Transactions of the Materials Research Society of Japan 28 [3] 593-596 (2003)

Fabrication and optical properties of organic-inorganic ultra thin films by layer-by-layer self assembly method.

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Layer-by-layer self assembly method was used for fabricating organic-inorganic ultra hybrid thin films of polyelectrolytes and TiO_2 nanoparticles(7nm, anatase) on silicon and polystyrene substrates. In this study, we measured the optical properties of multilayer thin films. The hetero structure multilayer thin films which have a different refractive index(n) were deposited on substrates by the coating sequence of $[PAH/PSS]_{10}/[PAH/PVS/TiO_2/PVS]_{10}/[PAH/PAA]_{20}/[PAH/PVS/TiO_2/PVS]_{10}$. From the results of optical interfering method, the refractive index of organic [PAH/PAA] layer and inorganic $[PAH/PVS/TiO_2/PVS]$ layer were n=1.41and n=1.86. The cross sectional image was observed by a field emission transmission electron microscope(FE-TEM). The surface morphology and roughness measurement were carried out using a field emission scanning electron microscope(FE-SEM) and atomic force microscope(AFM).

Keywords: organic-inorganic hetero structure, layer-by-layer self assembly , polyelectrolyte, TiO_2 nanoparticles

1. Introduction

In the past several years there has been increasing interest in the layer-by-layer self-assembly(LBL-SA) method to fabricate the hetero-structure thin films consisted of ionic polymers and positively charged titanium dioxide TiO_2 nanoparticles[1-4]. Because the nanosized titanium dioxide(TiO_2) particles exhibit some of unique properties such as a very high refractive index[5], a high dielectric constant[6], and a remarkable photocatalystic behavior to decompose organic pollutants[7]. Therefore the hetero structure thin films consisted of TiO_2 nanoparticles and polyelectrolytes can be expected to apply to optical filters, air filter and self-cleaning coatings[8-10].

There are several coating methods to fabricate the TiO_2 thin films such as sol-gel synthesis[11], sputtering[12] and chemical vapor deposition(CVD)[13]. However these processes present undesirable conditions of a high temperature, a delicate vacuum system, limit of thickness and mechanical instability etc. In the other hand, the LBL-SA method using a sequential deposition of ionized polyelectrolytes and oppositely charged materials in aqueous solution has lots of merits such as simple process es, low temperature, needless of expensive equipments and no limit of thickness[14-15]. Moreover the thickness of thin films can be controlled with nano-order accuracy[16]. Because LBL-SA method is based on the self assembling nature of oppositely charged aqueous solutions and sequential adsorption processes.

In this study, we fabricated the organic-inorganic hetero structure thin films composed of TiO_2 nano particles and ionic polyelectrolytes and then measured the optical properties of films using a optical interfering method. In addition, the structural properties of thin films were measured by using a field emission transmission electron microscopy(FE-TEM), a field emission scanning electron microscopy(FE-SEM) and an atomic force microscopy(AFM). Now we wish to report the results herein.

2. Experimental details

2.1. Preparing substrates

Silicon(Si) wafers were immersed in potassium hydroxide solution(1wt. %) mixed with water and ethanol(2:3 in volume ratio) in ultrasonic for 5min to obtain a negative charged surface and then rinsed 3times in ultra pure water(>18MΩ•cm) for each 1min in ultrasonic. Polystyrene(Nalge Nunc International) substrates with a negatively charged surface were used for preparing the cross sectional specimens of FE-TEM. Finally the substrates were carried out Ozone(O_3)

treatment for 2h using UV-O_3(NLE, Japan). After these procedures, the surfaces of substrates were changed to be hydrophilic perfectly.

