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A layer-by-layer self-assembly method for organic-inorganic hybrid multilayer thin films

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Organic-inorganic hybrid multilayer thin films were fabricated by a layer-by-layer self-assembly method at room temperature and the surface morphologies, thicknesses, surface roughnesses and optical properties of multilayer thin films were measured. The high refractive index multilayer thin films were assembled using poly (diallyldimethylammonium chloride) (PDDA) and titanium (IV) bis (ammonium lactato) dihydroxide (TALH). TiO_2 crystallites ca. 5 nm in particle size were formed in the (PDDA/TALH) thin film by sequentially depositing PDDA and TALH solutions. The $(PDDA/TALH)_{20}$ multilayer thin films showed a high refractive index (n = ca. 1.81) and low surface roughness (RMS = ca. 4.5 nm). The $(PDDA/PSS)_{20}$ multilayer thin films with a low refractive index were assembled using poly (diallyldimethylammonium chloride) (PDDA) and poly (sodium 4-styrenesulfonate) (PSS). The refractive index of $(PDDA/PSS)_{20}$ organic layers was n = ca. 1.55 at 632 nm and the surface roughness was RMS = ca. 3.4 nm. In addition, these (PDDA/TALH) and (PDDA/PSS) multilayer thin films showed a high transmittance in visible range.

Key words: Layer-by-layer self assembly, Polyelectrolyte, TiO_2, refractive index.

Introduction

A layer-by-layer (LBL) self-assembly method using sequential adsorptions of ionized polyelectrolytes and oppositely charged materials in aqueous solutions has many advantages such as a simple process, low temperature deposition, no limit of thickness and thickness control on the nanoscale [1-6]. Therefore, organic-inorganic hybrid multilayer thin films fabricated by a LBL self-assembly method have been demonstrated to be new materials for with many applications [7-11]. Among the applications, it is especially important to control the thickness, surface roughness, refractive index and transmittance of multilayer thin films for optical devices.

From a previous report, the refractive index of organic multilayer thin films assembled with poly (acrylic acid) (PAA) and poly (allylamine hydrochloride) (PAH) was successfully controlled between 1.55 and 1.15 [12]. On the other hand, TiO_2 nanoparticles and titanium (IV) bis (ammonium lactato) dihydroxide (TALH) were used to fabricate multilayer thin films with a high refractive index by a LBL deposition method [13-14]. TALH solution has been an attractive precursor to fabricate titanium dioxide thin film by the LBL technique because TALH is stable and a double negatively charged inorganic precursor in water [15].

In this study, we fabricated organic-inorganic hybrid multilayer thin films consisting of polyelectrolytes and TiO_2 by controlling the coating sequence of multilayer thin films. The surface morphologies and optical properties of hybrid multilayer thin films were investigated.

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Experimental Details

Poly (diallyldimethylammonium chloride) (PDDA, 20 wt.% in water) was obtained from Aldrich as positively charged solutions and poly (sodium 4-styrenesulfonate) (PSS, Mw = 70,000, Aldrich) was used as an anionic polyelectrolyte. Titanium (IV) bis (ammonium lactato) dihydroxide (TALH, 50 wt.%, Aldrich) with a double negative charge was used for the deposition of inorganic layers. All materials were used without any further purification. The concentration of PDDA and PSS solution was adjusted to 0.01 M and TALH was adjusted to 1.0 wt. % with ultra pure water (> 18 MΩ·cm).

The inorganic multilayer thin films with a high refractive index were fabricated using the PDDA and TALH solutions and the organic multilayer thin films with a low refractive index were assembled by PDDA and PSS solutions.

Glass, polystyrene (Nalge Nunc International), and Si/SiO_2 substrates were ultrasonically agitated in a KOH solution (1.0 wt.%) mixed with water and ethanol (2 : 3 in volume ratio) for 5 minutes and then, rinsed in ultra pure water. From this treatment, we finally prepared negatively charged substrates.

The negatively charged substrates was immersed in PDDA for 10 minutes and then, rinsed with pure water with a rinsing procedure of 1 minute 3 times. Positively charged substrates by the deposition of PDDA were subsequently immersed into the negatively charged solutions, TALH or PSS, for 10 minutes and then, the same rinsing procedures (1 minute 3 times) were carried out. This coating sequence was repeated without stopping and automatically using a dipping machine until the desired thin films were deposited on substrates. Here, when we deposit material B over A, we describe it as (A/B). If we repeated this sequence 10 times, we describe it as $(A/B)_{10}$. After the deposition of solutions, the prepared thin films were annealed at 80 °C for 1 h.

The surface morphologies of multilayer thin films were investigated by a field emission scanning electron microscope (FE-SEM, Hitachi S-4700) and the cross-sectional images of hybrid multilayer thin films deposited on polystyrene substrates were obtained by a field emission transmission electron microscope (FE-TEM, Philips TECNAIF 20). The root mean square (RMS) surface roughnesses of film were measured by an atomic force microscope (AFM, Digital Instrument nanoscope a) in a tapping mode. The refractive index of hetero-structural films assembled on Si/SiO_2 substrates and the reflectance of films deposited on glass substrares were determined by ellipsometry (Film Tek 3000, Scientific Computing International). The absorbance and transmittance of prepared thin films deposited on glass were measured by a UV-vis spectrophotometer (UV mini-1240, Shimadzu).

