Room-Temperature Imprinting Poly(acrylic acid)/Poly(allylamine hydrochloride) Multilayer Films by Using Polymer Molds

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Layer-by-layer assembled polyelectrolyte multilayer films of poly(acrylic acid) (PAA)/poly(allylamine hydrochloride) (PAH) have been successfully patterned by room-temperature imprinting using a Norland Optical Adhesives (NOA 63) polymer mold. The proper amount of water in the PAA/PAH multilayer film can decrease the viscosity of the film and facilitate the imprinting. Many factors, such as imprinting pressure, length of imprinting time, and the structure and size of the patterns in the polymer mold, can produce an influence on the final imprinted pattern structures on multilayer films. A high imprinting pressure of 100 bar and elongated imprinting time of several hours is needed to achieve a patterned PAA/PAH multilayer film with a feature size of several tens of micrometers. With a twice imprinting, grid structures can be successfully produced when a NOA 63 mold having line structures is used. Room-temperature imprinting by using polymer NOA 63 mold provides a facile way to fabricate layered polymeric films with various kinds of pattern structures.

Introduction

Imprint lithography is a promising technology to fabricate pattern structures with a high-aspect ratio in the region of micro-/nanometers.[1,2] Because of its low-cost, easy operation, and high-throughput, imprint technology has become one of the emerging technologies in fabricating optoelectronics, microelectric devices, nanofluidics, and so forth. Recently, researchers have developed many additive approaches beyond this method to resolve critical issues that need to be addressed for the further progress of this technology, such as room-temperature imprint lithography.[3–10] One of the important issues is the useful lifetime of the mold. In conventional imprinting technology, a hard mold typically made of Si, SiO$_2$, and various metal materials is used to obtain certain hardness during the imprinting process. The problem encountered is that the conformal contact between the hard mold and the substrate is usually limited by the rigid nature of the mold material. Furthermore, cooling cycles and high pressure (50–130 bar) employed during imprinting produce stress and wear on the molds.[11] These issues would deteriorate the imprinted pattern fidelity. The use of the flexible polymer mold instead of the hard mold can provide better conformal contact with the

substrate to be patterned and reduce the pressure needed during the imprinting step.[12,13] Therefore, the use of soft polymer mold in imprinting technology is an alternative to solve the problems encountered in using hard mold.

To satisfy the application as a mold in imprinting technology, the polymer mold material must have a high modulus to withstand deformation of the mold during the imprinting. The composite poly(dimethylsiloxane) (PDMS) mold, which consists of a thin hard PDMS and a relatively thick soft PDMS, is a choice.[14] However, problems such as the brittleness of the hard PDMS and the thermal instability of the composite mold restrict the wide application of this kind of mold in nanofabrication. There are several reports about the fabrication of the soft polymer mold with high modulus in a relatively more easy way. Lee et al. reported the fabrication of amorphous fluoropolymer (Dupont Teflon AF 2400) mold with a feature size of sub-100 nm from a master mold of SiO$_2$/Si wafer. The fluoropolymer has a tensile modulus of ~1.6 GPa. Because of the high modulus, they successfully patterned densely populated features with a size as small as 80 nm and features with an aspect ratio up to 6:1 by using the fluoropolymer mold.[12,13] Norland Optical Adhesives (NOA 63) is a mercapto ester-type UV-curable prepolymer, which has outstanding optical and mechanical properties as well as a softening transition at mild temperatures. Kim et al. demonstrated that NOA 63 could be used as a promising material to manufacture polymer molds for transferring patterning nanostructures of high aspect ratio.[15] Hammond et al. used NOA 63 to make stamps for contact printing with a range of sub-micrometer to 80 nm features.[16] Polymer transfer printing of poly(acrylic acid) onto a polyelectrolyte multilayer platform has successfully resulted in chemically nanopatterned surfaces with well-defined structures and both positive and negative surface functionalities. UV-curable polyurethane acrylate is another choice for imprinting mold material because it has a Young's modulus of ~1.7×10^9 N m^{-2} and the mold can be easily fabricated by replicating a preformed master.[17] These soft molds will open a wider application in

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fabricating pattern structures by various methods of contact printing and imprinting lithography.

