

Notes

Patterning Polyelectrolyte Multilayers by AFM Nanolithography

Chang-Hyun Jang*

Gachon Bionano Research Institute, Kyungwon University,
Gyeonggi 461-701, Korea

Received July 17, 2006; Revised October 16, 2006

Introduction

Since Schmitt *et al.* demonstrated the basic principle in 1992,¹ it became possible to create highly tuned, ultra thin films with desired functional groups by sequentially adsorbing alternating charged polyelectrolytes on a hydrophilic substrate. Due to the versatility of the system with respect to the usability of various materials as building blocks, polyelectrolyte multilayer (PEM) has attracted broad attention in practical applications as well as in fundamental physical studies.²⁻⁷ The PEM procedure provides a simple and efficient route to make a uniform reversal of the surface charge and to deposit reproducible quantities of material on the surface.

In recent years, efforts have been devoted to the patterning of PEM based on the use of template surfaces with ionizable or charged regions for the construction of self-assembled arrays.⁸⁻¹¹ Hammond *et al.* demonstrated the first micropatterning approach for PEMs on chemically patterned surfaces created by microcontact printing techniques.⁸ Lu *et al.* showed that nanoimprint lithography can be applied for patterning polymeric multilayer films. A successful imprinting was achieved due to the high compressibility and fluidity of the layered polymeric films under high pressure.¹⁰ Hendricks *et al.* presented a process for creating copper patterns by combining PEM coatings, micro-contact printing, and electroless deposition.¹¹ Their method enables a creation of stable and selective copper patterns on flexible substrates. However, although there exists several methods for patterning of PEMs, increased level of miniaturization is still highly desirable to meet the demand for an effective route for nanoscale assembly of devices and new material systems.

In this paper, we report a simple and straightforward procedure that permits nanometer scale fabrication of PEM on

a patterned self-assembled monolayer (SAM) with a degree of assembly miniaturization an order of magnitude smaller than that which has previously been reported. We created a template pattern on the surface using the procedure of nano-grafting that was developed by Liu and co-workers.^{12,13} Layer-by-layer PEM coating has been then created by alternate adsorption of oppositely charged poly-ion molecules.

Experimental

Materials and Sample Preparation. The tri(ethylene glycol)-terminated thiol (HS(CH₂)₁₁(OCH₂CH₂)₃OH) and the carboxylic acid-terminated thiol (HS(CH₂)₁₁(OCH₂CH₂)₆OCH₂CO₂H) were synthesized. 11-Mercapto-1-undecanol, poly(allylamine hydrochloride) (PAH, $M_w \approx 15,000$ g/mol), and poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt] (PCBS, $M_w \approx 65,000$ -100,000 g/mol) were purchased from Aldrich.

Flat gold substrates were prepared by annealing a gold wire in a H₂/O₂ flame.^{14,15} The 1-mm diameter gold wire was cleaned with piranha solution (3:1 v/v ratio of H₂SO₄/30 wt% H₂O₂) for 20 min and thoroughly rinsed with pure water. Warning: Piranha solution should be handled with extreme caution; in some circumstances, most probably when it has been mixed with significant quantities of an oxidizable organic material, it has detonated unexpectedly. One end of the wire was then placed in a H₂/O₂ flame and allowed to melt until a 2.0-2.5 mm diameter droplet forms. The droplet was further annealed for several seconds in a cooler region of the flame and was cooled down to room temperature. The resulting gold surface shows large atomically flat <111> crystalline terraces and monatomic steps that are suitable for AFM nanolithography. Monolayers were prepared with tri(ethylene glycol)-terminated thiol. Immediately after being annealed in a H₂/O₂ flame, the gold substrates were immersed in a 2 mM ethanolic solution of thiol molecules for 24 h. The substrates were then placed into pure ethanol for several hours to remove the physisorbed layer and were ultimately dried in a N₂ stream.

