Journal of Sol-Gel Science and Technology (2018) 87:537–543
https://doi.org/10.1007/s10971-018-4715-x

ORIGINAL PAPER: FUNCTIONAL COATINGS, THIN FILMS AND MEMBRANES (INCLUDING DEPOSITION TECHNIQUES)

Additive-free alkoxide–water–alcohol solutions as precursors for crystalline titania thin films

Shinnosuke Yamazaki[1] · **Hiroaki Uchiyama**[1] · **Hiromitsu Kozuka**[1]

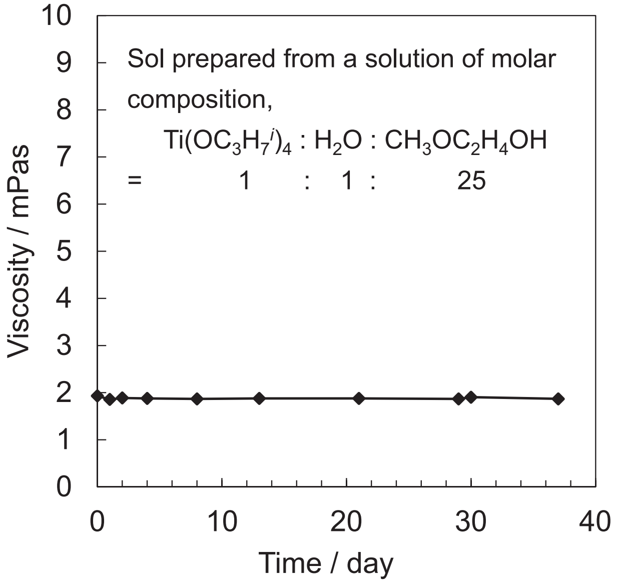
Received: 31 March 2018 / Accepted: 24 May 2018 / Published online: 19 June 2018

Abstract

When titanium alkoxides are hydrolyzed for preparing coating solutions for titania thin film deposition, chelating and peptizing agents such as acetylacetone and hydrochloric acid, respectively, are employed in order to suppress the formation of precipitates and obtain homogeneous sols. The present work demonstrates that precipitation can be avoided when 2-methoxyethanol is used as solvent for hydrolyzing titanium isopropoxide even without using chelating or peptizing agents. A sol obtained from a simple solution of molar compositions, $Ti(OC_3H_7^i)_4$:H_2O:$CH_3OC_2H_4OH$ = 1:1:25, was demonstrated to be stable in viscosity at least for >1 month. The stability and long pot life of the sol were evidenced in the identical characters including thickness, crystallite size and refractive index and the similar microstructure of the films prepared from the sols aged for 1 and 30 days at room temperature. The formation of homogeneous sol and its long-period stability were thought to result from chelation of the titanium atoms by 2-methoxyethanol molecules.

Graphical Abstract

An additive-free, simple sol prepared from a $Ti(OC_3H_7^i)_4$–H_2O–$CH_3OC_2H_4OH$ solution as a stable precursor for TiO_2 thin film deposition.



The original version of this article was revised: The figure 3 has been update.

✉ Hiromitsu Kozuka
kozuka@kansai-u.ac.jp

[1] Department of Chemistry and Materials Engineering, Kansai University, 3-3-35 Yamate-cho, Suita 564-8680, Japan

Highlights

- Sols from $Ti(OC_3H_7^i)_4$–H_2O–$CH_3OC_2H_4OH$ solutions are presented for titania thin film deposition.
- Neither peptizing nor chelating agents are needed to obtain transparent and homogeneous sols.
- The use of 2-methoxyethanol as solvent is the key.
- A sol prepared from a solution of molar composition, $Ti(OC_3H_7^i)_4:H_2O:CH_3OC_2H_4OH = 1:1:25$, was stable in viscosity and had long pot life as a precursor for crystalline titania thin films.
- Chelation of the titanium atoms by 2-methoxyethanol molecules may be the cause of the formation of homogenous sols and of the long pot life of the sol.

