

CHARACTERISTICS AND MICROPATTERNING OF SPIN SELF-ASSEMBLED ULTRATHIN MULTILAYERS

KOOKHEON CHAR*, SANGCHEOL KIM, JINHAN CHO,
HIESANG SOHN, and HONGSEOK JANG

*School of Chemical Engineering, Seoul National University
San 56-1, Shilim-dong, Kwanak-gu, Seoul, 151-744, Korea*

**khchar@plaza.snu.ac.kr*

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A new method is introduced to build organic/organic multilayer films composed of cationic poly(allylamine hydrochloride) (PAH) and negatively-charged poly(sodium 4-styrenesulfonate) (PSS) using the spinning process. The adsorption process is governed by both the viscous force induced by fast solvent elimination and the electrostatic interaction between oppositely-charged species. On the other hand, the centrifugal and air shear forces applied by the spinning process enhance significantly the desorption of weakly-bound polyelectrolyte chains and also induce the planarization of the adsorbed polyelectrolyte layer. The surface of the multilayer films prepared with the spinning process is quite homogeneous and smooth. Also, a new approach to create multilayer ultrathin films with well-defined micropatterns in short process time is introduced. To achieve such micropatterns with high line resolution in organic multilayer films, microfluidic channels were combined with the convective self-assembly process employing both hydrogen bonding and electrostatic intermolecular interactions. As a next step, we extended the spin SA to the fabrication of multilayer micropatterns with vertical heterostructure.

Keywords: Spin self-assembly method; multilayer thin films; micropatterns; microfluidic channels; convective self-assembly.

1. Introduction

Fabrication of multilayer thin films have attracted much interest since they are of great use in thin film devices based on the electrochemical processes such as sensors, integrated optics, rectifiers, or light-emitting devices (LED).^{1–5} For the applications of organic or organic/inorganic hybrid multilayer thin films to high performance devices, the internal structure of the films should be at the degree of high molecular order and the ability to pattern with at least micrometer-scale feature on the films are also required. Since the ionic layer-by-layer self-assembly (SA)

*Rm. 725, Bldg. 302, School of Chemical Engineering, Seoul National University, San 56-1, Shilim-dong, Kwanak-gu, Seoul, 151-744, Korea.

technique was introduced for the fabrication of polyelectrolyte multilayer, this self-assembling technique has been extended to conducting polymer composites, non-linear optical dyes, and the assembly of nanoparticles or biomolecular systems.^{6–9} This layer-by-layer deposition by dipping method is principally governed by the self-diffusion of adsorbing polymer and the rearrangement on the surface and thus various experimental factors should be taken into account in order to obtain the uniform surface coverage of a polymer layer adsorbing onto a substrate: adsorption time, pH, concentration of polyelectrolyte and amount of added ionic salt. After the adsorption of a polyelectrolyte layer, thorough washing using pure solvent is required because the weakly-adsorbed polyelectrolyte chains increase significantly the surface roughness of the multilayer films.

Until now, several methods of multilayer patterning have been reported, including template-directed selective deposition with microcontact printing, electric field-directed deposition, and water-based subtractive patterning. In these methods, however, chemically-patterned templates should be prepared on the substrates because the adsorption process is based on the self-diffusion and rearrangement due to the interactions between adsorbing molecules and the patterned templates.

In present work, we describe the new spin self-assembly (SA) method as an alternative for producing well-organized multilayer films in short process time. Through the analyses by UV-vis spectroscopy and AFM, the multilayer thin films fabricated by the spin SA method were compared with those prepared by the conventional dipping method. We have also investigated the micropatterning of multilayers based on both hydrogen bonding and electrostatic intermolecular interactions. Furthermore, the obtained patterns were then used as templates to produce multilayer micropatterns with vertical heterostructure