In the recent decade, layered polymeric ultrathin films fabricated by layer-by-layer (LbL) assembly technique[18] have attracted much attention in the materials science community because of their potential applications in areas such as antire-flection coatings,[19,20] biosensors,[21–24] drug delivery,[25] nonlinear optics,[26–29] solid-state ion conducting materials,[30] ion-perm-selective multilayer films,[31] organic light-emitting devices (OLEDs),[32] solar-energy conversion,[33,34] and so on. One of the critical steps that determine the final applications of polymeric ultrathin films, especially in miniaturized devices, is the ability to pattern these films in a simple, flexible, and economic way.[35–41] In our previous study, we have reported that LbL assembled polymeric multilayer films based on either electrostatic interaction or hydrogen bonding as driving force can be successfully patterned by room-temperature nanoimprint lithography using a rigid Ni mold.[42] The successful patterning of these films originates from the high compressibility and fluidity of the layered polymeric films under high pressure. Problems encountered for using Ni molds include incomplete patterning of the films because of non-conformal contact between the mold and the film caused by the rumples in the edges of the mold, the short lifetime of the mold, and so forth. Here, we examined the possibility of patterning the LbL assembled poly(acrylic acid) (PAA)/poly(allylamine hydrochloride) (PAH) multilayer films with flexible NOA 63 polymer molds. The success of using polymeric mold instead of rigid metal mold will, on the one hand, make the imprint lithography a high throughput way to fabricate patterned layered polymeric films with large area and, on the other hand, cut the cost of the patterning fabrication because the inexpensive polymer mold can be easily obtained by casting/demolding photocurable prepolymers of NOA 63 over a prefabricated master mold.

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Scheme 1. Schematic Illustrations of (a) the Fabrication of NOA 63 Polymer Mold from Replicating PDMS Master and (b) the Process of Room-Temperature Imprinting Layered Polymeric Films with NOA 63 Polymer Mold
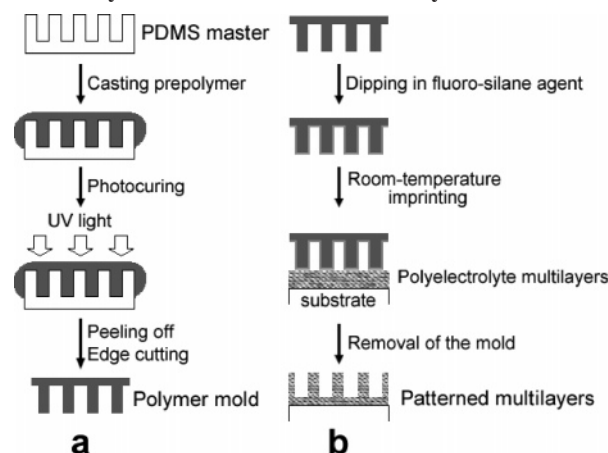
Experimental Section

Materials. A commercial mercapto ester type prepolymer, NOA 63 (Norland Optical Adhesives 63), was purchased from Norland Products Inc. 1*H*,1*H*,2*H*,2*H*-Perfluorooctyltriethoxysilane (POTS) was purchased from Degussa Corp. Poly(acrylic acid) (PAA, M_w ca. 2000), poly(allylamine hydrochloride) (PAH, M_w ca. 70 000), and poly(diallyldimethylammonium) (PDDA, 20 wt %, M_w ca. 100 000–200 000) were purchased from Sigma-Aldrich. All chemicals were used without further purification. The concentration of polymer solutions used for all experiments was 1 mg mL^{-1} made from 18 MΩ Millipore water, and further pH was adjusted with either 1 M HCl or 1 M NaOH.

Fabrication of PAA/PAH Multilayer Films. The LbL deposition of PAA/PAH multilayer films was conducted automatically by a programmable dipping machine (Dipping Robot DR-3, Riegler & Kirstein GmbH) at room temperature. A newly cleaned Si wafer was immersed in PDDA aqueous solution for 20 min to obtain a cationic ammonium-terminated surface and was ready for PAA/PAH multilayer deposition. Next, the substrate was immersed into aqueous PAA solution (pH 3.5) for 15 min to obtain a layer of PAA film. The substrate was then rinsed in two water baths for 1 and 1 min before the next layer deposition. Next, the substrate was immersed into aqueous PAH solution (pH 7.5) for 15 min to obtain a layer of PAH film. No drying step was used in the film deposition procedure. The adsorption and rinsing steps were repeated until the desired number of bilayers was obtained. Multilayers of PAA/PAH were immediately used to imprint, otherwise stored in a water bath.