Keywords Thin film · Titania · Viscosity · Chelating agent · Peptizing agent · 2-Methoxyethanol

1 Introduction

Titania thin films have attracted much attention for a long time as anti-reflective coatings [1], photocatalysts [2], photoelectrodes [3], and super-hydrophilic coatings [4]. Preparation of titania thin films by sol-gel method has long history [5–7]. Dip- or spin-coating is used in laboratory scale for fabricating gel films, and the gel films are converted into polycrystalline anatase or rutile films by firing. The most popular route for preparing coating solutions is to employ titanium alkoxides as the source materials, which undergo hydrolysis and condensation in alcoholic media to form polymerized species. Because titanium akoxides are very fast in hydrolysis reaction as in the case of other transition metal alkoxides, their uncontrolled hydrolysis results in precipitation in solutions. Then peptizing or chelating agents are added in the starting solutions prior to the hydrolysis in order to make sols available for coating by avoiding precipitation. Hydrochloric or nitric acids, for instance, are used as peptizing agents, where the acid-to-alkoxide mole ratios as large as 0.2 are employed [6–8]. Carboxylic acids and β-diketones such as acetic acid and acetylacetone, respectively, are used as chelating agents, where their chelation enhances the steric effects and retards the hydrolysis of titanium akoxides [9, 10].

We noticed that, when 2-methoxyethanol ($CH_3OC_2H_4OH$) is used as the reaction media in titanium alkoxide solutions, precipitation can be avoided even without peptizing or chelating agents. 2-Methoxyethanol is often used as solvent for alkoxides and salts of transition metals because of their high solubility in it. For example, one of the authors had an experience in preparing titania sol from titanium isopropoxide ($Ti(OC_3H_7^i)_4$) using 2-methoxyethanol as solvent, from which transparent and homogenous titania thin films could be prepared [11]. However, the major solvent was ethanol and a peptizing agent was employed there as is seen in the molar composition of the starting solution, $Ti(OC_3H_7^i)_4:H_2O:HCl:CH_3OC_2H_4OH:C_2H_5OH =$ 1:1:0.14:0.5:8.2. Sreemany and Sen [12] and Mahanty et al. [13], respectively, preWepared titania sols for fabricating transparent and homogenous titania thin films, where the molar compositions of the starting solutions were $Ti(OC_3H_7^i)_4:H_2O:CH_3COOH:CH_3OC_2H_4OH = 1:1.8:0.7:32$ and 1:1:0.3:40. Only 2-methoxyethanol was the solvent while a chelating agent, acetic acid, was employed there. Thus 2-methoxyethanol has never been recognized as the reaction media that can avoid precipitation during hydrolysis of alkoxides without the aid of peptizing or chelating agents. Then we demonstrate here the formation of transparent titania sols by hydrolyzing titanium alkoxide in 2-methoxyethanol without any additives. Preliminary comparison was also made with the solutions containing other types of solvents. The availability of the sol as the coating solution and its long pot life were also demonstrated by characterizing the thin films that were prepared from the sols aged for different periods of time.

2 Experimental

Titanium isopropoxide ($Ti(OC_3H_7^i)_4$) and nitric acid (69% HNO_3 aq.) purchased from Wako Pure Chemical Industries, Osaka, Japan and purified water were used as the starting materials. Methanol (CH_3OH), ethanol (C_2H_5OH), 2-propanol ($(CH_3)_2CHOH$), 2-butanol ($CH_3CH(OH)CH_2CH_3$), 2-methoxyethanol ($CH_3OC_2H_4OH$), 2-ethoxyethanol ($C_2H_5OC_2H_4OH$), and tetrahydrofuran (THF; C_4H_8O) all purchased from Wako Pure Chemical Industries were used as the solvents.

First, the solutions of the mole ratios summarized in Table 1 were prepared by the procedure shown in Fig. 1a. Titanium isopropoxide was added to 2/3 of the prescribed amount of the solvent, while water was added to the remaining solvent. The latter solution was added to the former that was cooled in iced water and continuously stirred. The resultant solutions thus obtained were kept in a sealed glass container at room temperature (24–26 °C).

