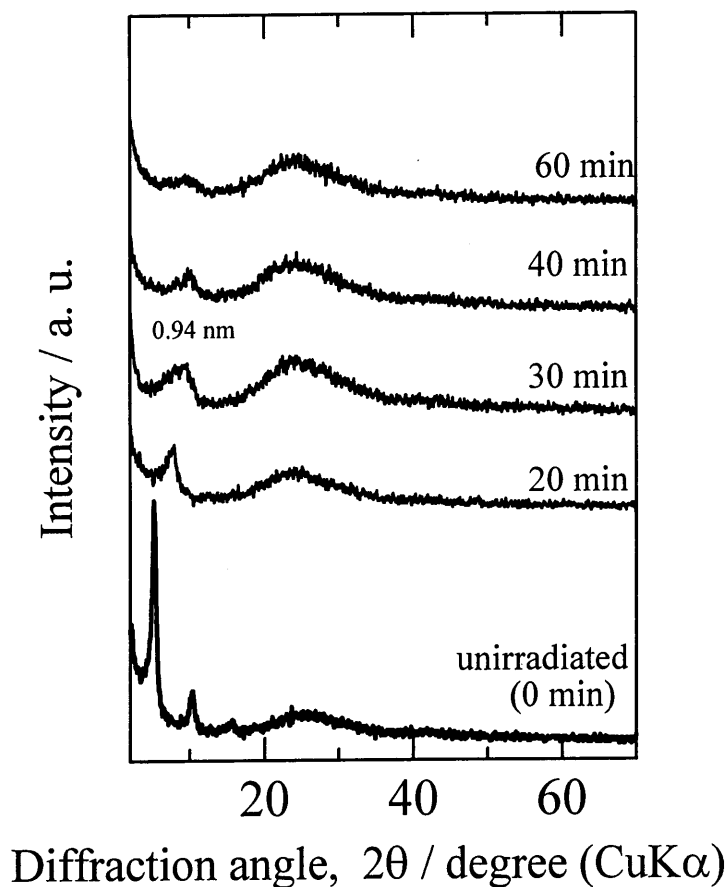


Figure 4. 2. Effect of photoirradiation on XRD patterns of the thin films prepared from 1.2 M TIP-TMAOH ( $R=0.4$ , sucrose 3 mol%) refluxed for 3 h.

indicating that the interlayer distances decreased. The  $d$  value (at  $9.40^\circ$ ) for the film irradiated for 30 min was 0.94 nm, being in good agreement with the (020) reflection of  $H_xTi_{(2-x/4)}□_{x/4}O_4 \cdot H_2O$ . This observation strongly suggests that the  $TMA^+$  ions located between the titanate layers were photochemically decomposed. After irradiation for 60 min, the film became almost amorphous.

When the film was irradiated with light at a wavelength above 300 nm through a cut filter, the film was dissolved in water and no changes in the solubility to water and refractive index were observed, regardless of the irradiation time. However,

when irradiated with light at a wavelength below 300 nm for 20 min or longer, the film became insoluble in water, but still soluble in aqueous TMAOH (15 %). Accordingly, it is concluded that the film had a photosensitivity below 300 nm and the layered structure was changed by photoirradiation.

When a film prepared from the refluxed TIP-TMAOH sol was heated after photoirradiation, its crystallization to anatase was not found until 500 °C.

On the other hand, films derived from commercial sols, STS-01 and STS-21 (Ishihara Sangyo Kaisha, Ltd., Osaka, Japan) containing crystalline  $\text{TiO}_2$  (anatase,  $d = 9$  nm) did not exhibit any change in solubility after photoirradiation, and opaque films were obtained; they dissolved in both water and the TMAOH solution, even after photoirradiation. These results indicate that the titanate solution is completely different from a simple colloidal  $\text{TiO}_2$  suspension.

#### **4.3.3. Effect of Photoirradiation on the Hardness and Refractive Indices of the Titanate Films**

Fig. 4. 3 shows the changes in the hardness and refractive indices of the TIP-TMAOH films with the irradiation time. The hardness data of the films prepared from an alcoholic solution of the TIP-DEA, which were irradiated for 0 and 40 min, are also included for a comparison. For TIP-TMAOH films, an abrupt increase in the hardness and refractive index was observed after 20 min of irradiation in accordance with the result of a decrease of the solubility to water. The films irradiated for longer than 30 min were hard (hardness 2H) with refractive indices of 1.95 to 1.98. This observation suggests that densification, a decrease of the solubility and hardening of the film simultaneously occurred with photoirradiation for about 20 min. The TIP-DEA films were much softer than the TIP-TMAOH films, even after 40 min of irradiation, as can be seen from Fig. 4. 3.

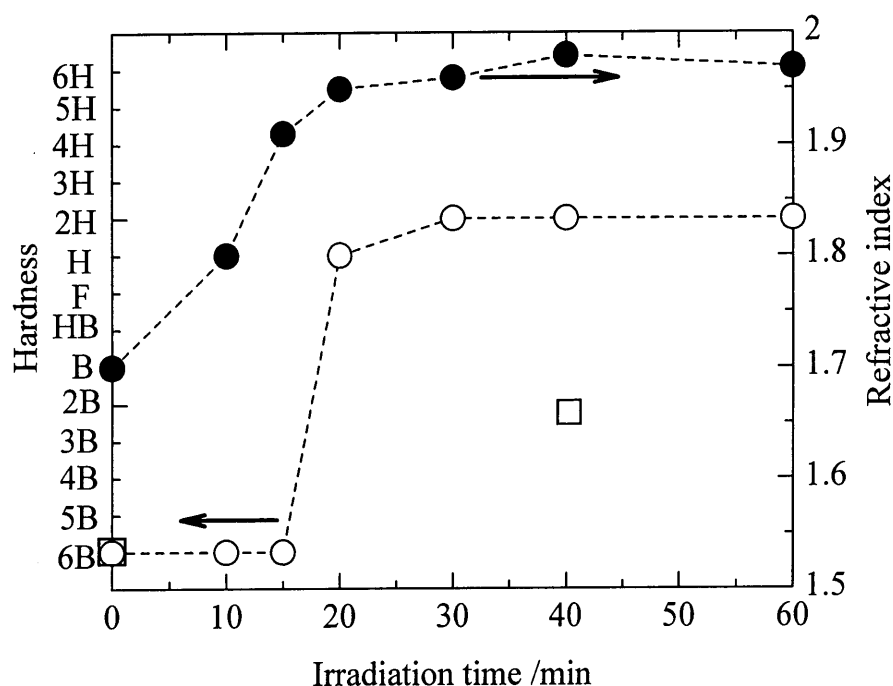


Figure 4. 3. Changes in the hardness and refractive indices of the TIP-TMAOH films on irradiation time. ○: hardness of the films; ●: refractive indices of the films; □: hardness of the films prepared form 2-propanol sol of 0.5 M TIP-DEA ( $R=2$ ).

Similarly, the changes in the hardness and refractive indices of the TIP-TMAOH films upon a heat treatment were examined as shown in Fig. 4. 4. A remarkable change in the hardness was observed between 200 and 250 °C, and a decrease in solubility was observed at 200 °C or above. The refractive indices of the films rapidly increased up to 350 °C, at which point crystallization to anatase was detected by XRD, as shown in Fig. 4. 1(a). On the other hand, the TIP-DEA film had already become hard at 200 °C, suggesting that the hydrolysis and condensation of the DEA-chelated TIP progress well by heating in air.

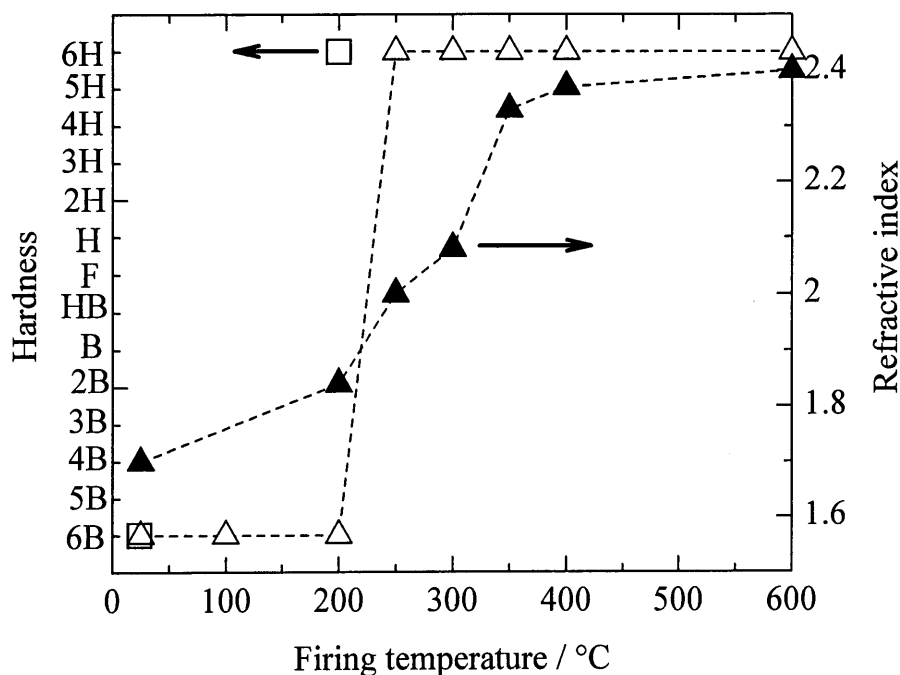


Figure 4. 4. Changes in the hardness and refractive indices of the TIP-TMAOH films on heat treatment.  $\triangle$ : hardness of the films;  $\blacktriangle$ : refractive indices of the films;  $\square$ : hardness of the films prepared form 2-propanol sol of 0.5 M TIP-DEA ( $R=2$ ).

Fig. 4. 5 shows the effects of photoirradiation and a heat treatment on the thickness and refractive index of TIP-TMAOH films. The thickness and refractive indices were calculated by both ellipsometry and UV-Vis spectroscopy. Along with the heating temperature, the thickness of both irradiated and unirradiated films decreased, and became almost constant above 400 °C. The reduction in thickness of the films upon a heat treatment was rather small in irradiated films. The refractive indices of the irradiated films were larger than that of the unirradiated films up to 300 °C, but were reversed above a certain temperature, being 2.35 and 2.40 at 400 °C for irradiated and unirradiated films, respectively.

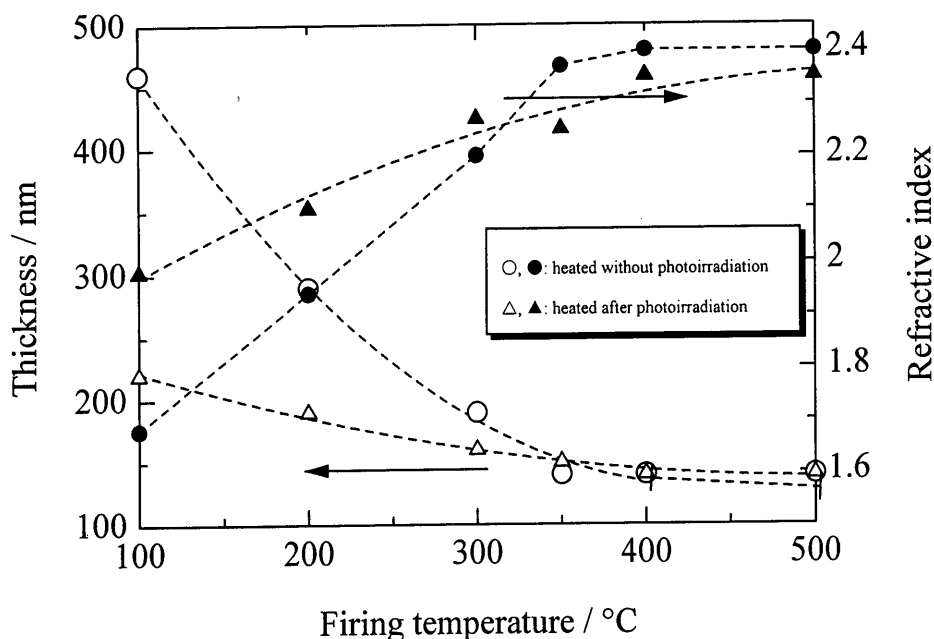


Figure 4. 5. Effects of photoirradiation and heat treatment on thickness and refractive index of the films, which were prepared from 1.2 M TIP-TMAOH ( $R=0.4$ , sucrose 3 mol%).