Fabrication of NOA 63 Polymer Mold. Scheme 1a shows the schematic for fabricating a polymer mold using a photocurable prepolymer NOA 63. To peel off the polymer mold from the PDMS master easily, the surface of PDMS master was treated with the fluoroalkylsilane POTS prior to casting the prepolymer. The liquid prepolymer is drop-dispensed on a master pattern. Subsequently, UV curing was conducted by irradiating with a 250 W UV lamp (λ = 365 nm) at a distance of 12 cm from the source. The Norland NOA 63 optical adhesive is a polyurethane oligomer having C=C unsaturation and can be cross-linked by a mercapto-ester oligomer upon exposure to ultraviolet light.[43] After the UV curing, the mold is removed from the master by being peeled. Trimming the edges completes the preparation of the replica mold, which is the negative of the PDMS master.

Room-Temperature Imprinting PAA/PAH Multilayer Films and Their Characterization. A schematic of imprinting multilayer films with polymer mold by room-temperature imprinting technique is shown in Scheme 1b. The surface of the NOA 63 polymer mold was modified with POTS to lower its surface energy. As soon as the PAA/PAH multilayer films were taken out from water, the water

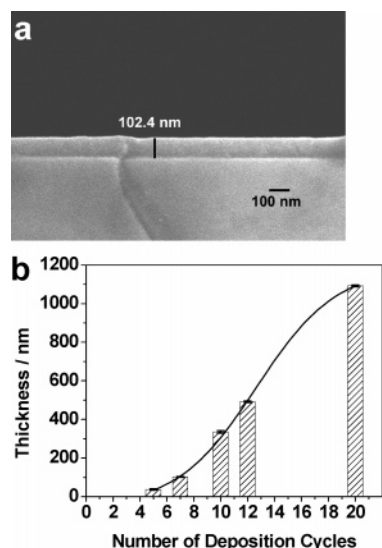(43) Straub, M.; Ventura, M.; Gu, M. *Thin Solid Films* **2004**, *453–454*, 522.

Figure 1. (a) Cross-sectional SEM image of the as-prepared (PAA/PAH)*7 multilayers film. (b) The thickness of the PAA/PAH multilayers as a function of the number of deposition cycles. The curve serves as a guide to the eye.

on the film surface was removed with a piece of filter paper, and the films were ready for immediate imprinting. All imprinting was carried out at room temperature (about 25 °C), and all imprinted samples were stored in ambient conditions before characterization.

The multilayer film-thickness determination was carried out on a JEOL JSM-6700F scanning electron microscope (SEM). All samples were coated with a thin alloy layer of gold and platinum prior to imaging. An Olympus optical microscope was used to obtain images of the imprinted PAA/PAH multilayer films. Atomic force microscope (AFM) images were taken with a Nanoscope IIIa AFM Multimode (Digital Instruments, Santa Barbara, CA) under ambient conditions. AFM was operated in the tapping mode with an optical readout using Si_3N_4 cantilevers (Nanoprobes, Digital Instruments). If not stated, the imprinting was carried out on a commercial Nanoimprinter (Obducat's 2.5 in. NIL system).

Results and Discussion

Imprinting PAA/PAH Multilayers by Polymeric NOA 63 Molds with Different Pattern Structures. To decrease the adhesion between the PAA/PAH multilayer films and the polymer mold, fluorosilane of POTS was used to modify the mold surface before imprinting. In this case, a layer of POTS was covalently bound to the NOA 63 mold surface via the reaction of an ethoxysilane group of POTS with the urethane group of NOA 63.[16] The modification of NOA 63 mold with POTS facilitates the lateral movement of the PAA/PAH layers and makes it much easier to separate the mold from the polymeric film surface in comparison to an untreated mold.[13,16,42]

