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Crystal Phase Control for Titanium Dioxide Films by Direct Deposition in Aqueous Solutions

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Crystalline titanium dioxide (TiO_2) was directly grown on a substrate via heterogeneous nucleation in aqueous solutions with titanyl sulfate at near room temperature. The crystal phase of TiO_2 films was essentially determined by the initial pH value and the Ti concentration of the precursor solutions. The rutile and anatase phases were produced in the solutions around their thermodynamic equilibrium conditions between Ti(IV) ionic species and the solid phases. The effect of the deposition rate on the crystal phases was not dominant in this system. On the other hand, the morphology of the TiO_2 products was influenced by the reaction rate controlled with the properties of anions as a ligand for titanium cations. Homogeneous rutile and anatase films consisting of highly oriented needlelike crystals were obtained with a relatively slow deposition rate.

1. Introduction

Titanium dioxide (TiO_2) is a highly valuable material because of its optical and catalytic properties. The rutile phase of TiO_2 with a high refractive index is especially useful for optical devices such as waveguides and thin film coatings. The photocatalytic activity of the anatase phase of TiO_2 is widely applied in many fields such as microorganism photolysis,[1] medical treatment,[2] and environmental purification.[3] Controlling the polymorphs on the preparation of TiO_2 is practically essential for producing excellent functions. Fabrication techniques for TiO_2 thin films are also important in terms of practical application fields. Conventionally, TiO_2 coatings have been prepared by casting TiO_2 crystalline powder with organic binder and subsequently heating for removal of the organics.[4] Chemical vapor deposition (CVD),[5,6] sputtering,[7] spray pyrolysis,[8] and sol−gel methods[9,10] are also applicable for the production of homogeneous thin films. In these cases, however, high processing temperatures are commonly needed for high crystallinity of the ceramic films.

In recent years, fabrication techniques for inorganic coatings analogous to biomineralization have been emphasized as low-energy and environmentally benign processes.[11] Film formation via heterogeneous nucleation in supersaturated aqueous solutions at near room temperatures was reported for silicon oxide,[12] titanium oxide,[13,14] tin oxide,[15] iron oxide,[16] and vanadium oxide.[17] Various plastics and other organic materials are available as a substrate because of low processing temperatures for deposition. Morphological control of metal oxide was easily achieved with this biomimetic film fabrication method by replication of template shapes.[18−20] Direct synthesis of crystalline TiO_2 thin films at near room temperatures was reported using aqueous solutions with ammonium hexafluorotitanate [$(NH_4)_2TiF_6$][13] and titanium tetrafluoride (TiF_4).[14,18,20] Most of these works using aqueous solutions have been limited for the preparation of the anatase phase. Recently, we have produced TiO_2 thin films consisting of the rutile phase in aqueous solutions with titanyl sulfate ($TiOSO_4$) at 60 °C.[21] The preparation of a rutile ultrafine powder was also reported using $TiCl_4$ as a starting reagent around room temperatures.[22−24] However, the mechanism to

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determine the polymorphs such as rutile and anatase in aqueous solutions has not been clarified. Controlling the crystal phases is essentially important for the synthesis of TiO_2 thin films at low temperatures for practical usage. In the present work, we successfully produced rutile and anatase phases of TiO_2 thin films in aqueous solutions near room temperature. The conditions for the phase control in solutions were clarified based on the thermodynamic study. The effects of coexisting species such as ligands and the surface properties of substrates are also discussed on the morphology of the thin films.

2. Experimental Section

Precursor solutions at Ti concentrations of 0.001−0.1 M were prepared by adding $TiOSO_4 \cdot xH_2O$ (Nacalai Tesque, Inc., $x_{av} = 4.6$) into aqueous solvents containing hydrochloric acid (HCl) or ammonium hydroxide (NH_4OH) and then stirring for approximately 1 h at room temperature. $TiOSO_4$ is chosen as a starting material because of its low cost, low reactivity with moisture, and lack of toxicity. The initial pH (pH_i) of the solutions after 1 h of stirring was adjusted in the range from −0.50 to +1.80. Substrates were immersed into the precursor solutions and then maintained at 60 °C. After an appropriate reaction time (1−10 days), the substrates deposited with TiO_2 were rinsed with purified water and dried at room temperature.