2.2. Fabrication of the hetero-structure thin films

The used starting materials were as follows: poly(allylamine hydrochloride) (PAH, Mw=70,000g/mol, Aldrich) was used for a cationic polyelectrolyte, poly(sodium 4-styrenesulfonate) (PSS, Mw=70,000g/mol, Aldrich), poly(acrylic acid) (PAA, Mw=~90,000g/mol, 25% aqueous solution, Polyscience), poly(vinylsulfonic acid, sodium salt) (PVS, 25wt.% solution in water, Aldrich) were purchased for anionic polyelectrolytes. TiO_2 colloidal solution (Ishihara, 30wt.%) that TiO_2 anatase nanoparticles were dispersed in solution uniformly was used.

For preparing the solutions of process, the density of all polymer solutions was adjusted to 0.01M and the pH value of solutions was adjusted to pH3.5 for [PAH/PSS] layer. In the other hand, for [PAH/PVS/Ti O_2/PVS] and [PAH/PAA] layers, polyelectrolytes solut ions were adjusted to pH2.5 with HCl. TiO_2 colloidal solution was adjusted to 0.15wt.% and pH2.5 with HNO_3[4]. The pH of ultra pure water for rinsing steps was also adjusted to the same pH value of each layers.

The dipping process was performed by the sequence of $[PAH/PSS]_{10}$/ $[PAH/PVS/TiO_2/PVS]_{10}$/ $[PAH/PAA]_{20}$ /$[PAH/PVS/TiO_2/PVS]_{10}$. For each layer, substrates were immersed in every polymers solution for 5min and 15min for TiO_2 colloidal solution. And then 3times rinse procedure was performed for each 1min. The substrates were annealed at 80℃ for 1h after the adsorption of $[PAH/PVS/TiO_2/PVS]_{10}$ layer.

2.3. Characterization of the hetero structure thin films

The surface morphology and roughness of hetero structure thin films were investigated by a field emission scanning electron microscope(FE-SEM, Hitachi S-4700) and an atomic force microscope(AFM, Digital Instrument, nanoscope IIIa). The refractive index and thickness of hetero structure multilayer films were calculated by an optical interfering method (Film Tek 3000, Scientific Computing International) at the wavelength of 632nm.

The deposited polystyrene substrate for observation of a field emission transmission electron microscope(FE-TEM, Philips, TECNAIF20) was covered with resin and then, an encapsulated specimen was trimmed with a glass knife and a NACC diamond knife(Micro Star Technologies) by using ultramicrotome(RMC, MT-XL).

3. Results and Discussion

3.1. The surface morphology and roughness of thin films.

Orgnic-inorganic hetro structure multilayer thin films consisted of polyelectrolytes and TiO_2 nanoparticles were successfully fabricated by controlling the pH of solution and the adsorption sequences of $[PAH/PSS]_{10}$/ $[PAH/PVS/TiO_2/PVS]_{10}$/$[PAH/PAA]_{20}$/$[PAH/PVS/TiO_2/PVS]_{10}$ at room temperature. We investigated the surface morphology of thin films containing of TiO_2 nanoparticles layer deposited by $[PAH/PSS]_{10}$/ $[PAH/PVS/TiO_2/PVS]_{10}$ using FE-SEM. Fig. 1 shows that TiO_2 nanoparticles were absorbed compactly on the surface of films with some of uniform clusters agglomerated from 7nm particles.

The polymer layer surface of $[PAH/PSS]_{10}$/$[PAH/PVS/TiO_2/PVS]_{10}$/$[PAH/PAA]_{20}$ was presented in Fig. 2. Polyelectrolytes of PAH and PAA were found to be white and a sphere.

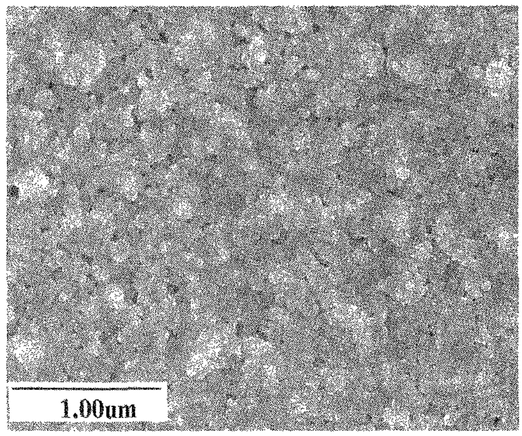

Fig. 1. FE-SEM image of a $[PAH/PSS]_{10}$/ $[PAH/PVS/TiO_2/PVS]_{10}$ thin film.

