

Dip-coating of TiO₂ films using a sol derived from Ti(O-*i*-Pr)₄-diethanolamine-H₂O-*i*-PrOH system

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Diethanolamine (DEA) can suppress the precipitation of oxides from the alcoholic titanium isopropoxide solution in its hydrolysis so that much water can be added to the Ti(O-*i*-Pr)₄-diethanolamine-*i*-propanol solution to give a clear solution. Addition of excess water converted the solution to the gel. The conditions for the formation of the clear solution and gel are examined. Uniform transparent TiO₂ films can be prepared by dip-coating with the clear solution. The limit of the thickness of uniform films was 200 to 240 nm. Films thicker than 1 μm can be prepared by repeating the coating cycle. These films were well densified. Diethanolamine has some positive effect on the densification of the TiO₂ crystals.

1. Introduction

Recently, metal alkoxide processes for the preparation of oxides have received special attention. These processes are applicable to good quality TiO₂ powders [1-3] and TiO₂-based mixed oxides, for example aluminium titanate [4, 5]. The sol-gel method belongs to one of these processes. This method enables the preparation of TiO₂ fibres [6] or bulk bodies [7, 8]. As far as oxide film coatings are concerned, the sol-gel process is superior to other coating methods, such as organometallic chemical vapour deposition [9-11], because it is possible to coat a substrate with a large area [12]. With this process, fibre [13] or glass bead coatings [14] and some SiO₂-TiO₂ mixed oxide coatings [15, 16] are also possible. So far several reports [17-20] on TiO₂ film coatings on the flat surface have been published. Generally alcoholic solution of metal alkoxides with a proper amount of water was used for the dip-coating of the oxide films. However, in this system, the amount of water seems to be very critical for the preparation of homogeneous films. When excess water was added to the solution, sometimes the solution was converted rapidly to the gel or sometimes precipitation of oxides took place. On the other hand, under conditions of water deficiency, discontinuous films tend to be formed [17, 18].

In the course of our investigation concerning the solvent effect of the hydrolysis of metal alkoxide, it was found that glycols or ethanolamines can suppress the precipitation of the oxides from the alcoholic solution of the metal alkoxide. When the compounds were added to the solution, large amounts of water can be added so as to control the degree of hydrolysis of the alkoxide and subsequent polymerization reaction, namely the viscosity of the homogeneous solution. Thus, using this technique homogeneous zirconia and mixed zirconia or spinel films could be prepared quite

easily. The results of these processes have been reported [21, 22].

In this paper dip-coating of the TiO₂ films using the Ti(O-*i*-Pr)₄-diethanolamine-H₂O-*i*-PrOH system is reported. TiO₂ films can be used as antireflection coatings and have an interesting application as an n-type semiconductor. The process described in this paper seems to be one of several interesting processes which can improve the shortcomings of conventional sol-gel methods.

2. Experimental procedure

Commercial extrapure grade titanium isopropoxide (TTIP), isopropanol (*i*-PrOH), *t*-butanol, ethanol and diethanolamine (DEA) were used without further purification. The water content in *i*-PrOH was estimated to be as low as 0.06% using Karl Fischer's method so that the water content is neglected when water/TTIP molar ratios are cited in this paper.

A given amount of TTIP was dissolved in *i*-PrOH (the concentration of TTIP was 0.2 to 1.2 mol l⁻¹) and subsequently a suitable amount of DEA (DEA/TTIP molar ratio $R = 1$ to 2) was added to the TTIP solution under a nitrogen atmosphere. After stirring the solution at room temperature for 2 h, a suitable amount of water-isopropanol (1:2 to 10) solution (water/TTIP molar ratio, $W = 0$ to 10) was added. TTIP concentrations cited in the text are the final concentrations after the addition of DEA and *i*-PrOH solution of water. When a clear solution was obtained after the addition of water, a substrate was dipped into the solution, pulled up at constant pull rate, dried in air for 24 h (0.5 at 100°C), and heated typically at 600°C for 30 min to prepare the uniform, transparent TiO₂ films. Other heating temperatures were examined to investigate their effect on the quality of the films and the modifications of TiO₂ crystals. In this case the

temperature will be specified in the text. The pull-up rate of 18 cm min^{-1} was applied mainly to one cycle coating, but for the preparation of thick films of good quality by repeating the coating cycle, the coating was carried out at a lower pull-up rate (6 cm min^{-1}).

The film thickness was determined directly by SEM observation of the fracture cross-sections of the films, with a surface-roughness meter or an ellipsometer. Sometimes the thickness was evaluated from the interference stripes observed in the visible spectra of the films on glass substrates (see text). These values for the thickness were generally well correlated.

The surface morphology of films was examined by SEM. X-ray diffraction was used to determine the modification of the TiO_2 crystals in the film. TEM also was used to investigate very thin films formed on KBr single crystals after dissolving the KBr in water. The refractive indices were evaluated using the ellipsometer or from the stripes (minimum or maximum of the reflectances and the wavelengths) in the visible spectra cited above.

