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# Optical Properties of Polyelectrolyte Multilayers Fabricated by Layer-by-layer Adsorption Processes

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The optical properties of ultra thin films fabricated by layer-by-layer (LBL) self-assembly processes using poly (allylamine hydrochloride)(PAH) and poly (acrylic acid)(PAA) were measured for optical applications. Refractive index dispersion of the thin films was dependent on the thickness, dipping cycle and deposition time. Relation of optical properties and these conditions (thickness and dipping cycle, deposition time) was studied. Based on calculation with the measured optical data, anti-reflection films were calculated by this measurement data, and fabricated by this LBL method.

Key words: layer-by-layer, polyelectroytes, refractive index dispersion, anti-reflection film

## 1. INTRODUCTION

Recently, with the current trend of technology moving towards optically transparent polymeric media and coatings, the need for anti-reflection technology and environmentally benign processing methods for polymeric materials independent of shape or size has become quite apparent. Layer-by-layer (LBL) self-assembly process[1, 2, 3] has many merits. For example, this method can be used at room temperature and normal pressure. Thickness can be controlled at nano meter order. As it is a wet process, it can be prepared with large area and is expected to realize the fabrication of the film at very low cost.

For application to optical devices and films (anti-reflection films[4, 5, 6] or IR-cut films or UV-cut films, and so on), optical properties such as refractive index as a function of thickness were needed. However, there has not been a detailed report about optical properties of poly (allylamine hydrochloride) (PAH)/ poly (acrylic acid) (PAA) fabricated by the LBL adsorption process. This versatile process is particularly amenable to the creation of large-area uniform coatings on essentially any kind of surface, permitting precise control of thickness.

The LBL process has a problem that dipping time is very long (about 40 minutes / cycle). In order to fabricate 100nm-thick film, it takes about 6 hours. Quarter wavelength optical thickness was needed for optical devices. Therefore, the purpose of this study is shortening of fabrication time with investigation of optical properties of films prepared by different dipping conditions.

In this study, we measured the optical thickness calculated from refractive index and film thickness that depend on dipping cycle. High-quality anti-reflection film was successfully designed by LBL self-assemble polyelectrolyte adsorption process. The thin films obtained are suitable for broadband anti-reflection coating and expected to provide a high performance, low-cost light control devices.

## 2. EXPERIMENTAL

PAH (MW=55,000) was purchased from Aldrich Chemical. PAA (MW=90,000) was obtained from Polyscience as a 25% aqueous solution. The polyelectrolytes were used without any further purification. Deposition bath for both polyelectrolyte was prepared as $10^{-2}$ mol/L (based on the repeat unit molecular weight) solutions using deionized water (R > 18MΩ). Aqueous solutions of PAH and PAA were adjusted to pH 7.5±0.1 with 1N NaOH and pH 3.5±0.1 with 1N HCl, respectively. Rinse bath was deionized water without adjusted pH.

The layer-by-layer deposition to prepare the multilayer thin films was completed via an automatic dipping process using Layer-by-layer adsorption process (Nippon Laser & Electronics Lab., NL-SA1010T). Silica-on-silicon type wafers (thickness of silica layer was about 300nm: hereafter denoted Si wafer) were ultrasonically agitated in a $H_2O$:EtOH (2:3) solution of KOH for 10min and then washed ultrasonically with deionized water (R > 18MΩ, pH 5.5~6.5) 2 times for 10 min. Si wafers were immersed in a polyelectrolyte solution (PAH first) for 15min followed by rinsing 3 times for 3, 1 and 1min, respectively. The Si wafers were then immersed into the oppositely charged polyelectrolyte solution for 15min and subjected to the same rinsing procedure. After a desired number of layers (from 1 to 30, arbitrary extraction) had been built on the Si wafer, the substrate were removed from the dipping cycle, dried with flowing $N_2$ gas, and dried again at 80℃ for 1h in vacuum. The thickness and refractive index of the above films were measured using the optical interfering method (Film Tek 3000, Scientific Computing International) and values were averaged for at least 3 separate measurements on each sample.

Anti-reflection film is 2-layer type, composed of which high transmission grade PET (100 $\mu$m) / high refractive index layer : (HI layer) / low refractive index layer : (LI layer). The thickness of high-refractive-index layer was calculated by $\lambda/4 = nd$ (n : refractive index, d : thickness, $\lambda$ =550nm, n=1.9, d=70nm. HI layer coated on PET film (hereafter denoted HI films) was immersed in a polyelectrolyte solution (PAH first) for 3, 5, 15 min followed by rinsing 3 times for 3, 1 and 1 min, respectively. The films were then immersed into the oppositely charged polyelectrolyte solution for 3 and 15 min and subjected to the same rinsing procedure. After the desired number of 8 or 11 layers had been built on the HI films, the substrate was removed from the dipping cycle, dried with flowing $N_2$ gas, and dried again at 80 ℃ for 1h in vacuum.