Second the solutions containing ethanol and/or 2-methoxyethanol shown in Table 2 were prepared. When both ethanol and 2-methoxyethanol were used as solvent, the procedure shown in Fig. 1b was employed. 2-Methoxyethanol and titanium isopropoxide were added to

Table 1 Appearance of the solutions containing various types of solvents

Solvent	Mole ratio			Appearance
	$Ti(OC_3H_7^i)_4$	Solvent	H_2O	
CH_3OH	1	16.6	—	White and opaque on mixing $Ti(OC_3H_7^i)_4$ with CH_3OH. Solidified in a few minutes
C_2H_5OH	1	25	1	White and opaque, followed by the formation of white precipitates
$(CH_3)_2CHOH$	1	25	1	Colorless and transparent on preparation, followed by the formation of colorless, crystal-like precipitates at the bottom and on the wall of the container in 1 day
$CH_3CH(OH)CH_2CH_3$	1	25	1	Light yellow and transparent, remaining at least over 1 month
$CH_3OC_2H_4OH$	1	25	1	Colorless and transparent, remaining at least over 1 month
$C_2H_5OC_2H_4OH$	1	25	1	Yellow and transparent, remaining at least over 1 month
C_4H_8O (tetrahydrofuran)	1	25	1	Opalescent, but colorless and transparent in 1 day with a trace amount of white precipitates, which disappeared within a few days. Transparency remaining at least over 1 month

2/3 of the prescribed amount of ethanol to form an alkoxide solution. Separately water and nitric acid were added to the remaining ethanol. The latter solution was added to the former that was cooled in iced water with continuous stirring. When only 2-methoxyethanol was the solvent, on the other hand, the procedure shown in Fig. 1a was employed.

Sols thus obtained and kept in a sealed glass container at room temperature (24–26 °C) for 1 or 30 days served as coating solutions. Gel films were deposited on cleaned Si (100) substrates ($20 \times 40 \times 0.625$ mm^3) by spin-coating at a spinning rate of 1000 rpm. Immediately after being deposited, the gel films were inserted in an electric furnace of 700 or 900 °C, kept there for 10 min, and then taken out of the furnace to the ambient atmosphere.

The viscosity of the sol was measured at room temperature using an oscillating-type viscometer (VM-1G, Yamaichi Electronics, Tokyo, Japan) at a frequency of 500 Hz. The thickness and refractive index were measured on the thin film samples using a spectroscopic ellipsometer (M-2000V-Kk, J. A. Woollam Company, Nebraska, USA) with a software (CompleteEASETM, J. A. Woollam Company). The measurement was conducted at three angles of incidence of 65°, 70°, and 75° over the spectral range of 370–1000 nm, and the analysis was made based on Cauchy model [14].

The crystalline phase of the thin film samples was identified by X-ray diffraction (XRD) measurement using a diffractometer (RINT-Ultima III, Rigaku, Tokyo, Japan) with Cu Kα radiation operated at 40 kV and 40 mA. The measurement was carried out with grazing incidence configuration at an incidence angle of 0.5°. The crystallite size of the films was obtained from the corrected half-height width of the diffraction peak using Scherrer's equation. The microstructure of the films was observed by a field emission scanning electron microscope (SEM) (JSM-6500F, JEOL, Tokyo, Japan). Osmium was deposited on the surface of the samples prior to the observation using an osmium coater