3. Results

When water less than $W = 1$ was added to the *i*-PrOH solution of TTIP, the solution was clear, but only very cloudy, powderlike TiO_2 films are obtained from the solution. In the case of water addition larger than $W = 2$, white precipitates separated from the solution. Only near $W = 2$ was a clear solution obtained, and from the solution uniform, transparent TiO_2 films could be obtained. This behaviour is very consistent with the observations of Yoldas [18]. Thus the water content is very critical and will be troublesome in extending the process to other TiO_2 -based mixed oxide preparation in which a greater water content would be needed. Furthermore, it is difficult to perform the process reproducibly.

In our previous papers [21, 22] it was reported that some additives such as glycols and ethanolamines can moderate the strict conditions and they retard the precipitation of oxides or hydroxides from zirconium or magnesium aluminium alkoxide even in the presence of excess water. Therefore, we examined whether glycols and ethanolamines can similarly stabilize the titanium isopropoxide- H_2O -*i*-PrOH system. The additives examined were: glycols [ethylene glycol (EG), ethylene glycol monoethyl ether (EGME), diethylene glycol (DEG), diethylene glycol monoethyl ether (DEGME), diethylene glycol diethyl ether (DEGDE)]; and ethanolamines [monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA)]. DEG had been very effective for zirconium alkoxide, but all glycols and derivatives had no positive effect on the suppression of the precipitations in the present case, probably due to the difference in coordination ability between zirconium and titanium ions with oxygen atoms. On the other hand, ethanolamines which have stronger dative nature, as a result of which they contain a nitrogen atom in the molecule, could stabilize the zirconium, magnesium and/or aluminium ion(s) in the alcoholic solution. Of these ethanolamines, DEA and TEA were found to retard effectively the precipitation of the oxides or hydroxides from the titanium

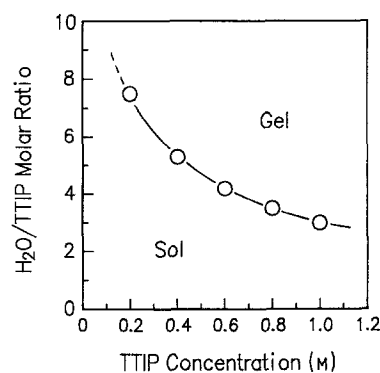


Figure 1 The relationship between the TTIP concentration and $\text{H}_2\text{O}/\text{TTIP}$ molar ratio for the sol-gel formation in constant DEA/TTIP molar ratio ($R = 1$) at room temperature.

isopropoxide- H_2O -*i*-PrOH mixture, and a clear solution was obtained in their presence even after the addition of water. If excess water was added to the TTIP-DEA-*i*-PrOH solution, the entire solution gelled rapidly (an opaque to white gel is formed). Not only can DEA and TEA suppress the precipitation, but they can also redissolve the precipitates in alcohol just after the precipitation by hydrolysis.

The conditions required to form the clear solution and gel are shown in Figs 1 and 2. The former indicates the TTIP dependence at constant R , and the latter explains the relationship between R and W at constant TTIP final concentration. It is very obvious from the figures that in the presence of DEA, excess water can be added to the solution. It was found that the gel formed at a lower water quantity was transparent and soft, while introduction of sufficient water gave the white, hard gel. TEA behaved in a similar manner to DEA, but in this case much more water was needed to form the gel, and the resultant gel appeared rather like precipitate aggregates. Unfortunately, we could not clarify the reason for the difference in the behaviour of DEA and TEA. It was found, by qualitative experiment, that more uniform TiO_2 films could be obtained in the presence of DEA than TEA. Therefore, dip-coating of TiO_2 films was done using the clear solutions which were formed with DEA, i.e. at conditions shown as "Sol" in the Figs 1 and 2.

The appearance of the resultant films formed at various R and W conditions by one dipping-drying-heating (600°C) cycle was examined qualitatively. It was found that at $R = 1$, $W = 1$ to 4 and alkoxide

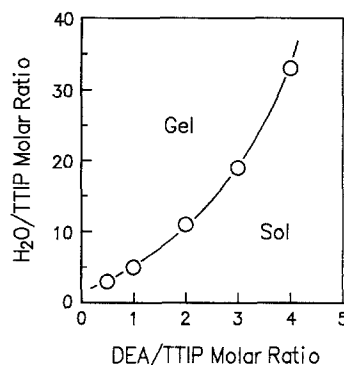


Figure 2 The relationship between the DEA/TTIP molar ratio (R) and $\text{H}_2\text{O}/\text{TTIP}$ molar ratio (W) for the sol-gel formation in constant final TTIP concentration of 0.5 M at room temperature.

