Modulating the Pattern Quality of Micropatterned Multilayer Films Prepared by Layer-by-Layer Self-Assembly

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Received July 28, 2005. In Final Form: October 27, 2005

Patterned multilayer films composed of poly(allylamine hydrochloride) (PAH) and poly(sodium 4-styrenesulfonate) (PSS) were prepared using dip and spin self-assembly (SA) methods. A silicon substrate was patterned with a photoresist thin film using conventional photolithography, and PAH/PSS multilayers were then deposited onto the substrate surface using dip or spin SA. For spin SA, the photoresist on the substrate was retained, despite the high centrifugal forces involved in depositing the polyelectrolytes (PEs). The patterned multilayer films were formed by immersing the PE-coated substrates in acetone for 10 min. The effect of ionic strength on the pattern quality in dip and spin multilayer patterns (line-edge definition and surface roughness of the patterned region) was investigated by increasing the salt concentration in the PE solution (range 0−1 M). In dip multilayer patterns, the presence of salt increased the film surface roughness and pattern thickness without any deformation of pattern shape. The spin multilayer patterns formed without salt induced a height profile of about 130 nm at the pattern edge, whereas the patterns formed with high salt content (1 M) were extensively washed off the substrates. Well-defined pattern shapes of spin SA multilayers were obtained at an ionic strength of 0.4 M NaCl. Multilayer patterns prepared using spin SA and lift-off methods at the same ionic strength had a surface roughness of about 2 nm, and those prepared using the dip SA and lift-off method had a surface roughness of about 5 nm. The same process was used to prepare well-defined patterns of organic/metallic multilayer films consisting of PE and gold nanoparticles. The spin SA process yielded patterned multilayer films with various lengths and shapes.

Introduction

Decher and Hong introduced the layer-by-layer (LbL) self-assembly (SA) technique based on the dipping process (i.e., dip SA) to produce multilayer films in 1992.[1−4] Since then LbL films formed through electrostatic interactions and hydrogen bonding have been used for selective area patterning,[5−11] as light emitting diodes,[12−19] for membranes,[20−22] for photonic crystals,[23−26] and for the surface modification of colloidal particles.[27−29] Multilayer patterns have attracted particular interest in fabricating devices with various electrical,[30−32] optical,[22−25] or biological properties.[33−35] Such patterns have been prepared by a photolithographic approach using UV irradiation[36−39] or by a non-

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10.1021/la052057a CCC: $33.50 © 2006 American Chemical Society
Published on Web 12/21/2005

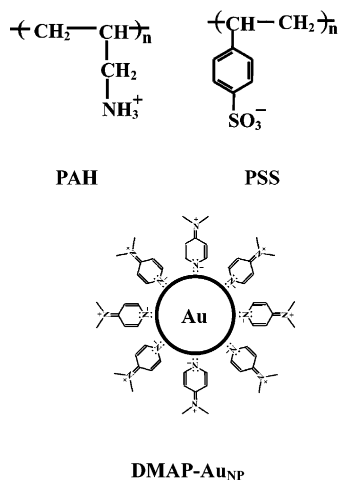
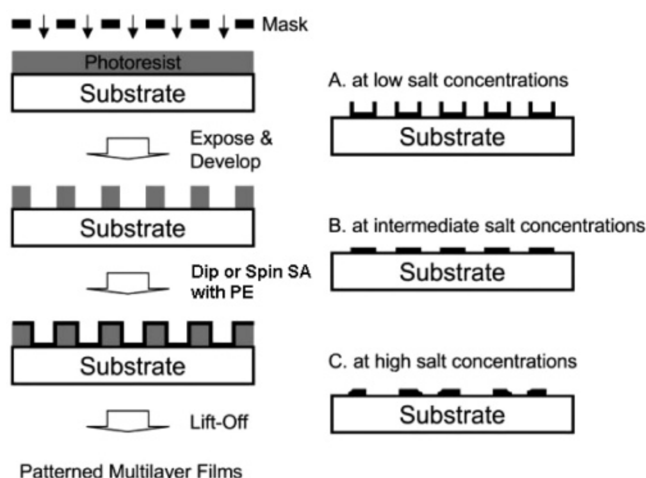


Figure 1. Chemical structures of PEs used in this study and schematic of DMAP-Au$_{NP}$.

Scheme 1



lithographic approach, such as microcontact printing.[40−43] For example, Hammond and co-workers reported that various LbL self-assembled layers could be built up onto specific regions without UV irradiation using chemically patterned templates.[5−10] They also demonstrated that selective adsorption of polyelectrolytes (PEs) or colloidal particles was significantly influenced by pH and ionic strength, which was closely related to changes in the charge density or charge screening. Jaffar et al. reported that multicomposition patterns composed of cationic and anionic nanoparticle bilayers can be prepared using quantum dots coated with oppositely charged PEs.[43] Conversely, Hua et al. reported that LbL multilayer patterns composed of PEs and nanoparticles could be obtained by combining photolithography and lift-off procedures.[36,37] For the dip SA multilayer patterns, a photoresist film is first patterned onto a substrate through a mask by UV irradiation. The entire substrate surface, including the photoresist pattern, is then coated with PE layers by the dip SA method. Following this, the substrate is immersed in acetone with ultrasonic treatment, which removes both the photoresist pattern and the LbL layers deposited over it, yielding a multilayer pattern on a selective region.[13] Although multilayer patterns based on the dip SA method can be easily applied to various devices, real applications will require films with high surface quality that can be rapidly processed.