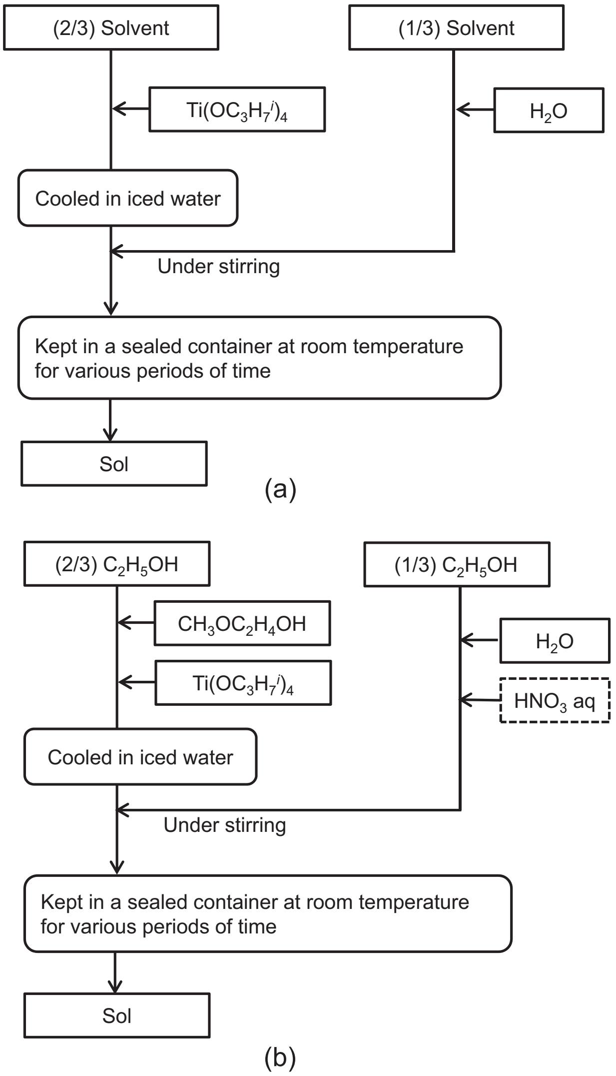


Fig. 1 Procedure for preparing the solutions. **a** For the solutions in Table 1 and for Solutions ME25-W0.5, ME25-W1 and ME25-W2 in Table 2, and **b** for Solutions ME2-ET25-W1 and ME2-ET25-W1-N0.2 in Table 2

Table 2 Appearance of the solutions with ethanol and/or 2-methoxyethanol

Solution	Mole ratio					Appearance
	$Ti(OC_3H_7^i)_4$	$CH_3OC_2H_4OH$	C_2H_5OH	H_2O	HNO_3	
ME2-ET25-W1	1	2	25	1	—	White and opaque
ME2-ET25-W1-N0.2	1	2	25	1	0.2	Colorless and transparent
ME25-W0.5	1	25	—	0.5	—	Colorless and transparent
ME25-W1	1	25	—	1	—	Colorless and transparent (even after 1 month)
ME25-W2	1	25	—	2	—	Colorless and transparent (Turning opaque within a few days)

(Neco-ST, Meiwafosis, Tokyo, Japan). Osmium coatings have extremely small granularity compared with those of gold and platinum and hence can avoid the detection of the granules of such coatings in SEM observation of high magnification [15].

3 Results and discussion

3.1 Appearance of the solutions

Table 1 shows the appearance of the solutions containing various types of solvents. When titanium isopropoxide was added in methanol, the solution became white and opaque and solidified in a few minutes. This may be due to the formation of titanium methoxide, which is solid [16], via ligand exchange reaction. When ethanol was the solvent, the mixed solution became white and opaque on the alkoxide hydrolysis, followed by precipitation of white powders. When 2-propanol was the solvent, the mixed solution was transparent at the beginning, but later crystal-like precipitates deposited at the bottom and on the inner wall of the container. These precipitates in ethanol- and 2-propanol-containing solutions may be formed by the fast hydrolysis of the alkoxide. When 2-butanol, 2-methoxyethanol, or 2-ethoxyethanol was employed as the solvent, the mixed solutions were transparent at least for over 1 month. When THF was used as the solvent, the mixed solution became white and opaque at the beginning but turned transparent in 1 day with a trace amount of white precipitates, which disppeared within a few days, and the transparency remained at least over 1 month. Thus transparent solutions were obtained even without peptizing or chelating agents when 2-butanol, 2-methoxyethanol, 2-ethoxyethanol, or THF was used as solvent.

The effect of 2-methoxyethanol on the formation of transparent solutions is also demonstrated in a series of solutions listed in Table 2. Hereafter the mole ratios of $CH_3OC_2H_4OH$, C_2H_5OH, H_2O, and HNO_3 to $Ti(OC_3H_7^i)_4$ are represented as $r_{CH3OC2H4OH}$, r_{C2H5OH}, r_{H2O}, and r_{HNO3}, respectively. The solution of $r_{CH3OC2H4OH} = 2$, $r_{C2H5OH} = 25$, $r_{H2O} = 1$, and $r_{HNO3} = 0.2$, for example, is denoted as ME2-ET25-W1-N0.2 as seen in Table 2. When ethanol was the major solvent ($r_{C2H5OH} = 25$ and $r_{CH3OC2H4OH} = 2$) and no peptizing agent, HNO_3, was added ($r_{HNO3} = 0$), the solution became white and opaque on hydrolysis (ME2-ET25-W1 in Table 2). This indicates that such a small amount of 2-methoxyethanol is ineffective in retarding the hydrolysis and in suppressing the formation of precipitates. When nitric acid was added at $r_{HNO3} = 0.2$, on the other hand (ME2-ET25-W1-N0.2 in Table 2), no precipitates were formed and the solution was transparent, which may be due to the peptization by the acid.