2. Experimental

2.1. Materials

Poly(allylamine hydrochloride) (PAH, $M_n = 50\,000 \sim 65\,000$), poly(diallyldimethyl ammonium chloride) (PDAC, $M_w = 100\,000 \sim 200\,000$), poly(sodium 4-styrenesulfonate) (PSS, $MW = 70\,000$), poly(4-vinylpyridine) (PVP, $M_w = 60\,000$) and poly(acrylic acid) (PAA, $M_v \sim 450\,000$) were purchased from Aldrich and used without further purification. 16-mercaptohexadecanoic acid was obtained from Aldrich and used in absolute ethanol solution. Poly(dimethylsiloxane) (PDMS) and curing agent were purchased from Dow Corning.

2.2. Multilayer preparation

Quartz substrates for the deposition of polyelectrolytes were initially cleaned by ultrasonification in a hot mixture of H_2SO_4/H_2O_2 (7/3) for three hours. They were then heated in a mixture of $H_2O/H_2O_2/NH_3$ (5/1/1) at $80^\circ C$ for 1 h, and then dried by N_2 gas purging. After this procedure, the substrates were negatively-charged

and used for the polyelectrolyte deposition starting with the cationic PAH. In the conventional layer-by-layer SA method, the substrates were immersed alternately in the cationic solution and in the anionic solution for 20 min for each deposition. After each deposition step, the surface of the self-assembled film was washed by dipping into the deionized water for 2 min and then blown dry with a stream of nitrogen. In the spin SA method, the deposition steps were carried out as follows: a few drops of polyelectrolyte solution were placed on the substrate and the substrate was then rotated at a fixed rotating speed (typically, 4000 rpm) for 8 to 15 s. After the deposition of each polyelectrolyte layer, the substrates were thoroughly rinsed twice with a plenty of deionized water. The spinning time and speed for the washing step were also identical to those for the layer deposition.

2.3. Micropatterning of multilayers

A silicon wafer was initially coated with a 1000 Å buffer layer of silicon oxide and followed by deposition of a 100 Å adhesive layer of titanium. A 1000 Å film of gold was then sputtered on the titanium surface. The COOH-terminated hydrophilic substrate was prepared by immersing the gold film into a 5 mM 16-mercaptohexadecanoic acid in absolute ethanol for 30 min. The multilayer deposition steps were carried out as follows: polymer solution was first allowed to fill the microfluidic channels, which were formed by the contact between a PDMS mold and a hydrophilic substrate, by the capillary pressure. The channel filling with a polymer solution also enables the polymer to adsorb onto the surface and the removal of residual solution is then carried out by the spinning process (typically, 6000 rpm for 2 min).

2.4. Characterization

The characteristics of multilayer films were analyzed by UV-vis spectrometer, atomic force microscope (AFM). An ellipsometer was also employed for the thickness measurement.

3. Results and Discussion

Figure 1 shows the difference in UV-vis absorbance of multilayer films prepared by both spin SA and dipping SA methods as a function of number of bilayers. Due to the contribution of the adsorbed PSS chains, the absorbance occurs at 225 nm in the UV region. The aqueous polyelectrolyte concentrations of PAH and PSS used in the two different deposition methods were all identical to be 10 mM (on the monomer unit basis). The dipping process was performed for an adsorption time of 20 min per layer in order to allow enough time for the saturated adsorption. In spin SA process, however, the amount of polymers adsorbed at each deposition step was found to be much larger. The film thickness per bilayer adsorbed by the dipping process and the spinning process was found to be about 4 Å and 24 Å, respectively, as determined from the ellipsometric measurement.