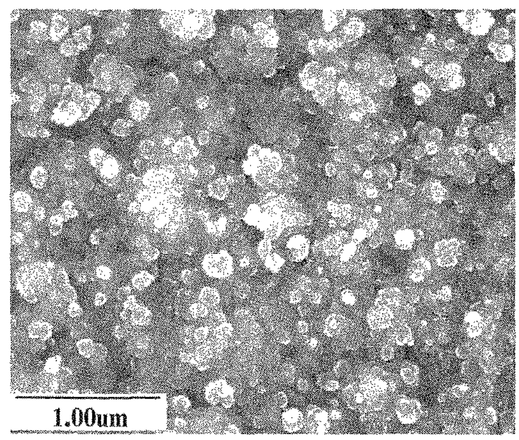

Fig. 2. FE-SEM image of a $[PAH/PSS]_{10}$/ $[PAH/PVS/TiO_2/PVS]_{10}$/$[PAH/PAA]_{20}$ thin film.

As shown in Fig. 1 and Fig. 2, the different surface morphology of films demonstrates the adsorption of $[PAH/PVS/TiO_2/PVS]_{10}$ inorganic layer and $[PAH/PAA]_{20}$ organic layer by sequential adsorption using the LBL-SA method at room temperature.

The surface roughness(Rms) of thin films fabricated in corresponding to the dipping sequence of each layer was measured by an atomic force microscope(AFM). The Rms of inorganic layer containing TiO_2 nanoparticles was about 24nm in Fig. 3.

Fig. 4 indicates the AFM image of a $[PAH/PSS]_{10}$/ $[PAH/PVS/TiO_2/PVS]_{10}$/$[PAH/PAA]_{20}$ thin films. The surface roughness of thin films layer was about 27nm.

After the deposition of inorganic layer, the Rms was increased to 22nm from 2nm of [PAH/PSS] layer. This result is considered to derive from the agglomeration of TiO_2 nanoparticles(7nm) in solution(pH2.5). However after the deposition of organic layer containing polyelectrolytes, the change of roughness was about 3nm.

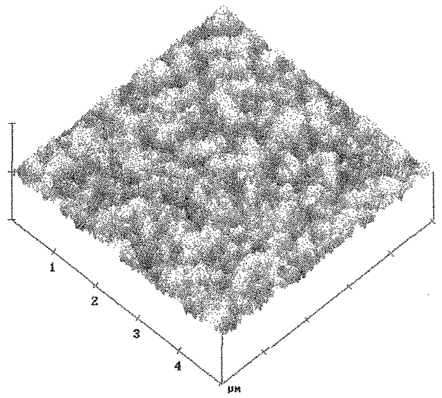

Fig. 3. AFM image of the surface of $[PAH/PSS]_{10}$/ $[PAH/PVS/TiO_2/PVS]_{10}$ thin film

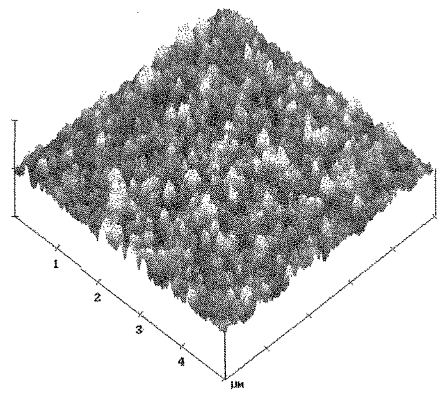

Fig. 4. AFM image of a $[PAH/PSS]_{10}$/ $[PAH/PVS/TiO_2/PVS]_{10}$ / $[PAH/PAA]_{20}$ thin films.