Recently, it was reported that well-defined multilayer films can be quickly fabricated by spin SA (15 s per layer).[44−53] However, the spin SA method has difficulty in adsorbing PE multilayers selectively onto patterned substrates using the microcontact printing method because the adsorption selectivity for patterning decreases as the number of PE layers increases. These phenomena can also be observed in dip SA PE multilayer patterns prepared from relatively high ionic salt concentration.[6] To overcome this decreased selectivity, spin SA multilayer patterning was prepared using microfluidic channels.[48] This method provides inherent selective adsorption control due to the use of the microfluidic channels, but it can be limited to line patterns because of the directionality of centrifugal force during the spinning process.[48] As a result, it has been recognized that this method has limited applications for fabricating devices with varied pattern shapes.

Herein, we show that well-defined multilayer patterns with various shapes can be fabricated through the combination of the spin SA and lift-off (spin SALO) methods at optimum ionic strength. Although our pattern method is similar to the combination of dip SA and lift-off (dip SALO) methods suggested by Hua et al.,[37] the current work is important because the dependence of ionic strength on pattern formation in spin SALO is significantly different from that produced from dip SALO. Dip SA multilayer patterns, which require relatively long adsorption time (5−20 min per layer) can be replaced by the spin SA method (about 15 s per layer). Also, few studies have examined the effect of ionic strength on pattern quality during the lift-off procedure, and the patterns formed using the spin SA method. Although the relationship between the ionic strength and the selective adsorption of dip SA multilayers onto chemically patterned substrates has been reported,[6,54] our study focuses on the effect of ionic strength on the pattern shape obtained from the selective removal of spin SA multilayers. The dependence of pattern formation on ionic strength was exploited to fabricate well-defined positive and negative multilayer patterns of PEs and densely adsorbed gold nanoparticles (DMAP-Au$_{NP}$). In addition, we investigated the effect of ionic strength on the film thickness on unpatterned substrates for both dip and spin SA methods. For this investigation, the ionic strength of the PE deposition solution was varied from 0 to 1.0 M NaCl and the adsorbed amount of PE was measured with increasing bilayer number as a function of ionic strength. Although our previous results show that the spin SA films are thicker than the dip SA films when assembled with no added salt, these phenomena are reversed with increasing the ionic strength of the PE deposition solution. Further, this trend has an effect on the feature height between dip and spin SA multilayer patterns. The relationship between the pattern quality and the

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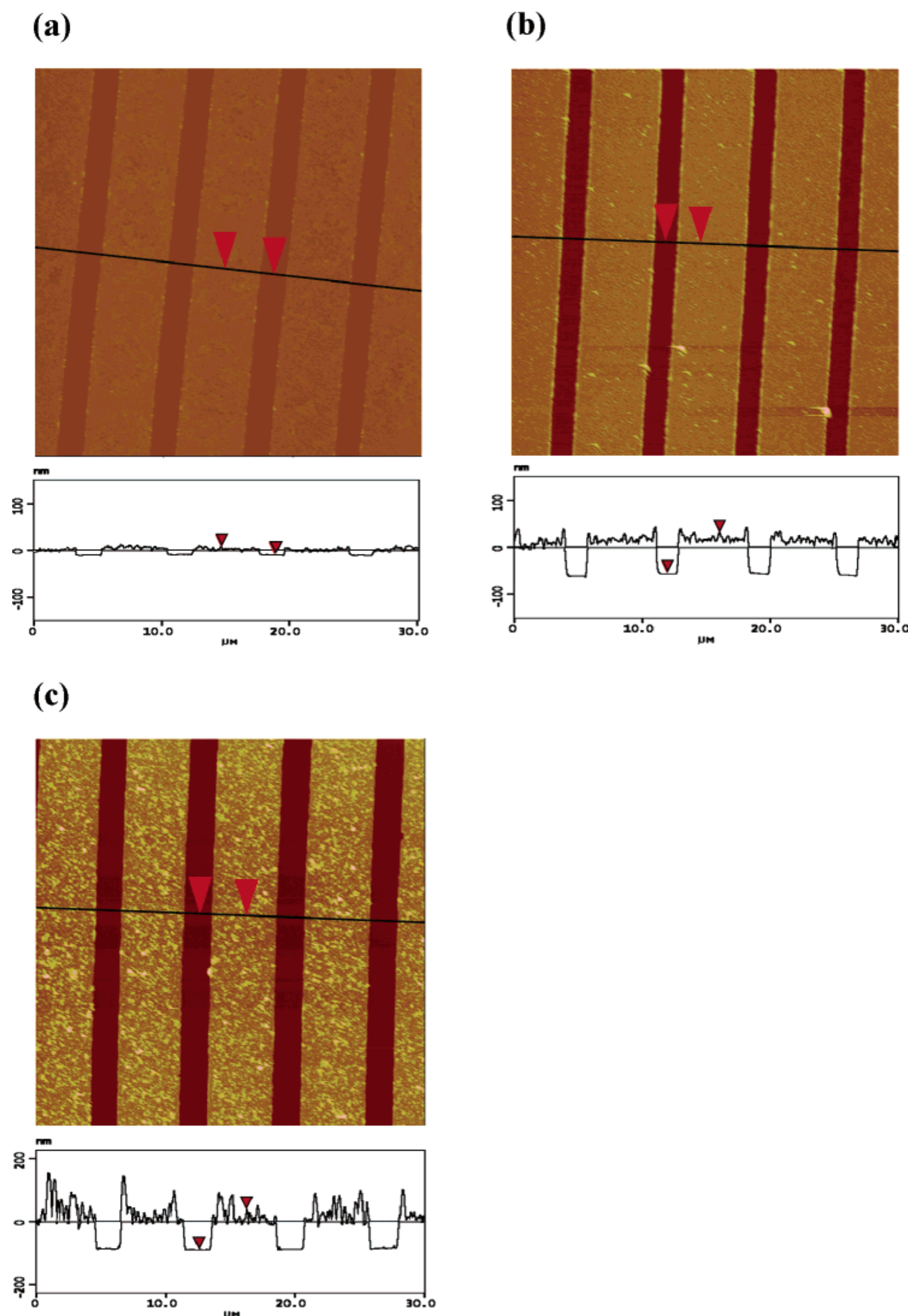

