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Fabrication of Antireflective Films Composed of High and Low Refractive Index Layers Using Layer-by-Layer Self-Assembly Method

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Abstract. We introduce a novel and versatile approach for controlling anti-reflective (AR) properties of multilayer films based on layer-by-layer (LbL) self-assembly (SA) method. For the fabrication of these films, blend (i.e., mixed) layers containing both polyanions (i.e., titanium precursor (TALH) and poly(sodium 4-styrenesulfonate) (PSS)) were assembled with polycation (i.e., poly(diallyldimethylammonium chloride) (PDAD)) for the formation of the high refractive index multilayers and on the other hand, the negatively charged silica particles with the diameter of about 100 nm were employed for low refractive index layer. The refractive index of TALH:PSS/PDAD multilayer was controlled by blending ratio and annealing temperature as TALH has the relatively high refractive index (n = 1.68) in comparison with that (n = 1.46) of conventional polyelectrolytes (PEs) at room temperature and furthermore these titanium precursors are partially changed into TiO_2 with relatively high refractive indices (n = 1.50 ~ 1.81) at annealing temperature of 250 ^{o}C. In the case of silica particle layer used for low refractive index layer, the calculated refractive index was about 1.35 due to much vacancy among the adsorbed silica colloids although the inherent refractive index of silica material is about 1.45. As a result, the films composed of TALH:PSS/PDAD multilayers with tunable refractive index and silica colloidal layer can easily modulate the optical properties of multilayer films by blending ratio and heat treatment.

Introduction

Antireflective (AR) coatings based on interference of the reflected light from film-substrate and air- film interfaces have been used to increase light transmission in various optical applications [1]. In these AR films, the minute control of refractive index and film thickness has an important role in improving light transmission in the desired wavelength range [2]. Recently, it was reported by many research groups that these films could be easily fabricated from layer-by-layer (LbL) self-assembly (SA) method allowing the thickness control at angstrom level [3]. However, to our knowledge, they have been focused on modulating the antireflective properties from the surface morphological change of LbL films induced by pH [3].

In our study, we report the antireflective properties of LbL AR films composed of high refractive index multilayers (i.e., the blend layer of anionic TALH and PSS) and low refractive index layer (i.e., silica colloidal particles). The optical properties of these films were easily controlled by heating temperature as well as the blend ratio between TALH and PSS. Additionally, we demonstrate that the small fraction of PSS in blend has a significant effect on refractive index and film thickness of blend multilayers.

Experimental Procedure

Poly(diallyldimethylammonium chloride) (PDAD, M_W = 100 000 ~ 200 000), Poly(sodium 4-styrenesulfonate) (PSS, M_w = 70 000) and Titanium(IV) bis(ammonium lactato) dihydroxide (TALH) were used as received from Aldrich. Aqueous SiO_2 colloidal solution (100 nm diameter) were purchased from Polyscience, Inc. The concentration of cationic PDAD, anionic blend (TALH:PSS) and anionic SiO_2 solutions used for all the experiment was 1mg·mL^{-1}, 1mg·mL^{-1} and 5.6 wt%, respectively. PDAD and blend solutions contained 0.1 M NaCl. The blending ratio of TALH:PSS solutions was adjusted to 100:0, 99:1, 95:5, 90:10 and 0:100 wt%, respectively.

Glass substrates or silicon wafers were cleaned with a concentrated H_2SO_4/H_2O_2 (7:3 v/v) solution and subsequently negatively charged by heating at 70 ^oC for 20 min in a 5:1:1 vol % mixture of water, hydrogen peroxide, and 29 % ammonia solution. These substrates were first dipped for 10 min in the cationic PDAD, then washed three times by dipping in deionized water for 2 min, followed by drying with a gentle stream of nitrogen. Negatively charged blend layers were subsequently deposited onto the positively charged substrates by using the same washing and drying procedure as described above. Negatively charged silica colloids were deposited onto $(PDAD/TALH:PSS)_n$ multilayers at 4 ^oC for 20 min [4].

Results and Discussion

Controlling High Refractive Index Layer. The refractive index of $[PDAD/(TALH:PSS)]_n$ multilayers can be controlled by the blending ratio between TALH and PSS because the TALH has relatively high refractive index (n = 1.68) in comparison with that of conventional PEs such as PDAD or PSS [5]. The annealing temperature can also play an important role in increasing the refractive index of multilayers based on TALH. Caruso *et al.* reported that TALH/PDAD multilayers are converted into titania anatase with refractive index of 2.57 (at 550 nm wavelength) at about 450^{o}C. These hypotheses suggest the possibility of easily controlling refractive index of multilayers [6].

