

Spin-coated ultrathin multilayers and their micropatterning using microfluidic channels

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Abstract

A new method is introduced to build up 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 significantly enhances desorption of weakly bound polyelectrolyte chains and also induce the planarization of the adsorbed polyelectrolyte layer. The film thickness per bilayer adsorbed by the conventional dipping process and the spinning process was found to be about 4 Å and 24 Å, respectively. 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 a 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. The channels were initially filled with polymer solution by capillary pressure and the residual solution was then removed by the spinning process.

Keywords : spin self-assembly method, multilayer, electrostatic attraction, hydrogen bonding, micropattern, microfluidic channel, convective self-assembly

1. Introduction

Fabrication of multilayer thin films have attracted much interest because they are of great use in thin film devices based on electrochemical processes such as sensors, integrated optics, rectifiers, or light-emitting devices (LED) (He *et al.*, 1999; Ho *et al.*, 1998; 2000; Hong *et al.*, 1998; Onitsuka *et al.*, 1996; Zhang *et al.*, 1999). For the applications of organic or organic/inorganic hybrid multilayer thin films to high performance devices, the internal structure of the films should be on 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) technique was introduced for the fabrication of polyelectrolyte multilayer (Decher, 1997), this self-assembling technique has been extended to conducting polymer composites (Kotov *et al.*, 1995), nonlinear optical dyes (Laschewasky *et al.*, 1997; Lenahan *et al.*, 1998), and the assembly of nanoparticles or

biomolecular systems (Lvov *et al.*, 1995). This layer-by-layer deposition by dipping method is principally based on 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: the adsorption time, the pH, the concentration of polyelectrolyte and the amount of added ionic salt (Cho *et al.*, 2000; Mendelson *et al.*, 2000). After the adsorption of a polyelectrolyte layer, thorough washing using a flow of a pure solvent is required because the weakly adsorbed polyelectrolyte chains significantly increase the surface roughness of the multilayer films.

Up 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.

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In this 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 the hydrogen bonding and electrostatic intermolecular interaction. These patterned multilayers are obtained by using microfluidic channels composed of poly (dimethylsiloxane) (PDMS) and hydrophilic substrate.

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, $M_w=70,000$), Poly(4-vinylpyridine) (PVP, $M_w=60,000$) and poly(acrylic acid) (PAA, $M_r\sim 450,000$) 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 and used as recommended from the literature.

2.2. Multilayer preparation

Quartz substrates for the deposition of polyelectrolytes were initially cleaned by ultrasonication in a hot mixture of H_2SO_4/H_2O_2 (7/3) for 3 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 hour, and then subsequently 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 then the substrate was rotated at a fixed rotating speed (typically, 4000 rpm) for 8 to 15 seconds. After the deposition of each polyelectrolyte layer, the substrates were thoroughly rinsed twice with a plenty of deionized water. The spinning time and the 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 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 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 microscopy (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 (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. It should be noted at this point that the multilayer film fabricated by the spin SA method is adsorbed onto only one side of a

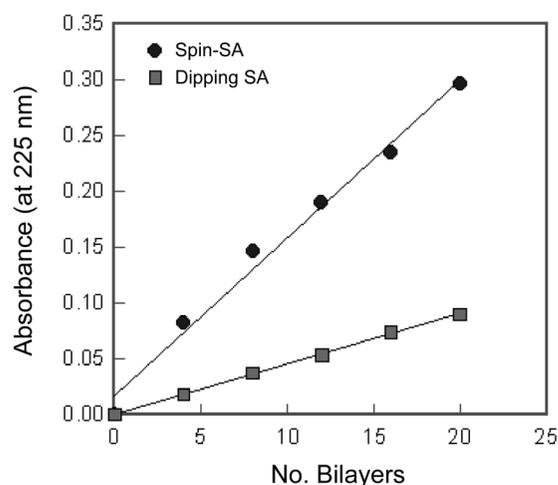


Fig. 1. Absorbance at 225 nm of PAH/PSS multilayers prepared by (●) spin SA method and (■) dipping SA method.

