Effect of the Addition of TiO_2 to SiO_2 Films with Concave–Convex Surface Derived by the Sol–Gel Method on Film Hardness and Application to Water-Repellent Glasses for Automotive Windows

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ゾル–ゲル法で作製した凹凸形状を有する SiO_2 薄膜の膜硬度に及ぼす TiO_2 添加効果と自動車用はつ水ガラスへの応用

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Silica-titania films with a concave-convex surface were prepared from a mixture of polymerized tetraethoxysilane (TEOS) sol containing tetraisopropoxytitanate and polymerized methyltriethoxysilane (MTES) sol in a molar ratio MTES/TEOS of 6. Film hardness was dependent on the composition of the coating sol, heat treatment temperature and time. The film obtained by introduction of 4 mol% TiO_2 to SiO_2 and by heat treatment at 620°C for 10 min was hard to be usable in engineering practice. New-type water-repellent glasses were produced by using these SiO_2 - TiO_2 films as an under layer combined with fluoroalkylsilane; the glasses showed an abrasion resistance for practical application as automotive windows.

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1. Introduction

There are many studies on sol-gel coating films showing various properties, such as electronic, optical, mechanical and chemical properties.^{1)–3)} There are, however, not so many studies on coating films having new functions derived from their surface morphologies instead of bulk properties.

The method utilizing phase separation has been studied to control a microstructure of a gel body. There are a lot of interesting studies on preparation of porous materials and control of their pore size.^{4),5)} Practical applications to supports for catalysts and filling materials for a column of gas chromatography have been examined. The sol-gel method is one of the important technologies to control the microstructure using phase separation, and to control a surface morphology of thin films. We have already reported that the mixture of two kinds of sols with greatly different average molecular weights derived from tetraethoxysilane ($\text{Si}(\text{OC}_2\text{H}_5)_4$, TEOS) and methyltriethoxysilane ($\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$, MTES) yielded the coating films with various surface morphologies.^{6),7)} In this study we examine the relationship between film hardness of silica based films with concave-convex surface and conditions for film preparation, such as TiO_2 concentration in the SiO_2 - TiO_2 system, heat treatment temperature and heat treatment time. Moreover we discuss about the effectiveness of SiO_2 - TiO_2 films to produce the water-repellent glass with an excellent abrasion resistance for automotive windows.

2. Experimental procedure

2.1 Preparation of silica based films

Figure 1 shows the preparation procedure of coating sols to obtain the silica based films with the concave-convex surface. A sol, called sol A, was prepared by mixing TEOS and hydrochloric acid of pH 2 with a molar ratio of $\text{TEOS} : \text{H}_2\text{O} = 1 : 4$ and by refluxing the solution at 60°C for 3.5 h. Another sol, called sol B, was prepared by mixing

MTES and acetic acid of pH 3 with a molar ratio of $\text{MTES} : \text{H}_2\text{O} = 1 : 3$ and by refluxing in the same manner. The alkoxide concentrations of sol A and sol B were adjusted to $0.75 \text{ mol} \cdot \text{l}^{-1}$ and $3.0 \text{ mol} \cdot \text{l}^{-1}$, respectively, by adding solvents mixed with 30 mass% of ethanol and 70 mass% of 2-propanol. A coating sol with a concentration of alkoxides of $0.15 \text{ mol} \cdot \text{l}^{-1}$ and with a molar ratio of $\text{MTES}/\text{TEOS} = 6$ was prepared by mixing sol A and sol B

Fig. 1. Procedure of preparing the coating sol.

with the addition of solvents mixed with 90 mass% of 2-propanol and 10 mass% of 1-butanol. In the case of the addition of TiO₂ to SiO₂ matrix, tetraisopropoxytitanate (Ti(O-*i*-C₃H₇)₄, TPOT) stabilized by acetylacetonate was added in the concentration ranging from 1 to 15 mol% against the sum of TEOS and MTES when sol A was prepared. Mean molecular weights were about 3000 for sol A and about 2000 for sol B, respectively.

The molecular weight of siloxane polymers was measured with a gel permeation chromatograph (GPC), TOSHO HLC-8020. The column consisted of TOSHO TSKgel types of one G-4000H-HR, one G3000H-HR and two G2000H-HRs (length: 0.3 m of each) and they were connected in series. The detector used was a differential refractometer. The temperature of the column and the detector were kept at 40 and 38°C, respectively. The mobile phase was tetrahydrofuran, which flowed at a rate of 1 ml/min. The molecular weight was determined by using the calibration curve obtained from retention time of standard compounds of polystyrene dissolved with tetrahydrofuran, of which molecular weight was already known.

Coating films were formed by a dipping-withdrawing manner on a clean soda-lime-silica glass substrate under a relative humidity of 58% at 25°C, and heated at 200°C for drying and then sintered at 530–700°C for 1–30 min.

