

Study of the Organic-inorganic Multi-layer Thin Films Fabricated via a Layer-by-layer Self Assembly Method for an Optical Filter

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Organic-inorganic hetero structure multi-layer thin film consisting of polyelectrolytes and titanium dioxide were successfully fabricated by a layer-by-layer self assembly(LBL-SA) method at room temperature in order to apply to an optical filter. In this study, we report the surface roughness, morphology, thickness, and transmittance of hetero structure thin film assembled by a different coating sequence. Finally, we obtained the multi-layer thin film showing a low surface roughness 17nm and 21nm, and a high transmittance by the measurement of atomic force microscope(AFM) and UV-Vis spectroscopy. By depositing the higher and lower refractive index layers sequentially, we fabricated the multi-layer thin film for an optical filter by the sequential wet process.

Keywords:Organic-inorganic hetero structure, LBL-SA method, polyelectrolyte, TiO₂ nanoparticles

1. INTRODUCTION

Recently, extensive studies have been carried out on the hetero-structure thin film consisting of ionic polyelectrolytes and positively charged titanium dioxide(TiO₂) nanoparticles by a layer-by-layer self assembly(LBL-SA) method.[1-2]. The TiO₂ nanoparticles show a very high refractive index[3] and a remarkable photocatalytic behavior to decompose organic pollutants[4]. Therefore, the thin film of organic/inorganic hybrid hetero structure using TiO₂ nanoparticles and polyelectrolytes can be applied for optical filters, air filters, antireflection films, self-cleaning coatings and materials to decompose organics and protect bacteria.[5-7].

Including sol-gel synthesis[8], sputtering[9], chemical vapor deposition(CVD)[10], several coating methods to fabricate the TiO₂ thin films have been reported. However, these processes had undesirable conditions of a high temperature, a high qualitative vacuum system, limit of thickness and mechanical instability etc. In addition, these processes are very expensive and difficult to control. However, the LBL-SA method using a sequential absorption of ionized polyelectrolytes and oppositely charged materials in aqueous solutions have lots of merits: simplicity of process, low temperature deposition, needless of complicated equipments and no limit of thickness[11-12]. In addition, the thickness of thin films can be controlled with nano-order accuracy[13]. Because LBL-SA method is based on the self assembling nature of oppositely

charged aqueous solution and sequential absorption processes. However, there have been few studies on controlling the surface roughness and morphology of thin films using polyelectrolytes and some of nanoparticles. Therefore, it would be of great interest to investigate the ways in order to control the properties of these thin films.

In this study, we fabricated the hetero structure thin film showing a higher or lower refractive index by the LBL-SA method in a wet process. And we measured the surface morphology, roughness, thickness, and transmittance of this multilayer thin film.

2. Experimental details

2.1. Substrate treatment.

Glass substrate obtained from Matsunami Ind., Ltd. with the size of 20 x 50 mm and about 1.5nm surface roughness(Root Mean Square: RMS) was immersed in potassium hydroxide solution(1.0 wt.%) mixed with water and ethanol(2:3 in vol. ratio) in ultrasonication to obtain a negatively charged surface and then subsequently rinsed in ultra pure water(>18MΩ·cm) in ultrasonication. After these procedures, substrate was perfectly converted to a negatively charged surface.

2.2. Fabrication of the hetero-structure thin films by LBL-SA method.

The used starting materials were poly(allylamine hydrochloride)(PAH, Mw=70,000g/mol, Aldrich) as cationic

polyelectrolyte, poly(acrylic acid)(PAA, $M_w \sim 90,000$ g/mol, 25% aqueous solution, Polyscience), and poly(phosphoric acid)(PPA, Wako) as an anionic polyelectrolyte. TiO_2 nanoparticles(ca. 7nm in primary particle size, anatase) were obtained from Ishihara Sangyo. For preparing the solutions of LBL-SA process, polyelectrolytes were dissolved in ultra pure water and then, adjusted to 0.01M and pH 2.5 using HCl or NaOH. TiO_2 nanoparticles were dispersed in ultra pure water and then, the solution was adjusted to pH 2.5 and carried out a centrifugal separation in 3000rpm for 30min. Finally, we obtained the TiO_2 coating solution of about 0.15wt.%. For 3 times rinse steps, ultra pure water(pH 5.5~6.5) was used. For the indication of the multi-layer film structures, we describe as follow: For example, when we deposit material B over A, we describe as (A/B). If we repeated 10 times of this sequence, we describe as (A/B)₁₀. If we deposited layers (A/B)₁₀ and (C/D)₁₅, we describe as (A/B)₁₀/(C/D)₁₅. The substrate was immersed in every polyelectrolytes and TiO_2 nanoparticles solutions for 15min by the coating sequence of $(\text{TiO}_2/\text{PPA})_{30} / (\text{PAH}/\text{PAA})_{50} / (\text{TiO}_2/\text{PPA})_{30}$ and then, the thin film was dried at 80 °C for 1h in vacuum after the adsorption of each block.