#### 4.3.4. IR and Liquid NMR Measurements

In order to investigate the change in the film caused by photoirradiation, IR spectra were recorded. Fig. 4. 6 shows the IR spectra of a powder obtained from films prepared from 1.2 M TIP-TMAOH ( $R=0.4$ ). The results of a powder prepared from 1.5 M TEOS-TMAOH ( $R=0.5$ ) sol are also shown for a comparison. For a powder prepared from the TIP-TMAOH film, two absorption bands were clearly observed around 950 and 1500  $\text{cm}^{-1}$  regions, which are assignable to the stretching vibration of the C–N bonds and the bending vibration of the C–H bonds in  $\text{TMA}^+$ , respectively. After 30 min of irradiation, these bands completely disappeared, indicating that  $\text{TMA}^+$  in the film was decomposed by UV irradiation. The powder obtained from the TIP-choline film revealed a similar decomposition behavior. On the other hand, the powder obtained from the TEOS-TMAOH film did not show any change in the IR spectra by photoirradiation, suggesting that the titanate layers play a crucial role in  $\text{TMA}^+$  decomposition. A liquid NMR measurement was

performed in order to detect the decomposition products formed by photoirradiation. The titanate solution was put in a silica test tube and photoirradiated with stirring for 1 h. In a TIP-choline solution, trimethylamine was detected, indicating that (2-hydroxyethyl)trimethylammonium ion (choline) was decomposed by photoirradiation in the titanate sol to yield trimethylamine. In the case of the TIP-TMAOH sol, no clear decomposition products were detected by NMR spectroscopy.

#### 4.3.5. Patterning of a Titanate Film using Photoirradiation

The results described above indicate that irradiated films became hard and insoluble in water, and that patterning of the film might be possible. Fig. 4. 7(a) shows a patterned  $\text{TiO}_2$  film, which was prepared from TIP-TMAOH ( $R=0.4$ , sucrose 3 mol%) by leaching the film after photoirradiation for 30 min through a mask pattern, and subsequently heating at 500 °C for 30 min. A negative pattern of the mask was clearly observed. In the same manner, patterning was possible in the TIP-choline, TIP- $\text{Et}_2\text{NH}$  and TIP- $\text{Et}_3\text{N}$  systems, but impossible in TEOS-TMAOH. In the TIP-choline system, the film became insoluble within 5 minutes of irradiation with the generation of a strong amine odor, being in good agreement with the NMR result.

When the film was made from titanate sols containing 30 mol% sucrose, the irradiated part of the film was insoluble as well, but readily peeled off by soaking the film in water. Hence, the irradiated film was directly fired at 500 °C in air without any leaching process. Interestingly, it was found that only the irradiated part of the film became colored dark brown, as shown in Fig. 4. 7(b). The colorless and colored parts of the film were found to be anatase and amorphous by XRD, respectively. Carbon was detected in the colored part of the film all over depth direction by XPS, which is shown in Fig. 4. 8. A further heat treatment at this temperature for more than 30 min made the colored film colorless, and led to the crystallization of anatase. This may have been due to the fact that the full decomposition of sucrose was rather difficult in the irradiated part of the film.

A wide variety of polyhydroxy compounds was examined in place of sucrose. However, only sucrose and raffinose, which are di- and tri-saccharides, were

effective for the coloring. The coloring of the irradiated film was not observed in the TIP-Et<sub>2</sub>NH, TIP-Et<sub>3</sub>N and TEOS-TMAOH systems.

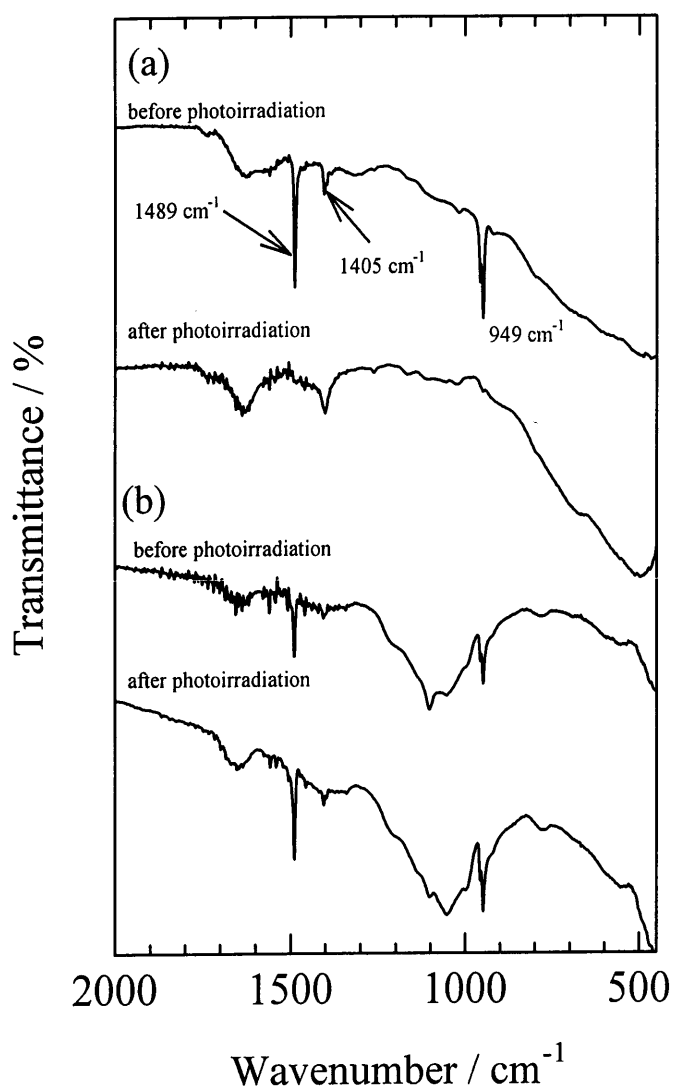


Figure 4. 6. IR spectra of the powder prepared from aqueous sols of (a) 1.2 M TIP-TMAOH ( $R=0.4$ ) and (b) 1.5 M TEOS-TMAOH ( $R=0.5$ ). The films were dried at room temperature and photoirradiation was carried out for 30 min.

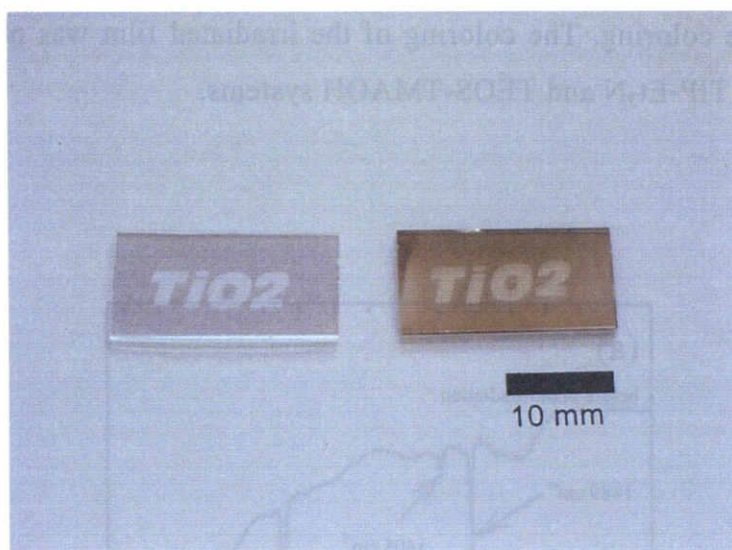


Figure 4. 7. Photographs of the patterned anatase films, which were prepared from the 1.2 M TIP-TMAOH ( $R=0.4$ , sucrose 3 mol%) sol, followed by firing at 500 °C for 30 min. (a) The unirradiated part of the film was removed by leaching and (b) The film was fired without leaching process. The irradiated part of the film was colored and amorphous, and unirradiated part of the film was anatase.

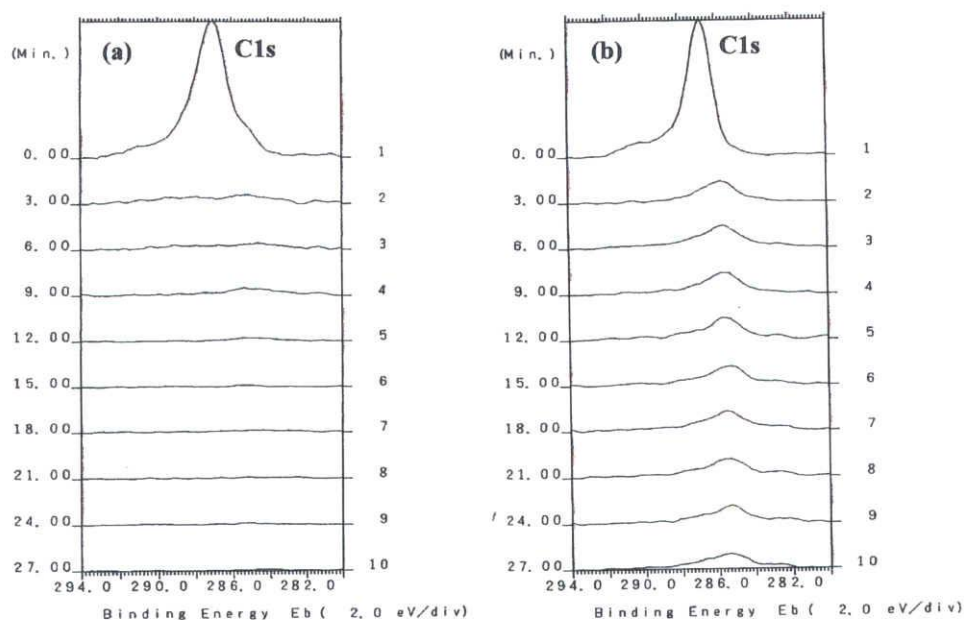


Figure 4. 8. ESCA depth profiles of the (a) unirradiated and (b) irradiated films, which were prepared from the 1.2 M TIP-TMAOH ( $R=0.4$ , sucrose 30 mol%) sol, followed by firing at 500 °C for 30 min.

## 4.4. DISCUSSION

### 4.4.1. Comparison of Photoirradiation with a Heat Treatment in Views of a Decrease in the Solubility, Hardness, and Crystallization to Anatase

The decomposition behaviors of layered titanate films prepared from 1.2 M TIP-TMAOH ( $R=0.4$ , sucrose 3 mol%) sol by photoirradiation and a heat treatment can be illustrated as in Fig. 4. 9; several of their properties are summarized in Table 4. 1.

Photoirradiation to the titanate films can decompose the  $\text{TMA}^+$  in the interlayer, but not accelerate crystallization to anatase, while a heat treatment of the titanate films can lead to anatase along with the decomposition of  $\text{TMA}^+$ .

Refluxing the sol did not influence the properties of the film, such as refractive index, thickness, hardness and patterning by photoirradiation and heat-treatment, although the crystallization temperature to anatase became higher than that of the film from the sol without reflux.

Once the TMA ions located between the layered titanates are decomposed by photoirradiation, the interlayer distance would contract from 1.71 to 0.94 nm, since the size of  $\text{H}^+$  or  $\text{H}_3\text{O}^+$  located between the layers is rather small compared to  $\text{TMA}^+$ , leading to a compound which is similar structure to  $\text{H}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4 \cdot \text{H}_2\text{O}$ . This formation of the protonated titanate is thought to be the main reason for the hardening, densification and decrease of solubility in water. In addition, it is reported that the protonated titanate can be dissolved or delaminated only in a highly basic aqueous solution, such as tetrabutylammonium hydroxide (TBAOH) and ethylamine.<sup>8,9</sup> The fact that the irradiated film was insoluble in water, but soluble in aqueous TMAOH, is in agreement with the property of the protonated titanate.

On the other hand, such photo-densification was not found for a film prepared from aqueous suspensions of crystalline  $\text{TiO}_2$  (anatase), indicating that the layered titanate sols are much different from the simple  $\text{TiO}_2$  suspension with respect to the structure and photosensitivity of colloids.

Table 4. 1. Comparison of the irradiated with heat treated films.

1.2 M TIP-TMAOH (R=0.4, sucrose 3 mol%)	Photoirradiation	Heat treatment (without irradiation)	Remarks
Decrease in solubility	20 min	200 °C	
Hardness	H (20 min)	6B (200 °C)	<sup>a</sup> 6H (250 °C)
Crystallization to anatase	500 °C	350 °C	
Refractive index	2.35 (500 °C)	2.37 (350 °C)	<sup>a</sup> 2.40 (500 °C)

The values in parentheses are irradiation time or firing temperature that the film was prepared.