Precursor solutions at 0.01 M of the Ti concentration were prepared by adding $TiOSO_4$ into HCl aqueous solvents at pH 0.50, and then urea (NH_2CONH_2; Junsei Chem. Co., Ltd.) was added into the solutions with the molar ratios (R = urea/Ti) of 0−500. In this case, the initial pH was varied from 0.48 to 1.59.

Barium chloride ($BaCl_2 \cdot 2H_2O$; Junsei Chem. Co., Ltd.) was added into the precursor solutions at the concentration of 0.03 M of $TiOSO_4$ to exchange sulfate anions with chloride anions through precipitation of barium sulfate and subsequent filtration. More than 98% of the sulfate anions in the solutions were removed by this procedure.

Glass slides, silicon wafers, polypropylene, polystyrene, polyethylene, and poly(ethylene terephthalate) sheets washed ultrasonically with diluted nitric acid and ethanol or acetone for 1 h, respectively, were used as substrates. Hydrophobized and hydrophilized glass slides were also exploited. Hydrophobized glass slides bearing methyl groups were prepared with a chloroform solution containing 5 vol % diethoxydimethylsilane [$(CH_3)_2Si(OC_2H_5)_2$; Kanto Chem. Co.]. Hydrophilization was conducted by ultrasonicating glass slides with a mixed solution of purified water (200 mL) and ethanol (300 mL) containing potassium hydroxide (5.0 g) for 5 min.

The crystal phases of TiO_2 deposited on the surfaces were identified by X-ray diffractometry (XRD; Rigaku) with Cu Kα radiation by 2θ and $\theta/2\theta$ scanning modes. The surface and cross section of the thin films deposited were observed using a field emission scanning electron microscope (FESEM; Hitachi S-4700). The specific surface area was calculated by the Brunauer−Emmett−Teller method based on N_2 adsorption with a Micromeritics TriStar 3000.

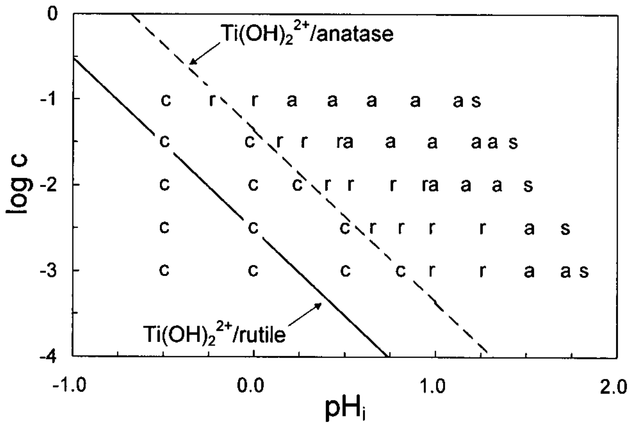

Figure 1. Relationship between the experimental conditions and crystal phases deposited on the surface. Clear solutions without both deposition and precipitation at least for 30 days were obtained at condition c. Suspension with insoluble species was observed from the solutions at condition s. The rutile, anatase, and their mixture were produced in the solutions at conditions r, a, and ra, respectively. The boundaries of $Ti(OH)_2^{2+}$/rutile (solid line) and $Ti(OH)_2^{2+}$/anatase (dashed line) were estimated by the thermodynamic equilibrium.