2.2 Observation of surface morphology

The surface morphology of the films prepared was observed with a field-emission type scanning electron microscope (FE-SEM; Hitachi, S-4500). Surface roughness (R_a /nm) was measured on area of 2.5 μm^2 by using an atomic force microscope (AFM; Seiko Instruments Inc., SPI-3700), where R_a was calculated by using Eq. (1).

$$R_a = (1/S_0) \iint |h(x, y) - Z_0| dx dy \quad (1)$$

where S_0 is the area of the measured plane to be ideally flat, $h(x, y)$ the height of each measured point, Z_0 the standard height to be satisfied with Eq. (2), respectively.

$$\iint |h(x, y) - Z_0| dx dy = 0 \quad (2)$$

2.3 Evaluation of film hardness

Film hardness of silica based films was evaluated by measuring the difference in haze ($\Delta H/\%$) before and after a Taber-type abrasion test referred to JIS R3212-3.7. A lower ΔH value means a higher film hardness. The films were abraded with an abrasive wheel of No. CS-10F by 20 revolutions. Haze was measured with a hazemeter (Nippon Denshoku Kogyo, NDH-20D). The film thickness was measured by using a thickness meter (Sloan Tech., Dek-tak-3030).

2.4 Measurement of IR spectra of films

Infrared spectra of the coating films were measured with an FT-IR spectrometer (Perkin Elmer, Auto Image System connected to PARAGON 1000) in the 4000–700 cm^{-1} region. The samples were prepared by coating sols on Si wafers and by heating at 350, 550 and 650°C for 10 min. The coating sol were composed of the sol A containing TPOT and the sol B, which formed the 96SiO₂·4TiO₂ film with the concave–convex surface for a water-repellent glass. The measurement was carried out in a transmission mode for 24 scans. The spectrum for a bare Si wafer was used as a background datum.

2.5 Preparation of water-repellent glass and evaluation of practical durability

The silica based film with 4 mol% TiO₂ and with concave–convex surface of $R_a=5.5$ nm was used as an under layer for a water-repellent glass. The 96SiO₂·4TiO₂ film was obtained by heat treatment at 620°C for 10 min. The

water-repellent glass was prepared by coating hydrolyzed heptadecafluorodecyltrimethoxysilane (CF₃(CF₂)₇CH₂CH₂Si(OCH₃)₃, FAS) with the concentration of 4 mass% in 2-propanol onto the silica based films and by curing the glass at 200°C for 10 min. The coating process was carried out by hand-rubbing method and under a relative humidity of 50% at 25°C.

The contact angle of a water droplet with a volume of about 2 μl on water-repellent glass was measured with a contact angle meter (Kyowa Interface Science Co., Ltd., CA-X200). Anti-abrasion resistance of water-repellent glass was examined by measuring the contact angles after the traverse-type abrasion test (load: 0.1 $\text{kg}\cdot\text{cm}^{-2}$, friction material: canvas JIS L3102-1206).

3. Results and discussion

3.1 Effect of introduction of TiO₂ on surface morphology

Figure 2 shows the AFM image of the surface morphology of the silica based film with TiO₂ concentration of 4 mol%. According to an AFM and an SEM observations, the surface has small roughness and R_a was 5.5 nm. In the range of TiO₂ concentration less than 10 mol%, the concave–convex morphology was observed. It was, therefore, confirmed that this unique surface morphology was also formed in the SiO₂–TiO₂ system as a result of the micro-phase separation into the silica network phase and the solvent phase in the mixture of TEOS and MTES as reported in our previous papers.^{1)–4)}

Figure 3 shows R_a values of the 96SiO₂·4TiO₂ films with concave–convex surface as a function of aging time of a coating sol, where aging time means the storage time of a coating sol after preparation in a clean beaker covered with a plastic wrapping film at 25–55°C.

The surface roughness (R_a) gradually increases with increasing aging time and this tendency becomes more remarkable with increasing aging temperature. At an aging temperature of 25°C, the surface roughness dose not change within 12 h and increases to 8 nm in 72 h. At an aging temperature of 55°C, the surface roughness increases to about 16 nm in 96 h and the film obtained was then hazy with a haze value of 1.2%. The ΔH values of film obtained from the coating sol aged for 96 h at 55°C and the sol as prepared were 0.8 and 0.2%, respectively. This means that the hardness of the film obtained from an aged sol became slightly lower than that of films obtained from a sol as prepared. According to GPC measurements, the retention

Fig. 2. AFM image of the surface morphology of the film with 96 SiO₂·4TiO₂ (mol%).

Fig. 3. Surface roughness (R_a) of the $96\text{SiO}_2 \cdot 4\text{TiO}_2$ films with concave-convex surface as a function of aging time of a coating sol at 25, 45 and 55°C.