Figure 2. AFM images of dip SA multilayer patterns of $(PAH/PSS)_{20}$ film prepared at different deposition conditions: (a) solution without salt, (b) 0.4 M NaCl solution, and (c) 1.0 M NaCl solution.

ionic strength has an important role in understanding the difference of adsorption behavior between dip and spin SA methods, and in turn the fabrication of patterned devices of high quality.

Experimental Section

Materials. Poly(allylamine hydrochloride) (PAH, M_w = 50 000–65 000) and poly(sodium 4-styrenesulfonate) (PSS, M_w = 70 000) were used as received from Aldrich. The mole concentration of PE solutions was fixed at 10 mM. 4-(Dimethylamino)pyridine (DMAP)-stabilized gold nanoparticle (Au_{NP}) dispersions were synthesized as reported by Gittins and Caruso.[55] The size of the DMAP-Au_{NP} dispersed in water is about 6 nm and displays a maximum in the surface plasmon band (λ_{max}) at 518 nm. This nanoparticle dispersion was used without dilution. The structures of the used PEs and the DMAP-Au_{NP} are shown in Figure 1.

Preparation of Photoresist-Coated Substrates. Silicon wafers were initially cleaned by ultrasonication in a mixture of H_2SO_4/H_2O_2 (7/3) for 60 min, followed by rinsing in water and drying with a gentle stream of nitrogen gas. (***Caution!*** *Piranha solution is highly corrosive. Extreme care should be taken when handling Piranha solution, and only small quantities should be prepared.*) After this cleaning treatment, the substrates were coated with hexamethyldisilazane (HMDS) to enhance the adhesion of photoresists. The photoresist films (AZ1512) spun on the HMDS-coated substrates were baked at 95 °C for 30 min and then exposed to UV light through a photomask MA6 aligner in vacuum contact mode (KARL-

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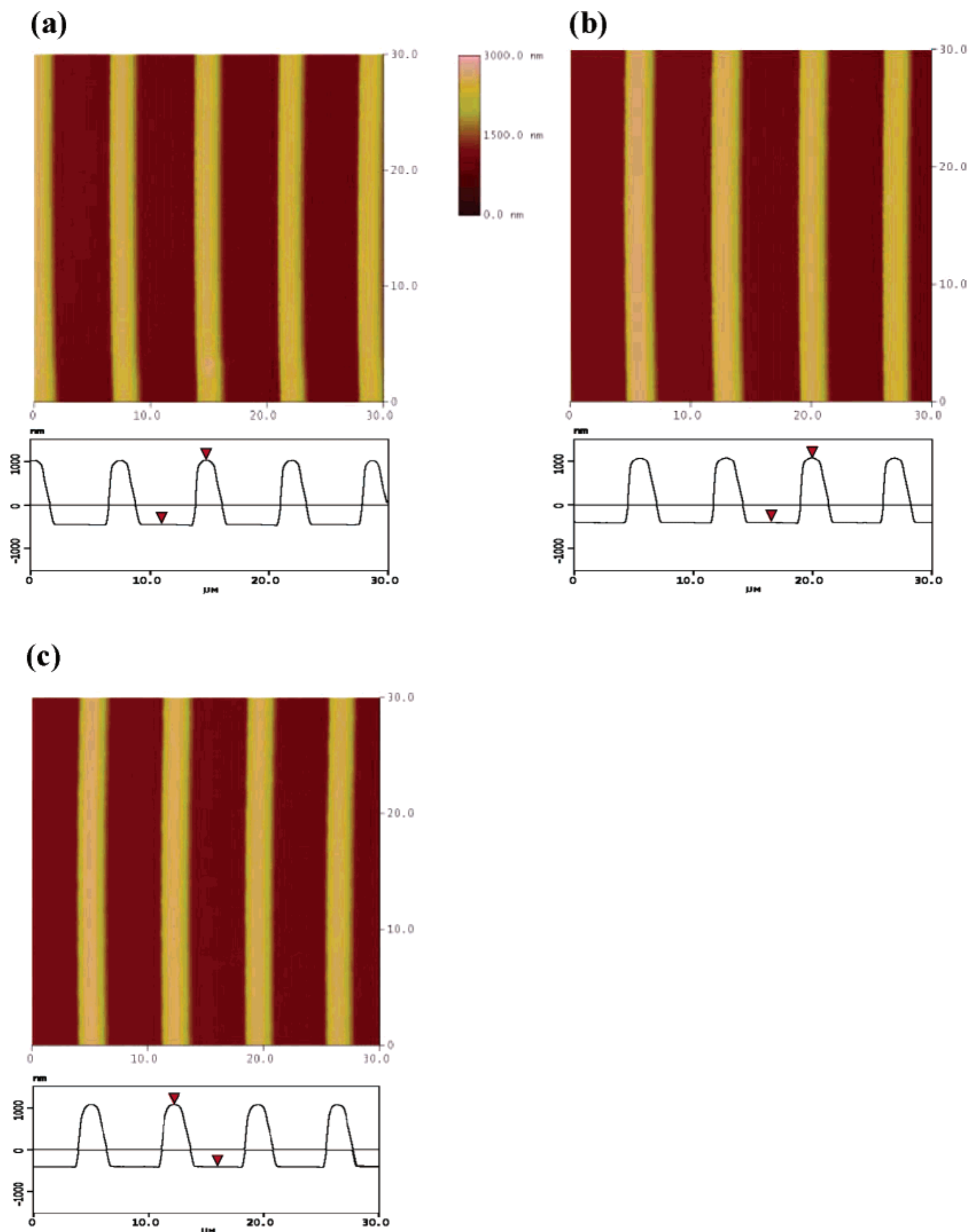