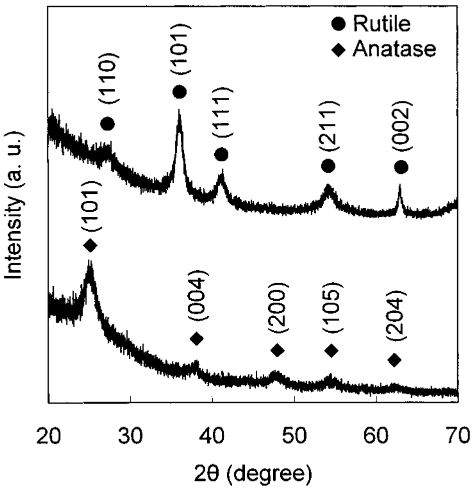

Figure 2. XRD profiles for TiO_2 deposited on glass slide substrates at conditions r and a: 0.01 M $TiOSO_4$ and pH_i 0.50 (a), 0.03 M $TiOSO_4$ and pH_i 1.30 (b). These XRD measurements were conducted by the 2θ scanning mode at the incident angle of 0.5°.

3. Results

3.1. Crystal Phases. The Ti source of 0.001−0.1 M was dissolved in HCl or NH_4OH aqueous solvents having various pH values. The acidity of the solutions gradually increased during stirring for 1 h because of hydrolysis of $TiOSO_4$. As shown in Figure 1, clear solutions were stable below pH_i −0.50−0.75 depending on the $TiOSO_4$ concentration (condition c). On the other hand, $TiOSO_4$ was insoluble in the solvents at high pH_i above 1.23−1.75 (condition s). After an appropriate reaction time (from several hours to 10 days), TiO_2 was grown on the surface of all kinds of substrates in the intermediate pH_i range between conditions c and s. XRD patterns as shown in Figure 2 revealed that both of the rutile and anatase phases were produced in these

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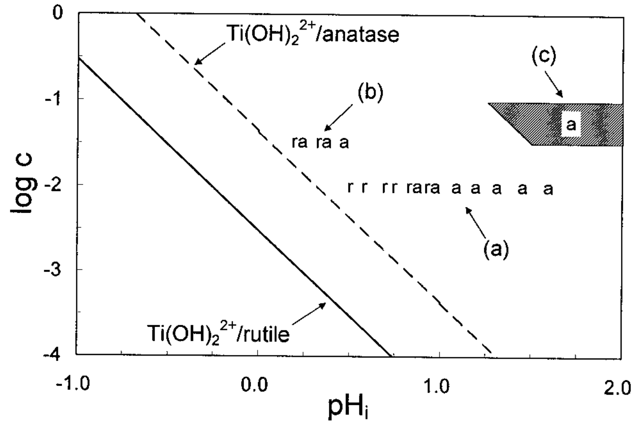

Figure 3. Relationship between the experimental conditions and crystal phases of TiO_2 prepared from various aqueous solutions: $TiOSO_4$ containing urea (a), $TiOSO_4$ solutions introduced with $BaCl_2$ (b), and TiF_4 (c). Symbols are the same as those shown in Figure 1.

Table 1. Morphology of Films Deposited from $TiOSO_4$, $TiOSO_4$ + Urea, and TiF_4 Aqueous Solutions on Various Surfaces

		morphology (crystallite shape)	
precursor solution	crystal phase	hydrophobic surface	hydrophilic surface
$TiOSO_4$	rutile	uniform (needle)	islandish (needle)
	anatase	uniform (sphere)	islandish (sphere)
$TiOSO_4$ + urea	rutile	uniform (needle)	islandish (needle)
	anatase	uniform (needle)	uniform (needle)
TiF_4	anatase	uniform (needle)	uniform (needle)

conditions. The rutile phase was obtained at a lower pH$_i$ region than that for the anatase at the same Ti concentrations. An induction time of several days was observed before deposition of the rutile phase on the surface. In this case, precipitation via homogeneous nucleation did not occur in the solutions. The anatase crystals were grown within several hours with massive precipitates.