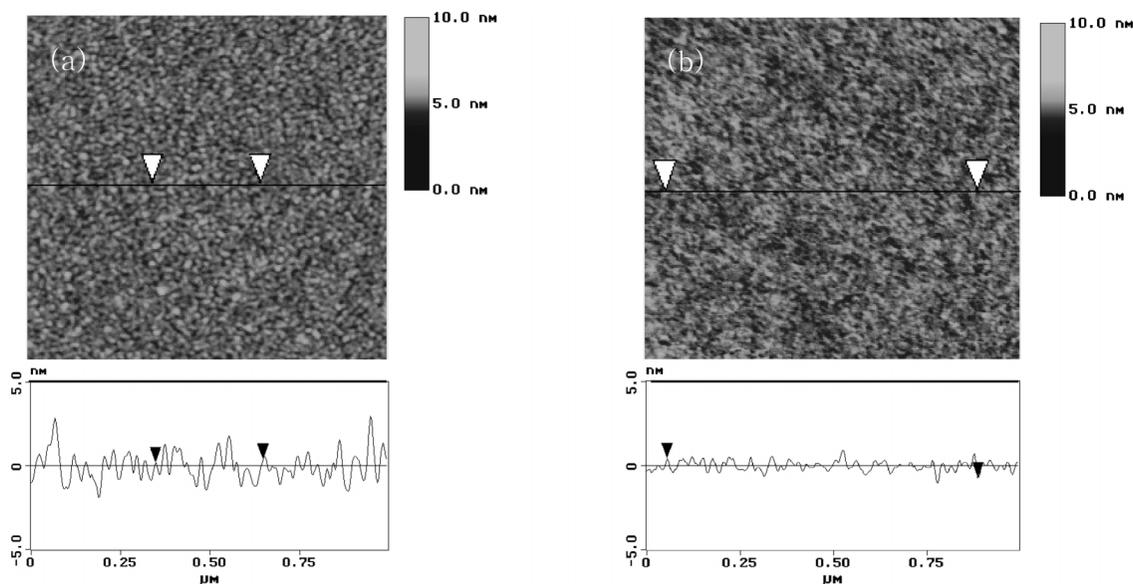


Fig. 2. Tapping mode AFM images (Digital Instruments, Nanoscope IIIa) of (a) a (PAH/PSS)₃₀ film prepared with the dipping SA and (b) a (PAH/PSS)₃₀ film fabricated with the spin SA.

quartz wafer while the film prepared by the dipping SA method is adsorbed onto both sides of a quartz wafer. 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.

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 (Chou *et al.*, 2000). 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 figure 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 driven by the spinning process significantly enhances 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. This also points to the fact that the film prepared with the spin process contains rather distinct interfaces between respective layers in contrast to the film obtained by the dipping method although no Bragg peaks in the X-ray reflectivity spectra of the PAH/PSS multilayer films to distinguish

such internal structure were observed due to the small electron density difference between PAH and PSS.

The significant difference in the adsorbed amount and the surface roughness between the dipping and the spinning method is caused by the different adsorption mechanism. The conventional SA method by the dipping process is principally based on the self-diffusion in which charged polyelectrolyte chains are adsorbed onto an oppositely charged surface and then rearranged owing to the electrostatic interaction. As the presence of water molecules in the assemblies screens the electrostatic attraction, the surface coverage of polyelectrolyte chains is restricted and the weakly adsorbed chains are produced. In the spin SA process, however, the adsorption and rearrangement of polyelectrolyte chains on the surface and the elimination of weakly bound chains from the substrate are almost simultaneously achieved by high spinning speed for a short time. Fast elimination rate of water by the spinning process significantly increases the concentration of polyelectrolyte solution during the short deposition time. It also improves the electrostatic attraction between oppositely charged polymers. As a result, the adsorption of polyelectrolyte chains is more enhanced and thicker layers are obtained although the thin layer is favoured by the centrifugal force and air shear force. The surface planarization of the multilayer films is also achieved because the weakly adsorbed chains are easily eliminated by the air shear force (Lawrence, 1988; Meyerhofer, 1978; Ohara *et al.*, 1989).