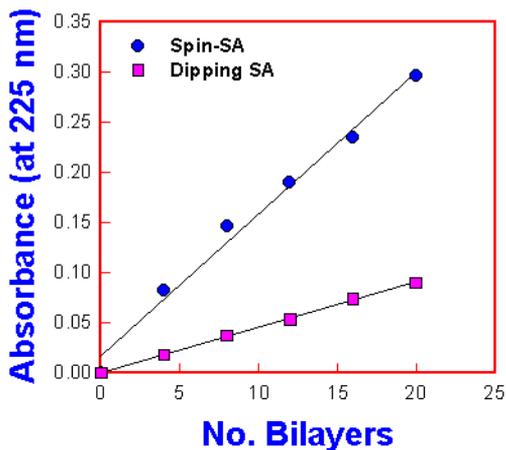


Fig. 1. Absorbance at 225 nm of PAH/PSS multilayers prepared by spin SA method and dipping SA method.

We also found that the spin SA method has a significant effect on the surface roughness of prepared multilayer films presumably due to the air shear force during the spinning process. In order to investigate this effect in detail, we measured the surface roughness of the self-assembled films using atomic force microscopy (AFM) in tapping mode as shown in Fig. 2. Although the flattened adsorption of a polyelectrolyte onto a substrate was obtained from a low ionic strength of the solution, the surface roughness of the dipping SA film composed of (PAH/PSS)₃₀ multilayer was measured to be about 8 Å.

On the other hand, the (PAH/PSS)₃₀ multilayer film prepared by the spin SA method shows a surface roughness of about 3 Å. These results are quite reproducible and clearly demonstrate that the air shear force imposed by the spinning process enhances significantly the surface planarization of the multilayer films. In addition, the surface roughness of about 3 Å and the bilayer thickness of 24 Å for the spinning process compared with 8 Å and 4 Å for the dipping process provides an indirect evidence that the internal structure of the spin SA films is highly ordered.¹⁰

To develop well-defined micropatterns of ultrathin multilayers in short process time, microfluidic channels were combined with the convective SA process (i.e., the self-assembling process in the presence of external flow) employing both electrostatic and hydrogen bonding intermolecular interactions.¹¹ The patterning is performed in two steps: polymer solution is first allowed to fill the microfluidic channels, which are formed by the contact between an elastomeric mold and a hydrophilic substrate, by the capillary pressure. The channel filling with a polymer solution also enables the polymer to adsorb onto the surface and the removal of residual polymer solution is then carried out by the spinning process.

The micropatterns of multilayer films with alternating PVP and PAA layers were prepared by the convective SA. As shown in Fig. 3, the micropatterns of ultrathin multilayers are significantly dependent on the solvent used. Micropatterns

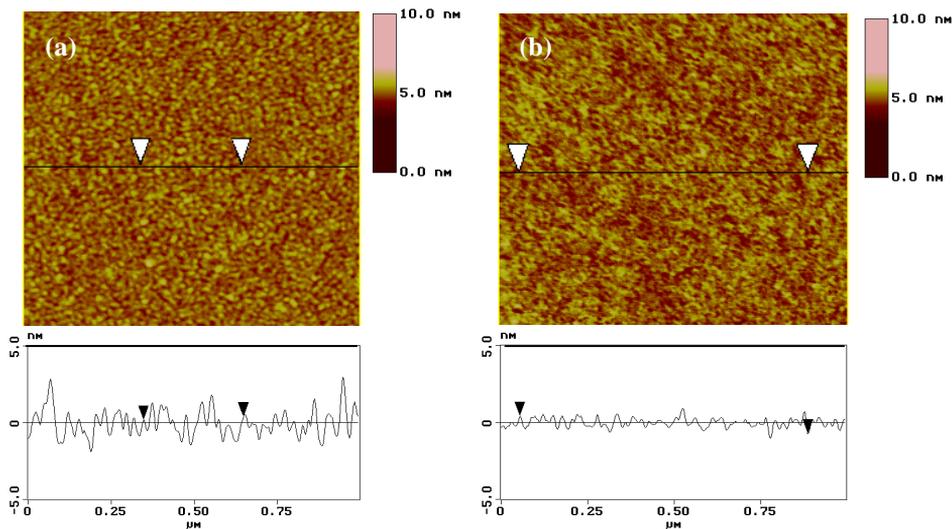


Fig. 2. Tapping mode AFM images of (a) a (PAH/PSS)₃₀ film prepared with the dipping SA and (b) a (PAH/PSS)₃₀ film fabricated with the spin SA.