<sup>a</sup> in the case of heat treatment

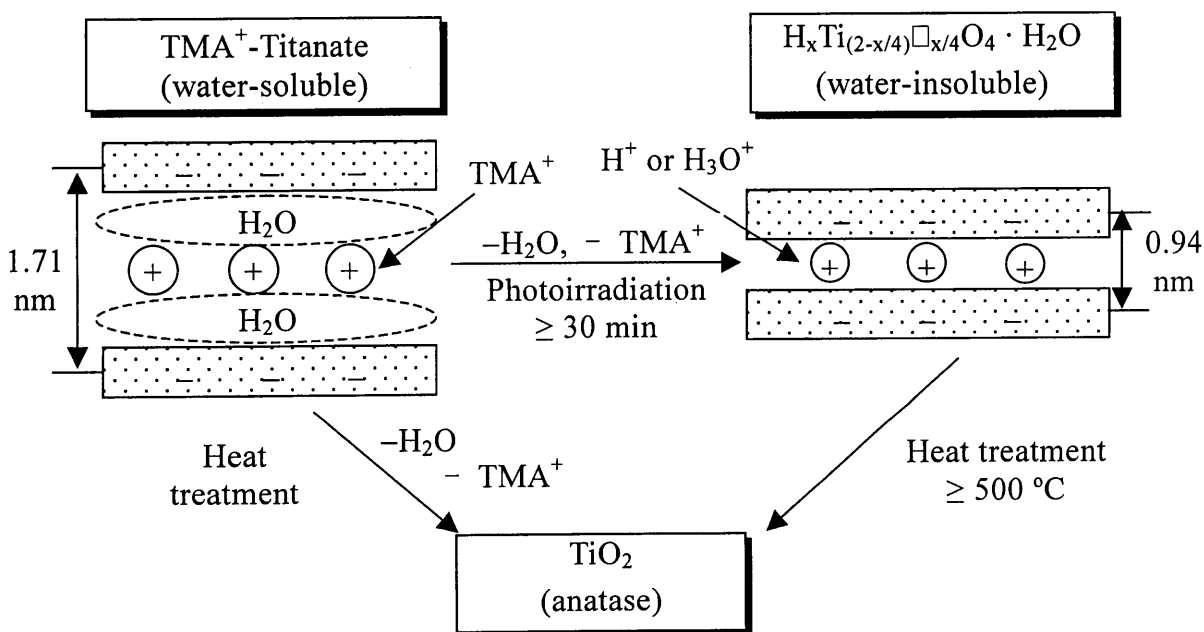


Figure 4. 9. The decomposition, decrease of solubility and densification of the gel films under photoirradiation and heat treatment.

#### 4.4.2. Patternability and coloring of a patterned film by sucrose

All of the layered titanate films used in this study were transparent (more than 90 %) above 320 nm, and the transmittance at 300 nm was about 55 %. The change due to photoirradiation was observed when the film was irradiated by light below 300 nm. It is reported in several papers that the  $\lambda_{\max}$  of a suspension and film prepared from  $H_xTi_{(2-x/4)}□_{x/4}O_4 \cdot H_2O$  was estimated to be 265 to 268 nm, and that the absorption started around 300 nm. Accordingly, the absorption of the film is assignable to that of the layered titanate, and the photocatalytic reaction of the titanates can occur at wavelengths below 300 nm. In the case of TEOS-TMAOH, the film was not affected by UV irradiation because it was transparent in the region of the light from a super high-pressure mercury lamp.

Coloring by polyhydroxy compounds was observed for only sucrose and raffinose, which are di- and tri-saccharides, respectively. Since the saccharides can be regarded as being carbon hydrates  $C_x(H_2O)_y$ , they may easily lose water to leave carbon when heated. As a matter of course, the photodecomposition of saccharides may occur, but it is thought that their excess amount in the layered titanate could not be completely decomposed after 30 min of irradiation. Actually, when sol containing 3 mol% of sucrose was photoirradiated, it turned yellow, indicating that photodecomposition might occur.

The type of starting sols is also related to the coloring of the irradiated film. Coloring occurred in films prepared from the aqueous sols from TIP-TMAOH and TIP-choline, while aqueous sols from TIP-Et<sub>2</sub>NH and Et<sub>3</sub>N, 1.0 M TIP-LA-NH<sub>3</sub> ( $R=1$ , 1) and TEOS-TMAOH were not observed. The films prepared from TIP-TMAOH and TIP-choline clearly showed a layered structure, and had refractive indices of 1.95 to 1.98 after photoirradiation, while films from TIP-Et<sub>2</sub>NH and Et<sub>3</sub>N had very broad peaks assignable to a layered structure by XRD and Raman, and had a lower refractive index ( $\sim 1.8$ ) even after photoirradiation. Films obtained from the TEOS-TMAOH system had no photosensitivity, as expected, and had a refractive index of about 1.4. A film prepared from TIP-LA-NH<sub>3</sub> was amorphous, but photosensitive. These results indicate that the presence of a well-defined, dense layered structure can be a crucial factor of this coloring. Therefore, it is thought that sucrose molecules were

confined within the host titanate layers densified by UV irradiation, and that the oxidation of the sucrose by oxygen in air was difficult under heating because the densified titanates suppressed the diffusion of oxygen.

In the TIP-choline system, the film became insoluble within 5 minutes of irradiation, while 20 minutes were required for the TIP-TMAOH system. TEOS-TMAOH did not show any change in the film property, and remained soluble after long-time photoirradiation. It is evident that the layered titanates have photocatalytic activity, and that (2-hydroxyethyl)trimethylammonium ion in titanate is photocatalytically decomposed much faster than  $\text{TMA}^+$ .

It can be assumed that the difference in the decomposition rate between  $\text{TMA}^+$  and (2-hydroxyethyl)trimethylammonium is partly related to their chemical structures. For example, it is possible to consider that choline is decomposed to generate trimethylamine in the same manner as Hoffmann degradation (elimination).<sup>25</sup> The degradation may proceed by an E2 reaction, that is, a thermal decomposition of quaternary ammonium hydroxides with a  $\beta$ -hydrogen atom, as viewed from nitrogen atom to yield alkenes, tertiary amines and water. According to this degradation reaction, it can be thought that choline with a  $\beta$ -hydrogen atom is decomposed faster than a TMA ion that has no  $\beta$ -hydrogen atom. Therefore, it is thought that the photocatalytic degradation reaction of choline can also occur faster than that of  $\text{TMA}^+$ .

The alcoholic sol of the TIP-DEA and aqueous sol of the TIP-LA- $\text{NH}_3$  system also have photosensitivity. The DEA and LA are known to make chelate compounds with Ti. Photoirradiation can break the Ti-O bonds in the chelate by LMCT. As a result,  $\text{Ti}^{4+}$  is destabilized and hydrolyzes to form an insoluble Ti-O-Ti polymer, but the extent of the polymerization would be lower than that takes place in the titanates.

#### 4.5. CONCLUSIONS

It was found that the alkylammonium ions between layered titanates could be decomposed by photoirradiation to lead to a decrease in the interlayer distance, hardening and densification of the films. Although photoirradiation did not accelerate the crystallization of anatase, the film became insoluble in water, and had

a high refractive index of around 2.0 and a hardness of 2H, indicative of some applicability as a surface modifier of plastics, etc. The addition of a large amount of sucrose to titanate sols made it possible not only to improve the film uniformity, but also to draw a pattern in the films.

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## *Chapter 5*

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### **AQUEOUS TITANATE SOLS FROM Ti ALKOXIDE- $\alpha$ -HYDROXYCARBOXYLIC ACID SYSTEM AND PREPARATION OF TITANIA FILMS FROM THE SOLS**

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## Chapter 5

### AQUEOUS TITANATE SOLS FROM Ti ALKOXIDE- $\alpha$ -HYDROXYCARBOXYLIC ACID SYSTEM AND PREPARATION OF TITANIA FILMS FROM THE SOLS

#### ABSTRACT

Aqueous titanate sols were prepared by reactions of titanium tetraisopropoxide (TIP) with  $\alpha$ -hydroxycarboxylic acids in water. Spin-coating of titania ( $\text{TiO}_2$ ) thin films prepared from these sols was examined. IR and Raman spectra, and elemental analysis of the powder obtained from the sols revealed that the carboxylates were chelated to titanium but the Ti species were polymerized to form a cluster that had a colloidal nature. Interestingly, it was found that (004) preferentially oriented anatase films with refractive index of 2.54 were obtained from TIP-Lactic acid- $\text{NH}_3$  (1:1:1) aqueous sol. This crystallographic orientation was characteristic of the TIP-Lactic acid- $\text{NH}_3$  (1:1:1) system, and was not affected by kinds of substrates used and heating rate of the film. TEM observation indicated that small anatase grains had already formed at 200 °C. Therefore, the crystallographic orientation might depend strongly on the structure of the chemical species of the precursor solutions.

#### 5.1. INTRODUCTION

Anatase-type titanium dioxide ( $\text{TiO}_2$ ) is attracting much attention to new applications such as self-cleaning, anti-fogging and/or hydrophilic films. Sol-gel processing including dip- or spin- coating is considered to be one of the conventional methods for the preparation of such films. In the processing, it is important to consider the stabilization of the precursor solution, and the use of water as a solvent and the reduction of organic content must be more benign for our environment.

The stabilization of titanium tetraisopropoxide ( $\text{Ti}(\text{OPr}^i)_4$ : TIP) using chelating

ligands has been reported in Chapter 1. It was found that acetoin (3-hydroxy-2-butanone), one of  $\alpha$ -hydroxyketones, had an extraordinarily strong stabilization effect for the 2-propanol solution of TIP, and an excess amount of water, in the molar ratio more than 30, could be added into the solution without occurrence of gelation or precipitation.<sup>1</sup> Furthermore, the reaction of TIP with lactic acid (Lac-H<sub>2</sub>) was found to give the aqueous solution even in the molar ratio of  $R=1$  ( $R=\text{Lac-H}_2/\text{TIP}$ ). Interestingly, the (004) preferentially oriented anatase films were obtained from the TIP-Lac-NH<sub>3</sub> ( $R=1:1$ ) system.<sup>2</sup>

The control of crystallographic orientation of the films is also important and essential issue. For instance, anatase is optically uniaxial crystal and shows double refraction ( $n_0=2.5612$ ,  $n_e=2.4880$ ).<sup>3</sup> Since the highest refractive index (2.56) of anatase can be observed in the direction of c-axis, higher refractive index can be expected in the form of the (00 $\ell$ ) oriented film than that of random orientation (2.52). In addition, it is reported that the (004) oriented anatase film that was prepared by MOCVD revealed high photocatalytic property.<sup>4</sup>

There are many papers and patents regarding water-soluble titanium complexes using oxalato, lactato and citrato ligands<sup>5-12</sup> based on the chemical formula:  $(\text{NH}_4)_2[\text{Ti}(\text{C}_3\text{H}_4\text{O}_3)_2(\text{OH})_2]$ , for example. Generally the titanium atoms are coordinated by two molecules of a ligand to satisfy six-coordination. However, the titanium complexes stabilized with a fewer ligand molecules are the better because higher titanium content would be economical starting materials for various compounds. So far, no reports relating to the orientation of the TiO<sub>2</sub> films prepared from aqueous solution have been published. In this chapter, the preparation and properties of aqueous titanate solution using TIP and  $\alpha$ -hydroxycarboxylic acids, and the factors to control the orientation were investigated.

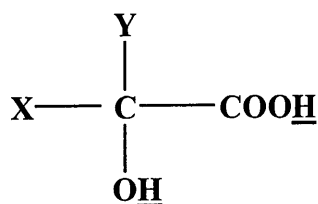
## 5.2. EXPERIMENTAL PROCEDURE

### 5.2.1. Preparation of Chelate-stabilized Titanate Sols

In this study,  $\alpha$ -hydroxycarboxylic acids were employed as chelating ligands for the preparation of aqueous titanate complexes, and the structure of which was shown in Fig. 5. 1. Abbreviation and substituents of the acids were also shown. “H<sub>2</sub>” in Gly-H<sub>2</sub>, for example, designates two dissociable protons: one is an active hydrogen with

carboxylic acid and the other is a hydrogen of  $\alpha$ -hydroxy group. In the free compounds (when they are not coordinated), the former is more protic than the latter. Oxalic acid, one of dicarboxylic acid  $\text{HOC(O)COOH}$ , was also examined because it can be regarded as an  $\alpha$ -hydroxycarboxylic acid.

All reagents used in this study were used as received from Wako Pure Chemical Industries, Ltd., Osaka, Japan. Titanium tetraisopropoxide ( $\text{Ti(OPr}^i\text{)}_4$ : TIP) was used after distillation under reduced pressure (3 mmHg, 80 °C). A preparation of aqueous titanate sols was examined by directly mixing TIP with the  $\alpha$ -hydroxycarboxylic acids in air at room temperature, followed by adding suitable amount of water so that the titanium concentration was adjusted to 1.0 M. The molar ratio of these additives to TIP is henceforth abbreviated as *R*.



$\alpha$ -Hydroxycarboxylic acids

$\alpha$ -Hydroxycarboxylic acids		substituents	
acids	abbrev.	X	Y
Glycolic acid	Gly-H <sub>2</sub>	H	H
DL-Lactic acid	Lac-H <sub>2</sub>	H	CH <sub>3</sub>
2-Hydroxyisobutylic acid	Hyd-H <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>
( $\pm$ )-Mandelic acid	Man-H <sub>2</sub>	H	C <sub>6</sub> H <sub>5</sub>
Oxalic acid	Ox-H <sub>2</sub>	= O	

Figure 5. 1. Structures of  $\alpha$ -hydroxycarboxylic acids used in this study.