It was found that the drying step during the film preparation had an obvious influence on the PAA/PAH multilayer deposition. As reported previously in our work, a 20-bilayer PAH/PAA film has a constant thickness of 84.4 nm with a drying step after each polyelectrolyte layer deposition.[42] For a (PAA/PAH)*7 film fabricated without a drying step, the cross-sectional SEM image reveals a uniform film with a constant thickness of 102.4 ± 1.9 nm (Figure 1a). The thickness of PAA/PAH multilayer films with different number of deposition cycles without a drying step during film fabrication is shown in Figure 1b. With the increase of the number of deposition cycles, the thickness of PAA/PAH multilayer films increases more rapidly than the normal linear behavior. The reason for the nonlinear growth behavior is not
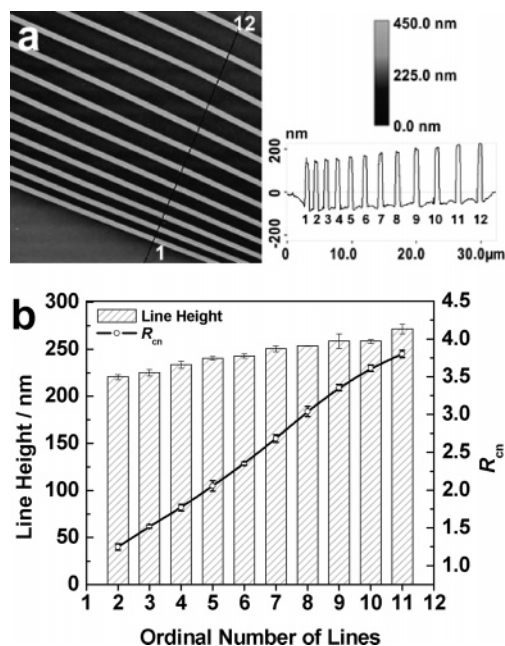

Figure 2. (a) AFM image (30 × 30 μm) and its cross-sectional analysis of an imprinted (PAA/PAH)*7 multilayer film on silicon wafer. (b) The line height and the area ratio of contact to noncontact region (R_{cn}) between the film and the mold as a function of the ordinal number of imprinted lines in (a).

very clear at present, but might be related to the serious interpenetration of the polyelectrolytes in the neighboring layers.[44−48]

The as-prepared (PAA/PAH)*7 film has a root-mean-square (rms) surface roughness of 0.8 nm, as determined by AFM. After the film was imprinted for 8 min under a pressure of 30 bar at room temperature, well-defined pattern structures can be observed. Figure 2a shows the AFM image of the imprinted (PAA/PAH)-*7 multilayers with 680 nm line-width and different spacing between the lines. The plan-view of the imprinted film shows well-defined pattern structures, which are the negative replica of the polymer NOA 63 mold used. From the cross-sectional AFM analysis, one can observe that the height of the line structures is not constant but increases with the increase of the spacing width. As shown in Figure 2b, the height of the line patterns and the area ratio of the contact to noncontact region (noted as R_{cn}) between the film and the mold (i.e., the ratio of the protruding and the concave areas in the polymer mold) are plotted against the selected line patterns in Figure 2a. The line height grows from 220.6 ± 2.7 to 271.5 ± 5.0 nm with increasing ratio value R_{cn} from 1.25 to 3.80. It is easy to understand that the wider is the contact region between the polymer mold and the PAA/PAH multilayer films, the more quantity of polymeric films is available to form the line patterns. Therefore, a larger R_{cn} leads to a higher line pattern.

The above patterned (PAA/PAH)*7 film with 680-nm line structures was also characterized with SEM. As shown in Figure 3, the cross-sectional SEM image shows that the line has a height of ∼235 nm, while the residual film contacted with the polymer mold has a thickness of ∼58 nm. The thickness of the residual

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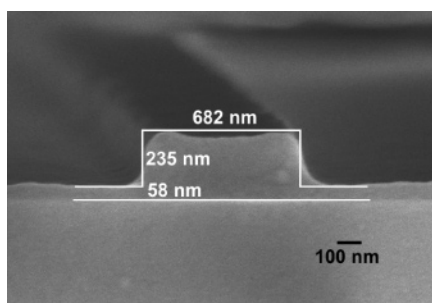
Figure 3. Cross-sectional SEM image of a (PAA/PAH)*7 multilayer film after imprinting under the pressure of 30 bar for 8 min.

film is much smaller than the original film thickness, while the height of the line pattern is much larger than the original film thickness.

