Preparation and Reflectivity of Self-Organized Nanograded 
SiO₂/TiO₂/PMMA Thin Films

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自己組織化する SiO₂/TiO₂/PMMA ナノ傾斜薄膜の成膜とその低反射特性

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Self-organized nanograded SiO₂/TiO₂/Polymethyl methacrylate (PMMA) thin film was successfully prepared by only one coating from the combination of Tetraethylyl orthosilicate (TEOS) and Titanium tetraisopropoxide (TTIP). Sufficient kinetics difference between two alkoxides was an important requirement for the processing of the graded thin film in this process. The film was colorless and transparent due to two gradual interfaces of three layers. The reflectance of the SiO₂/TiO₂/PMMA graded film was lower than 2% over a wide wavelength range, and this is attributed to the interference of lights reflected from both the SiO₂ layer and TiO₂ layer. Although further investigation and precise process control are required to further decrease reflectance, this film can be formed using only one coating process and has great potential as a new low reflective coating.

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1. Introduction

The low-reflectivity coating is one of the most significant techniques in the field of functional coatings. This low-reflectivity coating has been applied to various industrial items, such as monitors and windows, and is generally composed of a multilayer structure with high and low refractive indices. Due to the interference of lights reflected from each layer interface, apparent surface reflection is decreased. Thus, this coating requires strict adjustment of the thicknesses and refractive indices of each layer. Silica and TiO₂ are commonly employed for this application. Because of the easiness of the control of layer thickness and homogeneity in a large area, a dry process was initially utilized for the preparation of these coatings. Recently, the number of wet coatings required for this application has gradually increased.

Very recently, we have successfully developed an inorganic/organic nanograded thin film focusing on the adsorption-conformation of a polymer on a solid surface in a dilute solution. This film is formed by mixing a polymer solution and a hydrolyzed metal alkoxide (such as tetraethyl orthosilicate (TEOS)) solution. The polymer is prepared by radical polymerization of methyl methacrylate (MMA) and methacryloyloxypropyl trimethoxysilan (MPTMS). In the dilute solution, MMA-originated segments are expected to adsorb to the polymer substrate because of their affinity with organic surfaces. Then, MPTMS-originated segments preferentially oriented to the solvent side due to the formation of chemical bonding with hydrolyzed TEOS monomers in the solution. Thus, after coating in the hydrolyzed TEOS solution and subsequent drying, the inorganic/organic nanograded thin film was obtained on a polymer plate.

In this method, the inorganic layer was formed by hydrolyzing metal alkoxide, and various inorganic materials can be applicable to its surface layer. This coating possesses an ideal structure for the interface layer between inorganic coatings and plastics, and has been practically applied to photocatalytic TiO₂ coatings on PET films. In the present study, we have tried to prepare a laminated structure of SiO₂ and TiO₂ layers in the inorganic part by only one coating process by mixing and controlling the hydrolyzing rates of two metal alkoxides in our process for inorganic/organic nanograded thin film. Then, the performance of the film as a low reflective coating was examined.

2. Experimental

MMA (Wako Pure Chemical Industries, Tokyo) and MPTMS (Shin-Etsu Chemical Co., Tokyo) mixture, whose mixing ratio was 19:1, was polymerized by adding 2,2'-azobisisobutyronitrile (AIBN: Wako) at 70°C for 4 h. The weight average molecular weight (Mw) of the copolymer obtained was 80000, and the ratio of Mw to the number average molecular weight (Mn) was 2.2. Both Mw and Mn were evaluated by gel permeation chromatography with acetone solvent. (HLC-8120GPC system with TSKgel-GMHHR-H(S) column, Tosoh Co., Tokyo). Then, a 2.0 g/L acetone solution of the copolymer was prepared. Tetramethyl orthosilicate (TMOS: Shin-Etsu), TEOS, titanium tetrabutoxide (TTB: Wako), and titanium tetraisopropoxide (TTIP: Wako) were employed as the starting alkoxides for the inorganic parts. All these alkoxides were dissolved in methanol. All the concentrations of the solutions were fixed at 4.0 mol/L. These solutions were hydrolyzed for one hour using 35% aqueous HCl. The amount of HCl added was determined to obtain the molar ratio of H₂O/metal alkoxide of 2/1. The radius of gyration (s²) of the hydrolyzed alkoxides were evaluated using a static-light-scattering spectrophotometer (SLS-6000HL, Otsuka Electronics Co., Ltd., Osaka). Then one of the hydrolyzed Si
alkoxide solutions was mixed with one of the hydrolyzed Ti alkoxide solutions. The mixture was diluted with methanol to 8.0 g/L. As a comparison, each metal alkoxide solutions without mixing as also tested.