On the other hand, when solely 2-methoxyethanol was employed as solvent at $r_{CH3OC2H4OH} = 25$, transparent solutions were formed even without nitric acid (ME25-W0.5, ME25-W1 and ME25-W2 in Table 2). Solution ME25-W2 became opaque within a few days while Solutions ME25-W0.5 and ME25-W1 remained transparent even after 1 month. Thus 2-methoxyethanol as solvent has been demonstrated to allow titanium isopropoxide to be hydrolyzed without precipitation without the aid of chelating agents or peptizing agents.

3.2 Stability of the sol prepared from $Ti(OC_3H_7^i)_4$–H_2O–$CH_3OC_2H_4OH$ solution as the titania thin film precursor

Figure 2 shows the viscosity plotted vs. aging time for Solution ME25-W1 that was kept standing in a sealed container at room temperature. Solution ME25-W1 exhibited high stability in viscosity as seen in Fig. 2, where the viscosity was constant for over 35 days. Titania thin films were prepared on Si(100) substrates from Solution ME25-W1 via heat treatment at 700 or 900 °C for 10 min. The sol was aged at room temperature for 1 and 30 days in order to examine whether or not the aging time affects the nature of the thin film products. The thickness of the films is summarized in Table 3. The thickness was around 50 nm, and owing to the high stability of the sol viscosity, no significant difference was detected in thickness between the films prepared from the 1- and 30-day aged sols.

Figure 3a, b show the XRD patterns of the films heat treated at 700 and 900 °C, respectively. As seen in the figures, the films were anatase irrespective of the sol aging time as well as of the heat treatment temperature. The crystallite size calculated from the half height width of the anatase (101) peak was about 22 and 29 nm for the thin films fired at 700 and 900 °C, respectively (Table 3). The difference in sol aging time provided no difference in crystallite size, indicating that the sol is stable not only in viscosity but also as a titania thin film precursor.

Figures 4 and 5 show the SEM pictures of the surface of the films that were fired at 700 and 900 °C, respectively. Particles larger in size are seen in the films fired at 900 °C than in those at 700 °C, revealing the progress of grain growth at the higher temperature. More importantly, although not exactly the same, the microstructure was not remarkably different between the films prepared from the 1- and 30-day aged sols. Such similarity in microstructure reveals the stability, i.e., long pot life of the sol as coating solution.

The refractive index of the films is summarized in Table 3. Higher refractive indices were found for the films fired at 900 °C than for those at 700 °C. The higher refractive index may be due to smaller porosity resulting from sintering that was promoted at the higher temperature as well as to higher crystallinity that is revealed in larger crystallite size (Table 3) and larger grains (Figs. 4 and 5). The porosity, p, was calculated from the refractive index of the film, n_f, by the