Meanwhile, polymer NOA 63 mold with negative dot and square with different feature sizes were also employed to imprint PAA/PAH multilayer films. Figure 4 shows the AFM images of the imprinted (PAA/PAH)*7 multilayers under a pressure of 40 bar for 8 min and their corresponding cross-section analyses. When the diameter of the negative dots in the mold is about 1.67 μm, pillar-like dot pattern structures with the height of 221.8 $\pm$ 12.8 nm can be obtained (Figure 4a). For the negative square molds used, when the width of negative squares is 2.59 μm, a bowl-like square pattern structures can be obtained as shown in Figure 4b and c. In this case, the height of the pattern is 179.2 $\pm$ 8.1 nm as measured from the top edge of the squares to the top of the spaces. The center of the "bowl" is about 120-nm deep. By further increasing the width of the negative square to about 5.54 μm, an incompletely imprinted PAA/PAH film with wall structure is obtained. As shown in Figure 4d, only the films near the square edges undergo lateral movement and lead to the film wall structure. The primary conclusion is that pattern structures with large feature size are difficult to imprint for the PAA/PAH multilayers with definite number of layers and fixed imprinting time. Actually, the R_{cn} of the polymer mold is more important than the feature size of the mold to understand the above imprinting results. The R_{cn} is determined to be 13.0, 1.8, and 0.9 for polymer molds used in Figure 4a, b, and d, respectively. The larger is the patterned structure, the more amounts of polymer films are needed to fill the gap between the film and the polymer mold. For a polymer mold with a higher R_{cn}, the amount of polymer film that can undergo lateral movement to form the desired patterned structure is large enough. Therefore, homogeneous patterned structures can be formed as the one in Figure 4a. In contrast, for a polymer mold with a lower R_{cn}, the amount of polymer film that can be used to form the desired structure is very limited, and an incompletely imprinted structure as the one in Figure 4b and d will be obtained. Of course, for polymer molds with the same R_{cn}, the larger is the feature size, the more difficult is the imprinting. Interestingly, the incomplete imprinting of the polymer films provides a way to fabricate patterns with diminished feature size and structures different from that of the mold used.

The incompletely imprinted pattern structures as well as the fact that the height of the patterns after imprinting is much larger than the original thickness of the as-prepared films support our previous speculation that the imprinting of the layered polymeric multilayer films at room temperature originates from the high compressibility and fluidity of the layered films under higher pressure. The process of patterning the multilayer films is as follows: during imprinting, multilayer films in the contact regions are compressed under high pressure, and concomitantly these
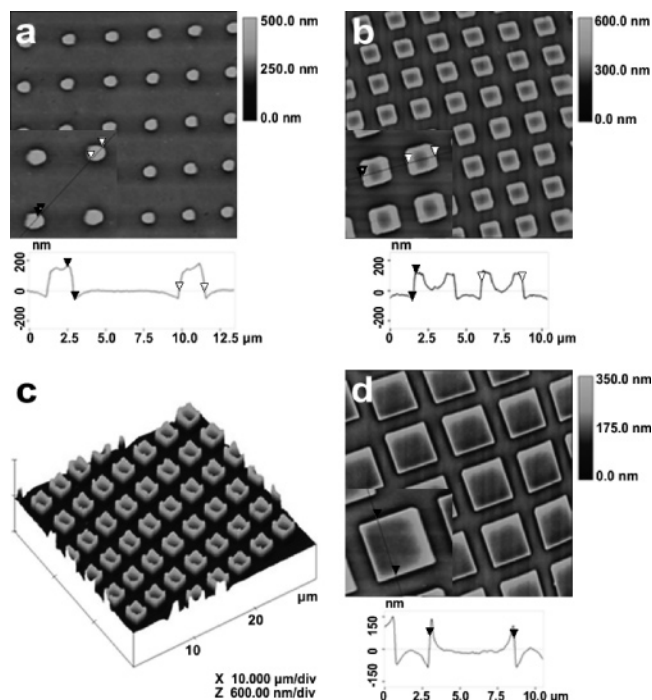