### 5.2.2. Preparation of TiO<sub>2</sub> Thin Films

TiO<sub>2</sub> thin films were prepared by a spin-coating method onto either borosilicate glass (Corning Inc, #7059) or aluminosilicate glass (Corning Inc, #1737). For spin-coating, the substrate on which the titanate solution (1.0 M, 50-200  $\mu$ l) was dropped and held for 30 sec, was rotated at 6000 rpm for 30 sec. The coated films were directly introduced into a horizontal furnace electrically heated at a given temperature in advance, and then heated in air for 30 min.

### 5.2.3. Characterizations

Infrared (IR) spectra of the powder dried from the solution were recorded with a spectrophotometer (PERKIN-ELMER System 2000 FT-IR) in the 4000-400  $\text{cm}^{-1}$  wavenumber range (KBr method). The chemical species in the solutions or precipitates were examined by elemental analysis (CHN CORDER MT-6, Yanako Analytical Instruments Co., Kyoto, Japan), and thermogravimetric and differential thermal analysis (TG-DTA, Models DTA 50 and TGA 50, Shimadzu, Kyoto, Japan) at a heating rate of 5  $^{\circ}\text{C}\cdot\text{min}^{-1}$  from room temperature to 800  $^{\circ}\text{C}$  under flowing dry air. Liquid-state  $^{13}\text{C}$ -NMR spectra (Model FT-NMR alpha-400, JOEL, Tokyo, Japan) were measured at room temperature under an external magnetic field  $H_0 = 9.4$  T with the internal standard of sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS). The specimens were mixed with D<sub>2</sub>O in a sample tube with a diameter of 5 mm. Aqueous titanate solutions were examined also by Raman spectroscopy (NR-1800, JASCO Co., Tokyo, Japan). The pH was measured by pH Meter F-13, Horiba Ltd., Kyoto, Japan. XRD patterns were recorded (Model Geigerflex, Rigaku Co., Tokyo, Japan) on using graphite monochromated  $\text{CuK}\alpha$  radiation with a scanning speed of 2 $^{\circ}$ /min over the 2 $\theta$  range of 2 $^{\circ}$ -70 $^{\circ}$ . The thickness and refractive index of films were measured by an ellipsometer (DVA-36VMW, Mizozojiri Optical Co., Ltd.) equipped with a He-Ne laser (632.8 nm), and UV-Vis spectrometer (Hitachi U-3500). The microstructures of the films were observed by TEM (Model H-8100, Hitachi, Tokyo, Japan), using an accelerating voltage of 200 kV. Samples for TEM observation of films were prepared using a conventional crushing method,<sup>13</sup> and all the observations were performed in a cross-sectional orientation. Changes in crystalline phase were determined using XRD and selected-area-electron diffraction (SAD) TEM patterns of the films.

#### 5.2.4. Reaction of TIP with $\alpha$ -Hydroxycarboxylic Acids and Examination of the Chemical Species Separated from the Solutions

##### 5.2.4.1. Reaction of TIP with Glycolic Acid

When 3.0 ml of TIP (10 mmol) was mixed with 1.52 g of glycolic acid (Gly- $H_2$ ,  $R=1$ , 10 mmol), followed by adding pure water, exothermic reaction instantly occurred to give a solid mass. After stirring for 24 h, the precipitates were centrifugally separated, and then washed by deionized water. This separation-washing process was repeated three times, and finally dried *in vacuo* at room temperature. The elemental analysis of the powder gave the results. Found: H: 2.03, C: 9.84, Ti: 40.68%. Calcd for  $C_2H_4O_7Ti_2$ ,  $Ti_2O_3(Gly) \cdot H_2O$ : H: 1.71, C: 10.19, Ti: 40.61%. For  $R=2$ , Found: H: 2.04, C: 12.50, Ti: 36.87%. Calcd for  $C_4H_8O_{12}Ti_3$ ,  $Ti_3O_4(Gly)_2 \cdot 2H_2O$ : H: 2.06, C: 12.26, Ti: 36.67%.

2-Hydroxyisobutylic acid (Hyd- $H_2$ ) and mandelic acid (Man- $H_2$ ) were found to behave similarly as glycolic acid and gave the following results. For Hyd- $H_2$  ( $R=1$ ), Found: H: 3.57, C: 25.25, Ti: 29.38%. For  $R=2$ , Found: H: 3.81, C: 27.95, Ti: 27.44%. Calcd for  $C_4H_8O_5Ti$ ,  $TiO(Hyd) \cdot H_2O$ : H: 4.38, C: 26.11, Ti: 26.02%. For Man- $H_2$  ( $R=2$ ) system, Found: H: 3.57, C: 41.22, Ti: 19.83%. Calcd for  $C_8H_8O_5Ti$ ,  $TiO(Man) \cdot H_2O$ : H: 3.48, C: 41.41, Ti: 20.63%.

##### 5.2.4.2. Reaction of TIP with Lactic Acid

When 3.0 ml of TIP (10 mmol) was mixed with 0.75 ml of lactic acid ( $R=1$ , 10 mmol), followed by adding pure water, exothermic reaction instantly occurred to give a solid mass. However, the solid product was gradually dissolved under stirring, and a clear solution with the concentration of 1.0 M was obtained within a few weeks. The solution was very stable for more than one year. An excess amount of 1-butanol to the solution caused precipitates. The precipitates were separated by filtration, washed several times by 1-butanol, and finally dried *in vacuo*. The elemental analysis of the powder gave the results. Found: H: 2.70, C: 13.12, Ti: 37.62%. Calcd for  $C_3H_8O_7Ti_2$ ,  $Ti_2O_3(Lac) \cdot 2H_2O$ : H: 3.20, C: 14.31, Ti: 38.02%. For  $R=2$ , Found: H: 3.06, C: 16.21, Ti: 30.54%. Calcd for  $C_9H_{18}O_{17}Ti_4$ ,  $Ti_4O_5(Lac)_3 \cdot 3H_2O$ : H: 3.07, C: 18.33, Ti: 32.47%.

##### 5.2.4.3. Reaction of TIP with Oxalic Acid.

3.0 ml of TIP (10 mmol) was directly added into 2.52 g of oxalic acid dihydrate

( $R=2$ , 20 mmol), almost exothermically affording an opaque colloidal solution under stirring. Then, the degree of transparency of the solution increased with time, and finally a clear solution (1 M) was obtained within a few hours. A precipitate was obtained by an addition of excess amount of 2-propanol to the solution, separated by filtration, washed 5 times by 2-propanol to remove unreacted oxalic acid, and finally dried *in vacuo*. In the case of  $R=1$ , the reaction of TIP with Ox- $H_2$  resulted in precipitate, the precipitate was separated by the same manner as  $R=2$ . The elemental analysis of both powders gave the same result. For  $R=1$ , Found: H: 2.22, C: 12.95, Ti: 24.42%. For  $R=2$ , Found: H: 2.12, C: 13.11, Ti: 25.20%. Calcd for  $C_2H_4O_7Ti$ ,  $TiO(Ox) \cdot 2H_2O$ : H: 2.15, C: 12.78, Ti: 25.48%.

#### 5.2.4.4. Reaction of Aqueous Titanate Solutions with Ammonia.

0.6 g of 28 % aqueous ammonia solution ( $R=1$ , 10 mmol) was added to the 20 ml of 0.5 M aqueous solution of TIP-Lac ( $R=1$ ), yielding colorless clear solution. After stirring for 24 h, the addition of large quantity of 2-propanol to the solution caused a precipitate. The precipitate was separated by filtration, washed by 2-propanol, and finally dried under vacuum at room temperature. The elemental analysis of the powder gave the results. Found: H: 4.18, C: 17.58, N: 5.54, Ti: 28.36%. Calcd for  $C_{15}H_{44}N_4O_{28}Ti_6$ ,  $(NH_4)_4Ti_6O_9(Lac)_5 \cdot 4H_2O$ : H: 4.37, C: 17.74, N: 5.52, Ti: 28.28%. For  $R=2$ , Found: H: 5.22, C: 23.00, N: 7.13, Ti: 19.07%. Calcd for  $C_{15}H_{42}N_4O_{21}Ti_3$ ,  $(NH_4)_4Ti_3O_3(Lac)_5 \cdot 3H_2O$ : H: 5.58, C: 23.76, N: 7.34, Ti: 18.94%.

Reaction of TIP-Ox ( $R=2$ ) with ammonia ( $R=2$ ) was found to behave similarly as TIP-Lac- $NH_3$  system and gave the following results. Found: H: 3.48, C: 15.76, N: 8.90, Ti: 15.88%. Calcd for  $C_4H_{10}N_2O_{10}Ti$ ,  $(NH_4)_2TiO(Ox)_2 \cdot H_2O$ : H: 3.43, C: 16.34, N: 9.53, Ti: 16.28%. In the case of TIP-Ox- $NH_3$  ( $R=1:1$ ), a precipitate derived from TIP-Ox ( $R=1$ ) was not dissolved by addition of ammonia. The precipitation was separated by filtration, washed by 2-propanol, and finally dried under vacuum at room temperature. Found: H: 2.96, C: 11.98, N: 6.30, Ti: 23.45%. Calcd for  $C_4H_{14}N_2O_{14}Ti_2$ ,  $(NH_4)_2Ti_2O_3(Ox)_2 \cdot 3H_2O$ : H: 3.44, C: 11.72, N: 6.83, Ti: 23.36%.

#### 5.2.4.5. Dried Powder from Commercial Aqueous Titanate Complex

Commercially available aqueous titanium complex, bis(ammonium lactato)

titanium dihydroxyde:  $[\text{CH}_3\text{CH}(\text{O}-)\text{COONH}_4]_2\text{Ti}(\text{OH})_2$  (ALT, Aldrich, 50 % aqueous solution) was precipitated by addition of excess amount of 2-propanol, and the precipitate was separated by filtration, washed by 2-propanol, and finally dried under vacuum at room temperature. Found: H: 5.50, C: 24.26, N: 7.14, Ti: 19.02%. Calcd for  $\text{C}_{15}\text{H}_{42}\text{N}_4\text{O}_{21}\text{Ti}_3$ , H: 5.58, C: 23.76, N: 7.34, Ti: 18.94%, which were almost the same as those for the sample obtained from TIP-Lac- $\text{NH}_3$  ( $R=2:2$ ) system.

### 5.3. RESULTS

#### 5.3.1. Reaction of TIP with $\alpha$ -Hydroxycarboxylic Acids

Table 5. 1 shows the effect of the carboxylic acids on the preparation of aqueous titanate solutions, together with the pH of the solution before and after TIP addition ( $[\text{Ti}] = 0.1 \text{ M}$ ). The  $\text{p}K_a$  values of the acids are also included in this table.<sup>14, 15</sup>

All of the reaction of TIP with the  $\alpha$ -hydroxycarboxylic acids were exothermic, yielding first white precipitates. The precipitates derived from the TIP-Gly, TIP-Hyd and TIP-Man remained undissolved regardless of  $R$  even after stirring for a long time. On the other hand, the precipitates prepared from the TIP-Lac ( $R=1$  and  $2$ ) and the TIP-Ox ( $R=2$ ) were slowly dissolved to give homogeneous clear solutions within a few weeks for the former and within a few hours for the latter. At least equimolar of lactic acid to Ti ( $R=1$ ) was required to form the aqueous titanate solution, and oxalic acid more than equimolar amounts was needed. Similarly, it was confirmed that aqueous titanate solution could be prepared using citric acid and tartaric acid. Interestingly, the aqueous clear sols were obtained irrespective of the order of addition among TIP, carboxylic acids and water. When a He-Ne laser (632.8 nm) was irradiated to these clear solutions, the trace of the light passage through the solutions was clearly observed, indicative of the colloidal nature. The pH values of the solutions or supernatant ranged from 0.84 to 2.34, which are slightly smaller than those of the solutions of  $\alpha$ -hydroxycarboxylic acid before TIP addition. The  $\text{p}K_a$  values of the acids did not have nothing to do with whether clear solutions were prepared or not. However, the substituents ( $X$  and  $Y$  in Fig. 5. 1) had a crucial effect on the formation of the aqueous solutions.

Interestingly, the precipitates were dissolved to give clear solutions when equimolar of ammonia, alkylamines and quaternary ammonium hydroxides was added to the

suspension. For instance, it was confirmed that tetramethylammonium dioxalato oxotitanate (IV) trihydrate:  $[(\text{CH}_3)_4\text{N}]_2[\text{TiO}(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$  could be prepared from TIP-Ox-TMAOH ( $R=2:2$ ).<sup>16</sup>

Table 5. 1. Effect of  $\alpha$ -hydroxycarboxylic acids on the preparation of aqueous titanate solutions.