2.3. Characterization of the hetero structure thin film.

The surface morphology, cross section, and surface roughness of multi-layer thin film were investigated by field emission scanning electron microscope(FE-SEM, Hitachi S-4700) and atomic force microscope(AFM, Digital Instrument, nanoscope IIIa) in tapping mode. The transmittance of thin film was measured by UV-Vis spectroscope.

3. Results and Discussion

3.1. The surface morphology and roughness of thin film.

First, we measured the ζ -potentials of TiO_2 anatase particles(0.15wt.%) as a function of the pH value in water as shown in Fig. 1. From this result, we selected the pH 2.5 condition(ζ -potential value=35.5mV) for the pH of TiO_2 solution to acquire an appropriate deposition condition[4]

As shown in Fig. 2(a), the TiO_2 nanoparticles of a $(\text{TiO}_2/\text{PPA})_{30}$ block appeared as dark and bright particles were absorbed on the surface of film and distributed with some of amorphous clusters of about 80nm. Fig. 2(b) shows the surface of $(\text{PAH}/\text{PAA})_{50}$ over $(\text{TiO}_2/\text{PPA})_{30}$ block.

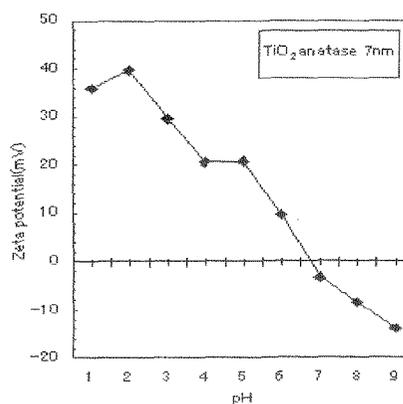


Fig. 1. ζ -potentials of anatase particles (0.15wt.%) as a function of the pH value in water.

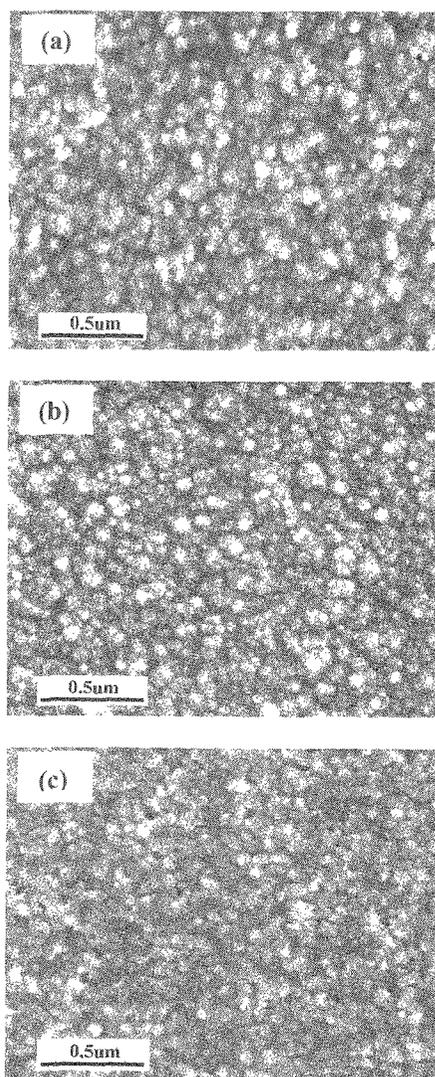


Fig. 2. FE-SEM images of hetero structure multi-layer thin films.

(a) $(\text{TiO}_2/\text{PPA})_{30}$, (b) $(\text{TiO}_2/\text{PPA})_{30}/(\text{PAH}/\text{PAA})_{50}$, (c) $(\text{TiO}_2/\text{PPA})_{30}/(\text{PAH}/\text{PAA})_{50}/(\text{TiO}_2/\text{PPA})_{30}$.