3.2 The refractive index(n) and thickness of multi-layer thin films.

Table I shows the thickness and refractive index of hetero structure multilayer thin films calculated using the optical interfering method.

Table I . Refractive index and thickness of hetero structure multi-layer thin film

Layers	Refrative index(n)	Thickness (nm)
$(PAH/PSS)_{10}$	1.27	30.3
$(PAH/PVS/TiO_2/PVS)_{10}$	1.86	190.0
$(PAH/PAA)_{20}$	1.41	99.1

The inorganic layer containing TiO_2 nanoparticles shows a higher refractive index(n=1.86) than that(n=1.41) of organic layers containing polyelectrolytes. From these results, it is possible to fabricate the multilayer that has different refractive index by layer-by-layer self assembly method.

3.3. The cross sectional images of hetero structure thin films

Fig. 5 demonstrates the organic-inorganic hetero structure multilayer thin films consisted of polymers and oppositely charged TiO_2 nanoparticles deposited on polystyrene by the LBL-SA method at room temperature. In the figure, organic and inorganic layer between $(PAH/PAA)_{10}$ and $(PAH/PVS/TiO_2/PVS)_{10}$ are distinguished obviously. Even if the interface of layers cannot be confirmed perfectly. Approximately, it is considered that the thickness of two organic layers of $[PAH/PSS]_{10}$ and $[PAH/PAA]_{20}$ are about 30-40nm and 80-100nm. And the thickness of inorganic layer, $[PAH/PVS/TiO_2/PVS]_{10}$ is about 180-200nm. These are consistent with the measurement of an optical interfering method.

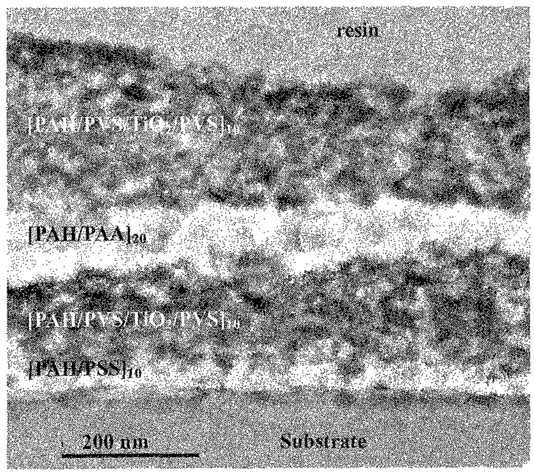

Fig.5. The cross sectional FE-TEM image of a $[PAH/PSS]_{10}/[PAH/PVS/TiO_2/PVS]_{10}/[PAH/PAA]_{20}/$ $[PAH/PVS/TiO_2/PVS]_{10}$ thin film

4. Conclusion

From these experimental results mentioned above, we conclude that organic-inorganic hetero structure thin films were successfully fabricated with the dipping sequence of $[PAH/PSS]_{10}$ / $[PAH/PVS/TiO_2/PVS]_{10}$ / $[PAH/PAA]_{20}$ / $[PAH/PVS/TiO_2/PVS]_{10}$ by a layer-by-layer self assembly method. The organic layers of (PAH/PSS) and (PAH/PAA) exhibited a low refractive index(n=1.27, n=1.41). However the inorganic layer containing TiO_2 nanoparticles showed a high refractive index(n=1.86). Therefore the hetero structure multilayer that retains a different refractive index was successfully fabricated by layer-by-layer self assembly method. By the observation of TEM, the heteo structure multilayer were confirmed definitely. Even if the interface of each layer is not flat perfectly. However these well developed thin films that show the hetero structure and a different refractive index are expected to have a lot of applications not only optical filters but also gas filters and photocatalystic material.

Acknowledgments

This work was partially supported by 21 century COE Keio University program(KEIO LCC COE21).

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(Received December 21, 2002; Accepted April 28, 2003)