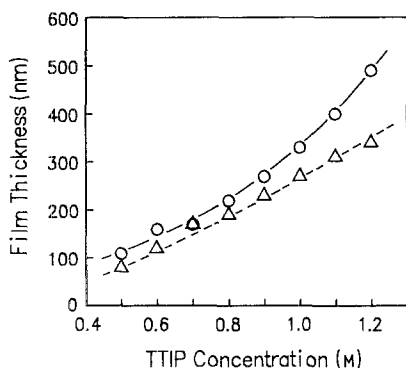


Figure 3 Effect of the TTIP concentration on the TiO₂ film thickness. TTIP:DEA:H₂O: (Δ) 1:1:0, (O) 1:1:2.

concentration smaller than 0.9 mol l⁻¹, uniform and transparent TiO₂ films could be formed. Thicker films tended to have fine cracks (see later). It was difficult to prepare thick and uniform films at lower W conditions probably due to insufficient hydrolysis and condensation. The condition of $W = 0$ to 2 was examined mainly because excess water induced the gelation especially at higher TTIP concentrations. At lower TTIP concentration, W conditions larger than 3 can also be applicable, where W has no positive effect on the morphology of the films. Excess DEA afforded discontinuous films. This is attributed to the properties of the gels formed at large R conditions. When heated above 100°C, these gels were melted to give viscous liquids so that their melting behaviour during the heat-treatment may cause the non-uniformity of the films.

The relationship between the TiO₂ film thickness and the TTIP concentration at constant R and W is shown in Fig. 3 (the heating temperature was fixed at 600°C). When $W = 2$, the film thickness increased exponentially with increasing TTIP concentration probably due to the increase of the TiO₂ concentration itself and the secondary effect of the viscosity increase of the solution with the TTIP concentration. Larger W gave thicker films at the same TTIP concentration. Films thicker than 200 to 400 nm were apt to have cracks. The thickness limit of uniform films obtained in one coating cycle was found to be about 200 to 240 nm at $W = 1$ to 2.

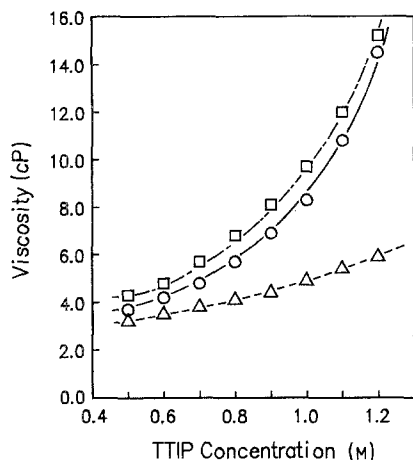


Figure 4 Effect of the TTIP concentration on the viscosity of the solution. TTIP:DEA:H₂O: (Δ) 1:1:0, (O) 1:1:2, (□) 1:2:2.

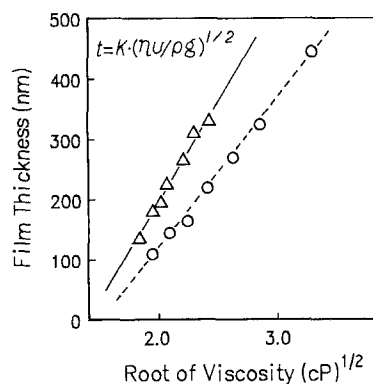


Figure 5 Effect of the viscosity of the solution on the TiO₂ film thickness. TTIP:DEA:H₂O: (O) 1:1:2, (Δ) 1:1:0.

The variation of viscosity of the solution with TTIP is shown in Fig. 4. The viscosity increased more sensitively with the TTIP concentration at $W = 2$ than at $W = 0$, because of the hydrolysis of TTIP and subsequent condensation. Increase of R has no effect on the concentration dependence of the viscosity except for the minor effect of the viscosity increase by the addition of viscous DEA.

The effect of viscosity of the solution on the film thickness is shown in Fig. 5. A dependence of the thickness on the square root of the viscosity is clearly found, being consistent with tendency reported in other dip-coating systems [23].

Much thicker films (above 1 μm) can be obtained by repeating the coating cycle: one cycle is composed of dipping, drying, and heating processes. The relationships between the number of coating cycles and the TiO₂ film thickness, and between the number and the film weight at constant R , W and TTIP concentration, are shown in Fig. 6. In both cases a linear relationship was observed. Therefore, the film thickness can be controlled by the TTIP concentration and the number of coating cycles. From Fig. 6 the relationship between the film thickness and weight can be derived as shown in Fig. 7. A moderately good linear relationship can be found. The slope of the line (3.9 or higher) corresponds to the density of the TiO₂ films. As will be described later, the films contain 30 to 50% rutile on heating at 600°C. Therefore, it can be concluded that the density derived from Fig. 7 is in good accordance with that of TiO₂ (anatase 3.9; rutile 4.27) [24], indicative of an ideal packing of TiO₂ crystals in the films. In other words, the films have no large pores.

The effect of the pull-up rate on the TiO₂ film thickness was examined roughly, and the dependence of the

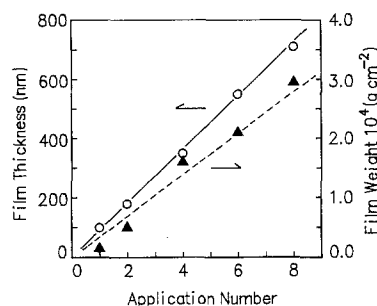


Figure 6 The relationship between the film thickness or film weight and the number of coating cycles at TTIP concentration 0.5 M.