Carboxylic acids	$\text{p}K_{\text{a}}$	$R$	$\text{pH}^{\text{a}}$	State ( $\text{pH}^{\text{b}}$ )
Gly- $\text{H}_2$	3.62	1	2.25	Precipitation (2.34)
		2	2.09	Precipitation (2.06)
Lac- $\text{H}_2$	3.64	1	2.08	Clear solution (2.03)
		2	1.94	Clear solution (1.86)
Hyd- $\text{H}_2$	3.77	1	2.32	Precipitation (1.77)
		2	2.18	Precipitation (1.39)
Man- $\text{H}_2$	3.41	1	2.01	Precipitation (1.71)
		2	1.86	Precipitation (1.38)
Ox- $\text{H}_2$	1.27	1	1.07	Precipitation (1.21)
		2	0.92	Clear solution (0.84)

<sup>a</sup> aqueous solution before TIP addition

<sup>b</sup> for homogeneous or supernatant solutions after TIP addition; total titanium concentration was 0.1 M

### 5.3.2. Chemical Composition of the Powder Prepared from TIP- $\alpha$ -Hydroxycarboxylic Acids

Elemental analysis was conducted in order to investigate the composition of the isolated solution species or the precipitates. Table 5. 2 shows the estimated chemical compositions of the powder prepared from aqueous sol of TIP- $\alpha$ -carboxylic acids, together with the ligand/Ti ratios (which is shown by  $R'$ ) that were based on the estimated composition. There were some cases that the calculated values were somewhat different from the observed values, indicating that the powder would not be a pure product but a mixture. Carboxylates were recognized in all samples even after

washing, suggesting that these acids are incorporated in the structural unit formed by Ti. If a reaction proceeded with its stoichiometry, the  $R'$  should be equal to  $R$ . Except for the TIP-Ox-NH<sub>3</sub> system, the ligand/Ti ratio ( $R'$ ) was smaller than the starting ratio  $R$ . In the TIP- $\alpha$ -hydroxycarboxylic acids except Ox-H<sub>2</sub>, the  $R'$  ranged from 0.5 to 1 regardless of  $R$ , and as the structure of the carboxylic acids was larger, the  $R'$  tended to be close to 1. From the magnitude of the  $R'$ , the order, Man-H<sub>2</sub> > Hyd-H<sub>2</sub> > Lac-H<sub>2</sub> > Gly-H<sub>2</sub> might be considered for the chelate strength and stability to Ti atom. The powder prepared from the commercially available aqueous titanate solution (ALT) had the same composition as that from the TIP-Lac-NH<sub>3</sub> ( $R=2:2$ ), but did not consistent to the nominal composition of the reagent  $[\text{CH}_3\text{CH}(\text{O}-)\text{COONH}_4]_2\text{Ti}(\text{OH})_2$ , suggesting that the lactato complex tended to release lactato ligands to polymerize. In the case of TIP-Lac system, clear solutions could be obtained even when 2-propanol was used as a solvent instead of water. The powder prepared by evaporation of the solution of TIP-Lac ( $R=2$ ) under reduced pressure had a composition of Ti: Lac = 1:2. When the same reaction was conducted in 2-propanol containing four times molar of water to Ti, a homogeneous solution was obtained. However the powder separated by evaporation of the solution was found to have a composition of Ti: Lac = 1:1. These observations suggest that the presence of water accelerated the hydrolysis and polycondensation of the Ti-Lac complex to yield the polymerized species and free lactic acid that could be removed in vacuo. Therefore, hydrolysis and polycondensation of Ti-Lac complex are thought to proceed in water solvent.

On the other hand, the powder prepared from TIP-Ox ( $R=1$  and 2) was estimated as  $\text{TiO}(\text{Ox}) \cdot 2\text{H}_2\text{O}$ , but the powder from TIP-Ox-NH<sub>3</sub> ( $R=1:1$  and 2:2) kept their stoichiometry. While the powder prepared from the TIP-Ox-NH<sub>3</sub> ( $R=1:1$  and 2:2) was readily soluble in water, the powder from both TIP-Lac ( $R=1$  and 2) and TIP-Lac-NH<sub>3</sub> ( $R=1:1$  and 2:2) took time to dissolve in water. These observations indicated that the chelate effect of oxalato ligand was larger than that of the other  $\alpha$ -hydroxycarboxylato ligands such as lactate, and stable oxalato titanium complex would be formed.

Table 5. 2. Estimated chemical composition of the powder prepared from TIP- $\alpha$ -hydroxycarboxylic acids.

System	$R$	Estimated chemical composition <sup>a</sup>	Ligand/ Ti ratio ( $R'$ )
TIP-Gly	1	$\text{Ti}_2\text{O}_3(\text{Gly})\cdot\text{H}_2\text{O}$	0.5
	2	$\text{Ti}_3\text{O}_4(\text{Gly})_2\cdot 2\text{H}_2\text{O}$	0.7
TIP-Lac	1	$\text{Ti}_2\text{O}_3(\text{Lac})\cdot 2\text{H}_2\text{O}$	0.5
	2	$\text{Ti}_4\text{O}_5(\text{Lac})_3\cdot 3\text{H}_2\text{O}$	0.8
TIP-Lac-NH <sub>3</sub>	1:1	$(\text{NH}_4)_4\text{Ti}_6\text{O}_9(\text{Lac})_5\cdot 4\text{H}_2\text{O}$	0.8
	2:2	$(\text{NH}_4)_4\text{Ti}_3\text{O}_3(\text{Lac})_5\cdot 3\text{H}_2\text{O}$	1.7
ALT	–	$(\text{NH}_4)_4\text{Ti}_3\text{O}_3(\text{Lac})_5\cdot 3\text{H}_2\text{O}$	1.7
TIP-Hyd	1 or 2	$\text{TiO}(\text{Hyd})\cdot\text{H}_2\text{O}$	1
TIP-Man	2	$\text{TiO}(\text{Man})\cdot\text{H}_2\text{O}$	1
TIP-Ox	1 or 2	$\text{TiO}(\text{Ox})\cdot 2\text{H}_2\text{O}$	1
TIP-Ox-NH <sub>3</sub>	1:1	$(\text{NH}_4)_2\text{Ti}_2\text{O}_3(\text{Ox})_2\cdot 3\text{H}_2\text{O}$	1
	2:2	$(\text{NH}_4)_2\text{TiO}(\text{Ox})_2\cdot\text{H}_2\text{O}$	2

<sup>a</sup>based on elemental analysis

### 5.3.3. TG-DTA

Decomposition behaviors of the powder prepared from the TIP-Lac-NH<sub>3</sub> ( $R=2:2$ ) and TIP-Ox-NH<sub>3</sub> ( $R=2:2$ ) are shown in Fig. 5. 2. In Fig. 5. 2(a), two main exothermic peaks with gentle mass loss were observed in the TIP-Lac-NH<sub>3</sub> system. The TG-DTA thermograms of the powder prepared from commercial ALT were almost the same as that of the TIP-Lac-NH<sub>3</sub> ( $R=2:2$ ), suggesting the same composition and structure. In Fig. 5. 2(b), the decomposition behavior of TIP-Ox-NH<sub>3</sub> ( $R=2:2$ ), was similar to that of  $(\text{NH}_4)_2\text{TiO}(\text{C}_2\text{O}_4)_2\cdot\text{H}_2\text{O}$ <sup>17</sup> and quite different from the TIP-Lac-NH<sub>3</sub> system. Three steps in mass loss were observed in the TG curve. The first two steps corresponded to the desorption and decomposition of water and ammonia and oxalato ligand. The last weight reduction was about 6 wt%, corresponding to the loss of one molecule of water.

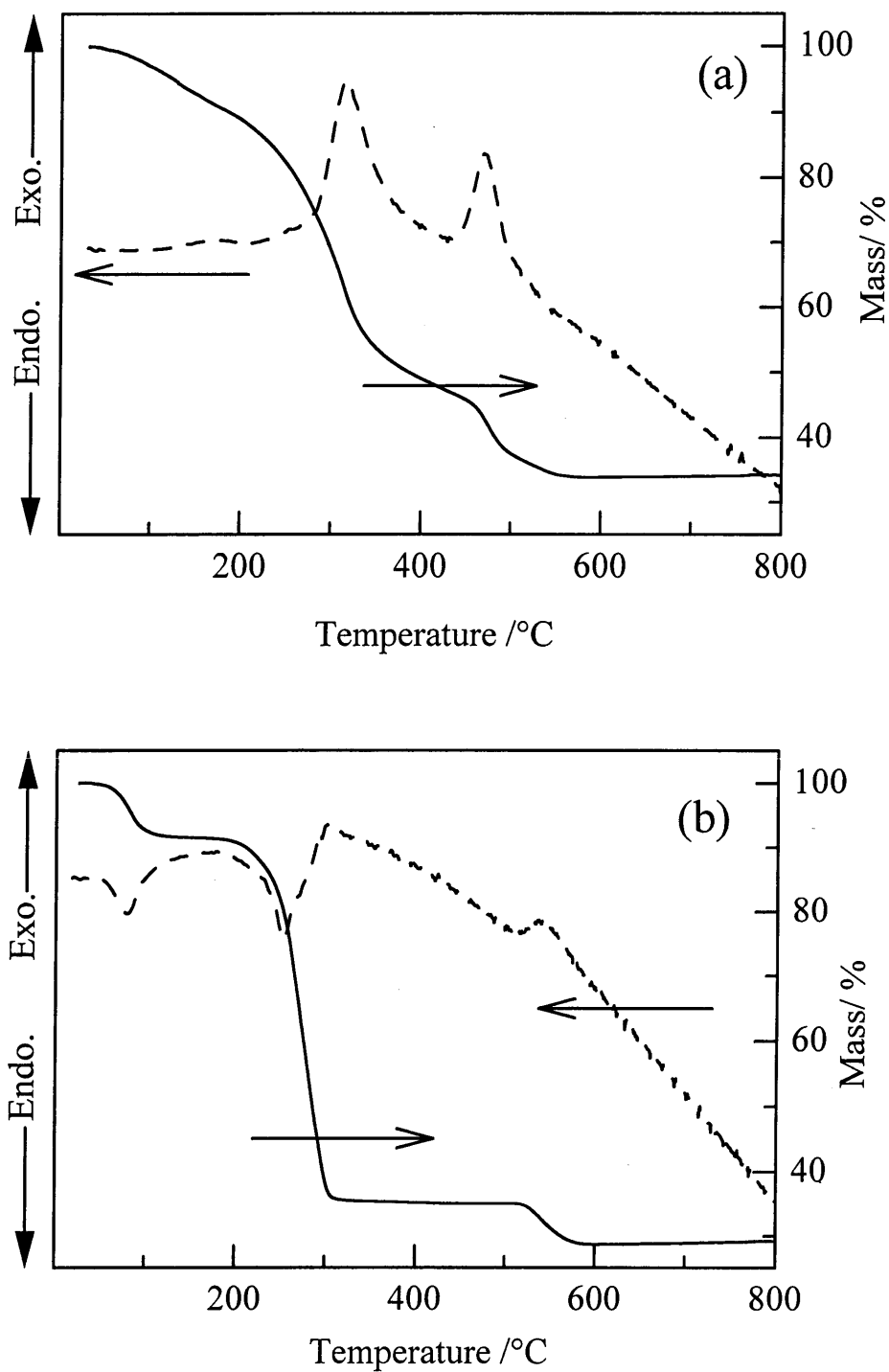


Figure 5. 2. TG-DTA of the powder prepared from the sols of (a) TIP-Lac-NH<sub>3</sub> ( $R=2:2$ ) and (b) TIP-Ox-NH<sub>3</sub> ( $R=2:2$ ).