Each of the two solutions were mixed and stirred for ten minutes. This mixture was used as the coating liquid. Polyethylene terephthalate (PET) film (Lumirror T-60, Toray, Tokyo) was selected as the coating substrate film, and the liquid was coated on the PET film by spin coating at 1500 rpm for ten seconds. The film was dried at 70°C for 10 h and subsequently heat-treated at 120°C for 10 h.

The thickness of the film was determined measuring the depth difference created by partially peeling off the film obtained. A scanning laser microscope (VF-7510, Keyence, Tokyo) was employed for this measurement. The depth profiles of C, Ti, and Si were evaluated through surface chemical composition analysis by X-ray photoelectron spectroscopy (XPS: PHI-5600 Perkin Elmer, U.S.A.) with Ar sputtering performed at a 3.0 kV beam voltage. The reflectivities of these films in the wavelength range from 400 nm to 800 nm were measured using a UV-Vis spectrometer (UV-2100: Shimadzu) before and after the heat treatment.

3. Results and discussion

The relationship between the thickness of the prepared film and the concentration of hydrolyzed TEOS in the coating liquid obtained is shown in Fig. 1. Film thickness increased linearly as the inorganic concentration increased. The film thickness when the inorganic concentration was 0% was estimated at approximately 40 nm, which was equal to the thickness of the graded structure determined through the direct observation by TEM and EDS on the SiO$_2$/PMMA graded film prepared using the coating liquid with 2% hydrolyzed TEOS. Detailed discussion on the self-organization and properties of graded structure will be described elsewhere.

Figure 2 shows depth profiles (Si concentration) measured by XPS with Ar sputtering on SiO$_2$/PMMA graded films prepared by changing the concentration of hydrolyzed TEOS in the coating liquid. All the Si degradation rates against sputtering time were almost the same. However, the starting times of the decrease in Si concentration were different. This means that each SiO$_2$ layer thickness on the graded layer is different. As the concentration of hydrolyzed TEOS in the coating liquid increased, the thickness of the inorganic part increased without affecting that of the graded part. This result indicates that the hydrolyzed TEOS concentration determines the thickness of the inorganic part in the prepared films. Therefore, by adjusting the concentration of hydrolyzed alkoxide in the coating solution, the film thickness of the inorganic part, which is one of the most important parameters for low-reflectivity coating is adjustable.

Figure 3 shows the depth profiles (C, Si, and Ti concentrations) measured by XPS with Ar sputtering of the films prepared using the mixture of Si alkoxide and Ti alkoxide as the inorganic source, in which the molar ratio of metallic element (Si/Ti) is fixed at 5/3. Figures 3(a), (b) and (c) show the depth profiles of the TMOS–TTB, TMOS–TTIP, and TEOS–TTIP films, respectively. The inorganic part was the mixture of SiO$_2$ and TiO$_2$ in the TMOS–TTB film. However, the concentration ratio of SiO$_2$ to TiO$_2$ in the TMOS–TTIP film changed gradually against with depth. The depth profile of the TEOS–TTIP film shows that the inorganic part of this film had a laminated structure in which a SiO$_2$-rich layer is located on the surface side and a TiO$_2$-rich layer is located on the interface side.