Urea is commonly used for homogeneous precipitation as a reagent increasing pH because of its decomposition. In this study, dissolution of urea into the reaction system slightly increased the initial pH value of the solutions by protonation because urea is scarcely decomposed at room temperatures.[25] A gradual increase in pH was induced by heating the solutions containing urea up to 60 °C. However, the organic molecule mainly acted as a freezing agent on reduction of the reactivity of the Ti source in the system. When urea was added into the precursor solutions with the molar ratios R of 0−500, pH$_i$ of the solutions at the Ti concentration of 0.01 M ranged from 0.48 to 1.59. As shown in Figure 3, the crystal phase of the deposits on the surface in the solutions was rutile, anatase, or their mixture. The dependence of the crystal phase on the pH$_i$ value is almost the same as that of the solutions without urea. Addition of urea remarkably increased the deposition time of anatase crystals from several hours to 3−7 days. On the contrary, the deposition rate of the rutile crystal was as long as that by the procedure without urea.

Introduction of $BaCl_2$ promoted the deposition in the solutions at the pH$_i$ producing the crystalline TiO_2. Deposition on the substrates and precipitation immediately occurred by heating the precursor solutions with $BaCl_2$ at pH$_i$ 0.25−0.45 up to 60 °C. Deposition of rutile containing a small amount of anatase was observed on the substrate at the lower pH$_i$ range while anatase was created with a lot of precipitate at the higher pH$_i$ (Figure 3).

3.2. Morphology. Macroscopic morphologies of TiO_2 films and crystallite shapes synthesized with various precursor solutions were affected by the preparation conditions such as the kind of substrate and component of the precursor solution. Table 1 summarizes the morphology of the films and the shapes of the crystallites composing the films. Figure 4 shows FESEM images of rutile crystals prepared on substrates in the solutions at condition r. Uniform thin films composed of fine needles perpendicular to the surface were formed on a relatively hydrophobic surface such as polypropylene, polystyrene, polyethylene, poly(ethylene terephthalate), a hydrophobized glass slide bearing methyl groups, and silicon wafer. Isolated clusters with diameters of ~2.0 μm consisting of fine needlelike crystallites with diameters of 10−20 nm were randomly deposited on a hydrophilic surface such as poly(vinyl chloride), a glass slide, and a hydrophilized glass slide. XRD profiles shown in Figure 2 suggest that the [101] or [001] direction of the rutile unit cell was oriented perpendicular to the surface of the substrates. Figure 5 shows FESEM images of anatase crystals deposited in the solutions at condition a. Uniform films consisting of fine spherical crystallites with diameters of 10−20 nm were observed on the hydrophobic surfaces. Orientation of the anatase crystals on the substrates was not identified from the XRD patterns. Clusters with various diameters of 0.1−1.0 μm consisting of spherical particles were scattered throughout hydrophilic surfaces. However, fine needlelike anatase crystals were formed in the solutions containing urea as shown in Figure 6. The [001] direction of the anatase crystallites in this film was oriented perpendicular to the surface (Figure 7).

4. Discussion

4.1. Crystal Phases. As shown in Figure 1, the crystal phase of deposited TiO_2 varied from rutile to anatase with increasing pH$_i$ at a constant Ti concentration. The solid and dashed lines denote the boundaries of $Ti(OH)_2^{2+}$/rutile and $Ti(OH)_2^{2+}$/anatase, respectively, which were estimated by the thermodynamic data of Lencka et al.[26] with the ideal solution approximation at 333 K. (The activity coefficients of all ionic species including H^+ and OH^- in the solutions are assumed to be equal to 1.00.) Because Ti(IV) ionic species are dominated by $Ti(OH)_2^{2+}$ at such high acidic conditions,[26] the solid and dashed lines were calculated on the basis of the following equilibrium:

$$Ti(OH)_2^{2+} \leftrightarrow TiO_2(s) + 2H^+ \qquad (1)$$

The experimental conditions producing rutile and anatase lie almost parallel to the solid and dashed lines in the phase stability diagram of the Ti(IV)−H_2O

