

## Polymer Heterostructure Using Sequential Adsorption Method of Polyelectrolyte

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Sequential adsorption process of polyelectrolyte was used to deposit on the substrate as the fabrication of ultra-thin films for wet process. In this study, in order to develop the functional devices such as one-dimensional photonic crystals or microcavity, multilayer structure was fabricated by depositing the high refractive index and low index materials polyelectrolytes periodically in the direction of the film thickness. The thickness of each layer was controlled by the frequency shift of quartz crystal microbalance. The cross sectional image of the hetero structure was observed with a transmittance electron microscope. The optical characteristic of the hetero structure was also investigated.

Key words : polyelectrolyte, transmission electron microscopy, hetero structure,

### 1. Introduction

To develop "nano-device" using nano-technology, the fabrication of ultra-thin films by wet process is strongly required because the running cost is less expensive than that of the dry process by carrying out at room temperature, normal pressure. Layer-by-layer sequential adsorption process of polyelectrolytes, which fabricated monolayer or multilayers hetero structure thin film by dipping the substrate successively in each polyelectrolyte solution (polyanion or polycation), is one of the promising techniques for the deposition of the ultra-thin organic films by the wet process [1,2].

In this study, low and high refractive index hetero structure was fabricated by this process. The cross-sectional organic hetero structure was observed by transmittance electron microscope (TEM). For 230°C annealed, the structure of each structure was maintained.

### 2. Experimental detail

A structural formula of polyelectrolytes is shown in Fig.1. Poly(acrylic acid) (mol. wt. 90,000), poly(allylamine-hydrochloride) (mol. wt. 70,000) and tetrahydro- thiophenium precursor of poly(p-phenylenevinylene) were used as the

polyanion and polycation. Each polymer is abbreviated as PAA, PAH and PPV-THT hereafter. PAH and PAA were purchased from Aldrich and Polyscience and no further purification. The synthesis of PPV-THT has been outlined by Paul L. Burn et al [3]. The concentration of the solutions of PAH and PAA was adjusted to  $10^{-2}$ M and that of PPV-THT was  $10^{-3}$ M. The pH of PAA and PAH solution was adjusted to pH 3.5 and that of PPV-THT solution was pH 5.5. The self-assembled film was deposited on a substrate using six steps: immersing in polycation solution; rinsing in water twice; immersing in polyanion solution; rinsing in water twice. Immersing time of each steps was 180 sec. These processes were executed by using the automatic dipping machine, which controlled the dipping time in each bath with a personal computer. The schematic illustration of the experimental set up is shown in Fig.2.

A schematic illustration of layer-by-layer sequential adsorption process was shown in Fig.3. In this study, weak polyelectrolyte was used and the mass of it's adsorption depend on the dissociation of ammonia group and carboxyl group. In the condition of pH 3.5, polyelectrolyte was relatively stretched in the solution as shown in Fig.3 (a). Therefore it adsorbed more uniformly to the substrate.

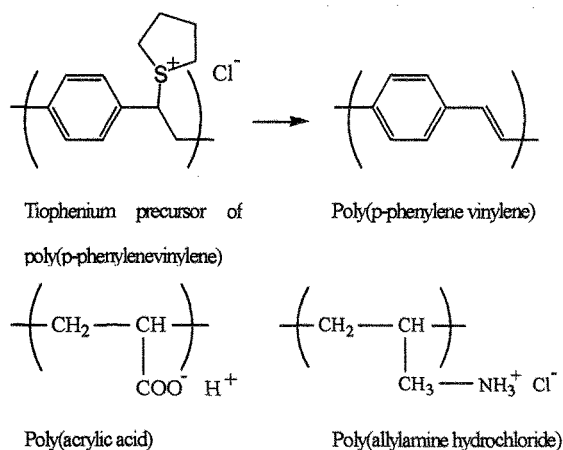


Fig.1: Structural formula of polyelectrolytes

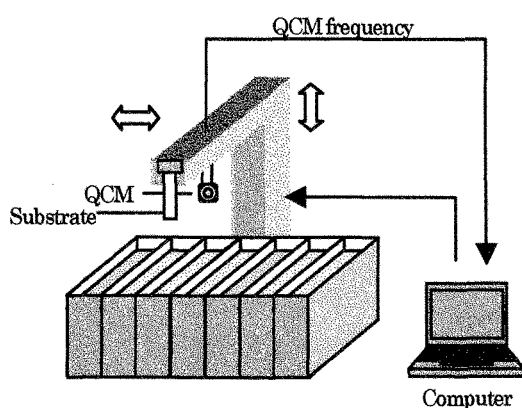


Fig.2: Schematic illustration of an automatic dipping machine with film mass monitoring in-situ QCM.