Figure 3. AFM images of patterned photoresists coated with $(PAH/PSS)_n$ multilayers: (a) $n = 0$, (b) $n = 2$, and (c) $n = 10$. In this case, $(PAH/PSS)_n$ multilayers are deposited onto the whole substrate, including unpatterned and patterned areas. The entire height gaps between two different triangles of the cross-sectional images are 1415 ± 5 nm.

SUSS) or an Ultrastep 1100 stepper. Finally, the wafers were developed by AZ developer, rinsed in water, and dried with nitrogen gas.

Fabrication of Patterned Multilayer Films. For the spin SA multilayer films, the total area (2 cm × 2 cm) of substrate carrying the patterned photoresist structure was wetted by a positively charged PAH solution.[44,46] After solution dropping (typically for 2−3 s), the substrate was immediately rotated with a spinner at a fixed rotating speed (typically, 4000 rpm) for a short period (typically about 15 s). After the film was sufficiently spin-dried at the same speed (typically about 15 s), the substrate was thoroughly rinsed twice with excess deionized water at a speed of 4000 rpm. A negatively charged PSS layer was next deposited onto the substrate using the same procedure. For the dip SA multilayer films, patterned substrates were first dipped for 20 min in the cationic PAH solution, and then dipped three times in deionized water for 2 min each time without drying. PSS and PAH were sequentially deposited onto the substrates using the same washing method mentioned above. For DMAP-Au_{NP} deposition, a PE-coated substrate with a top layer of PSS was immersed in a DMAP-Au_{NP} dispersion for 60 min, then washed with deionized water, and dried by spinning at 4000 rpm.

To prepare the spin SA multilayer patterns, the substrates were immersed in acetone and sonicated for 10 min, and then dried with a nitrogen stream. The surface morphology, the patterned height, and the root-mean-square (rms) surface roughness of patterned multilayer films were investigated by optical microscopy (Nikon OPTIPHOT-2POL in reflectance mode), scanning electron microscopy (Philips, XL30FEG), and atomic force microscopy (Digital Instruments, Nanoscope IIIa).