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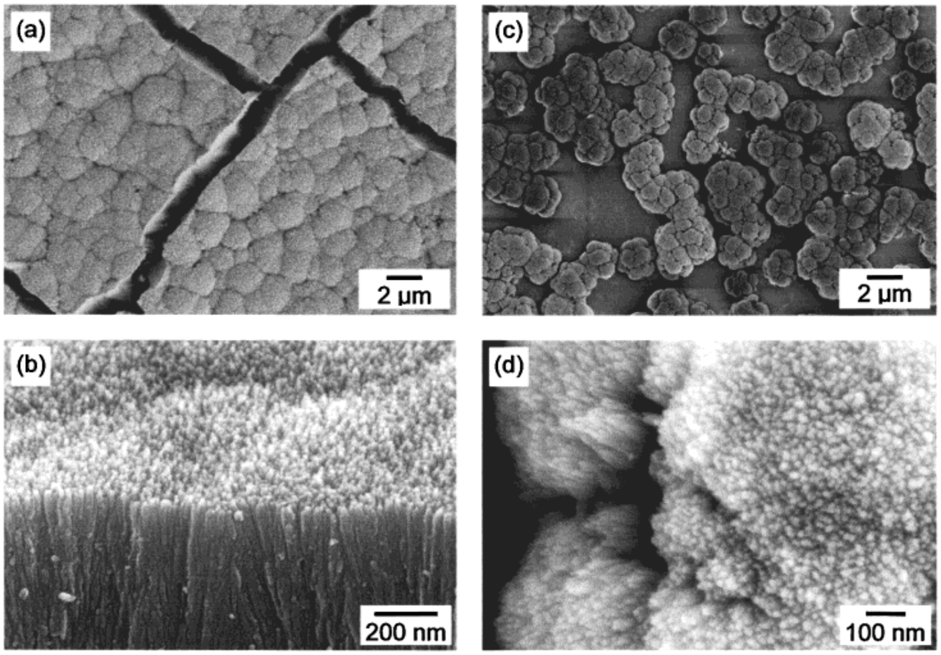

Figure 4. FESEM images for rutile crystals on a polyethylene sheet (a and b) and a glass slide (c and d). These crystals were prepared at 0.01 M $TiOSO_4$ and pH_i 0.50. Cracks in the films found in part a are considered to arise because of shrinkage during drying.