In order to reduce reflection of the back, the back of a film was rubbed by steel wool, and the rubbed side was colored black by an ink, and a black tape is stuck on the colored black layer.

The luminous reflection was measured using UV-Vis spectrophotometer (JASCO, V-570) and averaged for at least 3 separate measurements on each sample. The angle of incident light and the angle of detected light were 5 degree. The same thickness and refractive index for samples were used throughout the measurement. UV-Vis data was analyzed by optical interference method. This method simultaneously solves for refractive index, extinction coefficient, and thickness of multi-layer film structures. A self-consistent solution is obtained by using SCI's generalized dispersion formula to simulated fitted values of the dielectric function. This approach allows the user to model complex multi-layer structures with reflection/transmission data. This method optimizes both the reflectance and power density spectrum (FFT) simultaneously. This unique feature allows for accurate thickness determination over a wide range of thickness. The SCI dispersion model is a physical model derived from quantum mechanical principle that correctly obeys the Kramer-Kronig relationship. This model is applicable to metallic, semiconductor, amorphous, crystalline, and dielectric materials. For a single layer film, a single peak at a position corresponding to the optical thickness of the film is observed. For multiple layer films, multiple peaks are observed.

## 3. RESULTS AND DISCUSSION

(PAH/PAA) was fabricated by LBL method on Si wafer. The refractive index and thickness of the thin film were calculated from Figure 1 using the optical interfering method. The measured data was in agreement with simulated data. From simulated data, thickness and refractive index dispersion curves were determined. The check of reliability of data was used thickness of silica layer near 300nm. If a simulation was not converged, the thickness was calculated as 100 or 400nm, not 300 nm.

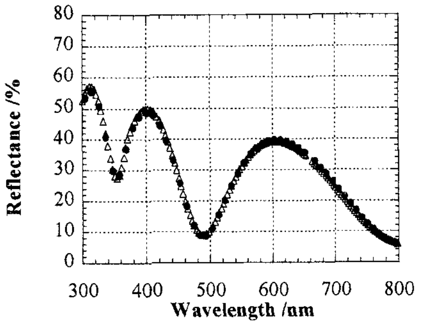


Fig. 1 Reflection as a function of wavelength
●:simulated, △:measured
Simulaed data was calclulated
by optical inetrference method.
Both data were overlap each other.

It is assumed that structure of the sample on Si wafer was 2 layers on silicon wafer, that structure was (PAH/PAA) / silica / silicon wafer.

Refractive index dispersion curves of silica layer were fixed at existing value measured by Film Tek 3000. Thickness of the silica layer was variable. Refractive index and thickness of the (PAH/PAA) layer were also variable. Refractive index dispersion curves were easily obtained with very short time (about 3 minutes /sample).

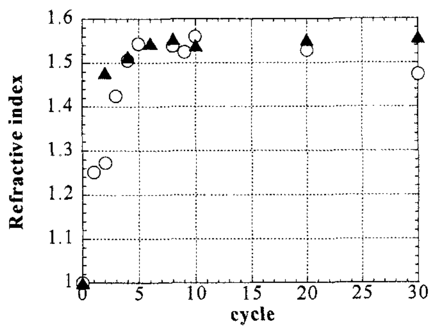


Fig.2 Refractive index as a function of dipping cycle
Dipping time was ○ : 15 minutes, ▲:5 minutes
Refractive index was saturated about 1.55 over 5cycles

Figure 2 shows the refractive index of (PAH/PAA) on Si wafer as a function of dipping cycle. Between 1 to 4 cycles, refractive index (at 632nm) was increased to 1.5. At over 5 cycles, refractive index was saturated at 1.5. This means that in the first step (PAH/PAA) was not adsorbed uniformly on Si wafer surface and in second step (PAH/PAA) was adsorbed uniformly on Si wafer surface.

At sample of 15 minutes deposition time, scattering loss was increase and reflectance was decreased in proportion to dipping cycle more than 10 cycles. Therefore, refractive index of the sample is decreased.

As refractive index of both samples was about 1.55 at 20 cycles, it is suggested that both samples have equivalent optical properties.