To understand quantitatively the formation of multilayers in spinning process, the effects of polyelectrolyte concentration and spinning speed were investigated. Figure 3(a) shows that the absorbance increases linearly with the num-

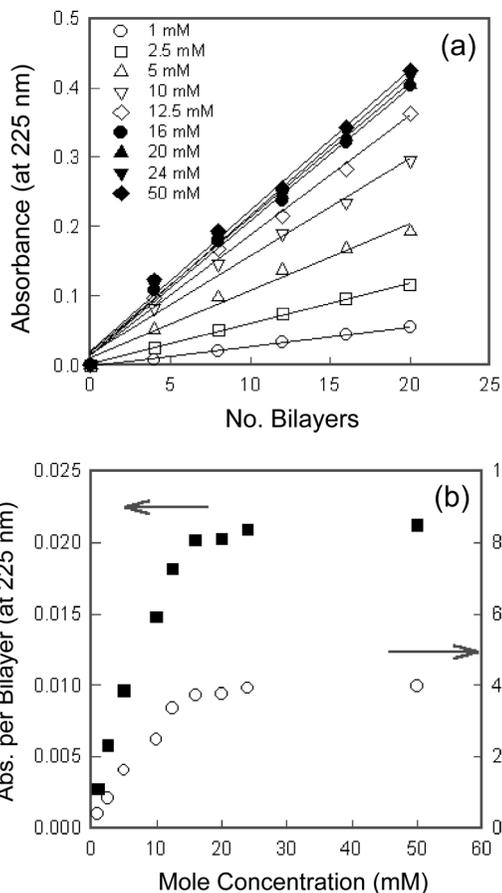


Fig. 3. (a) The increase of absorbance of $(\text{PAH/PSS})_n$ as a function of bilayer number. (b) The effect of mole concentration of polyelectrolytes on the adsorbed amount (■) and the thickness per PAH/PSS bilayer (○) prepared by spin SA method.

ber of bilayers for all the polymer concentrations employed in this study. The slope indicates the deposited amount of polyelectrolytes after a cycle of the spin self-assembly of both PAH and PSS. This amount is initially dependent on the concentration of polymer solution, then levels off above 16 mM. As shown in figure 3(b), the film thickness per bilayer increases from 5 Å to 40 Å and shows the same dependence on the solution concentration. This asymptotic behavior may be due to the saturation of polyelectrolytes on the surface. Although the increase of polymer concentration tends to produce a thicker adsorbed polymer layer due to the adsorption driving forces such as viscous and electrostatic forces, the excess adsorbed layer with weak binding sites is readily eliminated by the desorption driving forces such as centrifugal and air shear forces. This observation suggests that it is possible to precisely control the adsorbed amount of polyelectrolytes in multilayer films by simply changing a wide range of polymer concentration in spite of the strong repulsion among polyelectrolyte chains with the same charge.

According to the theoretical models and experimental results based on the spin coating of single-layer films, the film thickness (H) is dependent on the spinning speed (Ω) and the initial solution concentration (C_i) as follows:

$$H \sim \Omega^{-\alpha} C_i^\beta \quad (1)$$

When the thickness varies from micrometer to millimeter, the value of α is 0.5 and β has the value between 1.50 and 2.47. As mentioned above, the absorbance (A) is linearly proportional to the film thickness. Thus, by substituting A for H , the equation (1) is examined for the spin SA multilayer thin films. At a fixed solution concentration, the absorbance per bilayer decreases linearly with the spin speed as shown in figure 4(a) and the exponent of α is found to be 0.34. The polyelectrolyte concentrations are used only below 16 mM, above which the surface is fully saturated and is not affected by the concentration as confirmed in figure 3. Figure 4(b) represents a log-log plot of