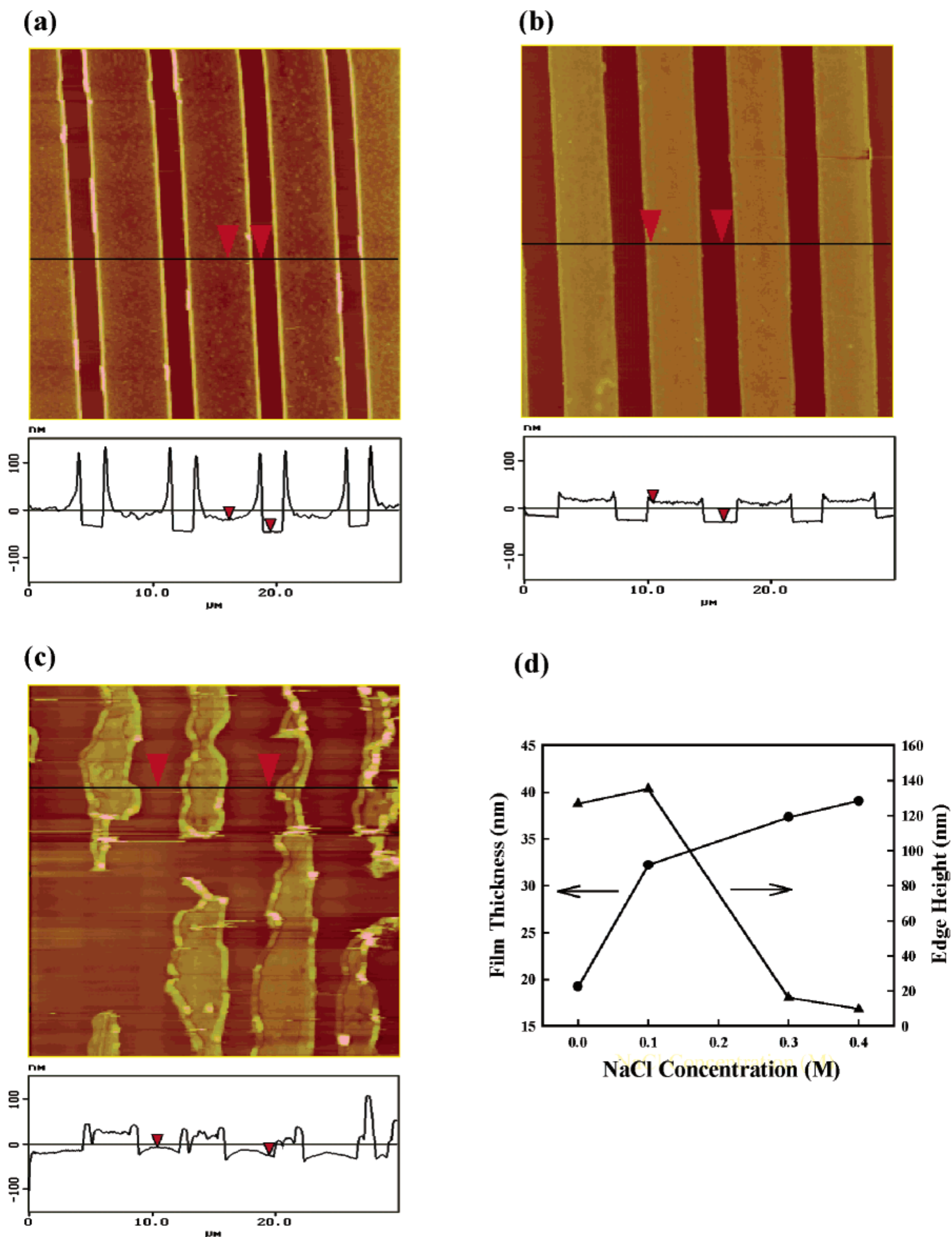

Figure 4. AFM images of patterned multilayer films of $(PAH/PSS)_{20}$ prepared at different deposition conditions: (a) solution without salt, (b) 0.4 M NaCl solution, and (c) 1.0 M NaCl solution. (d) Profiles of the film thickness (●) and edge height (▲) as a function of salt concentration. All the points in (d) are the average values for at least four different measurements.

Measurement of Contact Angle. The contact angle of water on the self-assembled films was measured using an Advanced Surface Technology video contact angle device.

Results and Discussion

To investigate the difference in pattern formation between the dip and spin SA methods, the multilayer patterns were fabricated by two different methods. As shown in Scheme 1, a patterned photoresist was fabricated on a silicon substrate using photolithography, and PAH/PSS multilayer films were deposited by the dip and spin SA methods. Deposition of PAH as a first layer led to instability, due to the low incomplete surface charge of the chemically patterned substrate. However, PE deposition of more than two bilayers of PAH/PSS yielded uniform buildup of multilayers, as determined from the periodically oscillating water contact angles (i.e., about 6° for PAH and 19° for PSS). After repeating this deposition process, the PAH/PSS multilayers uniformly coated the whole silicon substrate including the photoresist. Then, to eliminate the photoresist pattern and the

adsorbed multilayer films, the substrate was dipped into acetone and sonicated for 10 min, and then dried with nitrogen.

Figure 2 shows the AFM images of $(PAH/PSS)_{10}$ multilayer patterns prepared from the dip SALO method. By increasing the ionic strength of PE deposition solutions, the heights and the root-mean-square (rms) roughness of the multilayer pattern regions (measured from patterned area) are significantly increased without any collapse at the edge line of the multilayer patterns. The pattern height and rms roughness were 11 and 5 nm for 0 M NaCl, 70 and 5 nm for 0.4 M NaCl, and 99 and 35 nm for 1 M NaCl. Similarly, Hua et al. reported that dip SA multilayers composed of silica particles in 0.2 M NaCl and PE multilayers (poly(diallylammonium chloride)/PSS) in 0.5 M NaCl can be distinctly patterned after the lift-off process.[37] They also suggested that the omission of the drying process after multilayer deposition and water rinsing causes easy separation of the polymer chains, and that ultrasonic treatment breaks the links between the PE chains. However, in our system, the pattern edge lines are destroyed above 1 M NaCl despite the increase of pattern thickness and roughness. When using the conventional dip SA method, an increase in ionic strength changes the PE chain conformation from a flat (or rather extended) structure to a coiled conformation. This results in the increase of weakly adsorbed PE chains, due to the screening of charge repulsion along the chain.[56−61] The excess increase of ionic strength then causes partial removal of weakly bonded PE chains at the edge of the photoresist, due to entanglement with PE chains adsorbed onto the photoresist during ultrasonic treatment for the lift-off process.

Previously, we established that the adsorption mechanism, the degree of interdigitation between adjacent layers, the layer thickness, and the surface roughness formed from the spin SA method were totally unlike those from the dip SA method.[44,47,53] These differences can significantly affect the formation and quality of the PE multilayer pattern. To confirm these hypotheses, the spin SALO method was used to fabricate ultrathin multilayer patterns. First, it was investigated whether the stability of the chemically patterned photoresist is influenced by the strong external forces (i.e., centrifugal, air shear, and drag forces) operating during fast spinning of 4000 rpm for the deposition of PEs. Figure 3 displays AFM images of the patterned substrate for 0−10 PAH/PSS bilayer films. As shown in Figure 3a,b, it was observed that the consecutive spin deposition of PAH/PSS bilayers does not destroy the shape of the photoresist. Also, the height difference between the unpatterned and patterned photoresists is maintained at a fixed height of about 1415 ± 5 nm. These results indicate that spin self-assembled PEs are uniformly coated onto the whole region of the patterned substrate without any loss of photoresist, despite the high spinning speed.

Figure 4 shows the AFM images of spin SA multilayer patterns after the lift-off process, showing the profile of film thickness and the edge height as a function of ionic strength. For $(PAH/PSS)_{20}$ multilayer films prepared without any salt, the film thickness was 19 nm, the surface roughness at the center of multilayer pattern was 2 nm, and the edge height was 127 nm (Figure 4a). The edge height was measured relative to the height at the center of the multilayer pattern, and this height profile was consistently reproducible. Also, the film thickness of the $(PAH/PSS)_{20}$ multilayer pattern (i.e., 19 nm) is thinner than that reported for planar silicon substrates (i.e., 48 nm).[44] This difference in film thickness may be caused by the low surface charge[46] or by the residual hydrophobic HMDS of the patterned photoresist substrate (see Supporting Information S1); the silicon substrate after photoresist removal showed a contact angle of about 35° (compared with 10° for the substrate without photoresist treatment). It is also likely that the fluid motion containing PE on micropatterned surfaces during the high-speed spinning has an effect on the thickness of films deposited. Figure 4c shows the multilayer pattern formed with high ionic strength solution of 1.0 M NaCl. The multilayer pattern formed is extensively washed off the substrate (partial deformation of the multilayer patterns is also observed at 0.5 M NaCl; see Supporting Information, S2). This destruction of the multilayer patterns formed by the spin SALO method was not observed in the film pattern prepared from the dip SALO method at the same ionic strength (1.0 M NaCl). We attribute this difference to the increase in ionic strength due to the rapid water evaporation during spin deposition, and the resultant recrystallization of excess ionic salts formed after spin-drying. That is, the ionic strength of PEs during spin deposition is notably increased compared to the dip self-assembled PEs, despite the use of the same deposition solution

