

# Waterproof Anti-reflection films fabricated by layer-by-layer adsorption process

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## 1. Introduction

Recently, with the current trend of technology moving towards new coating method for controlled thickness at nano meter order. This technology is used for optical control devices (anti-reflection films or IR-cut films or UV-cut films, and so on). In the applications, we have reported high quality AR film fabricated by layer-by-layer (LBL) self-assemble polyelectrolyte adsorption process and a brief exposure to acidic aqueous solutions<sup>[1]</sup>.

Layer-by-layer (LBL) self-assembly process<sup>[2-4]</sup> is one of nano coating method and this method has many advantages. For example, this method can be used at room temperature and normal pressure and controlled thickness with nano meter order. As it is a wet process, it can be prepared easily with large area. It is expected that products coated on polymer film by LBL adsorption process get cheap.

With this process, exemplified by poly (acrylic acid) (PAA: anion) and poly (allylamine hydrochloride) (PAH: cation), one is afforded greater control over the physical state of the assembled polymers, such as their linear density, thickness, and conformation and the degree of interchain ionic bonding. In fact, layer thickness over 80 have been reported in weak PAA/PAH multilayers by depositing at a pH near the solution pKa of the polyelectrolytes<sup>[5]</sup>.

Further, micro porous thin films can be readily fabricated from layer-by-layer assembled multilayers of the weak polyelectrolytes PAA and PAH<sup>[6]</sup>. This transition to 3-D interconnected micro porous network is induced by a brief exposure to acidic aqueous solution at pH 2.3 - 2.5 and neutral water initiates a further reorganization that creates films with more discrete, rounded pores with radius sizes ranging from about 50 to 200 nm. The micro porous thin films are obtained low refractive index easily.

M. F. Rubner et al. reported that inorganic salts ( $MgCl_2$ ) have an effect on controlling micro porous diameter size, therefore micro porous film was appeared high transparency of AR film<sup>[7]</sup>.

However, the AR film was weak for water and rubbing. The surface of the AR film was included micro porous structure and PAH/PAA interaction was only ionic bonding. Changing dissociation ratio that was changed by moisture reorganized the micro porous structure and rubbing broke the micro porous structure.

In this study, we examined thermal cross-linking anion and cation of that micro porous structure and measured waterproof and rubbing stability

## 2. Materials

PAH ( $M_w=55,000$ ) was purchased from Aldrich Chemical. PAA ( $M_w=90,000$ ) was obtained from Poly science as a 25% aqueous solution. Carboxyl group and amino group were formed ionic interaction pair. The polyelectrolytes were used without any further purification. Both polyelectrolyte deposition bathes were prepared as  $10^{-2}$  mol/l (based on the repeat unit molecular weight) solutions using deionized water ( $> 18$  M Advantec water). PAH aqueous solution was adjusted to pH  $7.5 \pm 0.1$  with 1N NaOH and PAA aqueous solution was adjusted to pH  $3.5 \pm 0.1$  with 1N HCl. Rinse bath were deionized water, pH not adjusted. High-refractive-index layer coated on PET film (hereafter denoted HI films) were immersed in a polyelectrolyte solution (PAH first) for 15min followed by rinsing in three successive bathes of water (deionized water,  $>18$  M Advantec water, pH 5.5~6.5) for 3, 1 and 1min, respectively. The films were then immersed into the oppositely charged polyelectrolyte solution for 15 min and subjected to the same rinsing procedure. After the desired number of layers (from 7 to 9) had been built on the HI films, the substrate were removed from the automatic dipping machines, blown dry with compressed  $N_2$  gas, and subsequently oven dried at  $80^\circ C$  for 1h in vacuum.

As mentioned previously, the layer-by-layer deposition technique to prepare the multilayer thin films was completed via an automatic dipping process using an automated layer-by-layer adsorption system (Model NL-SA1010T, Nippon Laser & Electronics Lab.).

To effect porosity transformation, low-pH solution (pH = 2.5) was prepared by hydrochloric acid. The pH of the sample was confirmed with Horiba pH meter. Multilayer substrates were immersed into the acidic solution typically for 120 s, rinsed with neutral water for 1 min, blown dry, and then oven dried at  $80^\circ C$  for 1h in vacuum.

