

## Nano replica for inorganic porous structures using layer-by-layer self-assembly process of polyelectrolytes

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A new fabrication method of the titania anatase thin film deposit on the thin polymer films formed by layer-by-layer sequential adsorption is reported. Porous titania thin films are formed by using the systematically controlled nano structure of the layer-by-layer self-assembly films as the replica. It was also found that film thickness was controlled by the composition of the titania with the layer-by-layer self-assembly film. Titania nano particles with small diameter were obtained by the interaction of the titania with the polymer matrix.

Key words: titanium oxide, supersaturate, layer-by-layer, polyelectrolytes, thin film, self-assembly

### 1. INTRODUCTION

Anatase type crystal of titania is the famous material for its photo catalysis and various application such as antifouling, antifog, antimicrobial, deodorizing and photovoltaic effect are reported. Recently, dye synthesized titania compound is applied for the high efficiency, low cost materials for a solar battery [1-3].

Many fabrication process is proposed for anatase titania thin films. For example, sputtering, spray pyrolysis[4], sol-gel process[5]. In these processes, in order to have anatase crystal with sufficient crystallinity, the heat treatment at more than 400°C was unavoidable. Therefore, it was almost impossible to utilize organic substrate or organic materials with titania for these processes. Thus, anatase coatings on organic substrates and incorporation of organic molecules into the coatings were not directly achieved using these techniques. In general, crystalline films on organic substrates are prepared by coating of anatase powder mixed with appropriate organic binder [6].

In recent years, new techniques using supersaturated solutions have been developed for preparation of metal oxide films such as SiO<sub>2</sub>[7], SnO<sub>2</sub>[8], FeOOH[9] and V<sub>2</sub>O<sub>5</sub>[10]. These techniques produce dense oxide films through direct deposition on substrate from solutions at relatively low temperature. Preparation of amorphous titania thin films was demonstrated using aqueous solutions of ammonium hexafluorotitanate added with boric acid [11]. Baskaran et al. [12] reported that non-crystalline titania films were formed on sulfonated self-assembled monolayers using an aqueous titanium lactate. In these cases, however, crystallinity of the deposited films was not sufficient for the catalytic application.

In the previous study, it was reported that anatase films having excellent crystallinity were directly obtained on glass and various kinds of organic substrates at 40-70 °C using aqueous solutions of titanium tetrafluoride (TiF<sub>4</sub>) as a starting material [13]. In this method, however, a porous substrate is required to obtain a porous structure because of the direct adsorption from the solution. Therefore, the control of the porousness is the essential problem to have photo-catalytic property.

On the other hand recently, there are many reports on the fabrication method for organic thin films. Among the various fabrication methods, the layer-by-layer sequential adsorption technique of polyelectrolytes proposed in 1992 [14,15] is very promising because of its simplicity and the variety of the materials, which can be used in the technique. Just by the alternate dipping of the charged substrate to poly-cation and poly-anion solutions sequentially, multilayers of the organic thin films can be formed on the substrate. By using this technique, organic EL devices[16,17], nonlinear optical devices, solar batteries, sensors and filters[18] are fabricated. It was reported that by changing the solution pH of poly-cation or poly-anion, adsorption characteristics of the polyelectrolytes can be systematically controlled. In the case of weak polyelectrolytes, the surface wettability [19] or nano structure [20] are changed by adjusting the solution pH. Especially, the surface area can be control because the surface roughness of the films was systematically controlled by adjusting the solution pH.

In the present study, we report the new fabrication method of the titania anatase thin film deposit on the thin polymer films formed by layer-by-layer sequential

adsorption. Porous titania thin films are formed by using the systematically controlled nano structure of the layer-by-layer self-assembly films as the replica. It was also found that film thickness was controlled by the composition of the titania with the layer-by-layer self-assembly film. Titania nano particles with small diameter were obtained by the interaction of the titania with the polymer matrix.

## 2. EXPERIMENTSL SECTION

In this study, poly acrylic acid (PAA, Mw=90,000, Polyscience Inc.), as a polyanion, and poly allylamine hydrochloride (PAH, Mw=70,000, Aldrich Chemical Inc.), as a polycation, were used to fabricate the layer-by-layer self-assembly film. These materials were solved in 18.3M  $\Omega$  pure water, concentration of this solution was  $10^{-2}$ M both of same. Substrate was a silicon wafer, which had 2000 Å silicon oxide layer. By etched surface by using KOH solution, silicon oxide was charged negatively in these aqueous solutions. Solution pH, PAA solution was pH 2.5 - pH 4.5 and PAH solution was pH 6.5 - 8.5, was adjusted by the adding of HCl or NaOH.