Results and Discussion

Fig. 1 shows the surface morphologies of inorganic layers assembled with $(PDDA/TALH)_{20}$ and organic layers assembled with $(PDDA/PSS)_{20}$. As shown in this figure, the surface of inorganic layers was composed of clusters below ca. 50 nm in size and some of clusters ca. 100 nm in size. On the other hand, the surface of organic layers deposited with PDDA and PSS is flat and covered with a few clusters below ca. 30 nm in size.

Fig. 2 presents an image of TiO_2 crystallites obtained from TALH with alternative PDDA deposition. From this result, it was confined that inorganic layers consisting of dispersed TiO_2 crystallites ca. 5 nm in particle size were successfully fabricated by a LBL self-assembly method.

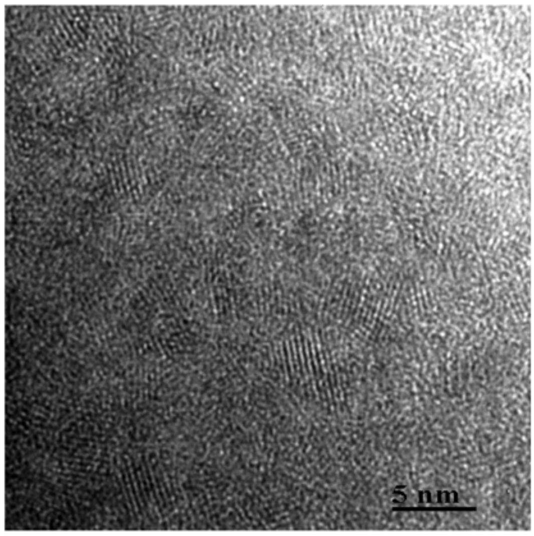
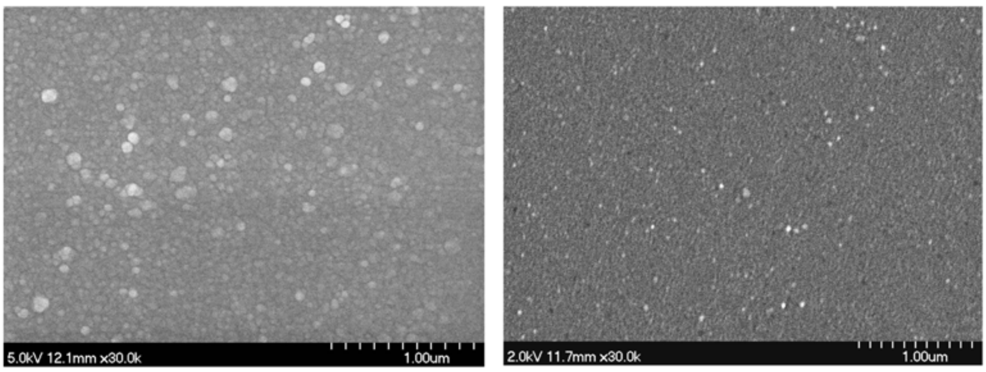


Fig. 2. FE-TEM image of crystallites obtained from the TALH precursor of the thin film consisting of PDDA and TALH. TiO_2 crystallites (ca. 5 nm) were formed in a thin film.

From the ellipsometer measurements, the thickness and the refractive index of a thin film deposited by $(PDDA/TALH)_{20}$ were 53 ± 2 nm and n = ca. 1.81, respectively. On the other hand, the thickness and the refractive index of organic layers assembled by $(PDDA/PSS)_{20}$ were 28 ± 2 nm and n = ca. 1.55, respectively.

The RMS surface roughnesses of prepared inorganic and organic thin films are shown in Fig. 3. The RMS values of inorganic and organic multilayers were ca. 4.5 nm and ca. 3.4 nm, respectively.

Fig. 4 presents a cross sectional image of hybrid multilayers assembled with 5 inorganic blocks of $(PDDA/TALH)_{20}$ and 4 organic blocks of $(PDDA/PSS)_{20}$ by the coating sequence of $[(PDDA/TALH)_{20}/(PDDA/PSS)_{20}]_{4.5}$. From this figure, it was confirmed that each inorganic or organic block with the same coating sequence were successfully deposited with almost same the film thickness by the LBL self-assembly method.



(a) (b)

Fig. 1. Surface morphologies of (a) inorganic multilayer thin films deposited by $(PDDA/TALH)_{20}$ and (b) organic multilayer thin films deposited by $(PDDA/PSS)_{20}$.