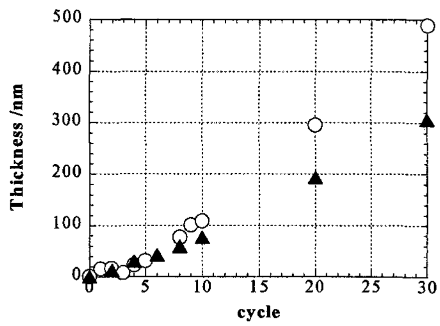


**Fig.3 Thickness as a function of dipping cycle Dipping time was ○:15 minutes, ▲:5 minutes The Growth rate was changed at 5 cycles each dipping time**

Figure 3 shows the thickness of (PAH/PAA) on Si wafer as a function of dipping cycle. As was in figure 2, the slope was changed at the 5 cycles, indicating that adsorption process changed at 5 cycles. From 1 to 4 cycles, only electrostatic attraction (Coulomb force) was dominate in adsorption. Over 5 cycles, physical attraction becomes also dominant and adsorption rate becomes fast. Thickness is growing linearly keeping almost the same refractive index.

The adsorption rate of 15 minutes and 5 minutes were different, because it depended on dipping time.

Thickness control was very easy from 1 to 4 cycles. Over 5 cycles, however thickness was not only controlled by dipping time but also by adsorption rate.

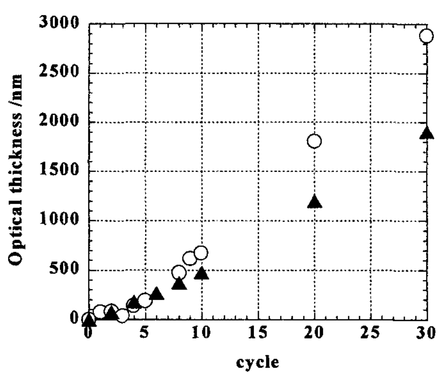


**Fig.4 Thickness as a function of dipping cycle Dipping time was ○:15 minutes, ▲:5 minutes The growth rate was changed at 5 cycles at each dipping time**

Figure 4 shows the optical thickness of (PAH/PAA) on Si wafer as a function of dipping cycle. The optical thickness is a multiply of thickness and refractive index. If optical thickness can be controlled near the quarter wavelength optical thickness, many optical applications are realized. The growth of optical thickness is changed at 5 cycles, too. Visible region is from 400 to 800 nm. The slope of the condition of 5 minutes compared with 15 minutes was smoothly, thickness was controlled easily from 400 to 800 nm using by the condition of deposition time of 5 minutes.

Based on these results of optical thickness, the most suitable thickness calculated for the LI layers in terms of dipping cycle was 8 cycles for dipping time of 15 minutes and 11 cycles for dipping time of 5 minutes. Anti-reflection films were fabricated according to these results.

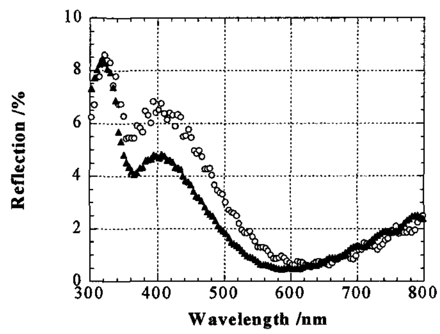


**Fig.5 Properties of AR films ○:8bilayers(15minutes), ▲ : 11bilayers(5minutes) Minimum reflectance was 0.47 at 5 minutes and 0.59 at 15 minutes. Luminous reflectance was 1.58 at 15 minutes and 0.93 at 5 minutes.**

Figure 5 shows reflectance of (PAH/PAA) on HI films as a function of wavelength. Dipping cycle was different between 5 and 15 minutes since adsorption rates were different. Absorption at 400nm depended on absorption of a metal oxide included in the HI layer.

Thickness of the HI layer was controlled for quarter wavelength optical thickness at 550nm. However wavelength of lowest reflectance was not 550nm in Figure 5. LI layer was (PAH/PAA) fabricated by LBL adsorption process. As the dipping cycle controlled the thickness, thickness was not continuous values. Minimum reflectance was 0.47 at 5 minutes and 0.59 at 15 minutes. Luminous reflectance was 1.58 at 15 minutes and 0.93 at 5 minutes. Wavelength of minimum reflectance of 8 bilayers (Figure 5) was different from that of 11 bilayers. Because of dipping rate, it is not able to control the same thickness. In respect that the high quality anti-reflection was realized and results of Figure 3 were reliable for optical applications.

## 4. CONCLUSION

From optical property of quarter wavelength optical thickness, thickness of low refractive index layer for anti-reflection film was calculated. Anti-reflection films were able to fabricate successfully by layer-by-layer self-assemble polyelectrolyte adsorption processes. Using the present methods, IR or UV cut films and various optical filters are able to be design easily. Since the method is wet process, it is expected that optical devices fabricated by this process become low cost in the near future.

## 5. AKNOWLEDGEMENT

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