The preparation and properties of CeO$_2$–TiO$_2$ film by sol–gel spin-coating process

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Abstract

Ultraviolet absorbing CeO$_2$–TiO$_2$ coatings were prepared by the sol–gel spin-coating process heat treated at 500 °C. The films obtained were brilliant yellow, adherent and had some pattern on the soda-lime glass substrate. The optical transmittance, thickness and hardness of the films as a function of the number of coatings, aging time (0, 24, 48, 96 h) or aging temperature (28, 35, 40, 50 °C) were determined, and surface microstructure of the films was observed by SEM. We found some pattern on the surface of films. This pattern was similar to that of the stage for fixing the substrate. The pattern on the surface of films would be caused by the difference of thermal conductivity to slide glass in the part of metal of the stage and hollow part of the stage.

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1. Introduction

It is well known that amorphous and crystalline coating can be prepared at relatively low temperature using a metal alkoxide by sol–gel process. Optical and other properties of thin films can be controlled easily by changing the physical and chemical conditions of preparation by sol–gel process [1,2]. In general two methods may be used to deposit a sol onto a substrate: dip coating [3,4] and spin coating [5–7]. These processes can be used to prepare thin films by sol–gel processing for various applications such as optical coating, electronic coating, electrochromic devices, thermochromic devices and protective coating. Especially the spin coating is used for precise preparation of thin film.

CeO$_2$–TiO$_2$ thin films have some properties of ultraviolet ray absorption and electronic properties and so on [7–9]. We reported the preparation and properties of CeO$_2$–TiO$_2$ thin films using the dip-coating process [10,11], which is a very simple technique. Dip-coating technique has some processing parameters that reflects on the porosity and refractive index of the resultant films. On the other hand spin-coating process has more various processing parameters than dip-coating process.

The processing parameter includes the viscosity, surface tension and amount of the sol, the speed and duration of the substrate rotation, the humidity and temperature of the surrounding atmosphere and so on [12–14]. And adjusting these parameters to suitable conditions is important for production of the film. Thus surface obtained by the precise spin-coating process is finer texture compared to surface obtained by dip-coating process and the precise spin-coating is applied for formation of coating film for memory disc and so on.

Present paper reports a preparation and properties of CeO$_2$–TiO$_2$ system film of ultraviolet ray absorption by the sol–gel spin-coating process. We have measured the microstructure of film by scanning electron microscopy (SEM), an absorption spectrum, hardness and thickness of films, and examined the surface pattern of the film.

2. Experimental

2.1. Coating the substrate slide glass

Titanium alkoxide solution containing Ce was prepared by dissolving 2.53 g (6.81 mmol) of CeCl$_3$·7H$_2$O in 30 ml C$_2$H$_5$OH and adding 1.93 g (6.81 mmol) of Ti(OCH(CH$_3$)$_2$)$_4$ to solution (Ce/Ti mol ratio = 1/1).
Glass slides were ultrasonically cleaned with an ethanol solution and dry. After the slide glass substrate was coated by spin-coating method apparatus (MIKASA 1H-DX2) with a spin speed of 3000 rpm, evaporated at room temperature, and heated in air at about 500 °C. If necessary, these procedures were repeated.

2.2. Measurement of properties

Thickness and transmittance of coating films were measured as a function of the number of coating, aging time (0, 24, 48, 96 h), or aging temperature (28, 35, 40, 50 °C). The surfaces of the coating films were observed by SEM. Thickness and roughness of the films was determined with a profilometer (Sloan Dektak3030). Hardness of the films was measured by Vickers hardness tester (SIMAZU HMV-2000). We measured 10 times and the mean values of the hardness were obtained.

3. Result and discussion

3.1. Solution and coating film

The C₂H₅OH solution containing CeCl₃ was colorless and transparent. When Ti(OCH(CH₃)₂)₄ was added, the color of solution changed to bright yellow. The solution is called ‘as-prepared’ solution. After the slide glass substrate was coated by spin-coating process, the sample color was slightly yellow and transparent or translucent. After the sample was heat-treated for 5 min at about 500 °C, and the film was bright yellow and very adherent to the substrate.

When the solution after aging for 24 h (called ‘24 h-solution’) was used, the films were not translucent and hazier than the coatings prepared from as-prepared solution. And when the solution after aging for 48 h (called ‘48 h-solution’) and 96 h (called ‘96 h-solution’) was used, the films were more transparent and clearer than other films of using the as-prepared solution.