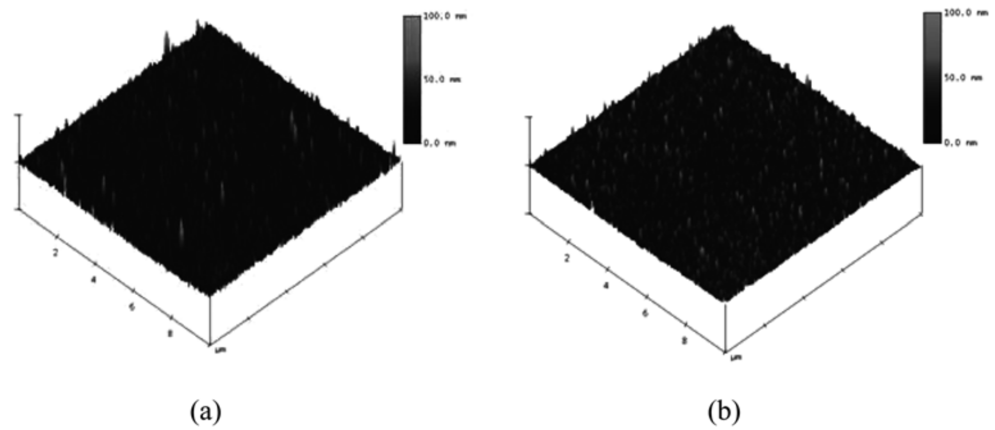


Fig. 3. AFM images of (a) inorganic multilayer thin films deposited by $(PDDA/TALH)_{20}$ and (b) organic multilayer thin films deposited by $(PDDA/PSS)_{20}$.

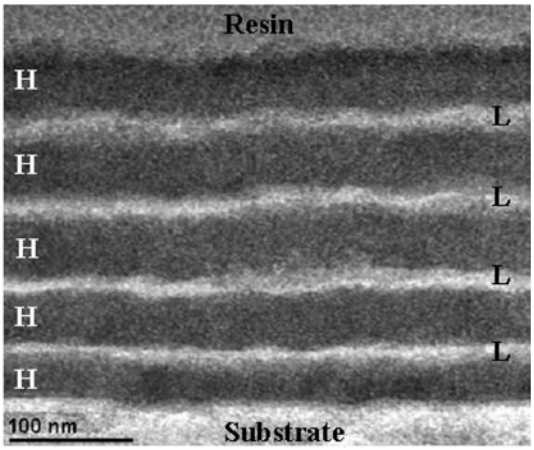


Fig. 4. Cross sectional image of hybrid multilayer thin films prepared with the coating sequence of $[(PDDA/TALH)_{20}/(PDDA/PSS)_{20}]_{4.5}$. H :$(PDDA/TALH)_{20}$, L: $(PDDA/PSS)_{20}$.

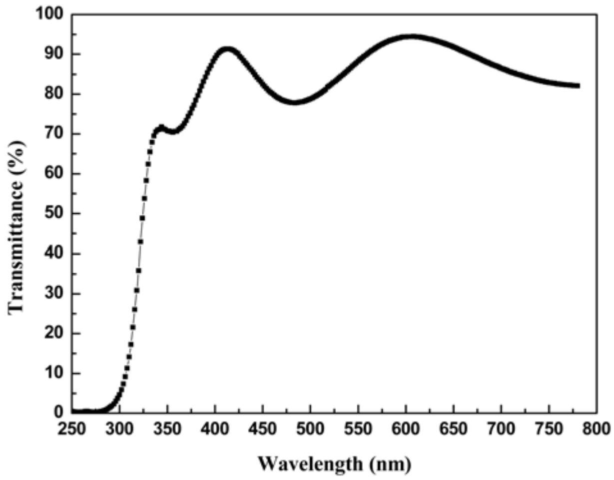


Fig. 5. Absorbance and transmittance of hybrid multilayer thin films prepared with the coating sequence of $[(PDDA/TALH)_{20}/(PDDA/PSS)_{20}]_{4.5}$.

Fig. 5 presents the transmittance of hybrid multilayer thin films prepared with the coating sequence of $[(PDDA/TALH)_{20}$ / $(PDDA/PSS)_{20}]_{4.5}$ on glass. This film showed a high transmittance above 94% at 430 nm and 630 nm wavelengths and UV light was cut to below 5% at 300 nm wavelength by the deposition of the TiO_2 thin film.

Conclusions

Inorganic-organic hybrid multilayer thin films with low or high refractive index were successfully fabricated by a LBL self-assembly method at room temperature. The inorganic layers composed of TiO_2 crystallites ca. 5 nm in particle size were obtained by the deposition of PDDA and TALH solutions. The refractive index of this film assembled by $(PDDA/TALH)_{20}$ was n = ca. 1.81 at 632 nm and the RMS roughness was ca. 4.5 nm. On the other hand, the refractive index of organic layers assembled by $(PDDA/PSS)_{20}$ was n = ca. 1.55 at 632 nm and the RMS roughness was ca. 3.4 nm.

From cross sectional images, it was found that the inorganic or organic layers were assembled with a constant growth thickness and the transmittance of hybrid thin films could be modified by controlling the coating sequence. Therefore these multilayer thin films with a high transmittance and low or high refractive index can be good materials for optical applications by controlling the film thickness.

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