Figures 4(a), (b) and (c) show the depth profiles of TEOS–TTIP films whose Si/Ti ratio is 1/1, 3/1 and 4/1, respectively. All of the inorganic parts of the prepared films had similar laminated structures, although the TiO$_2$ concentration profile in the hybrid layer was different. The TiO$_2$ concentration slope in the hybrid layer was sharp for the film with low TEOS concentration. Figures 3(c) and 4 indicate that the relative concentration of TEOS governs not only the thickness of the SiO$_2$-rich layer but also TiO$_2$ concentration in the hybrid layer.

These structural differences of the inorganic parts are related to the difference in reaction activity between the metal alkoxides. When the metal part is the same, the alkoxide with a high-carbon number alkyl group is generally stable. Moreover, the reactivity of the alkoxide is generally higher than Si alkoxide. Figure 5 shows the relationships between the radiuses of gyration of polymerized metal alkoxides and their reaction times. This result indicates that the reactivity of TTIP is the highest, that of TEOS is the lowest and those of both TMOS and TTB are regarded as almost the same. Thus, the reactivity order for the alkoxides employed here is regarded as follows: TTIP > TTB > TMOS > TEOS. In addition, the reactivity of the methoxy group in alkyl trimethoxy silanes
such as MPTMS is higher than that of tetramethoxy silanes in TMOS.\textsuperscript{9)}

In the case of the TEOS–TTIP film, the reactivity of the two metal alkoxides is quite different. It is deduced that TiO\textsubscript{2} from TTIP is initially formed and combined with the alkyl trimethoxy group in MPTMS located near the substrate due to polymer adsorption. During this reaction, TEOS is not hydrolyzed enough and does not react with other inorganic species. After completing the reaction of TTIP, the hydrolysis of TEOS will be initiated. Thus, TiO\textsubscript{2} or hydroxide from TTIP is located as the intermediate layer between the adsorbed polymer layer and SiO\textsubscript{2} from TEOS. In TMOS–TTB and TMOS–TTIP cases, the kinetics difference in the hydrolysis of alkoxides was insufficient and thus clear laminate structure was not attained.

On the other hand, in the depth profiles of the TEOS–TTIP films whose TEOS/TTIP molar ratio is higher than 3/1, as shown in Figs. 4(b) and (c), Si concentration increased not only on the surface side but also on the PMMA side. This is probably explained by the stability of a Ti–O–Si bond being less than that of a Si–O–Si bond. Thus, the relative reactivity of TEOS to bind to Si methoxide group included in MMA/MPTMS copolymer is probably higher than that determined only by the difference in reactivities between metal alkoxides. As the inorganic branches of the polymer grow, the relative TEOS reactivity decreases due to the substitution of Ti isopropoxide for Si ethoxide at the ends of the branches.

Fig. 3. Depth profiles by XPS of the films prepared by the mixture of Si alkoxide and Ti alkoxide in which the number ratio of Si/Ti is 5/3. (a) TMOS and TTB, (b) TMOS and TTIP, and (c) TEOS and TTIP.

Fig. 4. Depth profiles by XPS of the films prepared by the mixture of TEOS and TTIP in which the number ratio of Si/Ti is different. (a) Si/Ti = 1/1, (b) Si/Ti = 3/1 and (c) Si/Ti = 4/1.
Fig. 5. Relationship between the radius of the gyration of the polymerized metal alkoxide and its reaction time.

However, these results also indicate that this effect is negligible under the condition that TEOS/TTP molar ratio is 1/1.

Based on these results, it is elucidated that sufficient kinetics difference between two alcohols is an important requirement for the processing of the laminate structure.

The reflectivity of the SiO$_2$/TiO$_2$ laminate structure at wavelength $\lambda$ is minimized while the refractive index of SiO$_2$, $n_1$, thickness of the SiO$_2$ layer, $d_1$, refractive index of TiO$_2$, $n_2$, and thickness of the TiO$_2$ layer, $d_2$, satisfy $4n_1d_1=2n_2d_2=\lambda$.