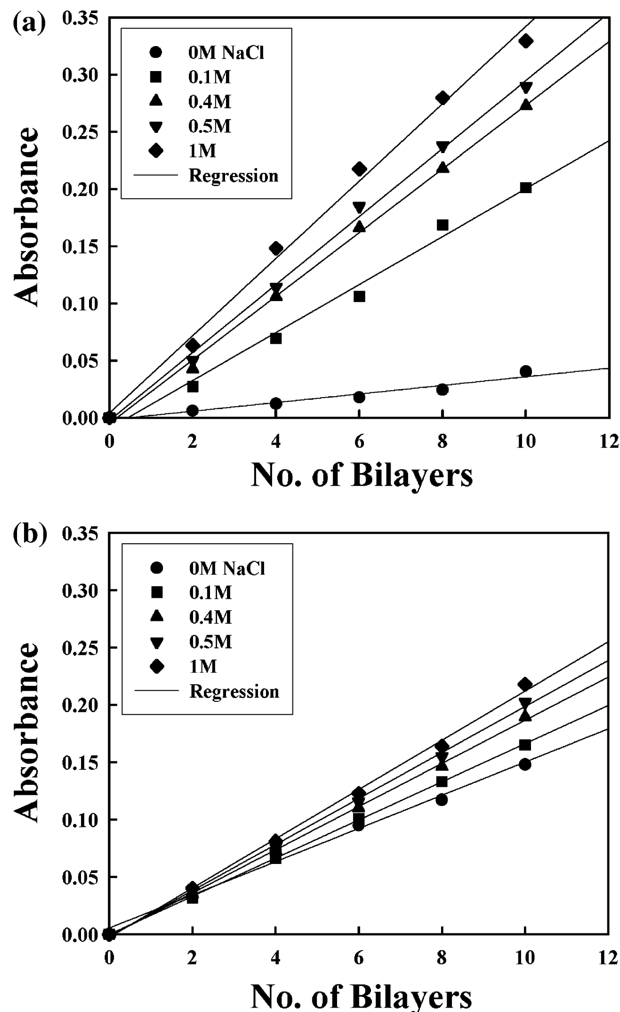

Figure 5. Absorbance measured at 225 nm of (a) dip and (b) spin SA $(PAH/PSS)_n$ films with increasing bilayer number at different salt concentrations. The absorbance values of dip SA films were divided by 2 for comparison with those of spin SA films, which are deposited on only one side of the substrate. These multilayer films were deposited onto planar quartz substrates without patterned photoresists.

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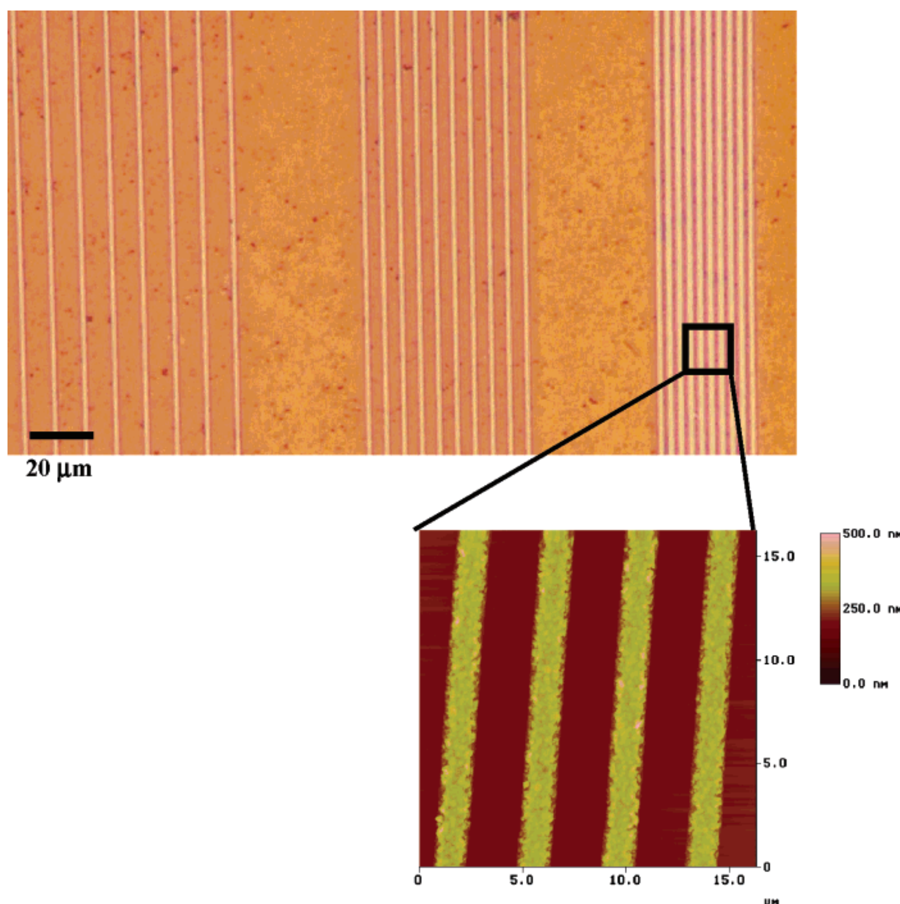