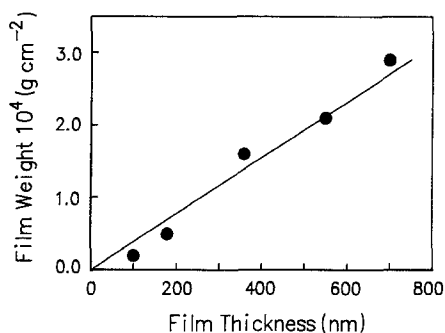


Figure 7 The relationship between the film weight and the film thickness at TTIP concentration 0.5M, $R = 1$ and $W = 2$. Slope = 3.9 g cm^{-3} .

thickness on the square root of pull-up rate was found [23]. A slow rate (6 cm min^{-1}) was preferable for the preparation of very uniform thick films by repeating the cycle.

The solvent of the TTIP solution has an effect on the film thickness as shown in Fig. 8. *t*-Butanol afforded the thickest films because of its highest viscosity.

The refractive indices of the TiO_2 films on silicon-wafer were examined using an ellipsometer, and were found to be in the range 2.0 to 2.3, a little smaller than the reported refractive indices of anatase (about 2.5) and rutile (2.6 to 2.9) [24]. This may be ascribed partly to the simultaneous contribution of the SiO_2 films formed on the silicon-substrate during the heat treatment in air at 600°C . Therefore, we intended to evaluate the refractive indices of the films formed on the glass plates (Corning Co., no. 7059) using the visible spectra. Typical examples of the visible spectra of pure anatase and rutile films (thickness values 775 nm for anatase film and 615 nm for rutile film: for their preparation, crystal modification and SEM images, see later) are shown in Fig. 9. The spectra indicate that anatase film is very transparent. The rutile films were slightly opaque due to the large grain growth of optically anisotropic rutile crystals. Because of the large refractive index of TiO_2 films, strong interference waves were observed in the visible spectra. The maximum and minimum transmittances (namely, minimum and maximum reflectances, respectively) are correlated with the equation [25]

$$n^2 = n_s(1 + R^{1/2})/(1 - R^{1/2}) \quad (1)$$

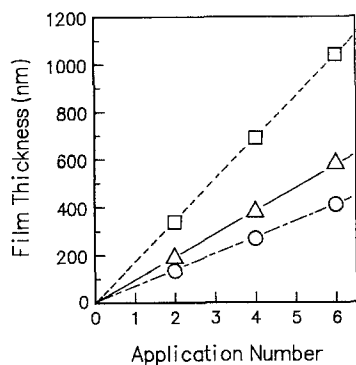


Figure 8 The effect of the solvent on the film thickness at TTIP concentration 0.5M, $R = 1$ and $W = 1$. (○) EtOH, (△) *i*-PrOH, (□) *t*-BuOH.

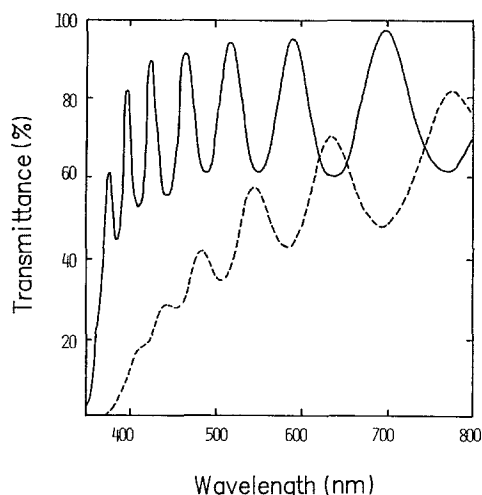


Figure 9 The visible spectra of (—) pure anatase and (---) pure rutile films formed on the glass substrates at 500 and 650°C , respectively.

where n and n_s are the refractive indices of the film and the glass substrate (in this case $n_s = 1.53$ at about 600 nm), respectively, and R is the reflectance. When the absorption of light by the film is negligibly small, namely the maximum transmittance was near 100%, the reflectance at the coating-glass interface can be estimated from the minimum transmittance, and then using Equation 1 we can obtain approximate refractive index of the film from the reflectance. Thus, values of 2.5 to 2.6 for the anatase film, and above 2.2 to 2.5 for the rutile film, were obtained.