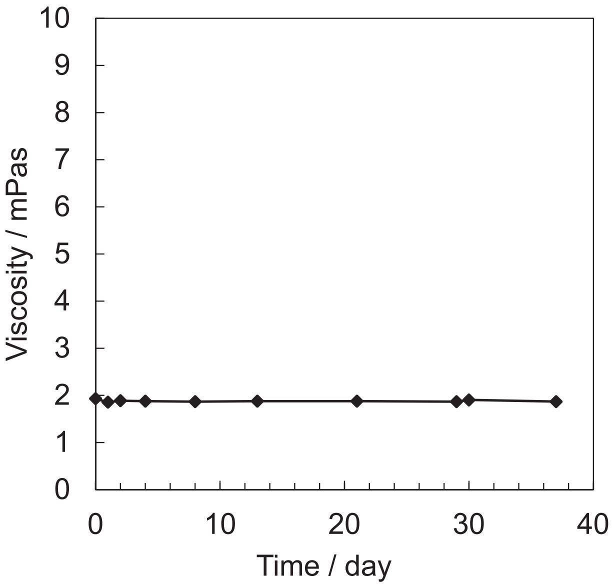


Fig. 2 Viscosity vs. aging time for Solution ME25-W1 at room temperature

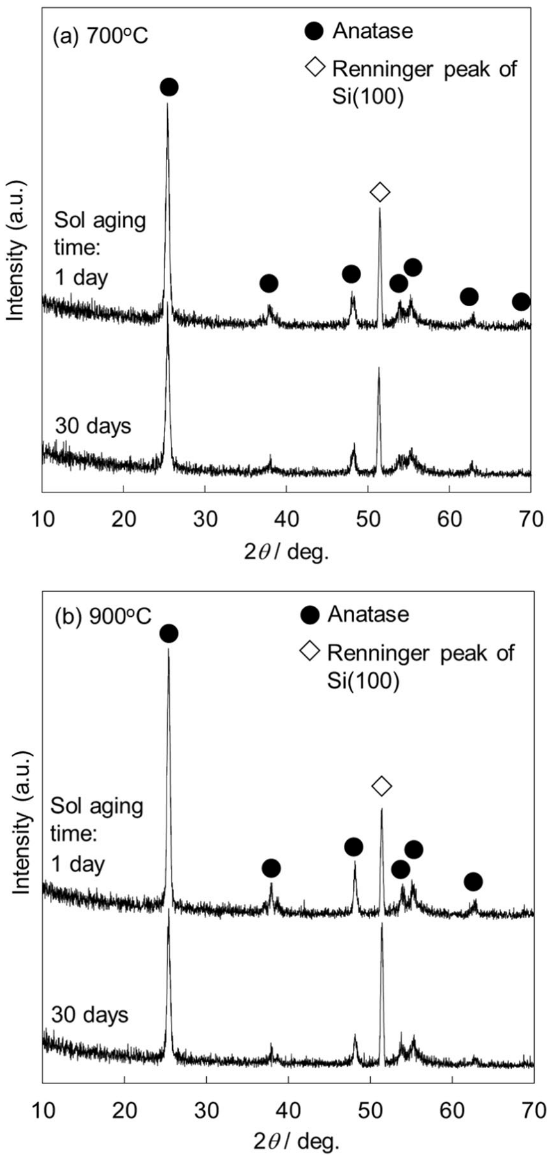


Fig. 3 XRD patterns of the titania thin films prepared from Solution ME25-W1 aged for 1 and 30 days. The gel films were fired at **a** 700 and **b** 900 °C

Table 3 Thickness, refractive index, and crystallite size of the thin film samples prepared from Solution ME25-W1 (Table 2) aged at room temperature for 1 and 30 days

Sol aging time (day)	Heat treatment temperature (°C)	Thickness (nm)	Refractive index	Crystallite size (nm)
1	700	54 ± 2	2.14 ± 0.01	23 ± 1
30	700	41 ± 4	2.22 ± 0.01	22 ± 2
1	900	49 ± 4	2.24 ± 0.01	29 ± 1
30	900	42 ± 6	2.27 ± 0.01	29 ± 2

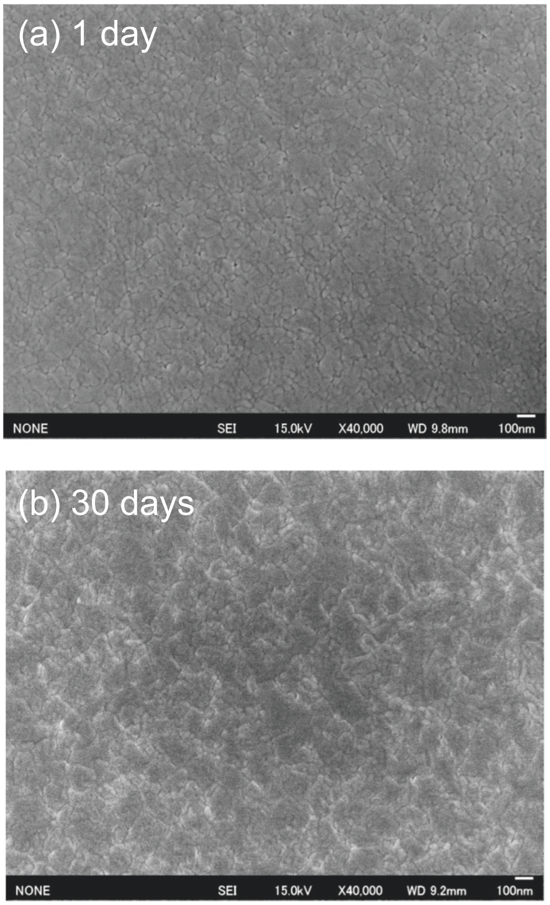


Fig. 4 SEM images of the titania thin films prepared from Solution ME25-W1 and fired at 700 °C. The sol was aged for **a** 1 and **b** 30 days