### 5.3.4. IR and Raman Spectra

Figure 5. 3 shows the IR spectra of the powder prepared from aqueous solution of TIP-Lac and TIP-Lac-NH<sub>3</sub> system. The spectrum for the powder prepared from Titanium(IV) bis(ammonium lactato) dihydroxide : [CH<sub>3</sub>CH(O-)CO<sub>2</sub> NH<sub>4</sub>]<sub>2</sub>Ti(OH)<sub>2</sub> (Aldrich, 50 % solution : ALT) is also shown for comparison. Lactic acid (Fig. 5. 3(f)) showed its characteristic absorption bands at 1733 and 1220 cm<sup>-1</sup> assignable to the stretch vibration of  $\nu(\text{C=O})$  and  $\nu(\text{C(O)-O})$ , respectively. The bands at 1130 and 1060 cm<sup>-1</sup> can be assigned to vibration of the methyl group  $\nu(\text{CH}_3\text{-C})$  and the  $\nu(\text{C-O})$  of the

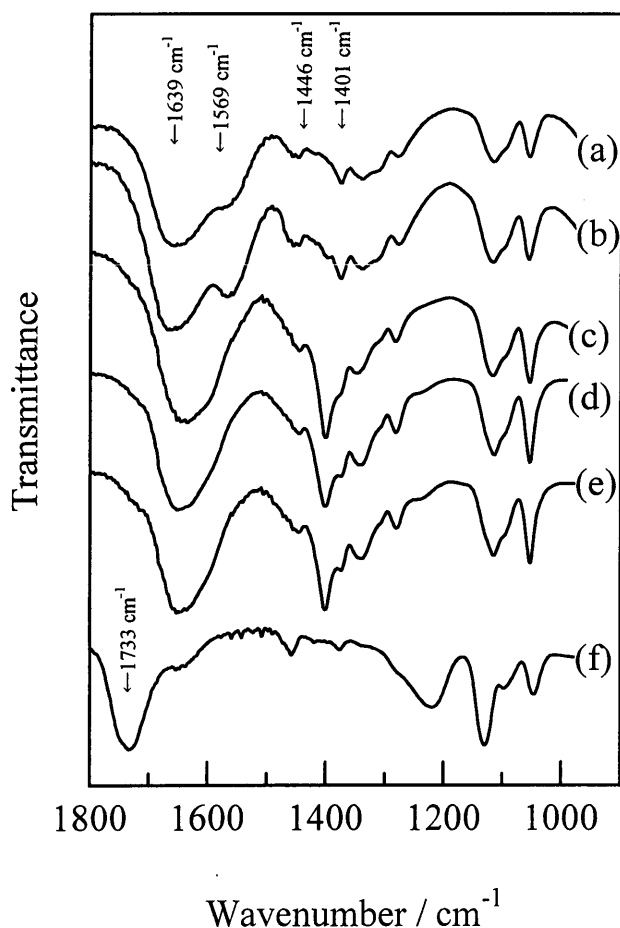


Figure 5. 3. IR spectra of the powder prepared from (a) TIP-Lac ( $R=1$ ), (b) TIP-Lac ( $R=2$ ), (c) TIP-Lac-NH<sub>3</sub> ( $R=1:1$ ), (d) TIP-Lac-NH<sub>3</sub> ( $R=2:2$ ) and (e) ALT, and of (f) neat lactic acid (liquid film method).

$\alpha$ -hydroxy group. When it reacted with TIP at  $R=1$  and 2, the  $\nu(\text{C}=\text{O})$  at  $1733\text{ cm}^{-1}$  was shifted to  $1659$  and  $1569\text{ cm}^{-1}$  as shown in Fig. 5. 3(a, b). The spectra showed absorption bands at  $1659$  and  $1569\text{ cm}^{-1}$  assignable to the antisymmetric stretch modes of the chelate and non-chelate (free lactate ion), respectively. Thus, two modes of interaction with Ti were observed in the TIP-Lac system. In Fig. 5. 3(c-e), the clear peak at  $1400\text{ cm}^{-1}$ , which was found for ammonium derivatives, is attributable to the bending vibration of  $\delta(\text{N-H})$  in  $\text{NH}_4^+$ . The spectra for TIP-Lac- $\text{NH}_3$  (Fig. 5. 3(c, d)) was completely the same as that for ALT.

Figure 5. 4 shows the Raman spectra of TIP-Lac- $\text{NH}_3$  system and ALT, and those of anatase, rutile and layered titanate  $\text{H}_2\text{Ti}_4\text{O}_9$  are also shown for comparison. The patterns

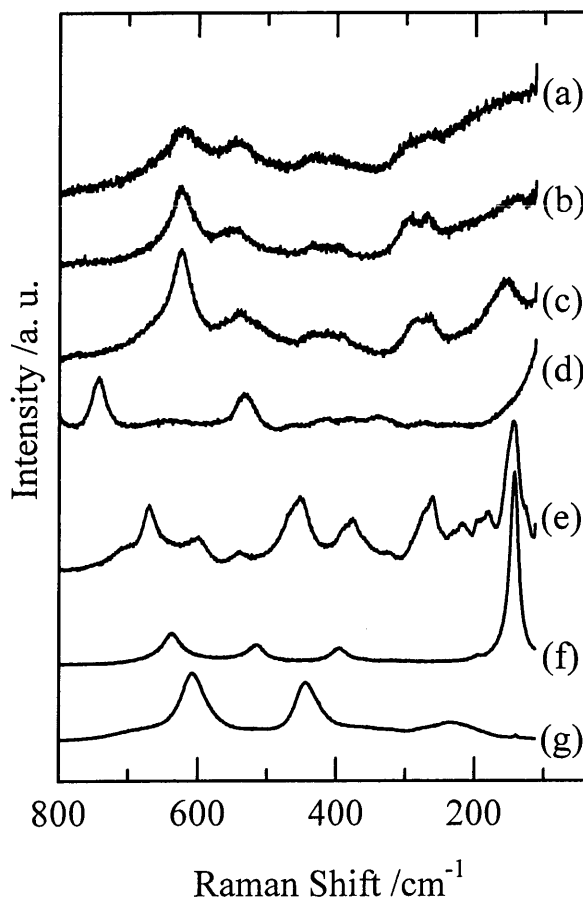


Figure 5. 4. Raman spectra of the powder prepared from aqueous sols of (a) TIP-Lac- $\text{NH}_3$  ( $R=1:1$ ), (b) TIP-Lac- $\text{NH}_3$  ( $R=2:2$ ), (c) ALT, (d)  $\text{H}_2\text{Ti}_4\text{O}_9$ , (e) anatase and (f) rutile.

for these titanate sols were completely different from those of lactic acid itself (Fig. 5. 4(d)), anatase (Fig. 5. 4(f)), rutile (Fig. 5. 4(g)) layered  $\text{H}_2\text{Ti}_4\text{O}_9$  (Fig. 5. 4(e)), and titanitic acid ( $\text{TiO}(\text{OH})_2$ , not shown) that prepared by hydrolysis of TIP, indicating the presence of a certain Ti-O framework controlled by the coordination of lactato ligands.

### 5.3.5. Liquid State NMR

Liquid state  $^{13}\text{C}$  NMR was measured to make sure of the state of the aqueous titanate sols. In the TIP-Lac ( $R=1$  or  $2$ ) system, the patterns were almost the same as that of free lactic acid. In the case of ALT and TIP-Lac- $\text{NH}_3$  ( $R=2:2$ ), the clear signals at 85 and 191 ppm assignable to methine and carbonyl carbon were observed but different from those of free lactic acid (69 and 181 ppm, respectively). The signals assignable to free ammonium lactate were also detected. These observations suggest that lactate acted as bidentate ligands, but existed equilibrium between lactato ligand and free lactate ion in aqueous medium.

On the other hand, the signals from carbonyl carbons of the TIP-Ox and TIP-Ox- $\text{NH}_3$  systems were observed only at 170 ppm, which is different from that of free oxalic acid (164 ppm) and ammonium oxalate (176 ppm), indicating that the oxalato complex was more stable than the lactato complex.

### 5.3.6. Preparation of $\text{TiO}_2$ Thin Films by Sol-Gel Technique

#### 5.3.6.1. Effect of Solution Species

Using the aqueous sols ( $[\text{Ti}] = 1.0 \text{ M}$ ) described above,  $\text{TiO}_2$  thin films were prepared on glass plate by spin-coating method. Figure 5. 5 shows the influence of the starting solutions on the crystal phase of  $\text{TiO}_2$  films heat-treated at 600 °C for 5 coatings. Whereas the films fired at 600 °C consisted of single-phase anatase, the film prepared from TIP-citric acid- $\text{NH}_3$  system gave both anatase and rutile. It is reported that the formation of rutile at lower temperature such as 600 °C partly related to the organic content of the chelate.<sup>1</sup> Comparing the intensities of the diffraction peaks of the films with the data from JCPDS, it was observed that the intensity of the (004) diffraction peak in the TIP-Lac- $\text{NH}_3$  ( $R=1:1$ ) system was rather strong and the intensity of the (101) diffraction peak was relatively weak instead, suggesting the orientation to (00 $\ell$ ). This strong orientation was not observed from ATL or the TIP-Lac- $\text{NH}_3$  ( $R=2:2$ ) and the

other aqueous sols used in this study. The film prepared from TIP-TMAOH ( $R=0.4$ ) seemed highly oriented to (101) but it was a cleavage plane. Therefore, it was found that the crystallographic orientation of the film was characteristic of the TIP-Lac-NH<sub>3</sub> ( $R=1:1$ ) system.

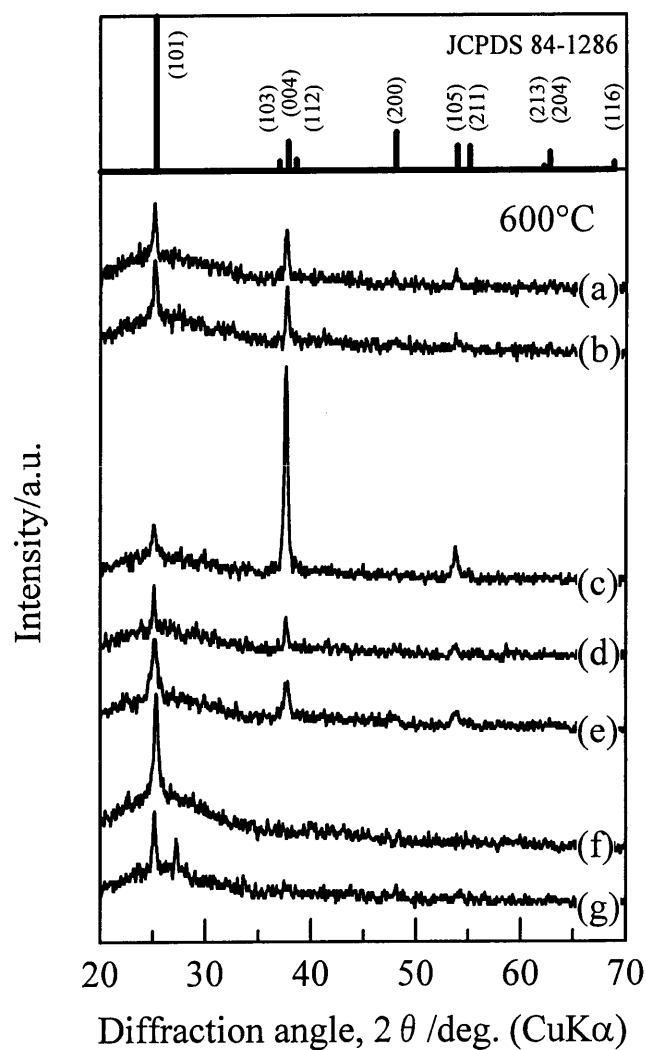


Figure 5. 5. XRD patterns of the thin films prepared at 600 °C from aqueous sols of (a) TIP-Lac ( $R=1$ ), (b) TIP-Lac ( $R=2$ ), (c) TIP-Lac-NH<sub>3</sub> ( $R=1:1$ ), (d) TIP-Lac-NH<sub>3</sub> ( $R=2:2$ ) (e) ALT, (f) TIP-TMAOH ( $R=0.4$ ) and (g) TIP-citric acid-NH<sub>3</sub> ( $R=1:1$ ).

### 5.3.6.2. Effect of Heat Treatment on the Crystallographic Orientation of $\text{TiO}_2$ Films

Figure 5. 6 shows the effect of firing temperature on the XRD patterns of the  $\text{TiO}_2$  thin films prepared from the TIP-Lac- $\text{NH}_3$  ( $R=1:1$ ) sol. Pure anatase films preferentially oriented to (004) plane were obtained from 500 to 700 °C, but the films prepared at 400 °C were brownish, indicative of carbonaceous residue. The intensity of the (004) peak was increased with firing temperature. The refractive index of the film fired at 700 °C was 2.54, which was comparable to the value of  $n_0$  (2.5612), and is considered to be the highest value in sol-gel method.

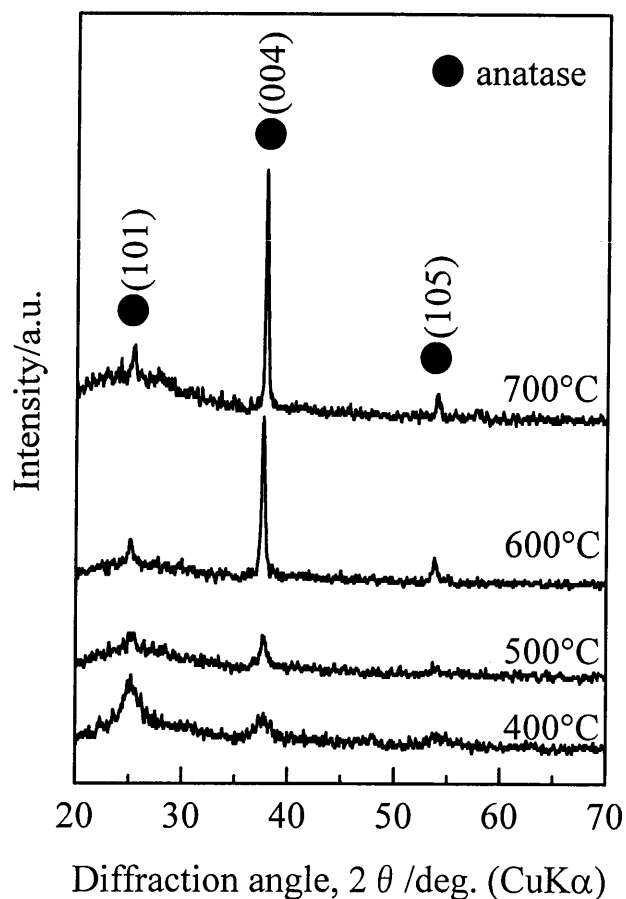


Figure 5. 6. Firing temperature dependence of XRD patterns of the  $\text{TiO}_2$  thin films from 1.0 M TIP-Lac- $\text{NH}_3$  ( $R=1:1$ ) system.