It is well known that the wavelengths at maximum or minimum reflectance are correlated with the thickness, t , and the refractive index, n , of the film by the equation [25]

$$n = \lambda_1 \lambda_2 / \{2t(\lambda_2 - \lambda_1)\} \quad (2)$$

where λ_1 and λ_2 denote the wavelengths of adjacent pairs of minima or maxima. The film thickness (t) can be evaluated directly by SEM observation (see later). So the refractive index can be calculated using Equation 2, and moreover its wavelength dependence can be derived at the same time using the various wavelengths of adjacent maxima or minima. The results of the such calculation are shown in Fig. 10, where each index was plotted against the mean values of adjacent wavelengths which were used for its calculation. The refractive indices decreased exponentially

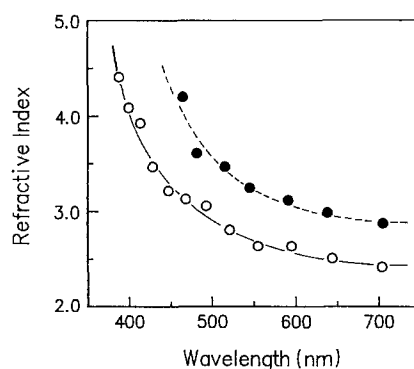


Figure 10 The wavelength dependence of refractive index of (○) pure anatase and (●) pure rutile films on the glass substrates derived from the visible spectra shown in Fig. 9.

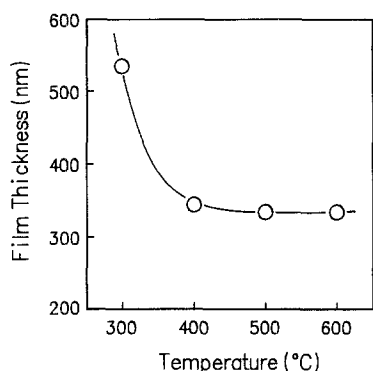


Figure 11 The effect of the heat treatment temperature on the film thickness: heating time at each temperature was fixed at 1 h. TTIP:DEA:H₂O = 1:1:1, 4 coatings.

increasing wavelength. This tendency is consistent with that reported [26] for TiO₂ film. The refractive indices around 600 nm can be read from Fig. 10 to be about 2.5 for anatase and about 2.9 to 3.0 for rutile, very close to those of the reported data, indicating that fully packed TiO₂ films are formed in this process. The DEA additive and alcoholic impurity can be eliminated effectively at the heating process. In ESCA measurement of the films, no carbon impurities were found except at the top surface.

In order to investigate the minimum heating temperature required to prepare the TiO₂ films, the variation of the film thickness with heating temperature was examined from the visible spectra using the assumed constant refractive index $n = 2.5$. The results are shown in Fig. 11. The film thickness decreased rapidly at 300 to 400°C, above which the thickness remained nearly constant. A small increase at 600°C can be ascribed to the partial transformation from anatase to rutile form. This tendency suggests that a minimum temperature of 400°C is required to eliminate the carbonaceous impurities. This temperature is consistent with that found in other systems [17].

The variation of X-ray diffraction pattern with temperature is shown in Fig. 12. At 400°C the crystallization of TiO₂ to anatase form takes place. This is lower than the crystallization temperature found for the films derived from Ti(OEt)₄-HCl-H₂O-EtOH system by other workers [20]. Near 550 to 600°C, trans-

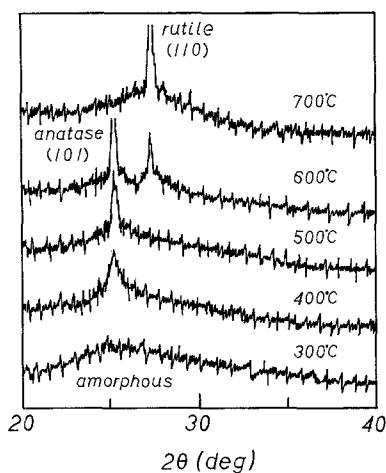


Figure 12 The effect of the heat-treatment temperature on the X-ray diffraction patterns of TiO₂ films.

formation to the rutile form begins, and above 650°C anatase modification disappeared completely. This transformation temperature seems to be much lower than that observed for the usual TiO₂ crystals (900 to 1000°C), and somewhat lower than that observed for TiO₂ films (720°C) prepared by the dip-coating from Ti(O-*i*-Pr)₄-HCl-H₂O-EtOH system [20]. Therefore, it can be suggested that chloride ion has a tendency to suppress the anatase-rutile transformation, and that DEA has no minor effects on the crystallization and transformation of TiO₂ films. In the X-ray diffraction patterns, the diffraction peaks assignable to higher Miller indices were very weak, being different from powder samples derived from the gels, indicative of the formation of highly oriented films. This tendency was clearly observed in the diffraction patterns of pure anatase and rutile films formed on the glass substrates, as shown in Fig. 13 (for both film preparations, see next section). The films lie on the *b*-axis for anatase and on the *c*-axis for rutile. This may contribute partly to the very high refractive indices of these films, especially in the case of the rutile film.