Fig. 1 shows the change in refractive index and thickness of $[PDAD/(TALH:PSS)]_{10.5}$ (TALH:PSS = 100:0, 99:1, 90:10 and 0:100) films as a function of heating temperature and blending ratio. Although the blending ratio of TALH:PSS = 90:10 and 0:100 wt% has no influence on the change in refractive index and thickness of the multilayer films, the films containing TALH:PSS = 100:0 and 99:1 evidently show the increased refractive index and the decreased thickness with increasing annealing temperature from 25 to 250 ^oC. It should also be noted that the presence of 1 wt% PSS in the TALH solution causes a significant difference in the refractive index and thickness from the equivalent film prepared with the addition of 10 wt% PSS (1.67 vs 1.48 for refractive index and 84 vs 30 nm for film thickness at 25 ^oC). This observation can be explained by the fact that PSS increases the total degree of ionization of blend TALH:PSS, leading to deposition of thinner layers and relative decrease of adsorbed TALH within blend layers.

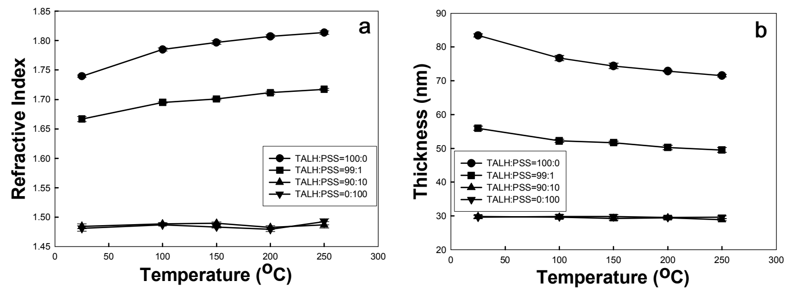

Fig. 1. The change in refractive index and thickness of [PDAD /(TALH:PSS)]$_{10.5}$ multilayer films prepared from various blending ratios and annealing temperature. In this case, the heat treatment was performed for 30 min in vacuum.

Antireflective Properties. Fig. 2 shows the tilted and plan SEM images of silica colloids (about 100 nm diameter) adsorbed onto $[PDAD/(TALH:PSS=95:5)]_{40.5}$ multilayers with n = 1.58 and 170 nm thickness. As shown in Fig. 2b, the deposited silica colloids yield sparse vacancy between neighboring colloids and resultantly induce the lower refractive index (n = 1.35) in comparison with the inherent refractive index (n = 1.45) of silica materials. This film structure can be applied to antireflective film that improve the light transmittance due to the destructive interference of the reflected lights from interfaces between different refractive index layers.

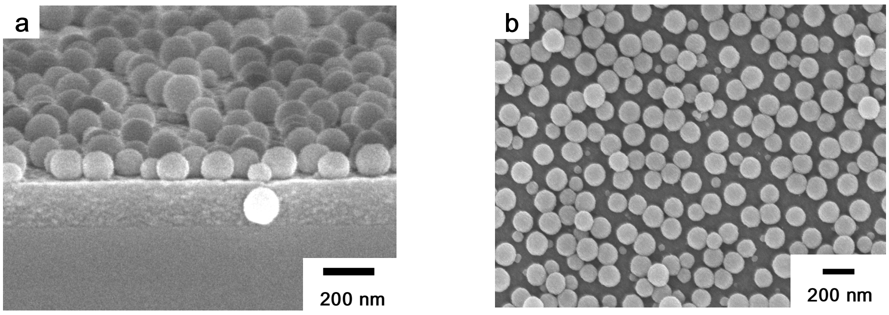

Fig. 2. SEM images of the silica colloidal layer coated onto the [PDAD/(TALH:PSS = 95 : 5)]$_{40.5}$ multilayer thin films on silicon wafer: (a) tilted view and (b) plan view.

In order to confirm this hypothesis, the antireflective properties of [PDAD/(TALH:PSS)]$_n$/ colloids multilayer films were investigated with increasing the fraction of PSS in blend as shown in Figure 3. In this case, the refractive index of blend multilayers decreased from 1.67 to 1.48 and on the other hand, the maximized light transmission was increased from 97 to 98.5 % in the visible wavelength range.