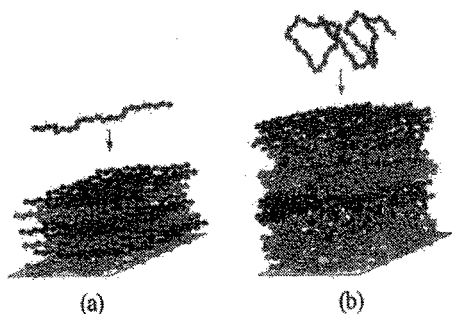


Fig.3: A schematic illustration of layer-by-layer sequential adsorption process.

Si, Glass and polymer (poly(styrene), poly(ether sulfone)) were used as a substrate. Si and Glass substrate were washed by KCl solution for 3 minutes in ultrasonic wave and washed by water appropriately. Polymer substrate was ozone cleaning for 3 hours. These surfaces were very hydrophilic. In order to obtain the

smooth initial polymer layer, we introduced poly(sodium 4-styrenesulfonate) (mol. wt. 70,000, abbreviated SPS). This strong polyelectrolyte dissolved at nearly 100% dissociation in the solution; therefore it adsorbed more uniformly as compared with weak polyelectrolytes [4,5]. Before constructing hetero structure, PAH/SPS was deposited to 3 bilayers (1 bilayer is consist of polyanion layer and polycation layer) onto the substrate. PAH/PAA 12 bilayers and PPV/PAA was assembled alternately and 7 blocks  $[(\text{PAH/PAA})_{12}/(\text{PPV/PAA})_{22}]_{3.5}$  polymer hetero structure was fabricated. Si, Glass and poly(ether sulfone) substrate was annealed for 3 hours at 230°C under vacuum. Poly(styrene) substrate was annealed for 3 hours at 100°C under vacuum. PPV-THT was converted to PPV over 200°C. Therefore the film on the former substrate was converted and that on the latter was not converted. Polymer hetero structure was analyzed by field emission transmission electron microscope (FETEM). For FETEM, it was difficult to recognize each polymer. Because the transmittance of each polymer was almost the same, it is necessary to enhance the contrast for polymers by use of a staining agent. Ruthenium tetroxide ( $\text{RuO}_4$ ) was an effective staining agent for FETEM. [6]. The phenylen group of PPV-THT or PPV was selectively stained with  $\text{RuO}_4$ , so PAH/PAA and PPV/PAA layer had different contrast at FETEM examination. Hydrated ruthenium dioxide ( $\text{RuO}_2 \cdot 2\text{H}_2\text{O}$ ) has been suggested as the starting material for the preparation of  $\text{RuO}_4$  by a reaction with an excess of sodium periodate ( $\text{NaIO}_4$ ) in water. The FETEM sample was stained by the  $\text{RuO}_4$  vapor for 18 hours.

### 3. Discussion

Frequency shift of quartz crystal microbalance (QCM) was shown in Fig.4 when the hetero structure of PAH/PAA and PPV/PAA was deposited to the substrate. As shown in this figure, the deposited mass of each blocks was constant. The average frequency shift of  $(\text{PAH/PAA})_{12}$  was 1380Hz and that of  $(\text{PPV/PAA})_{22}$  was 2350Hz. On the other hand, however, the frequency shift of the first block of  $(\text{PAH/PAA})_{12}$  was 1700Hz and this was larger than that of the other  $(\text{PAH/PAA})_{12}$  blocks. We considered that the surface charge was too high when the PAH/SPS bilayers were deposited as the preparation layers and the adsorbing mass of PAH/PAA was larger than that of the other

(PAH/PAA)<sub>12</sub> blocks.

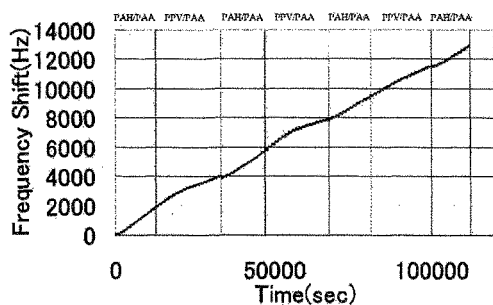
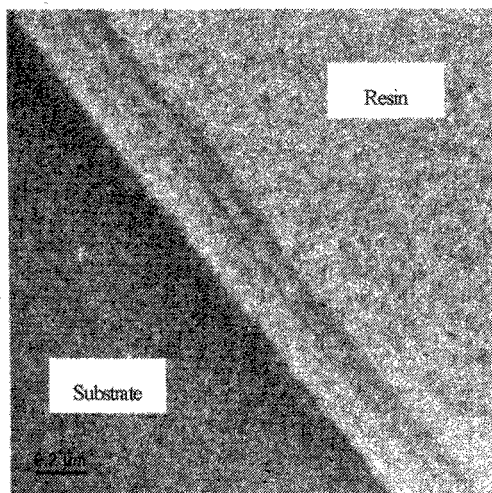
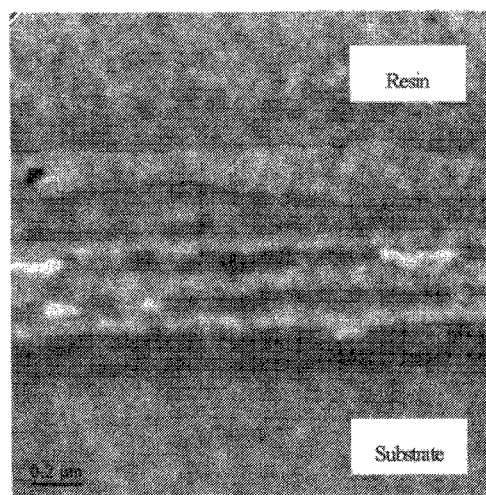