Anatase powders derived from the gel at 400°C transformed to rutile partly at 500°C and completely at 600°C within 1 h. The temperature of transformation is much lower than that found for usual TiO₂ crystals. On the other hand, a thick, pure anatase film (775 nm) can be prepared at 500°C on the glass by repeating the coating cycle, and it did not transform to rutile even after additional heating at 650°C for 2 h, but slowly transformed on heating at 700°C for as long as 10 h. Films thinner than 500 nm have a similar transformation temperature (550 to 600°C) to that of powders. Thus thick rutile films can be prepared by repeating the coating cycle with successive heat treatments around 650°C. The difference in the transformation temperatures of powders or thin films and thick films may be ascribed to the fraction of surface atoms in a body. The higher the fraction, the more easily the framework can rearrange to result in easy transformation. The formation of slightly non-stoichiometric oxides during heating the gel due to reduction by the organic compounds may also contribute partly to lower the transformation temperature.

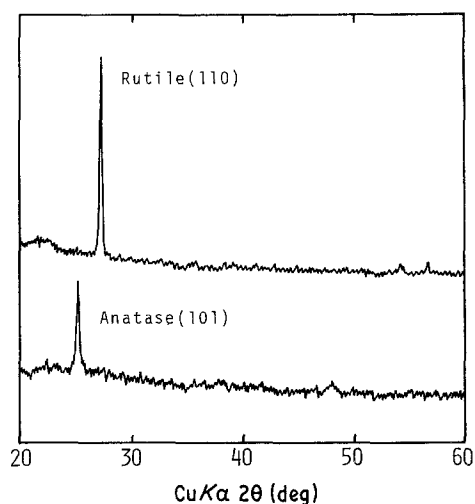


Figure 13 The X-ray diffraction patterns of pure anatase and rutile films formed on the glass substrates at 500 and 650°C, respectively.

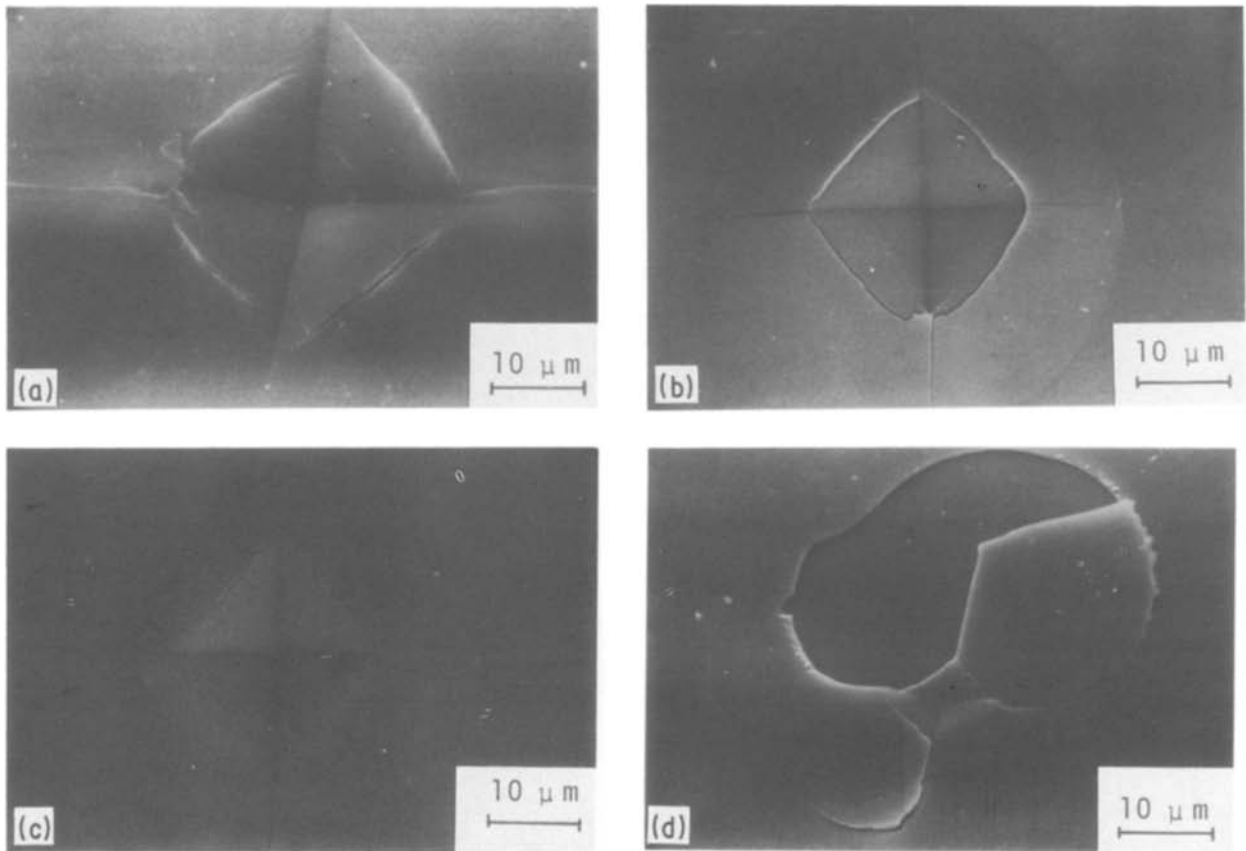


Figure 14 Scanning electron micrographs of (a) the surface of the glass itself and the films on the glass plates with indenter traces of Vickers hardness meter (25 g load was applied), (b) almost all anatase film (660 nm thick) obtained at 600°C, (c) pure rutile film (600 nm thick) obtained at 650°C, (d) a thick, anatase and rutile mixed film ($> 1 \mu\text{m}$).