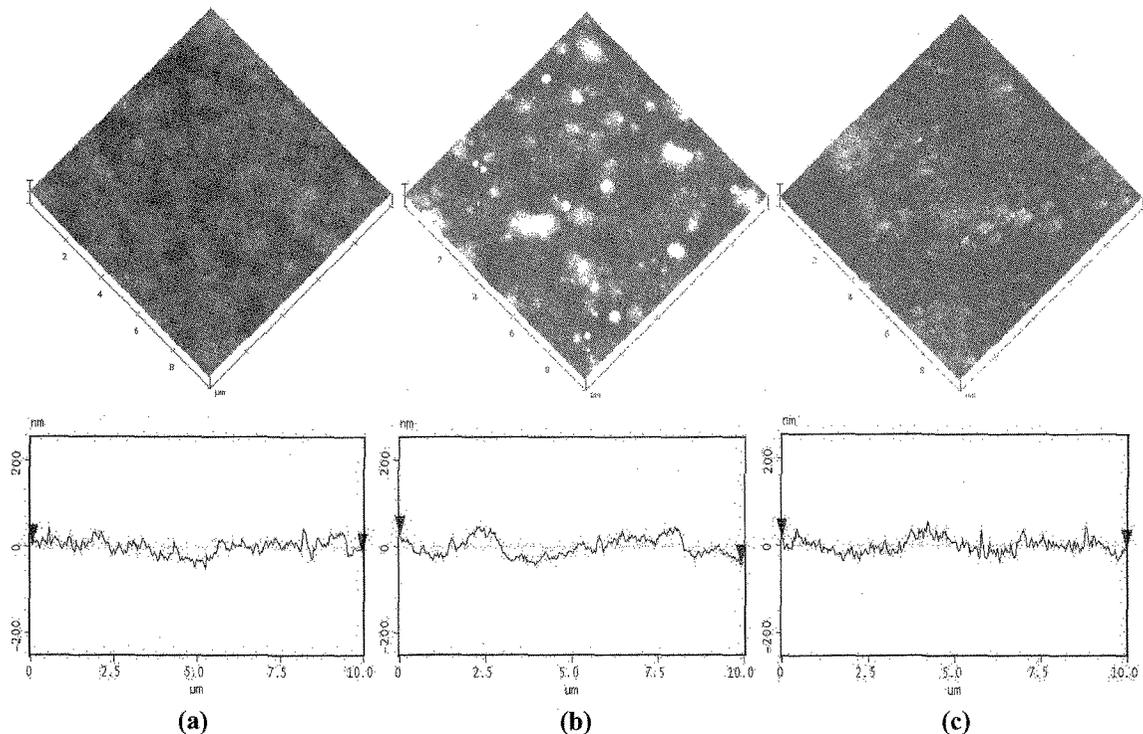


Fig. 3. AFM images of hetero structure multi-layer thin films measured in tapping mode. Scan size is $10\mu\text{m}$. Height is 500nm .

(a) $(\text{TiO}_2/\text{PPA})_{30}$, (b) $(\text{TiO}_2/\text{PPA})_{30}/(\text{PAH}/\text{PAA})_{50}$, (c) $(\text{TiO}_2/\text{PPA})_{30}/(\text{PAH}/\text{PAA})_{50}/(\text{TiO}_2/\text{PPA})_{30}$.

We can know that the thin film consisting of polyelectrolytes forms the broad size range of clusters than that of TiO_2 nanoparticles in pH 2.5. Fig. 2(c) presents the surface of the third block of $(\text{TiO}_2/\text{PPA})_{30}$ fabricated on the $(\text{PAH}/\text{PAA})_{50}$ block. This shows the almost same morphology with the first block deposited by same coating sequence. We suppose that these different surface morphologies demonstrate the deposition of hetero structure multi-layer thin film with different coating conditions.

As shown in Fig. 3(a), the RMS value of the first block assembled by $(\text{TiO}_2/\text{PPA})_{30}$ was about 17nm . We think that the roughness of this film depends on the dispersion of nanoparticles without an agglomeration in solution. Fig. 3(b) shows the surface roughness of $(\text{PAH}/\text{PAA})_{50}$ block. The RMS value of this block was about 21nm . This result agrees with the FE-SEM image showing the broad range distributions of polyelectrolytes clusters. The RMS value of third block, $(\text{TiO}_2/\text{PPA})_{30}$ was about 17nm as shown in Fig. 3(c). This film shows the same RMS value if thin film is fabricated with the same coating conditions. It was found that the surface roughness of the both polymer layers is larger than that of the layers composing TiO_2 .

3.3. Cross sectional image and transmittance of thin film.

The cross sectional image of thin film deposited on a glass substrate was observed by FE-SEM. We can distinguish the hetero structure multi-layer thin film obviously with the coating sequence of $(\text{TiO}_2/\text{PPA})_{30} / (\text{PAH}/\text{PAA})_{50} / (\text{TiO}_2/\text{PPA})_{30}$ in Fig. 4.