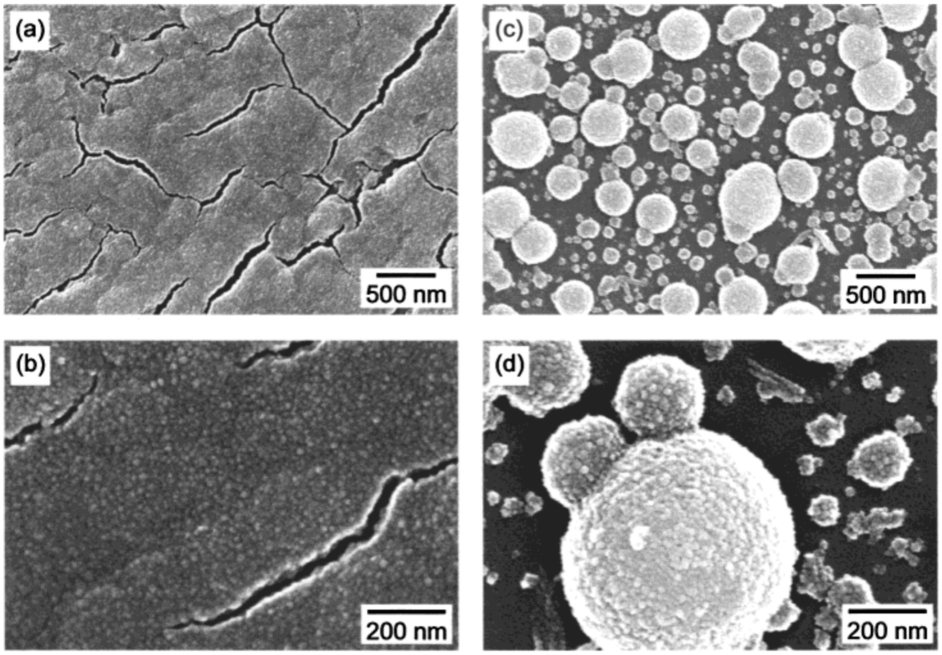

Figure 5. FESEM images for anatase crystals from a $TiOSO_4$ aqueous solution on a polyethylene sheet (a and b) and a glass slide (c and d). These crystals were synthesized at 0.03 M $TiOSO_4$ and pH_i 0.95. Cracks in the films found in part a are considered to arise because of shrinkage during drying.

system. Considering the activity coefficients of a variety of ionic species in the aqueous solutions, these calculated boundaries approach the experimental conditions while retaining their gradients. Therefore, the rutile and anatase phases are inferred to be formed at the conditions close to the thermodynamic equilibrium of $Ti(OH)_2^{2+}$/rutile and $Ti(OH)_2^{2+}$/anatase, respectively. The stable solutions were obtained in the pH_i region below the boundary of $Ti(OH)_2^{2+}$/rutile because titanium exists as soluble $Ti(OH)_2^{2+}$. At a pH_i slightly higher than the thermodynamic equilibrium of $Ti(OH)_2^{2+}$/rutile, the chemical potential of $Ti(OH)_2^{2+}$ (μ_i) is slightly larger than that of the rutile phase (μ_r). Consequently, rutile crystals are constructed in the solution because the stable Ti−O structures are gradually formed with condensing and redissolving due to the small difference in the chemical potentials between μ_i and μ_r. At the pH_i values higher than the thermodynamic equilibrium of $Ti(OH)_2^{2+}$/anatase, the chemical potential of anatase (μ_a) is slightly lower than μ_i. The order of magnitude of the chemical potentials changes from $\mu_r < \mu_i < \mu_a$ to $\mu_r < \mu_a < \mu_i$ around the dashed line. A phase commonly transforms into a state having the nearest chemical potential following Ostwald's step rule. Thus, the formation of the metastable anatase phase is achieved in the solutions at the relatively high pH_i region.

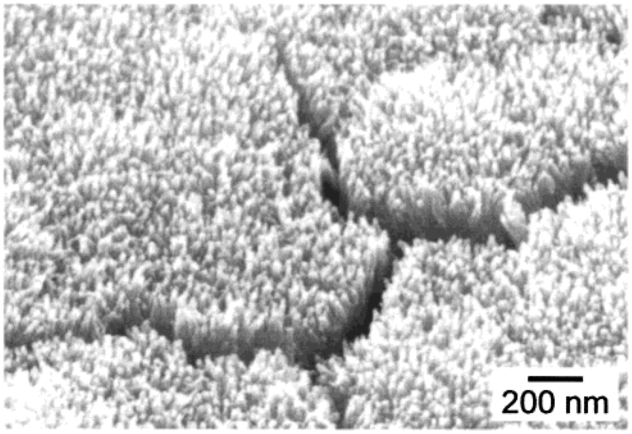

Figure 6. FESEM image for an anatase thin film prepared from a $TiOSO_4$ aqueous solution with urea at $R = 200$ on a glass slide. The condition of the film fabrication was at 0.01 M $TiOSO_4$ and pH_i 1.10.