Fig. 4. Relationship between R_a and heat treatment temperature of the $96\text{SiO}_2 \cdot 4\text{TiO}_2$ films with concave-convex surface.

Fig. 5. Relationship between thickness and heat treatment temperature of the $96\text{SiO}_2 \cdot 4\text{TiO}_2$ films with concave-convex surface.

time of the strongest peak due to polymerized silica species of an aged coating sol became earlier with increasing aging time and temperature. For example, the molecular weights calibrated by standard polystyrene of an aged coating sol for 96 h at 55°C and of a coating sol as prepared were 12600 and 6200, respectively. The phenomenon of increasing R_a

Fig. 6. SEM images of the film with $96\text{SiO}_2 \cdot 4\text{TiO}_2$ (mol%) heat-treated at 500°C (a) and 700°C (b).

values and decreasing hardness of the films thus seems to happen as a result of increasing the polymerization degree of silica species in a coating sol. Therefore, we used a coating sol within about 12 h at 25°C after preparation to avoid any changes of R_a values and hardness of the films in this study.

3.2 Effect of heat treatment conditions on R_a

The relationships between R_a and heat treatment temperature and also between thickness and heat treatment temperature of the $96\text{SiO}_2 \cdot 4\text{TiO}_2$ films with concave-convex surface are shown in Fig. 4 and Fig. 5, respectively. The SEM photographs of the films obtained by heat treatment at 500 and 700°C are also shown in Figs. 6(a) and (b). The surface roughness and film thickness are drastically decreased with increasing heat treatment temperature; the roughness is decreased from 8.5 to 0.8 nm and the thickness from 95 to 20 nm with the heat treatment at 700°C, and at the same time the surface morphology changes from concave-convex to almost flat. The higher heat treatment turned silica based films more dense, and the surface roughness, as a result, becomes small to be almost zero. It is thus important to precisely control the heat treatment temperature in order to obtain the films with a concave-convex surface.

3.3 Composition dependence of film hardness

Figure 7 shows the composition dependence of ΔH in the SiO_2 - TiO_2 films. The films coated and dried were heated at

Fig. 7. Composition dependence of ΔH in the SiO₂-TiO₂ films.

620°C for 10 min. Addition of 1–5 mol% TiO₂ to SiO₂ matrix decreases ΔH values and gives a minimum value of 0.2% in the TiO₂ concentration of 3–5 mol%. In this range, there was no change in the surface morphology. On the other hand, addition of TiO₂ more than 10 mol% increases ΔH to 0.5%. This means that the silica based films of 96 SiO₂·4TiO₂ (mol%) is the optimum composition to achieve the lowest ΔH value, i.e., to obtain hard enough films. The silica based films with the composition of 96SiO₂·4TiO₂ in mol% is further examined as the under layer for water-repellent glasses in an automotive use.

This improvement can be explained by the change of thermal expansion and IR spectra of the bulk glasses derived from the sol-gel technique in the SiO₂-TiO₂ system reported by Kamiya and Sakka.^{(8),(9)} They report that the addition of TiO₂ to SiO₂ less than about 10 mol% was easy for the preparation of homogeneous glass and that the thermal expansion coefficient decreased to the lower value than that of SiO₂ glass and an additional absorption peak at around 950 cm⁻¹ appeared in this composition range. On the other hand, more than about 10 mol% TiO₂ oppositely increased the thermal expansion coefficient. They concluded that Ti⁴⁺ ions in the glasses are 4-fold coordinated with oxygens, constructing three-dimensional networks together with Si⁴⁺ ions, that is to say, the peak at 950 cm⁻¹ assigned to Si-O-Ti bonds was formed in the SiO₂-TiO₂ glassed with the relatively small concentration of TiO₂. In the case of the TiO₂ concentration more than about 10 mol% the TiO₂ component tended to isolate from SiO₂ matrix as the precipitation of TiO₂ crystal.

Figure 8 shows the IR transmission spectra in the 1500–700 cm⁻¹ region of the 96SiO₂·4TiO₂ (mol%) films heated at 350, 550 and 650°C for 10 min. The absorption peaks for each spectrum at around 1080 and 800 cm⁻¹ are assigned to the asymmetric Si-O and symmetric Si-O stretching vibrations, respectively. For the spectra of the films heated at 350 and 550°C, the absorption peaks at around 1275, 1100, 900 and 780 cm⁻¹ are observed, which are related to Si-CH₃ groups and Si-C bonds, Si-OH groups and Si-C bonds, respectively,^{(10),(11)} as shown in the figure. This indicates that a lot of organic components and active Si-OH groups are still present in the films heated even at 550°C and the densification of the films has not completed yet. On the other hand, for the spectrum of the film heated at 660°C, those three absorption peaks almost disappear and new absorption peaks at 950 cm⁻¹ due to Si-O-Ti bonds and at 800 cm⁻¹ due to Si-O-Si bonds appear. This indicates that the densification of the film has effectively occurred.