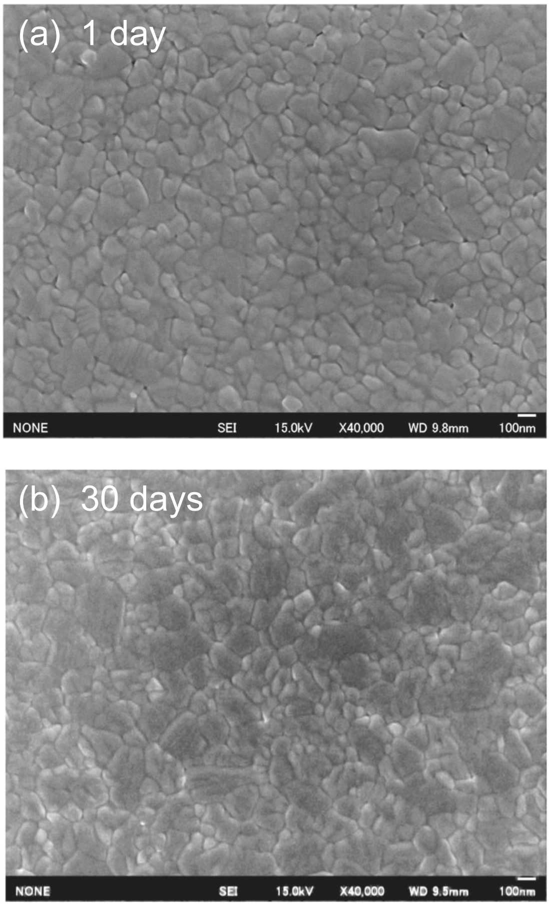


Fig. 5 SEM images of the titania thin films prepared from Solution ME25-W1 and fired at 900 °C. The sol was aged for **a** 1 and **b** 30 days

following equation [17],

$$1-p=\frac{\left(n_{\mathrm{f}}^{2}-1\right)\left(n_{\mathrm{c}}^{2}+2\right)}{\left(n_{\mathrm{f}}^{2}+2\right)\left(n_{\mathrm{c}}^{2}-1\right)}$$

where n_{c} is the refractive index of the solid phase, which was assumed to be 2.52, i.e., the refractive index of anatase [18]. The calculated porosity was 12–15 and 9–11% for the films fired at 700 and 900 °C, respectively. More importantly, no significant difference was seen in refractive index between the films prepared from the 1- and 30-day aged sols, again revealing the long pot life of the sol as coating solution.

2-Methoxyethanol provided the stability and the long pot life of the sol. A 2-methoxyethanol molecule has two oxygen atoms, both of which can coordinate metal atoms. Thus 2-methoxyethanol can act as a chelating agent as is reported, for example, in the structural analysis of a compound, $\mathrm{Ti(OC_3H_7{}^i)Cl_3(HOCH_2CH_2OCH_3)}$ [19]. When the titanium atom of the alkoxide is chelated by a 2-methoxyethanol molecule, the hydrolysis of the alkoxide may possibly be retarded due to the steric hindrance. This would lead to the retardation of the time-dependent increase of the sol viscosity as well as the suppression of the precipitation of rapidly polymerized species. The same explanation can also be made on the transparency and homogeneous nature of the 2-ethoxyethanol-containing sol (Table 1). For the 2-butanol- and the THF-containing sols (Table 1), on the other hand, further studies and discussion should be made on the origins of their transparency and homogeneous nature from the viewpoint of the structure and reactivity of chemically modified alkoxides. The thin film formability as well as the stability as coating solutions is another issues for the 2-butanol- and the THF-containing sols.

4 Conclusions

Starting solutions of mole ratios, titanium isopropoxide: water:solvent = 1:1:25, were prepared with various types of solvents, and the appearance of the resulting sols was observed. Titanium isopropoxide mixed with methanol became opaque and was solidified. When ethanol or 2-