Fig. 1. Transmittance of the films (A) using as-prepared, 24 h-solution, 48 h-solution, 96 h-solution at 28 °C; (B) using solution of aging temperature 28, 35, 40 and 50 °C; (C) using as-prepared solution at 28 °C; (D) using 96 h-solution at 28 °C.
solution. The films of solution of using aging temperature (28, 35, 40 and 50 °C) were also the same tendency.

3.2. Transmittance

Transmittance of the uncoated slide glass substrate was measured and compared with that of the coated samples after aging time (0, 24, 48, and 96 h) or after one, two, and three coating. Fig. 1(A) shows that the transmittance of curve for the samples that were coated using as-prepared solution, 24 h-solution, 48 h-solution, 96 h-solution at 28 °C. Fig. 1(B) shows the transmittance curve for the samples that were coated a time using solution for aging for 24 h at 28, 35, 40 and 50 °C. The transmittance of wavelength in visible region increases with rising the aging temperature.

The transmittance curves for 96 h-solution at 28 °C and solution of aging for 24 h at 50 °C are different from other curves in Fig. 1(A) and (B). In these solutions the hydrolysis of titanium alkoxide took place during the aging and the resultant microcomposite structures of the films would be the reasons the difference in the transmission curves.

Fig. 1(C) shows the transmittance curves for the samples that were coated using as-prepared solution. It is noteworthy that the samples (CeO2–TiO2 coating samples) hardly transmit the light between 300 and 350 nm in comparison with uncoated slide glass. Fig. 1(D) shows the transmittance curves for the samples that were coated using 24 h-solution. Fig. 1(C) and (D) showed that transmittance of each wavelength in visible region decreases with increasing the number of coating. The color of the films becomes brighter. The reasons for these changes in transmittance and color would be mainly the increase in the thickness of the coated films.

3.3. Film thickness

The thickness of films coated 1–6 times was measured shown in Fig. 2. Fig. 2(A) shows that the thickness of the films using as-prepared solution, 24 h-solution,
48 h-solution and 96 h-solution at 28 °C. Fig. 2(A) and (B) shows the thickness of the films coated 1–6 times of aging temperature 28 and 40 °C solution. Fig. 2(C) shows the thickness of the films using solution for aging for 24 h was measured. Almost linear relationship between thickness of the films and number of coating was found. It is shown that the thickness of the film obtained by one coating is about 200 nm which is nearly same value for other coating by the sol–gel process.

3.4. Microstructure

The surface microstructure of films of coating one times is shown in Figs. 3–6. The surface of the film using as-prepared solution at 28 °C (Fig. 3(A)) is not of finer texture compared to the surface of film using 24 h-solution at 28 °C (Fig. 3(B)). The surface of the film using 96 h-solution at 28 °C (Fig. 3(C)) is not of finer texture compared to the surface of film using 96 h-solution (Fig. 6(C)). The reason

Fig. 3. The microstructures of surfaces of films from (A) as-prepared solution and 24 h-solution; (C) 96 h-solution at aging temperature 28 °C.

Fig. 4. The microstructures of surfaces of films (A) as-prepared solution and 24 h-solution; (C) 96 h-solution at aging temperature 35 °C.
for this difference in microstructure would be caused by the difference in the extent of hydrolysis of titanium alkoxide solution.

3.5. Hardness

Hardness values of the films are shown in Fig. 7. Hardness of slide glass and heat-treated slide glass at 500 °C was 536 and 531 kg/mm², respectively. Hardness of films is decrease with increasing number of coating. The hardness of the films coated one time is nearly same with that of slide glass. Since thickness of their films is very thin (about 200 nm), the hardness values not only hardness of films but also hardness of substrate was measured simultaneously. We thought that hardness value of the films coated 6 times is that of CeO₂–TiO₂ films. Hardness and thickness of films coated 6 times is shown in Table 1. Hardness of films became harder with increasing aging time and temperature. Hardness of films would become harder by decreasing the porosity of film. The surface microstructure of films...
(Figs. 3–6) was finer texture with increasing aging temperature and aging time. It appears that porous surface microstructure of films becomes densely with increasing the aging temperature and aging time.