Figure 6. Optical microscopic and AFM images of a patterned $[(PAH/PSS)_3/DMAP\text{-}Au_{NP}/PSS]_5$ film. Scale bar corresponds to 20 μm.

containing 1.0 M NaCl. Also, the recrystallized ionic salts within adsorbed layers can deteriorate the surface of multilayers due to redissolution during the water-washing step. Hence, these consecutive phenomena shown in multilayer deposition may cause extensive loss of the spin SA multilayer pattern after the lift-off process. Without salt, long-range intra- and interchain charge repulsion allow the PE chains to adsorb on the substrate in a flat conformation, fully covering the surface.[44−46] Although this adsorption trend depending on ionic strength in the spin self-assembled films is partially similar to that of dip SA multilayer films, the adsorption mechanism in the spin SA method, which causes a densely packed layer due to strong centrifugation and viscous driving forces as well as electrostatic interaction during the spinning process, is very different from that caused by only electrostatic interaction in the dip SA method.[62−65] This difference causes the dissimilar desorption behavior in the lift-off process.

Consequently, the relatively high edge profile obtained without NaCl addition in the spin SALO method suggests that a large amount of PAH/PSS layers formed on the photoresist film are not completely removed. Instead, an edge pattern is formed on both sides of a line even after lift-off of the photoresist film, as shown in Figure 4a. For PAH/PSS multilayers deposited from high ionic strength solutions, the lift-off process removes the multilayer films adsorbed onto the substrate with and without a photoresist pattern since the multilayers presumably carry the excess amount of weakly bound PE chains (by the significant increase of ionic salt concentration during spin deposition and the dissolution of recrystallized ionic salts after spin deposition)

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Based on the behavior at high and low ionic strength, it is expected that the spin SA layers deposited on the photoresist area can be completely removed without damaging the PE multilayers on a desired film pattern area at an intermediate ionic strength. As shown in Figure 4b, the optimum NaCl concentration of 0.4 M used in our system provides a well-defined multilayer pattern with a low edge height of 7 nm with a rms surface roughness of 2 nm. By increasing the ionic strength from 0 to 0.4 M, the film thickness of the patterned area is increased from 19 nm to about 39 nm but the edge height is decreased from 127 to 7 nm, as shown in Figure 4d. Furthermore, the surface of the multilayer pattern formed from the spin SALO method in 0.4 M NaCl (shown in cross-sectional surface image of Figure 4b with a rms roughness of 2 nm) was flatter than those (with a rms roughness of 5 nm) prepared from the dip SALO method in 0 or 0.4 M NaCl.

It was previously reported that the thickness of spin self-assembled PAH/PSS bilayers is thicker than that of dip assembled PAH/PSS bilayer deposited without salt.[44,45] However, at the intermediate ionic strength of 0.4 M NaCl, the feature height of the spin SALO pattern (39 nm) is lower than that of the dip SALO pattern (70 nm). This reverse trend of film thickness with salt addition is also found on planar substrates without photoresist patterns, as shown in Figure 5. More specifically, the adsorbed amount of PAH/PSS deposited by spin SA is lower than that of PAH/PSS deposited by dip SA in the range of 0.1 and 1.0 M NaCl. This results in the relatively thin spin SALO pattern at high ionic strength (specifically, 0.4 M NaCl) due to relatively strong desorption forces (i.e., centrifugal and shear forces) due