Atomic Force Microscopy. All imaging and patterning were carried out in a desired solution with a NanoScope IIIa AFM (Digital Instruments, Santa Barbara, CA). 85 μ m long, 18 μ m wide, V-shaped Si₃N₄ cantilever (Park Scientific Instruments) with a force constant of 0.5 N · m⁻¹ and a radius of < 20 nm were used for both imaging and patterning. Prior to use, cantilevers were exposed to an UV lamp for 10-15 min to remove organic contaminants. SAM samples were mounted inside a fluid cell with a homemade sample holder (Figure 1). The sample holder was fabricated from Teflon in order to minimize contamination from the cell. This fluid cell was fabricated to hold the gold balls that were used as the

*Corresponding Authors. E-mail: chjang4u@kyungwon.ac.kr

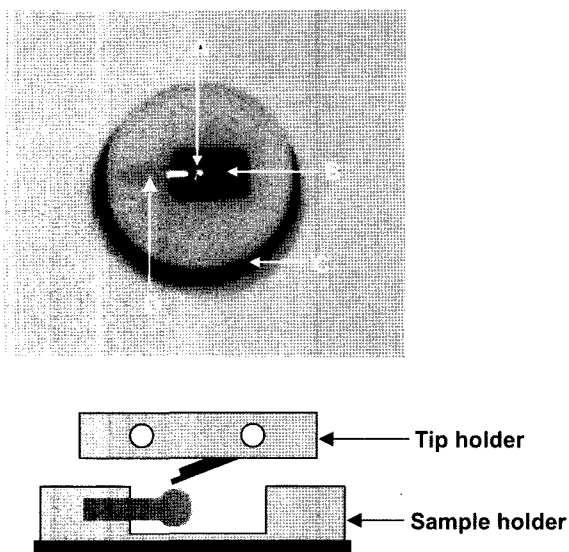


Figure 1. The homemade sample holder. The bottom of this sample holder is attached to the AFM piezoelectric scanner and the top presses against a silicon O-ring to seal against the tip-holder. (A) Gold ball. (B) Liquid pool. Solution is delivered from the tip holder. (C) A metal plate for securing the sample holder to the magnetic stage of AFM scanner. (D) Hole for holding gold wire.

support for the SAMs. A conventional fluid cell is too shallow (< 1 mm) to hold the gold ball ($r = 1$ mm). The cell has a recessed bath (Figure 1(B)) to fit the ball and a cylindrical hole (Figure 1(D)) to hold the gold wire. The wire is press-fitted into the hole, which allows the ball to be rotated in one dimension. This enabled the selection of a suitable area of the surface for AFM studies. The scanner was operated by a NanoScope IIIa SPM controller (Digital Instruments). To minimize the mechanical and thermal drift, the AFM probe and the sample were equilibrated in a solution for 2-3 h before imaging or the fabrication procedure.

Nanopatterning of Polyelectrolyte Multilayers. Polyelectrolytes were dissolved in water in a concentration of 10 mM with respect to the monomer repeat unit. The solution pH values of PAH and PCBS were adjusted to 7.5 and 7.0 respectively. The template patterns were produced with the hexa(ethylene glycol)-carboxylic acid ((EG)₆CO₂H)-terminated thiol on the tri(ethylene glycol) ((EO)₃OH)-terminated thiol SAM.¹⁶ Liu and co-workers' nanografting technique was used to produce patterns of the desired size, shape, and functionality.^{12,13} Sequential adsorption of polyelectrolytes was performed by hand dipping the patterned surface into each solution. The deposition time of each layer was 4 min. The surface was rinsed with pure water between alternate exposures to two polymer solutions. A total of two bilayers (PAH-PCBS-PAH-PCBS) were deposited on the surface (Figure 2). After careful rinsing with pure water, the surface was set into the AFM. The formation of PEM on the patterned

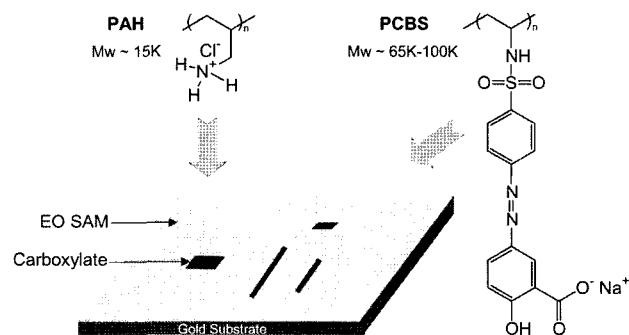


Figure 2. Schematic representation of nanofabrication of polyelectrolyte multilayers.

area was investigated using tapping mode imaging. The thickness for the multilayer determined by cross-sectional AFM images was compared with the ellipsometry data.