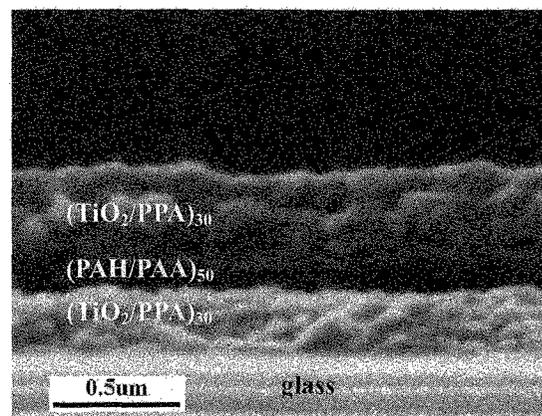


Fig. 4. The cross sectional image of a $(\text{TiO}_2/\text{PPA})_{30}/(\text{PAH}/\text{PAA})_{50}/(\text{TiO}_2/\text{PPA})_{30}$ thin film.

As shown in Fig. 4, by repeating the layer-by-layer sequential deposition 30 times for (TiO₂/PPA), 50 times for (PAH/PAA), and 30 times for (TiO₂/PPA), total thickness of the film over 0.7μm was deposited on the substrate. This means that by repeating the nano scale growth of the films, we can finally obtain the film with submicron scale thickness, though the film shows a small surface roughness by introducing the inorganic nanoparticles such as TiO₂.

The two blocks of (TiO₂/PPA)₃₀ were assembled with the thickness range of 400nm~500nm approximately and a (PAH/PAA)₅₀ block was fabricated with the thickness range of 100~200nm approximately and we can not see any cluster of polyelectrolytes by the measurement of cross section using FE-SEM. However, the interface of (PAH/PAA)₅₀ and third block (TiO₂/PPA)₃₀ is seemed to be rougher than that of first block (TiO₂/PPA)₃₀ and (PAH/PAA)₅₀. we think that this result is derived from the surface roughness of a (PAH/PAA)₅₀ block.

Fig. 5 shows the transmittance of multi-layer thin film measured by UV-Vis spectroscopy. In the Fig. 5, these results are shown the transmittance of top, middle, and bottom of multi-layer thin film. This film showed a high transmittance compared with that of glass substrate and there were almost no difference in the transmittance between the location of the deposition film(20mm x 50mm). In addition, this graph showed the right shift of wavelength about 50nm after depositing the multi-layer thin film on substrate.

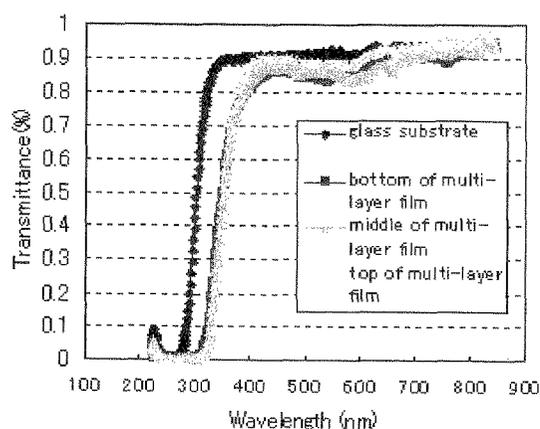


Fig. 5. Transmittance of multi-layer thin film of (TiO₂/PPA)₃₀/(PAH/PAA)₅₀/(TiO₂/PPA)₃₀.

This means that optically uniform thin film was deposited on the substrate by LBL-SA method. From these results, we consider that this hetero structural and transparent thin film fabricated by a LBL-SA method can be used for an optical filter.

Because we suppose that the thickness of each block can be controlled by using a quartz crystal microbalance(QCM) technique[13], which affects optical properties of thin film in order to make a desirable optical filter.

4. Conclusion

From the result of cross sectional image, we found that organic/inorganic hetero structure multi-layer thin film exhibiting a different refractive index was fabricated with the coating sequence of (TiO₂/PPA)₃₀ / (PAH/PAA)₅₀ / (TiO₂/PPA)₃₀ by a layer-by-layer self assembly method. In addition, this multi-layer thin film showed a high transmittance by the measurement of UV-Vis spectroscopy. Therefore, if we control the thickness of hetero structure multi-layer thin film, this well developed multi-layer thin film will be expected to be an application of optical filter.

Acknowledgments

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