Fig.4: Frequency shift of QCM hetero structure

A cross sectional FETEM image was shown in Fig.5 (a) and (b). The sample of Fig.5 (a) and Fig.5 (b) was 100°C annealing and 230°C annealing. The structures consist of a (PAH/PAA)<sub>12</sub> block (gray) and (PPV/PAA)<sub>22</sub> blocks (black). Since the existence of Ru in the (PPV/PAA)<sub>22</sub> blocks was higher than that of (PAH/PAA)<sub>12</sub> blocks, the penetration ratio of the electron beam of the former was much lower than that of the latter. Therefore, the former was shown much darker than the latter. Each 3 blocks of (PAH/PAA)<sub>12</sub> and (PPV/PAA)<sub>22</sub> was recognized in Fig.5 (a). The contrast between the outermost layer and resin was not clear. As shown in Fig.5 (a), the smooth hetero structure was observed. The hetero structure of [(PAH/PAA)<sub>12</sub>(PPV/PAA)<sub>22</sub>]<sub>3.5</sub> was maintained over the glass transition temperature of each polyelectrolyte.



(a)



(b)

Fig.5 : Cross sectional image of [(PAH/PAA)<sub>12</sub>(PPV/PAA)<sub>22</sub>]<sub>3.5</sub>  
(a)annealed at 100°C (b)annealed at 230°C

#### 4. Conclusion

(PAH/PAA)<sub>12</sub> and (PPV/PAA)<sub>22</sub> successfully accumulate to the substrate by layer-by-layer sequential adsorption process of polyelectrolyte. We can see a multilayer of 7 blocks from FETEM examination. The smooth hetero structure was observed from cross sectional image. The hetero structure of [(PAH/PAA)<sub>12</sub>(PPV/PAA)<sub>22</sub>]<sub>3.5</sub> was maintained over the glass transition temperature of each polyelectrolyte.

The subject of this study is the fabrication of dielectric optical multilayer filter by using this process [7,8]. Almost of polyelectrolyte have generally low refractive index, however, PPV is known as a high refractive index polymer. We try to fabricate this multilayer as an optical filter to stacks low refractive index layer (PAH/PAA)<sub>12</sub> and high refractive index layer (PPV/PAA)<sub>22</sub> each other. The reflectance of quarter wave stacks is shown in Fig.6 when an optical length is designed as  $nd = \lambda/4$  ( $n$ : refractive index,  $d$ : film thickness,  $\lambda = 550\text{nm}$ ). The maximum reflectance at 550 nm is successfully fabricated. We can see an optical filter is fabricated by using layer-by-layer sequential adsorption process which has advantage of the fabrication at room temperature and room pressure as compared with dry process such as vacuum evaporation, molecular beam epitaxy and chemical vapor deposition.

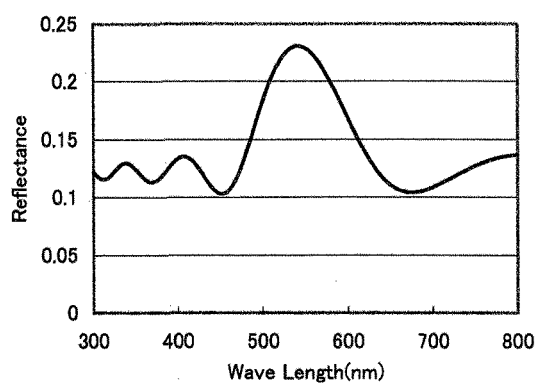


Fig.6: The simulation of reflectance of  $[(\text{PAH}/\text{PAA})_{12}/(\text{PPV}/\text{PAA})_{22}]_{3.5}$  multilayer

### 5. Acknowledgements

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