propanol was employed as solvent, precipitation was formed on hydrolysis. Stable transparency was found, on the other hand, for the sols with 2-methoxyethanol, 2-ethoxyethanol, 2-butanol, or THF as solvent. The stability as the precursor for crystalline titania thin films was examined for the sol prepared from the titanium isopropoxide–water–2-methoxyethanol solution. The sol was stable in viscosity at least for over 1 month. The long pot life of the sol was evidenced in the identical thickness, crystallite size, and refractive index as well as in the similar microstructure of the films that were prepared from the sols aged for 1 and 30 days at room temperature. The formation of homogeneous sol from the 2-methoxyethanol-containing solution and the stability of the resulting sol were thought to result from the chelation of the titanium atoms of the alkoxides by 2-methoxyethanol molecules.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Jeong SH, Kim JK, Kim BS, Shim SH, Lee BT (2004) Characterization of SiO_2 and TiO_2 films prepared using RF magnetron sputtering and their application to anti-reflection coating. Vacuum 76:507–515
2. Yu JG, Yu HG, Cheng B, Zhao XJ, Yu JC, Ho WK (2003) The effect of calcination temperature on the surface microstructure and photocatalytic activity of TiO_2 thin films prepared by liquid phase deposition. J Phys Chem B 107:13871–13879
3. Murakami TN, Kijitori Y, Kawashima N, Miyasaka T (2004) Low temperature preparation of mesoporous TiO2 films for efficient dye-sensitized photoelectrode by chemical vapor deposition combined with UV light irradiation. J Photochem Photobiol A Chem 164:187–191
4. Carp O, Huisman CL, Reller A (2004) Photoinduced reactivity of titanium dioxide. Prog Solid State Chem 32:33–177
5. Schroeder H (1969) Oxide layers deposited from organic solutions. Phys Thin Films 5:87–141
6. Pettit RB, Brinker CJ, Ashley CS (1985) Sol-gel double-layer antireflection coatings for silicon solar cells. Sol Cells 15:267–278
7. Yoko T, Kamiya K, Yuasa A, Sakka S (1986) Formation of H_2O_2 at the illuminated TiO_2 film electrode prepared by the sol-gel method and its chemical states. J Electroanal Chem 209:399–404
8. Barbé, CJ, Arendse F, Comte P, Jirousek M, Lenzmann F, Shklover V, Grätzel M (2005) Nanocrystalline titanium oxide electrodes for photovoltaic applications J Am Ceram Soc 80:3157–3171
9. Doeuff S, Henry M, Sanchez C, Livage J (1987) Hydrolysis of titanium alkoxides: modification of the molecular precursor by acetic acid. J Non Cryst Solids 89:206–216
10. Kowada Y, Noma N (2009) Electronic state and photosensitivity of metal alkoxides chemically modified with β-diketones. J Sol Gel Sci Technol 52:166–169
11. Hu L, Yoko T, Kozuka H, Sakka S (1992) Effects of solvent on properties of sol–gel-derived TiO_2 coating films. Thin Solid Films 219:18–23
12. Sreemany M, Sen S (2007) Influence of calcination ambient and film thickness on the optical and structural properties of sol–gel TiO_2 thin films. Mat Res Bull 42:177–189
13. Mahanty S, Roy S, Sen S (2004) Effect of Sn doping on the structural and optical properties of sol–gel TiO_2 thin films. J Cryst Growth 26:177–181
14. Johs BD, McGahan WA, Woollam JA (1994) Optical analysis of complex multilayer structures using multiple data types. Thin Solid Films 253:25–27
15. Park B-D, Singh AP, Nuryawan A, Hwang K (2013) MRT Letter: High resolution SEM imaging of nano-architecture of cured urea-formaldehyde resin using plasma coating of osmium. Microsc Res Technol 76:1108–1111
16. Sun S, Lu P, Fuierer PA (1999) Oriented bismuth titanate thin flms by single-solid-source metal-organic chemical vapour deposition. J Cryst Growth 205:177–184
17. Riter E (1975) Dielectric film materials for optical applications. In: Hass G, Francombe MH, Hoffmann RW (eds) Physics of thin films, vol 8. Academic Press, New York, p. 1
18. Kingery WD, Bowen HK, Uhlmann DR (1976) Introduction to ceramics, 2nd edn. Wiley, New York
19. Lee C-S, Kuo C-N, Shao M-Y, Gau H-M (1999) Reactions of Ti(O-*i*-Pr)Cl_3 with bidentate ligands containing hydroxy and methoxy groups. The crystal structure of Ti(O-*i*-Pr)$Cl_3(HOCH_2CH_2OCH_3)$ and the ^1H variable-temperature NMR studies of solution structures of Ti(O-*i*-Pr)$Cl_3(HOCH_2CH_2OCH_3)$ and Ti(O-*i*-Pr)$Cl_3(CH_3OCH_2CH_2OCH_3)$. Inorg Chim Acta 285:254–261