Results and Discussion

In this study, we first coat a very smooth gold sphere with a monolayer of HS(CH₂)₁₁(OCH₂CH₂)₃OH by deposition from ethanol solution for 24 h. The ethylene oxide groups are known to resist the adsorption of polyelectrolytes due to repulsive hydration forces and enthalpic penalties for disruption of the hydrogen bonding that ethylene glycol forms with water.^{17,18} Figure 3(A) shows a nanometer-scale pattern of two squares (100 × 100 nm² and 200 × 200 nm²) and two line patterns (length: 500 and 300 nm, line width: 30 nm) that was nanografted in the tri(ethylene glycol) ((EO)₃OH)-terminated SAM using a hexa(ethylene glycol)-carboxylic acid ((EG)₆CO₂H)-terminated thiol. The brighter region is patterned carboxylate and the rest of area is the monolayer of ethylene glycol. Note that the carboxylic acid has a longer oligo(ethylene oxide) segment than the ethylene glycol, so the patterned carboxylate should protrude from the surrounding area. However, it is interesting that the carboxylic acid molecules produce such high contrast (~2.5 nm) in the AFM image despite the chain length difference between the two molecules being only ~1.2 nm. It is reasonable to expect enhanced contrast of a charged group because of electrostatic interactions with the negatively charged AFM tip.

The pattern was then modified through a sequential adsorption of two bilayers (PAH-PCBS-PAH-PCBS) of polyelectrolytes. Figure 3(B) shows that the polymer molecules are preferentially adsorbed on the carboxylate patch by electrostatic interactions. Small amounts of nonspecifically bound polymers were initially observed outside the patterned region. However they were bound to the surface loosely enough to be removed by gentle scraping of the surface using AFM contact-mode imaging.

The corresponding cursor profiles show that the height of

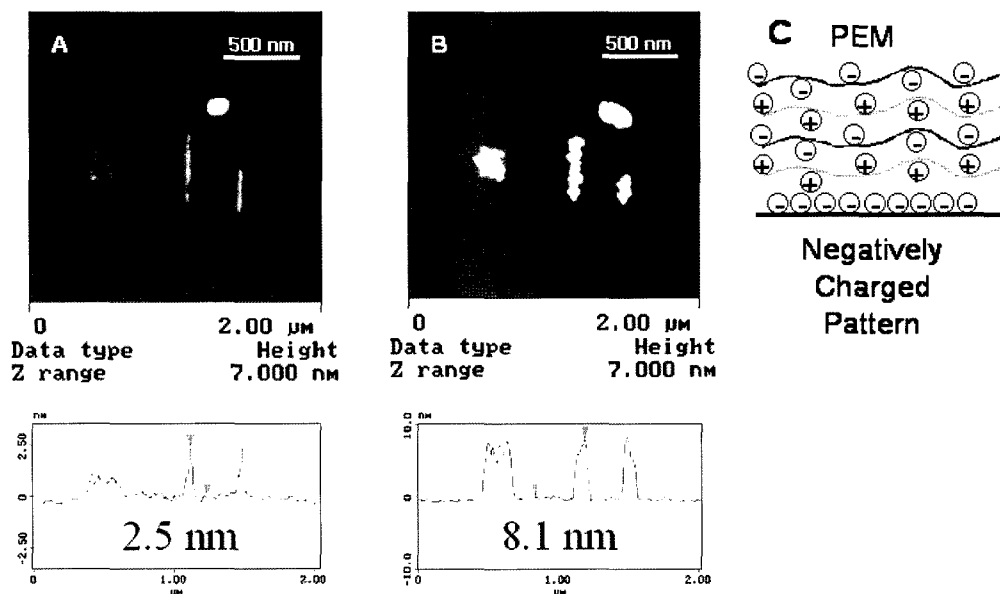


Figure 3. Tapping-mode AFM images with cross-sections showing the formation of PEM on a patterned carboxylate patch. (A) The brighter areas are hexa(ethylene glycol)-carboxylic acid-terminated thiol ($\text{HS}(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_6\text{OCH}_2\text{CO}_2\text{H}$) pattern nanografted into a tri(ethylene glycol)-terminated thiol ($\text{HS}(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_3\text{OH}$) surface. (B) The same surface was imaged after the deposition of two bilayers (PAH-PCBS-PAH-PCBS). PEM were preferentially formed on the patterned area. Corresponding cross-sectional lines show the height of each patch. Both images have a 7 nm Z-range. (C) Schematic of the polyelectrolyte layers on the nanografted pattern.