Figure 4. (a−d) AFM images (30 × 30 μm) of the imprinted (PAA/PAH)*7 multilayers with different feature sizes. The inset images are 10 × 10 μm, and their corresponding cross-sectional analyses are also given. (c) is the three-dimensional AFM image of sample (b).
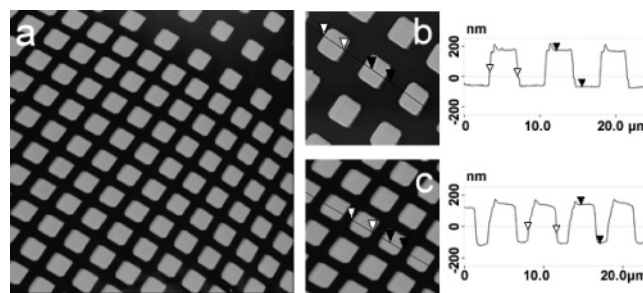

Figure 5. AFM images of the imprinted (PAA/PAH)*20 multilayers under a low pressure of 20 bar for 8 min. The NOA 63 polymer mold used has negative squares with a size of 3.72 μm, which are separated by spaces of 3.4 and 1.37 μm, respectively. (a) A whole image with a scan size of 50 × 50 μm. (b) and (c) are enlarged partial AFM images of (a) with a space of 3.4 and 1.37 μm, respectively, and their corresponding cross-section analyses. The scan size for (b) and (c) is 30 × 30 μm.

films undergo lateral movement toward the noncontact regions. As a result, the films in the contact regions are compressed, and in the noncontact regions they raise up.[42] The structures of the imprinted multilayer films finally developed. Furthermore, the lateral movement of the multilayers occurs first at the edges of the gap between the mold and the polymer films, and then gradually extends to the center, which can be determined from the cross-sectional analyses of AFM images in Figure 4b and d.

Factors Affecting the Imprinting of PAA/PAH Multilayers. Besides the size of the pattern structures in the polymer molds, many factors such as water content in PAA/PAH multilayer films, imprinting pressure, length of imprinting time, and so forth can produce an influence on the final imprinted pattern structures of PAA/PAH multilayer films.

The influence of the water content in PAA/PAH multilayer films was first investigated. After the (PAA/PAH)*7 films were dried in an oven for 1 h at 90 °C, and then exposed to ambient
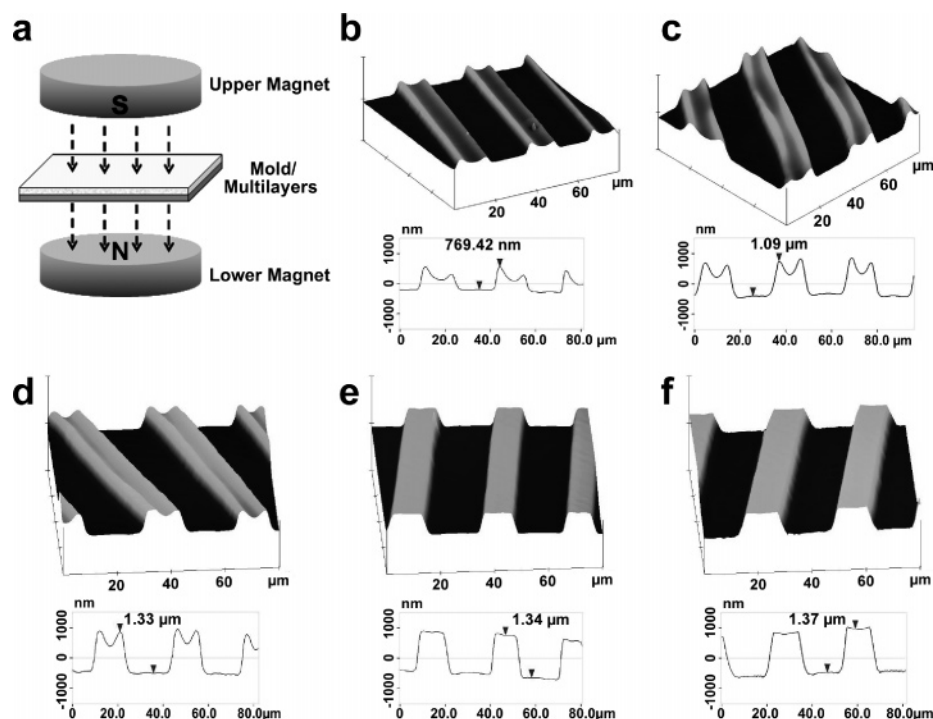
Figure 6. (a) Schematic illustration of imprinting PAA/PAH multilayer films with a homemade magnetic device. (b–f) AFM images of a (PAA/PAH)*20 multilayer film when imprinted at room temperature for 8 min, 30 min, 2 h, 3 h, and 6 h, respectively. For all three-dimensional AFM images, the Z-scale is 3000 nm.