For thermal cross-linking, reaction temperature was measured by DSC (Seiko instruments Inc., EXSTAR 6000), and checking finished cross-linking measured by FT-IR (Thermo Nicolet Japan Inc., Avater 330). That sample was film mixed PAA : PAH = 1 : 1 and dried at  $100^\circ C$  30 min in vacuum.

Composition of AR film is high transmission grade poly(ethylene terephthalate) (Toray Industries, Inc. T60,  $100 \mu m$ )/ high-refractive-index layer/ low-refractive-index layer. The thickness of high-refractive-index layer is controlled optical thickness using cerium oxide nano

particles in acrylic polymer. Low-refractive-index layer was fabricated (PAH/PAA) by LBL process.

The surface structure of (PAH/PAA) surface on silicon wafer and that of AR film was observed by AFM (Digital Instruments, Nano Scope a).

In order to lose reflection of the back, the back of a film was rubbed by steel wool, and the rubbed side was colored black by magic, and a black tape was stuck on the colored black layer. The luminous reflection was measured using UV-Vis spectrophotometer (JASCO, V-570). The incident angle and the angle of detected light were 5 degree, respectively. The same samples as measurement of thickness and refractive index were used for measurement. The values reported represent an average of at least 3 separate measurements on each sample at each experiment.

### 3. Results and discussions

The transition temperature is about 167 from DSC measurement. Therefore formation of amide binding was measured by FT-IR over 170 for 2 hours.

Table1 shows refractive index of micro porous (PAH/PAA) films before and after annealing.

Table1 Effect of annealing refractive index (PAH/PAA) on silicon wafer

Annealing	After a brief exposure to HCl
Before	1.25 1.43
After	1.25 1.25

[Immediately after making micro pores]

[After keeping the sample in distilled water for one week]

Refractive index of micro porous structure (PAH/PAA) on silicon wafer was 1.25 after a brief exposure to HCl solution. Before annealing, refractive index was changed from 1.25 to 1.43 at a brief exposure to distilled water for one week. That reason is considered that dissociation ratio of PAA is increased and ionic interaction of PAH/PAA is increased. Therefore micro porous structure was changed by reorganization of PAH/PAA. However, after annealing at 200 for 2 hours, refractive index was not changed in a brief exposure to distilled water for one week. For measurement of FT-IR, amide bonding was produced and PAH/PAA interaction is changed from ionic bonding to covalent bonding. Therefore dissociation ratio is not dependent on pH, the other words, micro porous structure is not dependent on pH.

Table 2 shows degradation of AR effect by rubbing. Rubbing points was covered by BEMCOT (Asahi Kasei Co.). Rubbing Pressure was about 100g/cm<sup>2</sup>. Rubbing times was over 1000. AR film for rubbing test sample was fixed on the flat table. Rubbing weight was moved horizontal, not curved. Before a brief exposure to HCl, rubbing test was good. The surface of AR film was no change before and after annealing.

Table2 Maximum reflectance of AR films after rubbing (Go and return for 1000 times, 500g weight, surface was covered by BEMCOT)

	A brief exposure to HCl	
Annealing	Before	After
Before	4.6 %	< 0.5 %
After	2.2 %	2.1 %

After a brief exposure to HCl and before annealing, the scratch on the surface was appeared at rubbing less than 100 times. Because of the surface scratch, reflectance of the AR film was not detected. This reason is that the surface was micro porous structure and surface strength was weak.

However, after annealing, the reflection was no change. This reason is that amide bonding was produced and PAH/PAA interaction is changed from ionic bonding to covalent bonding.

We demonstrated the new method of high quality and waterproof of AR film.

### 4. Conclusions

In this study, we examined thermal cross-linking anion and cation of that micro porous structure. Amide binding was confirmed in the micro porous structure by FT-IR spectra for thermal cross-linking.

The micro porous structure of the AR film's surface had been not changed as deposited in water for one week. Further, surface of the AR film became strong for rubbing.

Using the present methods, IR or UV cut films and various optical filters are able to be good water stability. Since the method is wet process, it is expected that optical devices fabricated by this process become low cost in the near future.

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