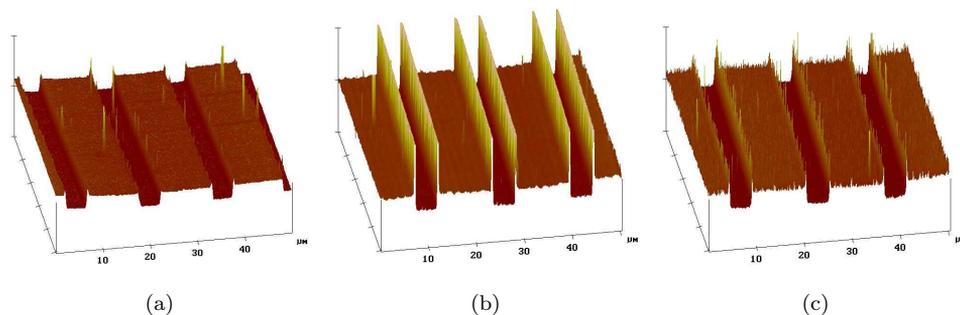


Fig. 3. AFM topography images of micropatterns of (PVP/PAA)₅ multilayers prepared with (a) DMF, (b) ethanol, and (c) ethanol/H₂O (9/1, v/v).

with sharp edge boundaries and small ridges were developed by using DMF as a solvent. For ethanol, high ridges are observed at the edges of the patterned lines, while the ridge was remarkably reduced by mixing ethanol with water. In previous works, the ridge formation phenomena were also observed in chemically-patterned films and were attributed to the retraction of a thin film of polymer from the resist alkanethiolate. However, in the case of the microfluidic channels employed in the present work, the ridge formation is due to the wetting of a solvent on the PDMS walls. It is consistent with the fact that the contact angle of ethanol on the PDMS is 31°, much lower than that of DMF (63°).

The alternate deposition of PDAC and PSS using the electrostatic intermolecular interactions was carried out by the spin SA on the patterned (PVP/PAA)₅