Assuming the refractive indices of SiO$_2$ and TiO$_2$ are 1.3 and 2.3, the suitable thickness ratio of TiO$_2$/SiO$_2$ can be estimated at approximately 1.13. In practice, the refractive index of TiO$_2$ is lower than the assumption. Thus, a suitable laminate structure is realized as a composition close to that shown in Fig. 3(c).

The reflectivities of several graded films before and after heat treatment at 120°C for 10 h are shown in Fig. 6. Figures 6(a), (b) and (c) refer to the cases of the SiO$_2$/PMMA, TiO$_2$/PMMA, and SiO$_2$/TiO$_2$/PMMA systems, respectively. The reflectivity of SiO$_2$/PMMA graded film slightly decreased with the heat treatment. On the other hand, reflectivity was increased by approximately 1% in the case of the TiO$_2$/PMMA system by the heat treatment. These reflectivity changes were probably caused by the removal of organic groups and densification in the inorganic part during heating. The refractive index of the shrunk SiO$_2$ layer is lower than that of the previous SiO$_2_{x-y}(OR)_y$ layer and that of the shrunk TiO$_2$ layer is higher than that of previous TiO$_2_{x-y}(OR)_y$ layer. Therefore, while SiO$_2$/PMMA graded film was heat-treated, the refractive index of its SiO$_2$ part was slightly decreased, so that the film’s reflectivity slightly decreased. On the other hand, the refractive index of the TiO$_2$ part of the TiO$_2$/PMMA graded film was increased by heat treatment, so that its reflectivity increased.

It should be noted that the reflectivity of the SiO$_2$/PMMA graded film is even lower than that of the PET substrate film itself. This is caused by low reflection due to the surface silica layer with a low refractive index. Moreover, the reflectance of the SiO$_2$/TiO$_2$/PMMA graded film prepared by the mixture of TEOS and TTIP was decreased by approximately 0.5% by the heat treatment, and was lower than that of SiO$_2$/PMMA graded film. This result suggests that the low refractive performance of SiO$_2$/TiO$_2$/PMMA graded film is attained not only by the substitution of silica on its surface, but also by the interference of light reflected from both the SiO$_2$ layer and TiO$_2$ layer.

The reflectivity of the prepared SiO$_2$/TiO$_2$/PMMA graded film was also influenced by the concentration of the hydrolyzed TEOS and TTIP mixture whose Si/Ti ratio was constant at 5/3. This result indicates that not only the thickness ratio of TiO$_2$/SiO$_2$ but also thicknesses of both the SiO$_2$ layer and TiO$_2$ layer is important for low reflectance. In this system, the ideal concentration of hydrolyzed TEOS and TTIP mixture was 4%.

Furthermore, it should be noted that the wavelength range of low reflectance is wide for the SiO$_2$/TiO$_2$/PMMA graded film. Similar results have been reported by several researchers.
both theoretically and experimentally, and this is a typical merit of the graded structure of low and high refractive index materials for the application as low-reflectivity coating.\(^\text{2,11}\) Although further investigation and precise process control is required for the attainment of lower reflectance, this film is colorless and transparent due to two gradual interfaces of three layers, and has great potential as a new low-reflectivity coating.

4. Summary

In the present paper, self-organized nanograded $\text{SiO}_2/\text{TiO}_2$/PMMA thin film was successfully prepared using only one coating from the combination of TEOS and TTIP. Sufficient kinetics difference between two alkoxides is an important requirement for the processing of the graded thin film in this process. In addition, the relative concentration of TEOS governs not only the thickness of the $\text{SiO}_2$-rich layer but also $\text{TiO}_2$ concentration in the hybrid layer. The film is colorless and transparent due to two gradual interfaces of three layers. The reflectance of the $\text{SiO}_2/\text{TiO}_2$/PMMA graded film was lower than 2% over a wide wavelength range, and this is attributed to the interference of lights reflected from both the $\text{SiO}_2$ layer and $\text{TiO}_2$ layer. Although further investigation and precise process control is required for the attainment of lower reflectance, this film can be formed using only one coating process and has a great potential as a new low-reflectivity coating.

References

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