The increase in SiO₂-TiO₂ film hardness during a heat treatment is caused by the decomposition of methyl groups,

Fig. 8. IR transmission spectra in the 1500–700 cm⁻¹ region of the 96SiO₂·4TiO₂ (mol%) films heated at 350, 550 and 650°C for 10 min.

by the condensation of Si-OH groups and by the formation of Si-O-Ti bonds. Especially, the formation of Si-O-Ti bonds at a higher temperature of 650°C is closely related to the film densification, which is well consistent with the results reported by Kamiya and Sakka.^{(8),(9)}

The abrasion resistance is closely related to the microstructure of the films and it is effectively enhanced by densification of the films during heat treatment. The addition of 3–5 mol% TiO₂ to SiO₂ matrix can make the films more densified by the formation of Si-O-Ti bonds. However, in the case of the addition of 10 mol% TiO₂ or more, we deduce that TiO₂ crystal tends to precipitate in SiO₂ matrix and the microstructure of the films becomes less homogeneous. This less homogeneity may lead to the deterioration of the abrasion resistance of the films with the TiO₂ concentration of 10 mol% or more. In order to make our deduction clear, the further investigation will be required.

3.4 Dependence of heat treatment conditions on film hardness

Figure 9 shows the contour lines of ΔH of the 96SiO₂·4

Fig. 9. Contour lines of ΔH of 96SiO₂·4TiO₂ films with different heat treatment temperatures and times.

Fig. 10. Change of contact angle during the traverse type abrasion test for the water-repellent glasses.

TiO₂ films with different heat treatment temperatures and times. Lower haze values mean higher film hardnesses and the films with ΔH of 0.3% or less have a great possibility to be practically used as the under layer for the automotive water-repellent windows.

The film hardness is dependent on heat treatment conditions; higher temperatures reduce treatment time to achieve a given film hardness. If the treatment temperature is in 620 to 640°C, the film hardness becomes hard in a short time less than 10 min. For example, the films with ΔH of 0.3% or less can be obtained by heat treatment at 620°C for 10 min or at 640°C for 3 min. This means that the films with ΔH of 0.3% or less can be produced through tempered or bending furnaces in a mass production process. This improvement in film hardness is related to densification of the films by heat treatment at such high temperatures.

3.5 Application of the silica based film to water-repellent glass

The silica based film obtained with ΔH of 0.3% or less can be applied to the under layer for durable water-repellent glasses. The practical durability of the water-repellent glass was evaluated. Figure 10 shows the change in contact angle of two different samples during the traverse-type abrasion test. The compositions of under layers of water-repellent glasses are 96SiO₂·4TiO₂ (mol%) and pure SiO₂. The initial contact angle of both two types of the water-repellent glasses is 110–113°. The contact angle after this test should be kept as large as possible; for example, it is preferable to be at least 90° after 20000 rubbing passes in this traverse-type for the automotive windows.

In the case of SiO₂ (triangle), the contact angle gradually decreases by rubbing passes and finally peeling of the film was observed. The abrasion resistance of this sample was too low to be used for automotive windows. On the other hand, abrasion resistance was improved by using 96SiO₂·4TiO₂ (circle) film as an under layer for water-repellent glasses; the contact angle of 100° is maintained after 20000

rubbing passes, which must be a satisfactory resistance for water-repellent automotive windows. This improvement of the practical durability of a water-repellent glass results in the improvement of film hardness of an under layer with addition of TiO₂ to SiO₂ matrix. The under layer of 96 SiO₂·4TiO₂ film with concave-convex surface can, therefore, work as an ideal coupling layer between fluoroalkylsilane and glass surface, of which concave-convex surface can hold a large amount of water-repellent agent (polymerized fluoroalkylsilane). This new type water-repellent glass with the controlled surface morphology of the SiO₂-TiO₂ film has a great advantage to be used for automotive windows.

4. Conclusions

The silica-titania films with concave-convex surface were prepared from a mixture of polymerized tetraethoxysilane (TEOS) sol containing 4 mol% tetraisopropoxytitanate and polymerized methyltriethoxysilane (MTES) sol in a molar ratio MTES/TEOS=6, and the following conclusions were obtained.

- (1) Film hardness was dependent on composition of a coating sol and heat treatment conditions such as temperature and time. The film obtained was hard enough to be practically used for automotive windows by introduction of 4 mol% TiO₂ to SiO₂ and by heat treatment at 620°C for 10 min.
- (2) The effect of addition of TiO₂ to SiO₂ on the abrasion resistance of the films obtained was related to the microstructure of the films. A small amount of TiO₂ introduced to SiO₂ densified the film by the formation of Si-O-Ti bonds.
- (3) The new type water-repellent glass was produced with an excellent abrasion resistance for automotive windows.

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