atmosphere for 24 h at room temperature, the PAA/PAH multilayers cannot be imprinted under a high pressure of 40 bar for 15 min with the same NOA 63 mold in Figure 2. The thermo-treatment cannot lead to the thermal cross-linking of the PAA/PAH film but can release the interior water in the film. Furthermore, PAA/PAH multilayers dried in a nitrogen stream for 1 min to remove the apparent water on the surface could not be imprinted, too, whereas by immersing the films in deionized water for about 24 h, both the thermally treated and the N_2-dried films could be imprinted again under the same conditions. Therefore, interior and apparent water in the films is critical to make the multilayer films to be imprinted at room temperature with NOA 63 polymer mold. The reason is that the water molecules as a kind of solvent in the multilayers can decrease the viscosity of the polymeric films, which in turn facilitates the compression and movements of the polyelectrolyte multilayers during the imprinting process.[6,49] The imprinted PAA/PAH multilayer films are stable and do not lose their patterned structures when stored in ambient conditions. Yet the imprinted pattern structures disappeared after being exposed to water vapor for 24 h because of the swelling and rearrangement of the polyelectrolyte chains. Thermal cross-linking can stabilize the imprinted patterns on the PAA/PAH multilayer films.[50]

The imprinting of the polymeric multilayer films is also dependent on the pressure. Under a high pressure, the multilayer films undergo a vertical compression and concomitantly a lateral movement. In this case, the height of the pattern structures is larger than the original thickness of the films, as the case in Figure 2, while under low pressure, only vertical compression takes place for the multilayer films. Figure 5a shows the AFM images of a (PAA/PAH)*20 multilayer film with a thickness of 1.09 μm after imprinting under a 20-bar low pressure for 8 min. The NOA 63 polymer mold used has negative squares with a

size of 3.72 μm, which are separated with spaces of different width. The R_{cn} value for Figure 5b and c, which are enlarged partial images in Figure 5a, is 2.66 and 0.87, respectively. The cross-sectional analyses show that the square patterns with the same height of 245.6 $\pm$ 14.0 nm are imprinted in Figure 5b and c. The resultant pattern structures here are vertical compression of the PAA/PAH multilayer films with no lateral movement of the film taking place.

To fabricate a patterned multilayer film with feature size of several to several tens of micrometers by imprinting lithography, both high pressure and elongated imprinting time are very necessary. To easily elongate the imprinting time, a homemade imprinting device that consists of two pieces of 30-mm diameter magnet was used, as shown in Figure 6a. The silicon wafer deposited with PAA/PAH multilayer films was covered with a NOA 63 polymer mold, and then they were put between two pieces of magnets. The two pieces of magnets were put with their opposite polarity near each other to produce a magnet force. In this way, a constant attractive force is produced between the PAA/PAH multilayer films and the polymer mold. The pressure is estimated to be ~100 bar. A (PAA/PAH)*20 film was imprinted with 8 min, 30 min, 2 h, 3 h, and 6 h, respectively. Their corresponding three-dimensional AFM images are shown in Figure 6b–f. The feature size of the line pattern structure determined with cross-sectional analysis is 13.6 $\pm$ 1.2-μm line and 18.7 $\pm$ 1.2-μm space. Clearly, the height of the lines increases with elongating the length of the imprinting time. The line structures imprinted with a period of time no longer than 2 h show a saddle-like profile, and the height of the lines increases with the imprinting time going on, indicating an incomplete lateral movement of the multilayer films under pressure. After 3 h imprinting, homogeneous line pattern structures with a flat top surface were obtained. The height of the lines is 1.34 μm, which is larger than the original thickness of the films. With further elongating the imprinting time to 6 h, the height of the lines increased to 1.37 μm, while the shape of the lines remains almost