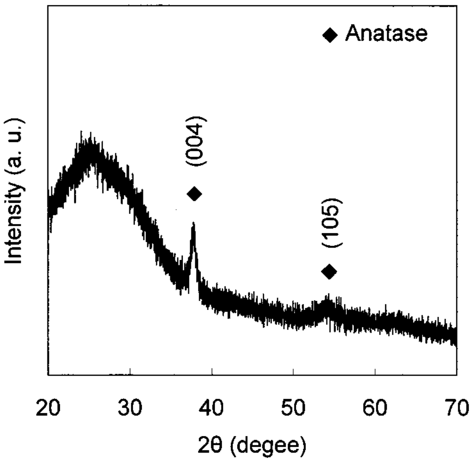

Figure 7. XRD profile for anatase thin film prepared from a $TiOSO_4$ aqueous solution with urea ($R = 200$) at 0.01 M $TiOSO_4$ and pH_i 1.10. This XRD measurement was conducted by the $\theta/2\theta$ scanning mode to investigate the orientation.

As mentioned above, addition of urea into the precursor solutions greatly reduced the deposition rate in the solutions. However, the dependence of the crystal phases obtained on pH_i (Figure 3) was almost consistent with that without urea (Figure 1). One of the authors has reported the deposition of anatase TiO_2 using TiF_4 aqueous solutions.[14] The anatase phase was prepared in the solutions with TiF_4 at pH_i ranging over 1.25–2.50 as shown in Figure 3, while the deposition slowly occurred within ~12 h. These facts suggest that the crystal phase of deposited TiO_2 is fundamentally determined by the thermodynamic equilibrium between $Ti(OH)_2^{2+}$ and the solid phases. The TiF_4 solutions were stable without deposition and precipitation at the pH_i region in which rutile crystals were produced from $TiOSO_4$ solutions. This phenomenon will be discussed in the following section on the basis of the nature of ligands.

Exchange of the counteranions from SO_4^{2-} to Cl^- by addition of $BaCl_2$ promoted the deposition and precipitation in the solutions (Figure 3). In this case, the products contained a small quantity of anatase, although the pH_i values of the solutions were in the range of condition r. Because the rapid condensation prevents the formation of the most stable structures at the growing surface, the metastable phase would be produced under highly supersaturated conditions. Thus, the influence of the reaction rate on the determination of the crystal phase cannot be completely ignored in the solution system.

4.2. Morphology. Figures 4 and 5 indicate that rutile and anatase grown in the $TiOSO_4$ solutions show needlelike and spherical shapes, respectively. According to the XRD analysis, the former crystallites were oriented on the surface but the latter was not. The deposition of spherical anatase particles was usually accompanied with massive precipitates. On the other hand, the oriented needlelike anatase crystallites were prepared from the $TiOSO_4$ solutions containing urea and from the TiF_4 solutions. The deposition of the anatase crystals in the $TiOSO_4$ solutions without urea occurred more rapidly than the others. Accordingly, the morphology of the crystallites is affected by the reaction rate regardless of the crystal phases. A high reaction rate results in the production of the nonoriented spherical particles with massive precipitates via homogeneous nucleation. In contrast, deposition with a relatively low reaction rate predominantly gives rise to heterogeneous nucleation and induces the formation of the highly oriented needlelike crystals. Because the XRD peaks of the rutile (101) and (002) planes and the anatase (004) plane were emphasized for the needles, the growth along with the *c* axis of the crystals is presumed to be promoted in these systems. As described in the following section, the coordination of coexisting species as a ligand for ionic Ti species is essential for controlling the deposition rate. Ultrafine needles showing a high specific surface area of about 150–300 m^2/g, independent of the crystal phases, were produced, although the deposition rate was extremely slow. This suggests that selective adsorption of the coexisting species, such as SO_4^{2-} and F^-, on specific surfaces parallel to the *c* axis prevents the crystal growth perpendicular to the *c* axis.