3.6. Pattern

We observed pattern in the surface of film after producing films (Fig. 8(A)). This pattern was observed more clearly than films using sol with higher aging temperature and longer aging time. This pattern was similar to that of metal stage for fixing slide glass in vacuum (Fig. 8(C)). The surface microstructure of film on the circle A and the circle B in Fig. 9(A) were shown in Fig. 9(B) and (C), respectively. Roughness along line from \(X\) to \(Y\) in Fig. 9(A) was measured was shown in Fig. 10. The surface microstructure of film on the circle A and the circle B was same (Fig. 9(B) and (C)). The undulation in surface structure of film was show in Fig. 10. The position of high and low in Fig. 10 were coincidence with the part of metal of stage and the hollow part of the stage, respectively. Thus the patterns in surface of film were caused by the undulation.

At first we thought that this pattern in films was caused by the effect of reflection of transmitted light. Therefore, film was prepared in the conditions that film was irradiated by ultraviolet ray \((\lambda = 365\text{ nm})\) during spinning the slide glass, and also film was prepared in dark or using black color stage. However, this pattern of the surface films appeared. But when the film that does not transmit light was inserted between slide glass and the metal stage, it has observed that the pattern became thinner. Therefore, this pattern is not caused by the effect of reflection of the light. Secondly, we thought that the pattern was caused by the difference in the evaporation rate of solvent because of the difference of the thermal conductivity between the slide glass substrate and the part of metal of stage or hollow part of the stage. The coating films were prepared in condition that a plastic film of low heat conductivity is inserted between the slide glass and the metal stage. In this case the pattern on the surface of film was not observed as shown in Fig. 8(B). Thus the reason for the occurring some pattern of the spin-coating process would be the difference of the thermal conductivity to the slide glass from the metal stage.

We considered that during the spin coating, sol–gel solution vaporizes and the temperature of the film becomes lower by the effect of vaporization heat. There are temperature difference between the part of metal of the stage and the hollow part of the stage because the part of metal of the stage sticks to the glass of substrate and soon recovers the temperature of original temperature before the start of spin coating. Thus the thickness of the film for the part of metal of the stage is thicker as shown in Fig. 10. The pattern we observed is different from so-called the radiative striation during the spin coating. We observed the radiative striation during the spin coatings. But in order to get the reliable transmission, thickness and hardness values of the coating

![Fig. 7. Hardness of films (A) aging at 28 °C; (B) aging at 35 °C.](image-url)

| Aging temperature (°C) | Aging time (h) | Vickers hardness (kg/mm²) | Thickness (nm) |
|-------------------------|---------------|---------------------------|----------------|
| 24                      | 0             | 389                       | 831            |
| 24                      | 24            | 378                       | 751            |
| 48                      | 378           | 819                       | 612            |
| 96                      | 415           |                           |                |
| 35                      | 0             | 307                       | 1080           |
| 24                      | 395           | 1005                      |                |
| 48                      | 382           | 819                       |                |
| 96                      | 418           | 769                       |                |
| 40                      | 0             | 346                       | 119            |
| 24                      | 386           | 844                       |                |
| 48                      | 451           | 667                       |                |
| 96                      | 505           | 759                       |                |
| 50                      | 0             | 315                       | 1098           |
| 24                      | 417           | 653                       |                |
| 48                      | 386           | 654                       |                |
| 96                      | 403           | 872                       |                |
films we adopted two step method. The first step is to drop the solution to the substrate with slow spinning of 500 rpm for 3 s. The second step is to rotate the stage with higher rotating speed of 3000 rpm for 10 s. This two step method was determined by the many preliminary experiments and finally the radiative striation was not formed by this method.

4. Conclusions

(1) The yellow coating and ultraviolet ray absorbing CeO$_2$–TiO$_2$ films was prepared on slide glass by the spin-coating process using sol–gel solution.
(2) Films of about 200 nm in thickness were obtained by coating one time.
(3) The relation between films of thickness and coating times was almost linear up to 6 times coating.
(4) The microstructure of film becomes fine texture by the advance of the hydrolysis of titanium alkoxide solution.
(5) The hardness of film becomes harder as the hydrolysis of titanium alkoxide solution proceeds.

Fig. 8. (A) The surface of the film using 96 h-solution at 35 °C; (B) the surface of the film using 96 h-solution at 35 °C when insert film of low heat conductivity between slide glass and stage; (C) stage for fixing slide glass.

Fig. 9. The SEM of texture of the surface of film.

Fig. 10. The roughness of the surface of film.
(6) The surface of films was patterned by the difference of heat conduction to the slide glass by the spin-coating during the substrate rotation.

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