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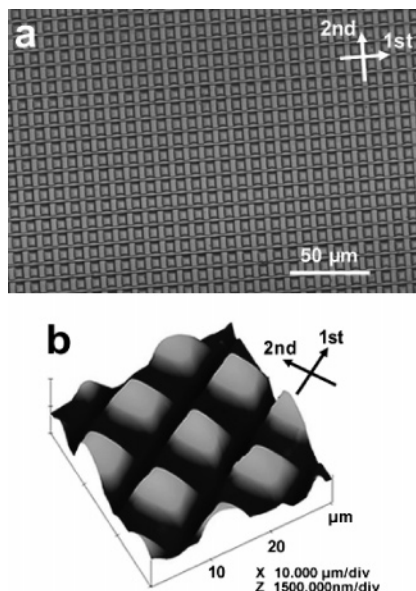(50) Harris, J. J.; DeRose, P. M.; Bruening, M. L. *J. Am. Chem. Soc.* **1999**, *121*, 1978.

Figure 7. Optical (a) and AFM (b) images of the twice imprinted (PAA/PAH)*20 multilayer films. For AFM image, the scan size is 30 × 30 μm.

the same as that of 3 h imprinting. Obviously, 3 h is the minimum length of time to get a completely imprinted (PAA/PAH)*20 film with a pattern structure of 13.6-μm line and 18.7-μm space. Meanwhile, 1 h is needed to realize a complete imprinting of (PAA/PAH)*20 film with a pattern structure of 6.5-μm line/ 3.5-μm space. Therefore, the broader is the width of a line or square, the longer imprinting time is needed to completely fill the gaps of the mold.

Multiple Imprinting of PAA/PAH Multilayer Films. The fact that PAA/PAH multilayer films can be imprinted at room temperature makes it possible to fabricate patterned PAA/PAH multilayer films with complex structures by multiple imprinting. As a proof-of-concept test, a (PAA/PAH)*20 multilayer film was first imprinted under a pressure of 100 bar for 1 h with a mold having 3.5-μm line and 6.5-μm space pattern by using a homemade magnetic device. Next, the film was imprinted again under the same conditions with the same mold rotated about 90°. The optical and AFM images of the twice imprinted (PAA/ PAH)*20 multilayer films are shown in Figure 7. As shown in Figure 7a, a large area pattern with square structure is obtained. The width of the spaces produced in the second imprinting is about 3.5 μm, which coincides well with the width of lines in the NOA 63 mold. Yet the width of the spaces produced in the first imprinting is about 3.0 μm, which is smaller than the width

of the lines in the polymer mold. The lateral movement of the first imprinted lines in the direction parallel to the lines in the polymer mold during the second imprinting led to the spaces with diminished width. The three-dimensional AFM image shown in Figure 7b indicates that the depth of the space produced in the first and second imprinting is about 1.6 and 1.2 μm, respectively. The smaller depth produced in the second imprinting than in the first one is due to the increase in the modulus of the film lines after the first imprinting. Our initial results show that room-temperature multiple imprinting provides an opportunity to produce patterned polyelectrolyte multilayers with complex structures. Further investigation in this aspect is underway.

Conclusions

It is demonstrated in this paper that LbL assembled multilayer films of PAA/PAH can be imprinted with a NOA 63 polymer mold. Many factors such as water content in multilayer films, imprinting pressure, length of imprinting time, and the structure and size of the patterns in the polymer mold can produce an influence on the final imprinted pattern structures in multilayer films. The successful imprinting of the multilayer film at room temperature originates from the high compressibility and fluidity of the layered film under high pressure, which makes it possible to fabricate patterned multilayer films with complex structures through multiple imprinting. The use of polymer NOA 63 molds instead of metal molds provides an inexpensive way to fabricate patterned layered polymeric films with large areas. Although the preparation of patterned PAA/PAH multilayer films with feature size ranging from several hundreds of nanometers to several tens of micrometers is proved to be successful, we believe that the present method is suitable to prepare patterned films with even smaller feature sizes for LbL assembled polymeric multilayer films based on electrostatic interaction and other kinds of driving forces, for example, hydrogen bonding and so forth. Therefore, we believe that room-temperature imprinting lithography has opened an experimentally simple but universal way to pattern LbL assembled polymeric multilayer films.