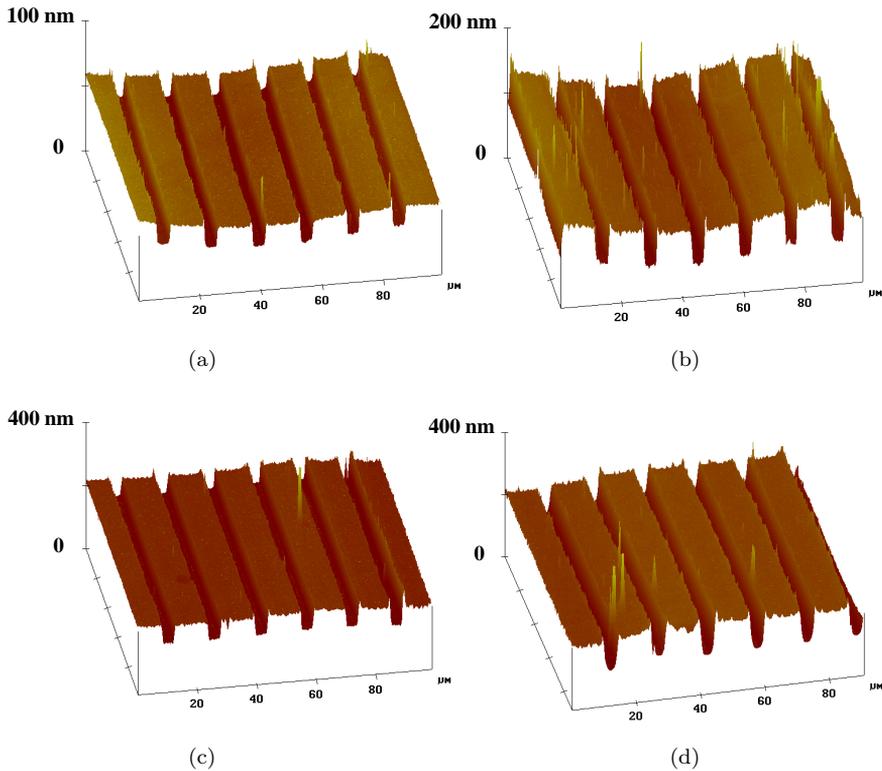


Fig. 4. Contact mode AFM images of patterned multilayer of $(\text{PVP/PAA})_5(\text{PDAC/PSS})_n$. (a) $n = 4$, (b) $n = 8$, (c) $n = 20$, and (d) $n = 40$.

multilayer template, initially prepared by using DMF as a solvent.¹² Carboxylate groups of PAA, an outmost layer of template, are partially ionized and thus allow the adsorption of cationic polyelectrolytes. The AFM topography images of 4, 8, 20, and 40 bilayers consisting of PDAC and PSS bilayers are shown in Fig. 4. The feature heights are 24, 30, 49, and 86 nm, respectively. These multilayer micropatterns with vertical heterostructure maintain high line resolution and small ridges. The surface of the micropatterns is also found to be quite homogeneous and smooth.

4. Conclusions

In summary, we have demonstrated for the first time that the spin SA process utilizing the centrifugal force, viscous force, air shear force and intermolecular interactions causes the adsorption, the rearrangement of polymer chains onto a substrate and the desorption of weakly-bound chains in a very short time of approximately 10 s. This new ultrathin film-forming process yields a highly-ordered internal structure far superior to the structure obtained by the conventional dipping SA process and it is much simpler and faster. It also allows us to precisely control and predict

the bilayer thickness as well as the surface roughness. The patterned multilayer films employing the hydrogen bonding and the electrostatic attractions can also be fabricated by the convective SA method combined with microfluidic channels. The well-defined micropatterns were obtained and then used as templates for the additional spin SA. Finally, the vertically heterostructural multilayer micropatterns with high line resolution and small ridges were produced.

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References

1. P. K. Ho, J.-S. Kim, J. H. Burroughes, H. Becker, S. F. Y. Li, T. M. Brown, F. Cacialli, and R. H. Friend, *Nature* **404**, 481 (2000).
2. X. Zhang and J. Shen, *Adv. Mater.* **11**, 1139 (1999).
3. J. D. Mendelson, C. J. Barrett, V. V. Chan, A. J. Pal, A. M. Mayes, and M. F. Rubner, *Langmuir* **16**, 5017 (2000).
4. Laschewasky, E. Wischerhoff, M. Kauranen, and A. Persoons, *Macromolecules* **30**, 8304 (1997).
5. Y. He, S. Gong, R. Hattori, and J. Kanicki, *Appl. Phys. Lett.* **74**, 2265 (1999).
6. G. Decher, *Science* **277**, 1232 (1997).
7. K. M. Lenahan, Y. X. Wang, Y. J. Liu, R. O. Claus, J. R. Hefflin, D. Marciu, and C. Figura, *Adv. Mater.* **10**, 853 (1998).
8. N. Kotov, I. Dekang, and J. H. Fendler, *J. Phys. Chem.* **99**, 13065 (1995).
9. Y. Lvov, K. Ariga, I. Ichinose, and T. Kunitake, *J. Am. Chem. Soc.* **117**, 6117 (1995).
10. J. Cho, K. Char, J. D. Hong, and K. B. Lee, *Adv. Mater.* **13**, 1076 (2001).
11. H. Jang, S. Kim, and K. Char, *Langmuir* **19**, 3094 (2003).
12. S. Kim, H. Jang, and K. Char, *Mol. Cryst. Liq. Cryst.*, submitted.