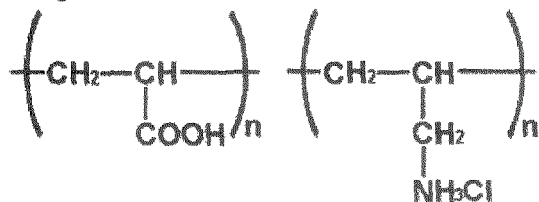


Fig.1 Polymer structures of PAA and PAH

After each the 15 minutes' adsorption of the polyelectrolytes, substrates were rinsed by pure water for 1 minute, three times. 50 bilayers of the layer-by-layer sequentially adsorbed film was deposited on the thermally oxidized films on the Si wafers. After the deposition, the self-assembled films are dried at 70 °C, for 1 hour in vacuum. The nano structure fabricated self-assembled films are transformed by dipping the diluted HCl solution at pH2.9. Titania was adsorbed into the porous structure of the fabricated polymer films. Detail of the fabrication is reported in the previous [13]. 0.248 g of  $\text{TiF}_4$  was dissolved in the 50ml pure water. By adding the aqueous ammonia, pH of the solution was adjusted at the value between 1.8 to 2.0 as the initial pH value. A substrate was stayed in the solution for 3 hours at 60 °C. Then the substrate was removed from the solution and rinsed with pure water in a supersonic bath.

The surface of the fabricated thin films were observed with an atomic force microscope (AFM, nanoscope IIIa, Digital Instruments), a scanning electron microscope (SEM, S-4700, Hitachi) and a transmission electron microscope (TEM, TECNAI F20, Philips). Si cantilever was used for the tapping mode of the AFM.

## 3. RESULTS AND DISCUSSION

The surface nano structures of the layer-by-layer sequential adsorption of the film are shown in Fig.2. By

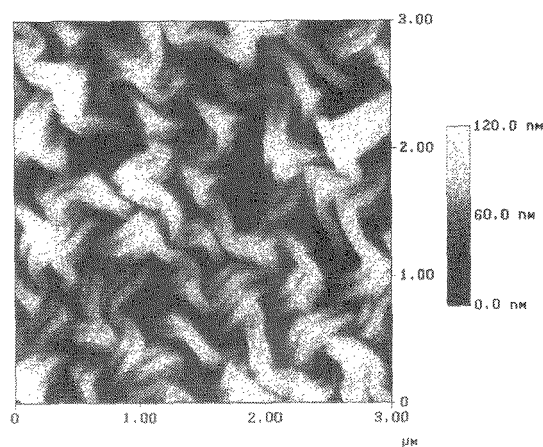


Fig.2 AFM image of PAH(pH7.5)/PAA(pH3.5) film surface (10 bilayers)

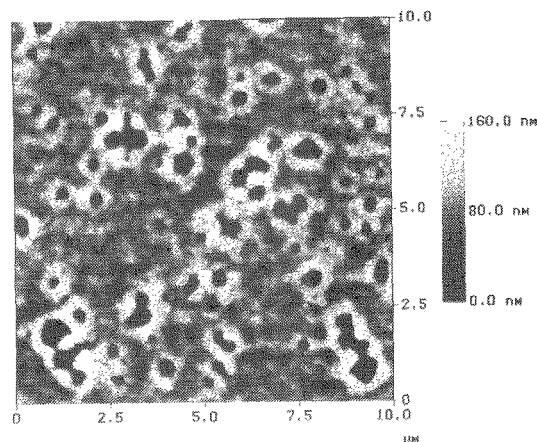


Fig.3 AFM image of PAH(pH7.5)/PAA(pH3.5) film surface after the soaking into pH2.9 diluted HCl

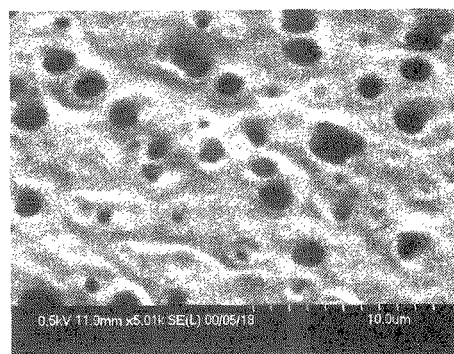


Fig.4 SEM image of PAH(pH7.5)/PAA(pH3.5) film surface after the soaking into pH2.9 diluted HCl

the systematic controlling the PAH solution pH from 2.5 to 4.5 and the PAA solution pH from 6.5 to 8.5, the surface roughness of the film was the largest when the pH of the PAH solution was 3.5 and the pH of the PAA solution was 4.5. The RMS value of the surface roughness obtained from the image shown in the Fig.2 was 20nm. The RMS value of the surface roughness formed by the other fabrication condition was less than

10nm. The peak to bottom surface roughness was approximately 150nm. Considering the result that the general surface roughness was approximately 30nm, a remarkably rough surface was obtained at this fabrication condition.