When the film prepared at 400 °C was fired at 700 °C for 30 min, the intensity of the (004) diffraction peak became strong as shown in Fig. 5. 7, suggesting that the small anatase grain suitable for (00 $\ell$ ) orientation may already existed in the film, and the further heat-treatment at higher temperature accelerated the grain growth. The heating rate of the film on firing had no effect on the crystal orientation.

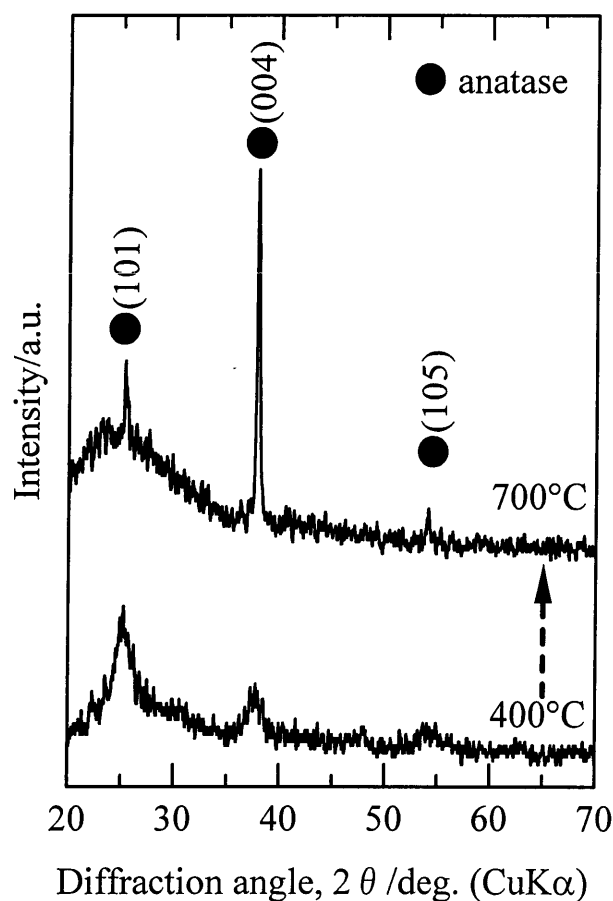


Figure 5. 7. Effect of post heat-treatment of the film prepared at 400 °C for 5 coatings.

### 5.3.7. Effect of Substrate on the Crystallographic Orientation of $\text{TiO}_2$ Films

Kato et al. reported that the (004) orientation was induced by the generation of carbon dioxide and the thermal expansion difference in the quartz-glass substrate and  $\text{TiO}_2$  film.<sup>18, 19</sup> In this study, five kinds of substrates (Corning #7059, #1737, quartz-glass, single crystal  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$ ) were examined. Figure 5. 8 shows the XRD patterns of  $\text{TiO}_2$  thin films coated 5 times on various substrates. No significant differences in orientation were observed at 600 °C. While single-phase of rutile was obtained on  $\text{SiO}_2$  substrate at 1000 °C, both anatase and rutile were observed on  $\text{Al}_2\text{O}_3$  substrate. Therefore, it is concluded that the substrate had no effect on the anatase crystal orientation.

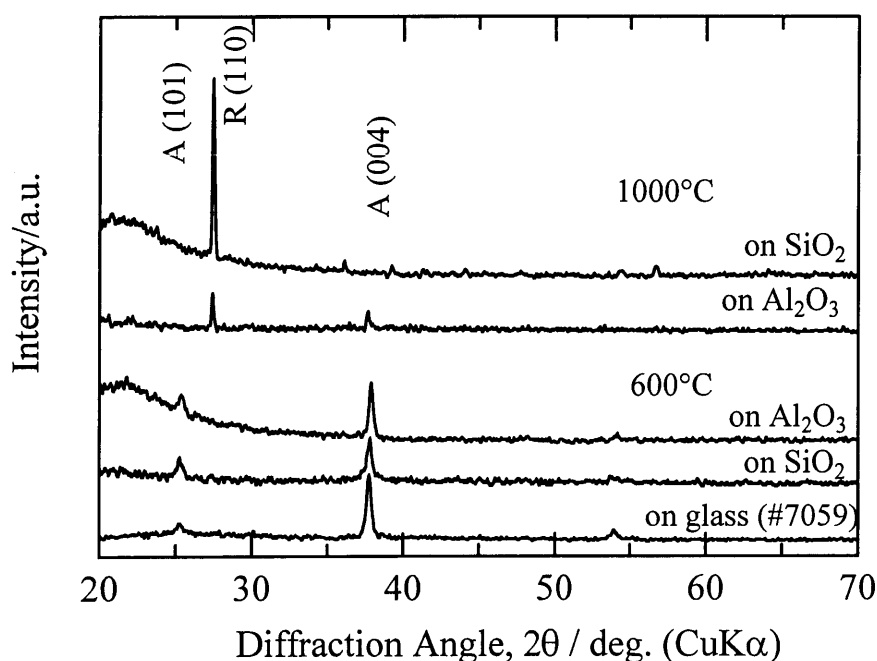


Figure 5. 8. Effect of substrates on XRD patterns of the thin films prepared at 600 and 1000 °C from 1.0 M TIP-Lac- $\text{NH}_3$  ( $R=1:1$ ) system.

### 5.3.8. TEM Observation

Figure 5. 9 shows TEM images of the  $\text{TiO}_2$  thin film prepared at 700 °C from 1 M TIP-Lac- $\text{NH}_3$  ( $R=1:1$ ). The film consisted of pure anatase with granular grain about 40 nm. The selected-area electron diffraction (SAD) pattern revealed the existence of (101) as well as (004) diffraction of anatase, suggesting the incomplete orientation. It was confirmed that the anatase film prepared from aqueous sol of TIP-TMAOH ( $R=0.4$ ) also consisted of granular grain with 30 nm.

Figure 5. 10 shows the SAD pattern of the powder prepared at 200 and 400 °C for 30 min. Both patterns showed the diffraction of anatase, indicating that anatase already formed at 200 °C.

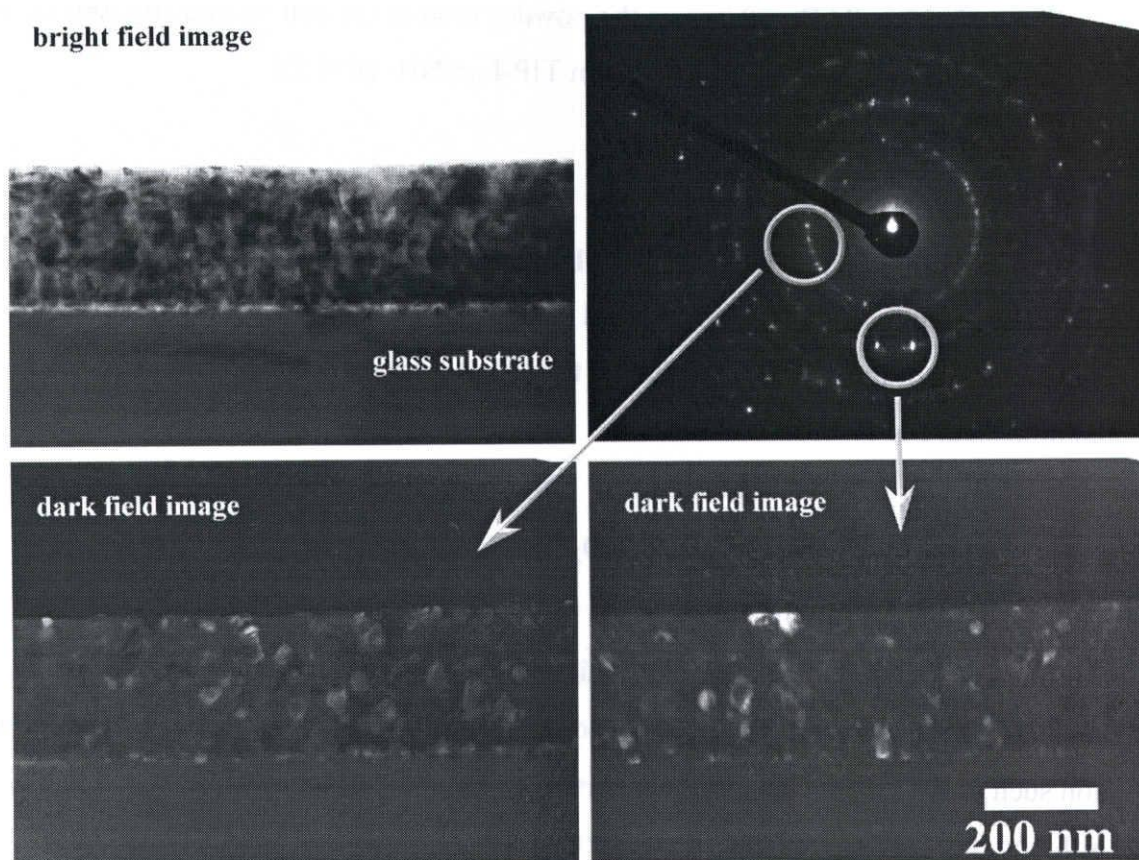


Figure 5. 9. TEM images and SAD pattern of the  $\text{TiO}_2$  thin film fired at 700 °C from 1.0 M TIP-Lac- $\text{NH}_3$  ( $R=1:1$ ) system.

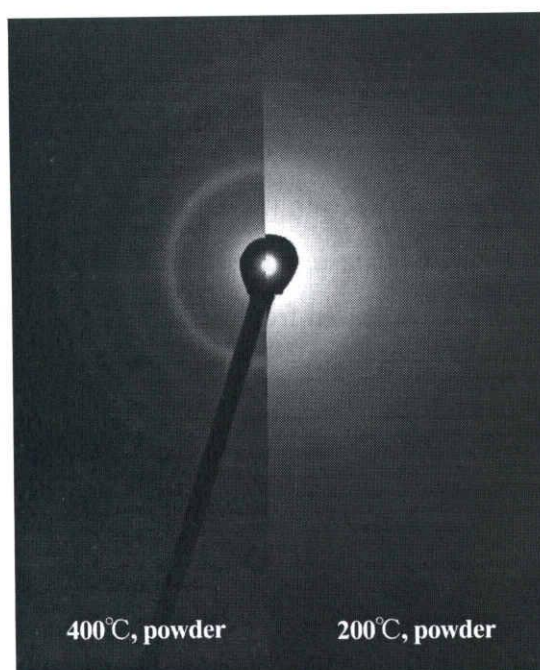
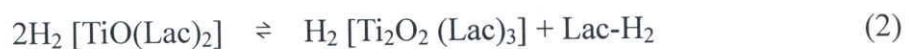
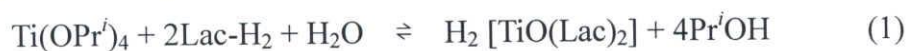


Figure 5. 10. SAD patterns of the powder fired at (a) 400 °C and (b) 200 °C for 30 min. The powder was prepared from TIP-Lac-NH<sub>3</sub> (*R*=1:1).

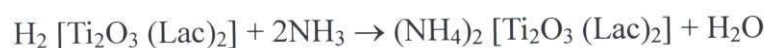
## 5.4. DISCUSSION

### 5.4.1. Reaction of TIP with Carboxylic Acids in Water

The reaction of TIP with lactic acid in water may consist of both hydrolysis of TIP and chelation of the acid to Ti, although the actual reaction is considered to be more complicated. For *R*=2,



In aqueous medium, there may exist a dissociation equilibrium between lactato complex and lactic acid as shown by eq. (2). Accordingly, excess amount of lactic acid or lactate ion such as *R*=2 would act as a stabilizer of the complex. If ammonia is added to the solution (eq. (1)), neutralization reaction occurs.



Lactic acid as a chelate ligand is considered to have a moderate chelating ability. The lactato complexes of titanium were hydrolyzed and polymerized to some extent (eq. (3)),

forming a cluster. The cluster is stabilized by the chelates and becomes  $\text{TiO}_2$  by heat treatment. It can be thought that the geometric structure of the cluster mainly depends on R and type of the chelate used and pH. On the other hand, although the reaction of TIP with oxalic acid is considered to be the same manner described above, the stability constant of the oxalato complex would be much larger than that of the lactato complex. Actually, it is reported that the stability constants of some oxalato complex are larger than that of lactato's.<sup>15</sup>

#### 5.4.2. Influence of a Cluster Formation on the Crystallographic Orientation and Particle Growth of $\text{TiO}_2$ Thin Films

There are several papers relating to the  $\text{TiO}_2$  films with oriented (004) plane. Koumoto et al.<sup>20</sup> reported that the crystal planes (004) tetragonal unit cell were highly oriented parallel to the substrate by liquid phase deposition (LPD) process using aqueous  $(\text{NH}_4)_2\text{TiF}_6$  solution, and the orientation was due to the heterogeneous surface nucleation and growth process.