The nature of the surface of the substrates also influences the morphology of the deposited TiO_2 crystals. Macroscopically uniform thin films can be obtained on relatively hydrophobic surfaces regardless of the crystal phases. On the other hand, islandlike clusters of rutile crystals were frequently observed on relatively hydrophilic surfaces. This morphological variation is ascribed to the difference of the number of nuclei formed on the surfaces. It was recently reported that rutile TiO_2 surfaces have amphiphilicity, i.e., hydrophilicity and oleophilicity.[27] As mentioned above, the coexisting species are covering the relatively hydrophilic surfaces parallel to the *c* axis of the crystals. In this case, the *c* axis of the active crystal nuclei is perpendicular to the substrate surface because the growth along the *c* axis is only permitted because of the adsorption of the species. Because the bottom (001) plane of the crystal nuclei is relatively hydrophobic,[28] the number of the nuclei increases on the hydrophobic surfaces. Although uniform and macroscopically continuous films were prepared on hydrophobic surfaces, the adhesion of the films was poor because of the absence of the covalent

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bonds between the films and the surfaces. Homogeneous films consisting of anatase needlelike crystals were achieved even on hydrophilic surfaces using TiF_4 and $TiOSO_4$ with urea. This fact is attributed to the fact that the bottom (001) plane of anatase nuclei is less hydrophobic than that of rutile.

4.3. Effects of Coexisting Species. The morphology of the deposited TiO_2 was profoundly affected by the coexisting species, such as SO_4^{2-}, F^-, Cl^-, and urea. This dependence of the morphology is ascribed to the coordination or adsorption of coexisting species. In aqueous chemistry, inorganic or organic anionic species as additives are often used in order to control the precipitation process. Because the complexation of metal cations with such anionic species gives new precursors with different chemical reactivity toward hydrolysis and condensation, morphology and the size of the particles are affected by the additives. The pH ranges for coordination of anions to the Ti^{4+} cation were calculated on the basis of the partial charge model by Livage et al.[29,30] According to the model, the coexisting SO_4^{2-}, F^-, and Cl^- form a complex with Ti^{4+} cations in pH ranging over −4.5−10.0, −3.7−8.1, and 4.2−9.1, respectively. Because both SO_4^{2-} and F^- are able to coordinate to Ti^{4+} cations at conditions r and a in Figure 1, the hydrolysis and condensation rates are reduced because of the complexation by these anions. The chemical bond of M−X ordinarily becomes less ionic and more covalent upon decreasing the mean electronegativity of anion X^- [$\chi(X^-)$]. In a highly acidic condition, such as conditions r and a, SO_4^{2-} exists as protonated form HSO_4^-. Because $\chi(F^-)$ and $\chi(HSO_4^-)$ are 2.42 and 2.64, respectively, coordination of F^- to the Ti^{4+} cation remains more stable than that of SO_4^{2-}. Thus, F^- effectively reduces the hydrolysis and condensation rates of Ti^{4+} cations by complexation. Using TiF_4 as a raw material, therefore, the solutions were stable without precipitation and deposition at condition r and anatase was slowly produced at condition a. Urea is also inferred to complex Ti^{4+} cations with amino groups as a freezing agent because the deposition rate was drastically decreased with the addition of urea into the system. Accordingly, the slower deposition rate with the coordination of urea leads to the gradual formation of the anatase crystals. On the contrary, the conditions for producing the crystalline TiO_2 are out of the pH range for coordination of Cl^-. Thus, rapid precipitation occurred through promotion of hydrolysis of Ti^{4+} and subsequent condensation with exchange of the anions from SO_4^{2-} to Cl^-.

5. Conclusions

The crystal phases of TiO_2 thin films were successfully controlled during direct deposition in aqueous solutions at a low temperature. The formation of the rutile and anatase phases is predominantly determined by the thermodynamic conditions, such as the pH_i and the Ti concentration of the solutions. The morphology of the crystalline films is influenced by the deposition rate depending on coexisting ionic species. Homogeneous films consisting of needlelike anatase and rutile crystals with diameters 10−20 nm were obtained in the solutions of $TiOSO_4$ with and without urea, respectively. Highly oriented fine crystals provide an extremely high specific surface area of about 150−300 m^2/g.

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