The surface nano-structure of the thin film was transformed when dipped in the water solution adjusted at various pH. Especially, the drastic change was observed when dipped in the HCl solution at pH2.9. The transformed nano-structure of the film surface was observed by AFM and SEM. The results are shown in Fig.3 and Fig.4. . By comparing the two images, it was found that there was no essential difference in the surface structures observed by the two evaluation methods, however, when using AFM, the nano structure of the film surface was observed more precisely. The textile structures as shown in Fig.2 is also observed in Fig.3, however they cannot be seen in Fig.4.

We consider that the efficiency of the photo-catalytic property of the titania will be much improved by using such porous structure as replica for titana thin film because the materials are easily penetrate into the polymer film, not only the surface. From the observation using an AFM, we consider that the pore of the film is penetrated through the thin film to the substrate surface.

50 bilayers of the layer-by-layer self-assembled films are formed by the fabrication condition described above. The surface of the thin film after adsorbing the titania is shown in Fig.5. As shown in the figure, the structure of the titania film surface is clearly traced the nano structure on the surface of the layer-by-layer self-assembled film. The side view of the SEM image of the titania film deposited on the self-assembled polyelectrolytes surface was shown in Fig.6 with the higher magnification than that Fig.5. As shown in Fig.6, titania nano particle grows not only on the surface of the polyelectrolytes films, but also inside of the films. We consider that this was caused by the crystallization of titania caused by the penetration of the  $TiF_4$  solution into the polyelectrolytes film because the surface of the self-assembled polyelectrolytes films are hydrophilic. In the figure, it is also shown that the penetrated titania nano particles form layer structures.

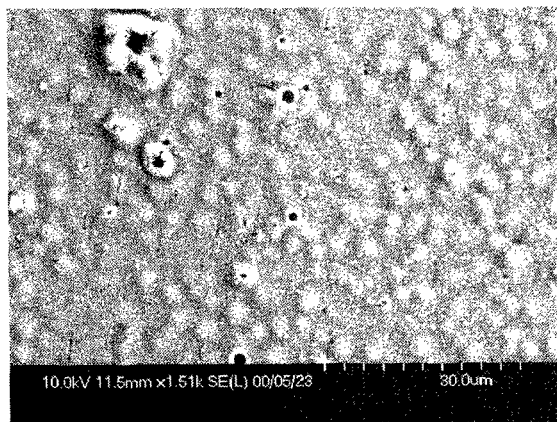


Fig.5 SEM image of titania film surface, which adsorbed onto the PAH(pH7.5)/PAA(pH3.5) film surface after the soaking into pH2.9 diluted HCl.

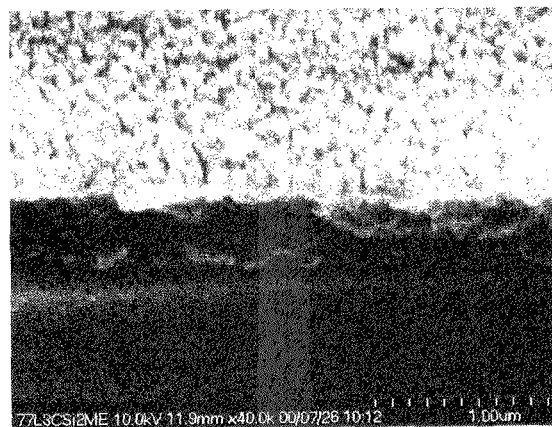


Fig.6 SEM image of titania film, which adsorbed onto the PAH(pH7.5)/PAA(pH3.5) film surface after the soaking into pH2.9 diluted HCl

Fig.7 is the SEM image of the structure of the titania nano particles formed on the surface on a glass substrate. By the comparison of the two images shown in Fig.6 and Fig.7, it was found that the diameter of the nano particle formed in the layer-by-layer self-assembled film is smaller than that formed on the surface.