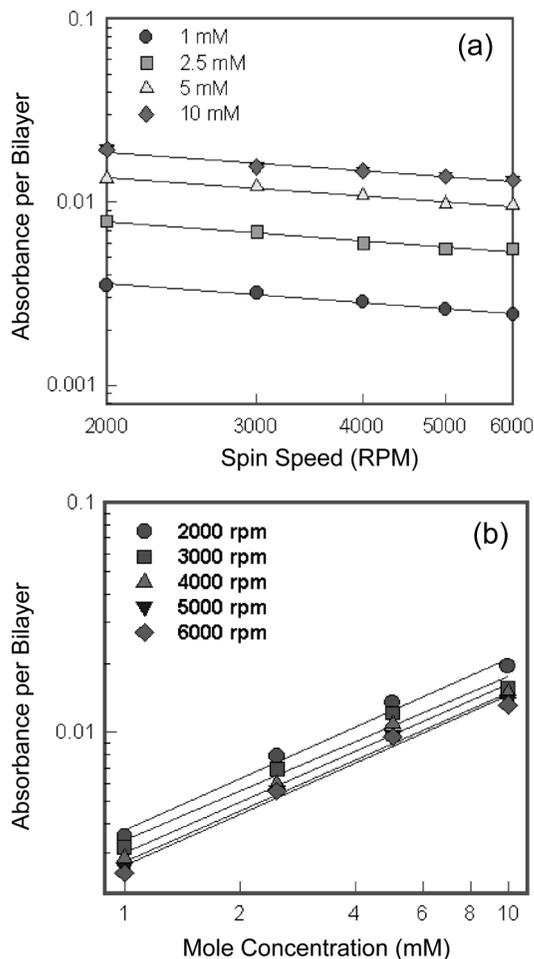


Fig. 4. The effect of spinning speed (a) and mole concentration of polyelectrolytes (b) ranging from 1 mM to 10 mM on the adsorbed amount of PAH/PSS bilayers prepared by the spin SA method. Each point in the figure represents the average absorbance per bilayer for up to 20 bilayers.

the average absorbance per bilayer as a function of mole concentration. For the spinning speeds ranging from 2000 to 6000 rpm, the absorbance increases with the polyelectrolyte concentration with a scaling exponent of 0.74. The difference in the power exponents with respect to both the spinning speed and the initial solution concentration may be caused by the characteristics of the spin SA method. In the spin self-assembled multilayer thin films, the weakly bound chains are thoroughly eliminated by the centrifugal force and air shear force during the washing step. As a result, the stable and ultrathin layer is obtained at each deposition step. It means that the next adsorption becomes strongly dependent on the interaction between a deposited sublayer (or a substrate) and a coating overlayer. Compared with a thick single layer, the adsorption and desorption forces, which are determined by only the spinning speed and mole concentration, become less important.

The dimension of each channel is 10 μm wide, 1.2 μm high, and 5 mm long. When a polymer solution fills the microfluidic channel with a rectangular cross section, the time τ taken to travel the channel with a length L is given by the following equation:

$$\Delta P = \gamma [\cos\theta_{\text{substrate}} + \cos\theta_{\text{PDMS}}] / a + 2\cos\theta_{\text{PDMS}} / b \quad (2)$$

$$C_g = \{ab / (a + b)\}^2 / 8 \quad (3)$$

$$\tau = \eta L^2 / (2C_g \Delta P) \quad (4)$$

where γ is the surface tension of liquid, θ is the contact angle of liquid, a is the height and b is the width of channel, η is the viscosity of a polymer solution, ΔP is the pressure drop across the channel and C_g is the geometric factor of the capillary channel. Generally, we note that the chan-

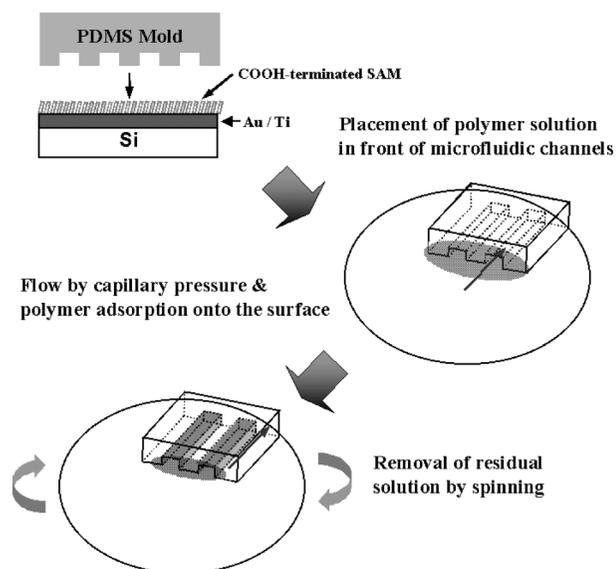


Fig. 5. Schematic of micropatterning of multilayer films using the convective self-assembly process.