In any case, these observations strongly support that the films prepared on the glass are fully packed.

The scanning electron micrographs of the surface and the fracture cross-section of the TiO_2 films on glass substrates are shown in Figs 14 and 15, respectively. In order to examine the adherence of the film to the substrate at the same time, a Vickers hardness microindenter was indented into the film with a load of 25 g, and the indentation traces were examined. As a reference, the glass substrate itself (without film coating) with an indenter trace is shown in Fig. 14a. Around the edges of the trace some microcracks are found, and further cracks proceed from the corners. In the films (Fig. 14b, $\sim 660 \text{ nm}$ thick, almost all anatase obtained at 600°C; Fig. 14c, $\sim 600 \text{ nm}$ thick, almost all rutile obtained at 650°C) which were

obtained by 10 to 15 coatings, analogous cracks are found, and the films with a very smooth surface seem to be held firmly on the substrates, suggesting that the films have good adherence to the substrate. However, a film thicker than about $1 \mu\text{m}$ (Fig. 14d) had a tendency to be partly broken by the indentation, indicative of the poor adherence induced by strong stresses within the film. The diagonal of the trace found on the film-coated substrate, especially on the substrate coated by a thick film (Fig. 14d), is smaller than that on the virgin glass, indicating that TiO_2 film has a larger Vickers hardness number than the glass. The appearances of the fracture cross-sections of the anatase and rutile films on the glass substrates (Fig. 15) also confirm the uniformity or the good adherence of the films.

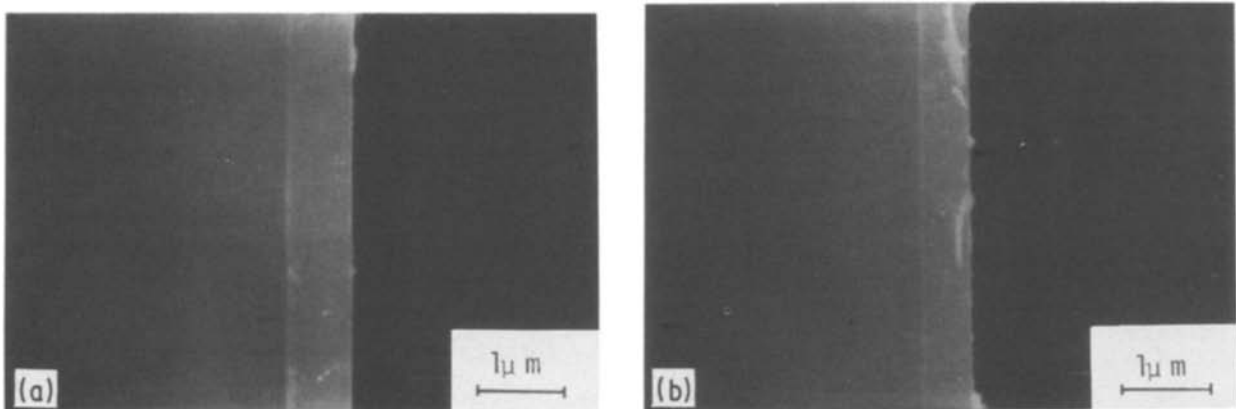


Figure 15 The fracture cross-sections of the films on the glass plates: (a) anatase film, (b) rutile film.