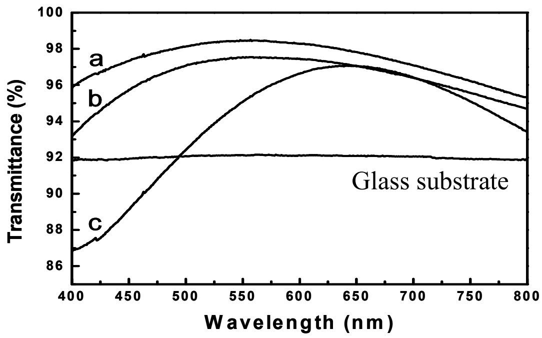

Fig. 3. Transmission spectra of the [PDAD/(TALH:PSS=X:Y)]$_n$/Silica colloids multilayer thin films deposited onto glass substrates : (a) X:Y = 95:5 (n = 40.5), (b) X:Y = 97:3 (n = 48.5) and (c) X:Y = 99:1 (n = 35.5).

Fig. 4 shows the change in the light transmittance curves of [PDAD/(TALH:PSS)]$_n$/colloids multilayer films with two different blending ratios (TALH:PSS = 99:1 and 95:5) as a function of annealing temperature. The broadness and red-shift of light transmittance curves indicates that the increase of heating temperature strongly induces the increase of refractive index and the decrease of thickness of blend multilayers due to the partial conversion from TALH to TiO_2 (see Fig. 1a and b). As a result, the antireflective properties as well as the refractive index and film thickness of [PDAD/(TALH:PSS)]$_n$/colloids multilayer films can be easily modulated through the blending ratio and heating treatment. Furthermore, we cannot exclude the possibility that optimized adsorption of silica colloids for achieving the lower refractive index than 1.35 can still more improve the maximum light transmittance of [PDAD/(TALH:PSS)]$_n$/colloid films. In the case of calculating the light transmittance of heterogeneous multilayer films composed of PDAD/(TALH:PSS) (n = 1.68) and colloidal layer with refractive index below n = 1.30 from the characteristic matrix theory, the maximum light transmittance increases up to above 99 %.

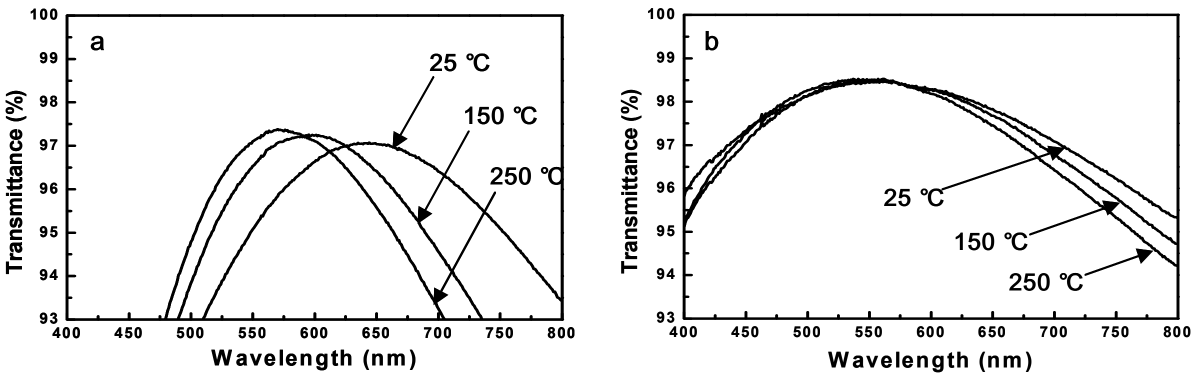

Fig. 4. Transmission spectra of [PDAD/(TALH:PSS)]$_n$/silica colloids ((a) TALH:PSS = 99:1, n = 35.5 and (b) TALH:PSS = 95:5, n = 40.5) multilayer thin films treated with different heating temperatures for 30 min in vacuum.

Conclusions

We demonstrate that the LbL multilayer films composed of blend multilayer and silica colloidal layer show the strong antireflective properties. The decrease of PSS fraction in the blend from 10 to 0% and the heating temperature induce the notable change in film thickness and refractive index of [PDAD/(TALH:PSS)]$_n$ films. Therefore, in the case of depositing silica colloidal layer onto blend multilayer, the antireflective properties of these films can be easily modulated using blending ratio and heating temperature.

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