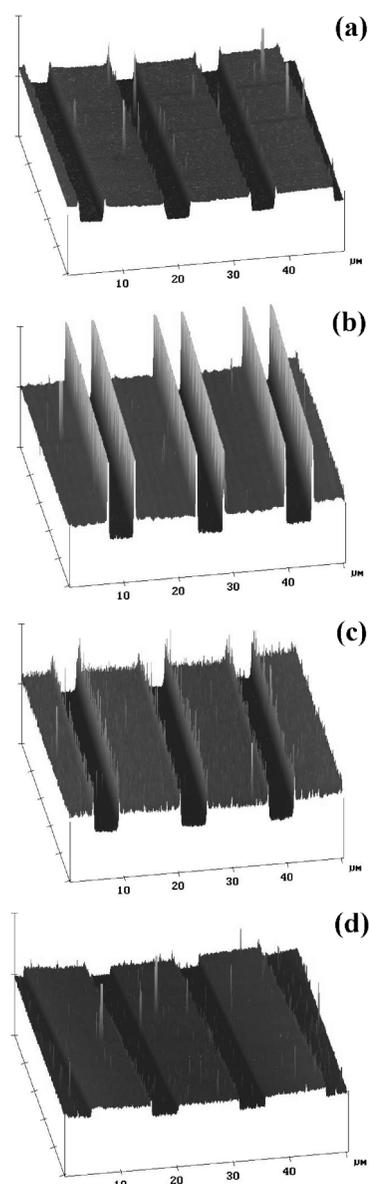


Fig. 6. AFM topography images of micropatterns of (PVP/PAA)₅ multilayers prepared with: (a) DMF, (b) ethanol and (c) ethanol/H₂O (9/1, v/v). (d) (PDAC/PSS)₅ multilayer in water (Height scale is 50 nm).

nel is filled in short time as far as the solvent preferentially wets the channel surface. For the case of *N,N*-dimethylformamide (DMF) as a solvent, the time taken for the complete filling was observed to be within 3s, which is in agreement with the time estimated by assuming $\eta_{\text{DMF}} = 0.794 \times 10^{-3}$ kg/ms, $\Delta P_{\text{DMF}} \approx 48$ kPa, and $C_g \approx 1.4 \times 10^{-13}$ m². The multilayers in the microfluidic channels are obtained by the convective SA method through the adsorption and rearrangement of polymer chains onto a substrate and the desorption of weakly bound chains in the presence of a shear field. In the spin SA process without mold confinement, there are several driving forces such as centrifugal

force, viscous force, and air shear force. Because the removal of the polymer solution in the microfluidic channels is restricted by the confined geometry, these forces are dependent on the position of the PDMS mold on a substrate. Typically, in present work, the mold is located near the rim of the SAM-coated silicon wafer and the channel direction is aligned in parallel with the radial direction.

By using the microfluidic channels, the patterning of multilayer films with alternating PVP and PAA layers was performed. As shown in figure 6, the micropatterns of spin-coating ultrathin multilayers are significantly dependent on solvent used.

Micropattern with clear edge boundaries and small ridges was developed by using DMF as a solvent. For ethanol, high ridge is observed at the edge 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 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 (i.e., 63°).

We also achieved the micropatterning of (PDAC/PSS)₅ multilayer, which is based on the electrostatic intermolecular interaction. Figure 6(d) shows the AFM image of (PDAC/PSS)₅ multilayer in aqueous solution. The feature height of the micropatterned multilayer is lower than that of (PVP/PAA)₅, but no ridge is observed. As mentioned above, the ridge formation at the edge boundary is suppressed by the poor wettability on the PDMS mold (i.e., the contact angle is about 108°).

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 electrostatic 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 seconds. This new ultrathin film-forming process yields a highly ordered internal structure far superior to the structure obtained by the conventional dipping SA process although 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 attraction can also be fabricated by the convective SA method combined with microfluidic channels. In the light of the wide application range of the ultrathin multilayer films, the spin SA process developed in the present study opens up new possibilities

for highly efficient electronic/photonics devices based on multilayer structures.

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