the carboxylate pattern has been increased by 5.5 nm after adsorption of the polymer. According to ellipsometry measurements, the thickness of one bilayer adsorbed on a homogeneous carboxylate surface is 1.5 nm. Therefore, the increment of height for the patterned site is 2.5 nm greater than that would be expected from the ellipsometry data. Two alternative explanations or the combination of both are possible for this observation. First, the top layer is covered by PCBS that has one carboxylate group per each ethylene-repeating unit. The charge density of the top polymer film could be higher than the one of the carboxylate pattern nanografted in the SAM. Higher negative charge density of PCBS causes a stronger repulsion to the negatively charged silicon nitride (Si_3N_4) AFM tip during the tapping-mode imaging, which results in the exaggeration of contrast. Second, extra amounts of polymer molecules may have adsorbed on each layer in the PEM. Kovacevic *et al.* reported that an increase of polymer adsorption occurs in the beginning of the layering procedure.⁶ The amounts of adsorption decrease and reach the equilibrium after several minutes. The duration of dipping (4 min) and the subsequent rinsing used in our PEM procedure may not be sufficient to achieve the equilibrium state and thus form a monolayer.

Figure 2 shows the increase of patch size after the formation of PEM as well, which indicates the lateral growth of polymer layers. This lateral growth is more obvious for the line pattern than the square pattern. Inspection of the plain-view and the cross-section of the multilayer pattern imaged by

AFM revealed the average line width of ~ 100 nm. Recently, Lu *et al.* reported the well-defined PEM structure with a line width of ~ 330 nm and a separation of ~ 413 nm that was fabricated by nanoimprinting lithography technique.¹⁰ To the best of our knowledge the feature size of the PEM pattern achieved by them has been the smallest. Thus, the nanometer scale patterning of PEM achieved in this study shows a degree of assembly miniaturization an order of magnitude smaller than that which has previously been reported.

In summary, we have shown that PEM combined with AFM nanolithography can be used to produce patterns with nanoscale features in 3 dimensions. Clearly, more experiments are required to understand the details of adsorption of the polyelectrolytes to nanografted patterns. At this stage we have simply demonstrated the template deposition of polyelectrolytes on the nanometer length scale. The combination of the two techniques shows great promise, because PEM procedure is relatively simple and a variety of materials can be used as building blocks. Increased levels of miniaturization demonstrated here are steps toward meeting the demand for the construction of structured nanodevices. Potential application of the patterned polymeric multilayers as a specifically positioned nanowire for the fabrication of nanocircuits is anticipated.

References

- (1) J. Schmitt, G. Decher, and J. D. Hong, *Thin Solid Films*, **210/**

- 211, 831 (1992).
- (2) Y. Liu and R. O. Claus, *J. Appl. Phys.*, **85**, 419 (1999).
- (3) C. W. Lee, J. G. Kim, and M. S. Gong, *Macromol. Res.*, **13**, 265 (2005).
- (4) Y. S. Yang, Y. M. Jeon, and C. W. Lee, *Macromol. Res.*, **14**, 251 (2006).
- (5) J. Schlenoff and S. T. Dubas, *Macromolecules*, **34**, 592 (2001).
- (6) D. Kovacevic, V. Burgh, A. Keizer, and M. A. C. Stuart, *Langmuir*, **18**, 5607 (2002).
- (7) J. Kim, J. M. Kim, and D. J. Ahn, *Macromol. Res.*, **14**, 478 (2006).
- (8) P. T. Hammond, *Adv. Mater.*, **16**, 1271 (2004).
- (9) S. L. Clark and P. T. Hammond, *Langmuir*, **16**, 10206 (2000).
- (10) Y. Lu, W. Hu, Y. Ma, L. Zhang, J. Sun, N. Lu, and J. Shen, *Macromol. Rapid Commun.*, **27**, 505 (2006).
- (11) T. R. Hendricks and I. Lee, *Thin Solid Films*, in Press (2006).
- (12) S. Xu and G. Y. Liu, *Langmuir*, **13**, 127 (1997).
- (13) S. Xu, S. Miller, P. E. Laibinis, and G. Y. Liu, *Langmuir*, **15**, 7244 (1999).
- (14) W. A. Hayes and C. Shannon, *Langmuir*, **14**, 1099 (1998).
- (15) C. -H. Jang, B. D. Stevens, R. Phillips, M. A. Calter, and W. A. Ducker, *Nano Lett.*, **3**, 691 (2003).
- (16) C. -H. Jang, B. D. Stevens, P. R. Caelier, M. A. Calter, and W. A. Ducker, *J. Am. Chem. Soc.*, **124**, 12114 (2002).
- (17) R. L. C. Wang, H. J. Kreuzer, and M. Grunze, *J. Phys. Chem. B*, **101**, 9767 (1997).
- (18) P. Harder, M. Grunze, R. Dahint, G. M. Whitesides, and P. E. Laibinis, *J. Phys. Chem. B*, **102**, 426 (1998).