In conventional sol-gel technique using alcoholic solution of chelate-stabilized titanium alkoxides, the nucleation and grain growth of the gel films are generally caused by decomposition of the chelates under heat treatment, because hydrolysis and condensation of the precursor solution are highly controlled by chelate ligands. Concerning the  $\text{TiO}_2$  thin films prepared from 2-propanol sol of TIP-DEA- $\text{H}_2\text{O}$ , Ohya et al.<sup>21</sup> reported that the way of particle growth strongly depended on the heating rate. Columnar grains were grown by rapid heating and granular grains by slow heating.

However, in the TIP-Lac- $\text{NH}_3$  ( $R=1:1$ ) and TIP-TMAOH ( $R=0.4$ ) systems, TEM observation showed that the films consisted of granular grains in spite of rapid heating. It is proposed that these differences are contributed to the solution species. In aqueous media, TIP is hydrolyzed and polymerized to form cluster in water solvent. Since the cluster or grain had already been in the film, it can be thought that the particle growth and crystallization would follow the geometric structure of the cluster, and the rate of particle growth during heating would be slower than that of the conventional gel derived from stable chelate compounds. As a result, it is considered that the crystallographic orientation of the film depended on the geometric structure of the cluster irrespective of the kind of substrates, and the formation of granular grain was preferred regardless of

heating rate. In the case of TIP-TMAOH system, the aqueous titanate sol with the composition of  $[(\text{CH}_3)_4\text{N}]_2[\text{Ti}_6\text{O}_{13}]$  has a layered structure, and the film prepared from which crystallized as low as 350 °C and had a excellent crystallinity small granular grains.

Therefore, the crystal form, orientation and crystallization of the  $\text{TiO}_2$  films were found to depend strongly on the chemical species of the starting solutions. However, the relation between the structure of the cluster prepared from TIP-Lac- $\text{NH}_3$  ( $R=1:1$ ) and the evolution of (004) plane remained unclear.

## 5.5. CONCLUSIONS

Aqueous titanate solutions were prepared by direct reaction of TIP with  $\alpha$ -hydroxycarboxylic acids in the presence of water. It was found that the chelate-stabilized species in water were polymerized to lead to a cluster. The  $\text{TiO}_2$  film fired at 700 °C, which was prepared from TIP-LA- $\text{NH}_3$  ( $R=1,1$ ), was single-phase anatase with a strong orientation of (004) plane and had a high refractive index of 2.54, which was considered to be the highest value in sol-gel method. The crystal form and crystallographic orientation of the  $\text{TiO}_2$  films were found to depend strongly on the structure of the chemical species of the starting solutions, but the relation between the chemical structure and the orientation of  $\text{TiO}_2$  film remained unclear.

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## *Chapter 6*

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### **CONCLUDING REMARKS AND FUTURE PERSPECTIVES**

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## Chapter 6

### CONCLUDING REMARKS AND FUTURE PERSPECTIVES

It has been found that the layered titanate sols could be easily prepared by the reaction of titanium isopropoxide with basic alkylamines and alkylammonium hydroxides in water, using an acid-base reaction between the amines and titanate acid derived from the alkoxide to yield ammonium titanates. Both the basicity of the amines and the sizes of the conjugate acid (ammonium cations) have been found to be crucial factors to determine whether the aqueous titanate solutions can be prepared. Similarly, aqueous oxo metallate solutions of V, Nb, Ta, Al, Si and Sn are easily prepared from the corresponding alkoxides. The chemical species in the titanate solutions were found to be a colloidal particle or sheet (15 nm) with a layered structure that is tetramethylammonium (TMA<sup>+</sup>) salts of  $H_xTi_{(2-x/4)}O_{4-x/4}$ . To our knowledge, this is the first report on the preparation of exfoliated, layered alkylammonium titanates by a solution method at room temperature. These aqueous metallate solutions are completely free from halogens, alkaline metal ions and chelates, and can be widely used as a source material to prepare various titanium compounds including  $K_2Ti_6O_{13}$  and  $KTiOPO_4$  (KTP). The solutions through sol-gel technique, may realize a novel, environmentally-friendly synthetic process of ceramic films, which can be applied to the preparation of photocatalysts, zeolites, optical and electronic materials.

Titania ( $TiO_2$ ) thin films from the aqueous solutions have been prepared by dip- or spin-coating method, and fully characterized. Chelate-modified aqueous titanate sols were also examined for comparison. The  $TiO_2$  films prepared from the TIP-TMAOH solution were already crystallized at 350 °C to anatase form and those formed at 600 °C had high transparency and higher refractive indices of 2.40. The pure anatase form was sustained up to 850 °C. Interestingly, it was found that (004) preferentially oriented anatase films with much higher refractive index of 2.54 were obtained at 700 °C from TIP-Lactic acid-  $NH_3$  (1:1:1) aqueous sol. Thus dense anatase film is of great interest

because oxide films prepared by sol-gel method usually tend to become porous. This index is considered to be the highest value observed for sol-gel derived  $\text{TiO}_2$  films. This crystallographic orientation was characteristic of the TIP-Lactic acid- $\text{NH}_3$  (1:1:1) system, and was not affected by kinds of substrates used and heating rate of the film. Therefore, it was found that the crystallographic orientation might depend strongly on the structure of the chemical species in the precursor solutions.

UV irradiation on the films prepared by a spin-coating method using aqueous titanate sols with layered structure has been investigated. Although photoirradiation to the gel film did not accelerate the crystallization of anatase, the film became insoluble in any solvent, and had a high refractive index of around 2.0 and a pencil hardness of 2H. It has been found that these phenomena were caused by the photocatalytic decomposition of alkylammonium ions located between the titanate sheets to form  $\text{H}_x\text{Ti}_{(2-x/4)}\text{O}_4$ . The film absorbs the light below 300 nm and can be applied to not only a surface modifier (hard coating) of plastics but also an UV cut film.

Lately, thin-film ceramics have become the center of wide interest, and it seems that as energy and global environmental issues are attracting the attention, solution methods such as sol-gel processing become more important. In the near future, preparation of ceramic thin films from aqueous solution will become the main current. All functional materials would be prepared from the aqueous solutions of the corresponding compounds. In this study, the aqueous solutions of Groups 4 and 5 have been developed. They are generally sparingly soluble in water by nature but the component elements are found in many functional materials. Research in this field may tend to be focused on the characterization of the final products. However, it is obvious that since the properties of starting materials have great influence on the final products (ceramics), we have to concentrate the solution chemistry of them on getting further information.

## *List of Publications*

1. **T. Ohya**, M. Ito, K. Yamada, T. Ban, Y. Ohya, and Y. Takahashi, "Aqueous Titanate Sols from Ti alkoxide- $\alpha$ -Hydroxycarboxylic Acid System and Preparation of Titania Films from the Sols", *J. Sol-Gel Sci. Technol.*, submitted.
2. **T. Ohya**, A. Nakayama, T. Ban, Y. Ohya, and Y. Takahashi, "Effect of Photoirradiation on the Properties of Layered Titanate Thin Films from Transparent Aqueous Titanate Sols", *Bull. Chem. Soc. Jpn.*, **76**, 429-435 (2003).
3. **T. Ohya**, A. Nakayama, Y. Shibata, T. Ban, Y. Ohya, and Y. Takahashi, "Preparation and Characterization of Titania Thin Films from Aqueous Solutions", *J. Sol-Gel Sci. Technol.*, **26**, 799-802 (2003).
4. **T. Ohya**, M. Kabata, T. Ban, Y. Ohya, and Y. Takahashi, "Effect of  $\alpha$ -Hydroxyketones as Chelate Ligands on Dip-Coating of Zirconia Thin Films", *J. Sol-Gel Sci. Technol.*, **25** 43-50 (2002).
5. **T. Ohya**, A. Nakayama, T. Ban, Y. Ohya, and Y. Takahashi, "Synthesis and Characterization of Halogen-free, Transparent, Aqueous Colloidal Titanate Solutions from Titanium Alkoxide", *Chem. Mater.*, **14**, 3082-3089 (2002).
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7. Y. Takahashi, A. Ohsugi, T. Arafuka, **T. Ohya**, T. Ban, and Y. Ohya, "Development of New Modifiers for Titanium Alkoxide-Based Sol-Gel Process", *J. Sol-Gel Sci. Technol.*, **17**, 227-238 (2000).

## *Oral Presentation*

1. Effect of Chelate Ligands on Dip-Coating of  $\text{ZrO}_2$  Thin Films,  
T. Ohya, T. Ban, Y. Ohya, and Y. Takahashi,  
11<sup>th</sup> Fall Meeting of The Ceramic Society of Japan  
(Nagoya Univ., Nagoya, Japan, October, 1998), p. 386, 2J12, 1998.
2. Effect of Chelate Ligands on Dip-Coating of  $\text{ZrO}_2$  Thin Films (Part II),  
T. Ohya, T. Ban, Y. Ohya, and Y. Takahashi,  
The 37<sup>th</sup> Symposium on Basic Science of Ceramics  
(The Hotel Shigyokuen, Kofu, Japan, January, 1999), p. 306-307, 2C-9, 1999.
3. Photoirradiation to the Gel Films Derived from Imine-Alkoxide System and Its Effect,  
T. Ohya, T. Arafuka, T. Ban, Y. Ohya, and Y. Takahashi  
Annual Meeting of The Ceramic Society of Japan, 1999  
(Seikei Univ., Tokyo, Japan, March, 1999), p. 496, 2J30, 1999.
4. Interaction between  $\alpha$ -Hydroxyketones and Metal Alkoxides,  
T. Ohya, N. Tsugawa, T. Ban, Y. Ohya, and Y. Takahashi  
Annual Meeting of The Ceramic Society of Japan, 2000  
(Tohoku Univ., Sendai, Japan, March, 2000), p. 79, 1H21, 2000.
5. Preparation of Aqueous Solutions of Transition Metals in Groups 4 and 5,  
T. Ohya, A. Nakayama, T. Ban, Y. Ohya, and Y. Takahashi,  
13<sup>th</sup> Fall Meeting of The Ceramic Society of Japan (Kitakyushu International Conference Center, West Japan General Exhibition Center, Kitakyushu, Fukuoka, Japan, October, 2000), p. 177, 2I16, 2000.
6. Preparation and Characterization of Aqueous Titanate Solutions,  
T. Ohya, A. Nakayama, T. Ban, Y. Ohya, and Y. Takahashi  
79<sup>th</sup> Chemical Society of Japan National Meeting, (Konan Univ., Kobe, Japan,

March 2001), p. 258, 2E2 11, 2001.

7. Effect of Addition of Saccharides on Dip-coating of  $\text{TiO}_2$  Thin Films from Aqueous Solutions,  
A. Nakayama, T. Ohya, T. Ban, Y. Ohya, and Y. Takahashi  
32<sup>nd</sup> Annual Meeting of Union of Chemistry-Related Societies in Chubu Area, Japan, (Gifu Univ., Gifu, Japan, October 2001), p. 136, 2J23, 2001.
8. Effect of Cation Size on the Stability of Aqueous Titanate Solutions with Layered Structure,  
T. Ohya, A. Sannomiya, T. Ban, Y. Ohya, and Y. Takahashi,  
15<sup>th</sup> Fall Meeting of The Ceramic Society of Japan (Akita Univ., Akita, Japan, September, 2002), p. 119, 2H05, 2002.
9. Preparation of Aqueous, Transparent Metallate Sols and Its Application to Ceramics Films,  
T. Ohya, A. Nakayama, T. Ban, Y. Ohya, and Y. Takahashi  
33<sup>rd</sup> Annual Meeting of Union of Chemistry-Related Societies in Chubu Area, Japan, (Nagoya Institute of Technology, Nagoya, Japan, October 2002), p. 168, 2J05, 2002.

### ***Poster Presentation***

1. Preparation of Concentrated, Halogen-free Aqueous Titanium Solutions,  
T. Ohya, T. Ban, Y. Ohya, and Y. Takahashi  
7th International Conference on Ceramic Processing Science (ICCPs)  
(Inuyama, Aichi, Japan, May, 2000).
2. Preparation and Characterization of Titania Thin Films from Aqueous Solutions,  
T. Ohya, A. Nakayama, Y. Shibata, T. Ban, Y. Ohya, and Y. Takahashi  
11<sup>th</sup> International Workshop on Glasses, Ceramics, Hybrids and Nanocomposites from Gels (Sol-Gel 2001), Abano Terme, Italy, September, 2001.

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