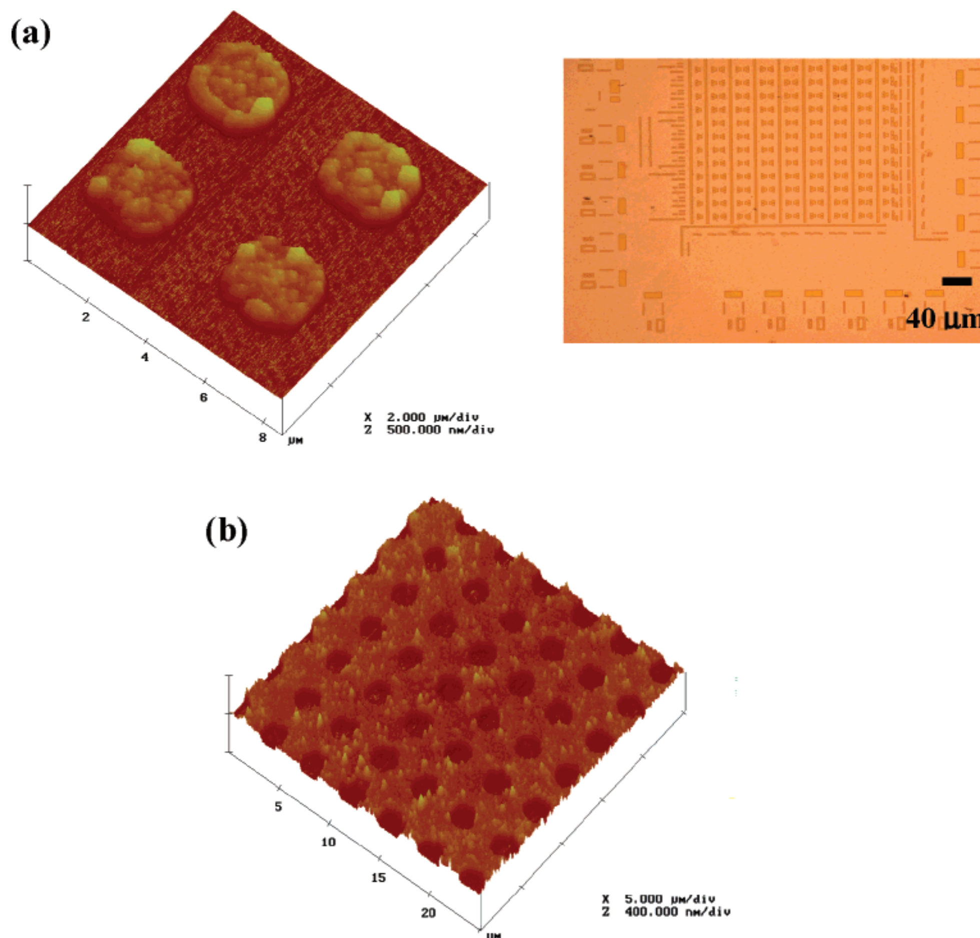

Figure 7. (a) AFM (left) and SEM (right) images of a positive pattern and (b) AFM image of a negative pattern of [(PAH/PSS)$_3$/DMAP-Au$_{NP}$/PSS]$_3$ films.

to the high spinning speeds. A similar trend is also observed with the PDADMAC/PSS multilayers (see Supporting Information, S3).

Using the optimized intermediate ionic strength used for the preparation of the PAH/PSS multilayer pattern, we patterned organic/metallic multilayer films involving ca. 6 nm Au nanoparticles. Positively charged Au nanoparticles stabilized with 4-(dimethylamino)pyridine (DMAP) were prepared as reported earlier.[55,66,67] The size of the Au$_{NP}$ was confirmed by transmission electron microscopy (TEM). Organic/metallic hybrid films with (PAH/PSS)$_3$/DMAP-Au$_{NP}$/PSS multilayers were fabricated by spin SA for the organic PE multilayers and by dip SA for the Au$_{NP}$ nanoparticle layer. The dip SA method was used for the deposition of the Au$_{NP}$ layer because it was found that the spin deposition of Au$_{NP}$ induces the crystallization of excess DMAP dissolved in the Au$_{NP}$ solution, which increased the surface roughness. For deposition of the Au$_{NP}$ layer, a PE-coated substrate was dipped into a solution containing Au nanoparticles for 60 min and then washed with deionized water and dried by spinning.

Figure 6 shows the [(PAH/PSS)$_3$/DMAP-Au$_{NP}$/PSS]$_5$ multilayer patterns with various line widths. The total film thickness is about 142 nm, and the thickness per [(PAH/PSS)$_3$/DMAP-Au$_{NP}$/PSS] layer is about 28 nm (measured from the AFM height profile). Using a (PAH/PSS)$_4$ film thickness of about 8 nm and DMAP-Au$_{NP}$ diameter of 6 nm, these results show that DMAP-Au$_{NP}$ are densely adsorbed onto the PE multilayers due to the infiltration of Au$_{NP}$ into the PAH/PSS film.[66,67] Also, the PE multilayers controlled with intermediate ionic strength have a significant effect on the formation of a well-defined PE/DMAP-Au$_{NP}$ multilayer pattern. The direction of the line pattern formed is not restricted to the centrifugal direction of the line patterns during the spinning process, as reported previously.[46] The spin and dip SA methods can be combined to produce the well-defined multilayer films.

Hybrid PE/Au multilayer patterns with arbitrary shapes can be prepared by the spin SA and lift-off process described in this study. Figure 6 shows various shapes achieved by the positive and negative patterns of [(PAH/PSS)$_3$/DMAP-Au$_{NP}$/PSS]$_3$ films. The AFM images in Figure 7 clearly show well-defined organic/metallic multilayer patterns using our method. Our spinning method for the formation of multilayer patterns is different from the polymer spin transfer printing method which transfers thick or thin spun-cast films from an elastomer stamp to other substrates.[68] Consequently, using optimum intermolecular forces between adsorbates, the spin SALO method can be used to improve the preparation speed and the pattern quality of the multilayers.

Conclusion

We demonstrated that the spin SA and lift-off method allows the quick and simple fabrication of well-defined multilayer patterns. The influence of ionic strength on the pattern formation

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for this process and the dip SA and lift-off process was also demonstrated. It is shown that optimum intermolecular forces between adsorbing species are crucial to produce well-defined patterns for organic/organic and organic/metallic multilayered films. The spin SA method may lead to the fast and simple fabrication of patterned multilayer devices requiring various optical and electronic functions with relatively low surface roughness.

Acknowledgment. This work was supported by the Ministry of Education through the Brain Korea 21 Program at Seoul National University, funded in part by the National Research Laboratory Program (Grant M1-0104-00-0191), and the Australian Research Council (Discovery Project and Federation Fellowship schemes). We are also grateful to R. Johnson (The University of Melbourne) for critical reading of the manuscript, J. Park for TEM measurements, U. Seong for SEM measurements, and D. Kim for the design of the photomask used in this study.

Supporting Information Available: UV−vis spectra of $(PAH/PSS)_n$ multilayer films deposited onto the substrates after RCA solution and after photoresist removal (S1), AFM image of patterned spin SALO multilayer films of $(PAH/PSS)_{20}$ prepared in 0.5 M NaCl (S2), and absorbance of dip and spin SA $(PDADMAC/PSS)_n$ films at 225 nm, increasing the bilayer number at different salt concentrations (S3). This material is available free of charge via the Internet at http://pubs.acs.org.

LA052057A