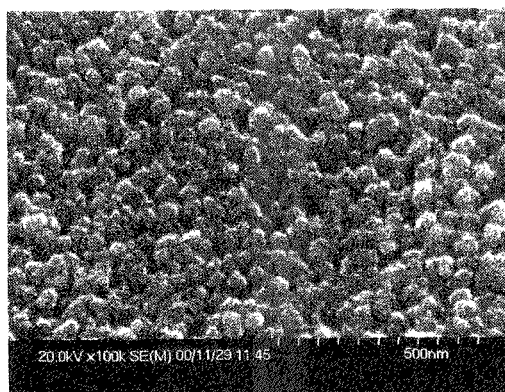


Fig.7 SEM image of titania film surface, which adsorbed onto glass plate

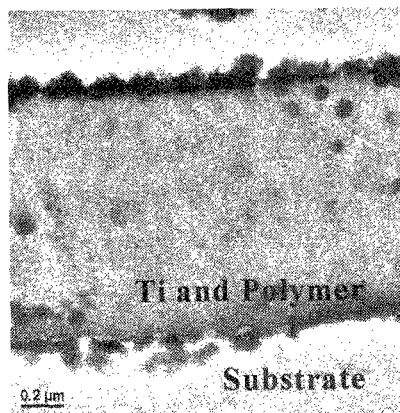


Fig.8 Cross-sectional TEM image of titania film, which adsorbed onto the PAH(pH7.5)/PAA(pH3.5) film surface after the soaking into pH2.9 diluted HCl.

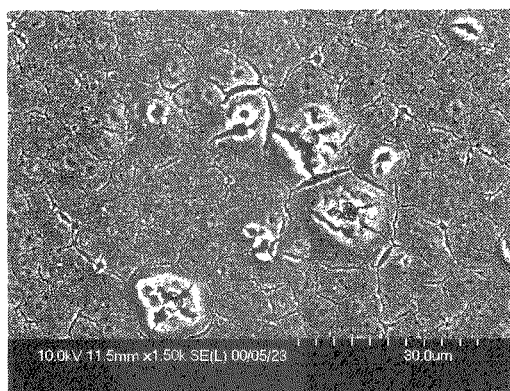


Fig.9 SEM image of titania film surface after burning polymers

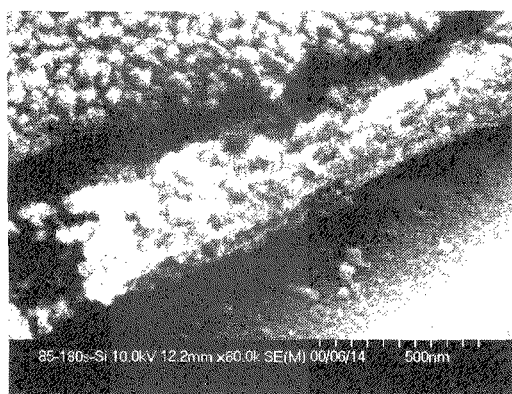


Fig.10 SEM image of titania film after burning polymers

The diameter of the former is 30nm and that of the latter was approximately 50nm for both. We consider that the nano particles, which are grown in the polymer matrix, did not increase its volume so much during the crystallization of the titania after the  $\text{TiF}_4$  solution penetrated into the polyelectrolytes self-assembled films. Since the  $\text{TiF}_4$  is not so stable in water solution, it is considered to be stabilized by forming the  $\text{TiO}_2$  molecules on the surface of the selfassembled polymer films.

The cross-sectional TEM image of the thin titania nano particles formed in the selfassembled polyelectrolytes films is shown in Fig.8. By the element analysis, Ti was detected on the whole thin film. This result demonstrates the penetration of the  $\text{TiF}_4$  solution into the polyelectrolytes films. Thickness of the formed film with titania nano-particles was almost the same with that of the layer-by-layer self-assembled film. On the other hand, it was found that titania was formed just approximately 200nm when it was grown on a glass substrate. Therefore, we can conclude that by the composition with the layer-by-layer selfassembled film, the total thickness of the titania is adjusted to the thickness of the selfassembled film.

The SEM images of the structures after burning the polymer with high temperature heating treatments are shown in Fig.9 and Fig.10. As shown in Fig.9, the unique nano-structure of the film surface was

maintained. In this case, the newly formed pores were also observed. We consider that these pores are formed when the gas inside of the film was removed by the heating treatment. These pores may make it easier for the transportation of the materials between the outside of the film and the inside of the film.

Layered structure of the titania was also observed in the pore by the magnified SEM observation. The cross-sectional image is shown in Fig.10. As already shown in Fig.6, titania nano particles penetrated into the inside of the film formed crystallized, layer structure.

Consequently, we consider that more titania nano particle can penetrate into the film through the pore when the pore was formed in the self-assembled polyelectrolytes film.

#### 4. CONCLUSION

The new method for the controlling the structure of titania thin film was proposed by using the layer-by-layer self-assembled polyelectrolytes film with nano pore as the replica for the titania film. The nano structure and the thickness of the titania film with the nano particles were successfully controlled by forming the crystallized anatase titania from supersaturated titania solution on/through the replica. Nano-scale control of the titania thin films is successfully carried out by using this new method.

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