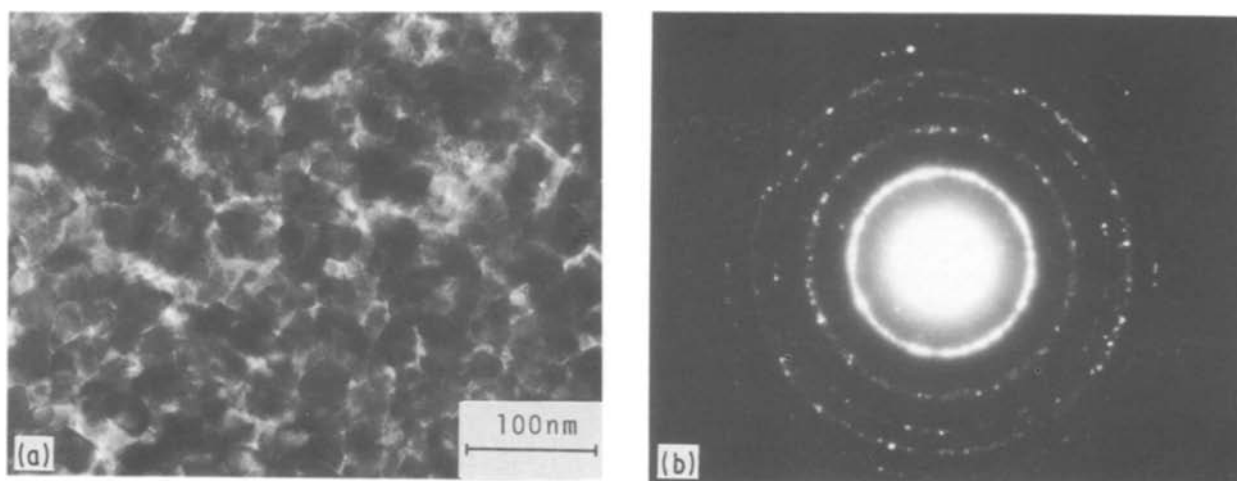


Figure 16 Transmission electron micrograph of a thin TiO_2 film formed on KBr single crystals at 600°C : (a) TEM images and (b) selected-area electron diffraction pattern.

The transmission electron micrograph of a thin TiO_2 film formed on KBr single crystal at 600°C is shown in Fig. 16a together with its selected-area electron diffraction pattern (Fig. 16b) which is consistent with that of anatase modification. TiO_2 crystals are found to be well developed. The size of the crystals is in the range 30 to 40 nm at 600°C . Some bright contrasts also exist between the crystals. The contrasts may be ascribed to openings (pores) rather than to the concentrations of carbonaceous compounds. The thickness of the thin films is comparable to the dimensions of the crystals. Because of the poor adherence of the film to the KBr crystal, the TiO_2 crystals migrate during the crystal growth to leave some pores. On the other hand, in the case of films on the glass substrate, where homogeneous nuclear formation can be expected and moreover the migration of TiO_2 on the glass may be slow, it is expected that very continuous and homogeneous crystal growth will occur concurrently with continuous crystal packing to give tightly packed films. The formation of films with a high refractive index and density of the films on the glass substrate described above can be explained by this mechanism. At 700°C almost pure rutile film is formed. The electron diffraction pattern showed rings composed of bright spots which were assignable to (1 1 0), (2 0 0), (2 2 0), (3 1 0), (4 0 0) diffractions. These data indicate that the film is oriented to the *c*-axis. The orientation of the film is different from that of the film on the glass substrate. Some effects of the KBr substrate on crystallization may exist.

4. Discussion

From the results described above, DEA can be concluded to be an effective additive in the sol-gel method in which the alkoxides were used as the starting materials not only in the sense that DEA can extend the conditions of the solution formation range, especially water content, but also in that DEA has rather some positive effect on the densification of the films. It is reported in a Patent [27] that when the TiO_2 gel films were treated with ethanolamines, much more transparent TiO_2 films could be formed after heating, than without the ethanolamine treatment. Ethanolamines and glycols are known to react with metal alkoxides to

give stable chelated glycolates and the like, through the alcohol exchange reaction [28]. Although we have no ideas concerning other roles of DEA for the stabilization of the solution and the apparently positive effect on the crystallization of TiO_2 , it is emphasized that DEA and related compounds can be used as effective modifiers to other sol-gel reactions. Use of acidic compounds as the modifier has been reported [8, 16, 19, 20]. But the acidic conditions may cause some trouble in the application to the coating on acid-sensitive substrates such as metals. In our case the solution can be thought to be nearly neutral or somewhat basic. So that the field of application may be wider than in the former acidic processes. Using this DEA-modified sol-gel method, other TiO_2 -based mixed oxides can be prepared much easier from the alkoxide, because sufficient water, and hence other inorganic compounds soluble in water, can be added at room temperature without the formation of precipitates. This possibility had been realized in the case of the preparation of ZrO_2 -based mixed oxide films. A study of this type of extension to TiO_2 is now in progress, and the results will be reported elsewhere.

5. Conclusions

1. Diethanolamine (DEA) can suppress the precipitation of oxides from the alcoholic solution in the hydrolysis of titanium isopropoxide so that much water can be added to the $\text{Ti}(\text{O}-i\text{-Pr})_4$ -diethanolamine-*i*-propanol solution to give a clear solution.
2. Uniform transparent TiO_2 films can be prepared by dip-coating with the solution. The thickness limit for uniform films obtained by one cycle was 200 to 240 nm. Films thicker than $1\ \mu\text{m}$ can be prepared by repeating the coating cycle.
3. Film thickness can be controlled by the TTIP concentration, viscosity of the solution ($\text{H}_2\text{O}/\text{TTIP}$ ratio), and substrate pull-up rate.
4. By controlling the heat-treatment temperature, pure anatase and rutile films can be obtained. The density of the films is equal to or is higher than 3.9. The refractive indices of considerably oriented anatase and rutile films were found to be 2.5 to 2.6 and about 2.9, respectively. These films were highly oriented and well densified.

5. Anatase and rutile films thinner than 1 μm adhered to the glass substrate more tightly than did the thick films.

6. Diethanolamine was found to have some positive effect on the high densification of the TiO_2 crystalline films.

Acknowledgement

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