

Functional Polymer Thin Films Based on the Layer-by-Layer Deposition

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Introduction

Since the layer-by-layer (LbL) self-assembly (SA) (i.e., dip SA) technique based on the dipping process was first introduced by Decher and Hong in 1992,¹⁻³ multilayer films prepared by various interactions employing electrostatic interaction and hydrogen bonding have been used for selective area patternings, light emitting diodes, membranes, photonic crystals, and the surface modification of colloidal particles. This LbL SA method is principally based on the self-diffusion process in which charged polyelectrolyte (PE) chains are adsorbed onto an oppositely charged surface due to the electrostatic attraction. As a result, the adsorption time, proper control of pH, PE concentration and the amount of added ionic salt should be carefully selected in order to increase the surface coverage of a polymer layer adsorbing onto a substrate.

In present study, we report a *spin self-assembly method* using a spinning process as an alternative to fabricate well-organized multilayer films in a very short process time.

Experimental

Materials. Poly(allylamine hydrochloride) (PAH; $M_w = 50\,000 - 65\,000$) as a cationic PE and poly(sodium 4-styrenesulfonate) (PSS; $M_w = 70\,000$) as an anionic PE were used as received from Aldrich. The mole concentration of PE solutions was fixed at 10 mM.

Build-Up of Multilayer Films. For the spin SA multilayer films, positively charged PAH solution was completely wetted on the total area (2cm x 2cm) of a substrate. Immediately after the solution deposition, the substrate was rotated with a spinner at a fixed rotating speed (typically, 4000 rpm) for a short period (typically about 15 seconds) until the sufficiently dried film was obtained and the substrate was then thoroughly rinsed twice at a speed of 4000 rpm with a plenty of deionized water. Negatively charged PSS layer was also sequentially deposited onto the substrate using the same procedure as mentioned above.

Results and discussion

Figure 1 shows the difference in UV/vis absorbance of multilayer films with alternating PAH and PSS layers prepared by both spin SA and dipping SA methods. In this case, the multilayer films prepared with the spin SA method are adsorbed onto only one side of a quartz wafer while the films prepared by the dipping SA method are adsorbed onto both sides of a quartz wafer. The film thickness per bilayer adsorbed by both the spinning process and the dipping process was found to be about 24 Å and 4 Å, respectively, as determined from ellipsometric measurement when the same mole concentrations of the polyelectrolytes were used. The significant difference in the adsorbed amount between the dipping and the spinning method is caused by different adsorption mechanisms. In the case of the conventional SA method by the dipping process, polyelectrolyte chains are allowed to diffuse toward the substrate due to the electrostatic interaction and then the adsorbed chains rearrange themselves on the surface. On the other hand, the adsorption and rearrangement of adsorbed chains on the surface and the elimination of weakly bound polymer chains from the substrate in the spin SA process are almost simultaneously achieved by a high spinning speed for a short time. Fast elimination of water during the spinning process significantly increases the mole concentration of PE solutions during the short deposition time and this increase in the polyelectrolyte concentration yields thick layers but molecularly smooth surface counterbalanced by the centrifugal force and the air shear force.^{4,5}

Figure 2 shows the change in water contact angles of dip and spin SA (PAH/PSS)_n films when the top-most layer is alternatively changed from PAH to PSS or from PSS to PAH. First, in the case of the dip SA film repeatedly deposited from PE solutions of 10 mM without the addition of ionic salt, all the contact angles measured on

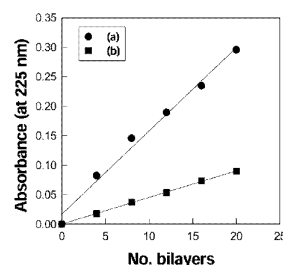


Figure 1. Absorbance at 225 nm of PAH/PSS multilayers prepared by (a) spin SA method and (b) dipping SA method.

PAH and PSS surfaces except the first two layers are within the range of 25 ~ 28° without evident periodic oscillation. The disappearance of the oscillatory trend of contact angles obtained from our experimental conditions reflects that the respective top surface layers form rather disordered layers composed of interdigitated PAH and PSS segments owing to the insufficient surface coverage. In contrast, for the spin SA multilayer films deposited from the five different mole concentrations of PE solutions, the increase in PE concentration significantly enhances the oscillation behavior of contact angles up to about 7 mM and then levels off at higher concentrations. This result indicates that the relatively thick top-most layers prepared by PE concentrations above 7 mM, fully covering the surface roughness of the sublayer, yields distinct and periodic oscillations in contact angles. It is also worthwhile to point out that the spin SA top-most layers with PE concentrations of 7, 10 and 16 mM demonstrate similar contact angles despite of the increase in individual layer thickness.⁵ These similarities in contact angles can be explained in light of physical and chemical characteristics.

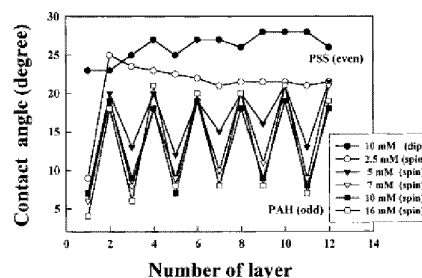


Figure 2. Water contact angles measured from PAH/PSS multilayers prepared with dip SA and spin SA methods. Odd and even numbers indicate the layers deposited with PAH and PSS, respectively.

Conclusion

We demonstrated that the spin SA process utilizing centrifugal force, viscous force, air shear and electrostatic interactions causes the adsorption, the rearrangement of PE chains onto a substrate and the desorption of weakly bound chains to occur in a very short time of approximately 10 seconds. This new ultrathin film-forming process, despite much simpler and faster in comparison with the conventional dipping SA process, yields a highly ordered internal structure far superior to the structure obtained with the dipping SA process.

Acknowledgement

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References

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