

Patterned Polymer Multilayers as Etch Resists

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This paper describes the synthesis and characterization of patterned polymer multilayers on self-assembled monolayers (SAMs) and the use of these structures as etch resists for gold. The procedure used to build polymer multilayers consisted of five steps: (i) A polar thiol—HS(CH₂)₁₅COOH—was patterned on gold or silver films by microcontact printing (μ CP) with a poly(dimethylsiloxane) (PDMS) stamp. (ii) The patterned surface was placed in a solution containing CH₃(CH₂)₁₅SH to form a nonpolar, methyl-terminated SAM on the remaining bare metal surface. (iii) The regions of the SAM patterned with CO₂H groups were activated for further chemical reaction by conversion into interchain anhydride groups. (iv) The activated substrate was allowed to react with poly(ethylene imine) (PEI, branched chain, M_w 750 000). (v) A second polymer layer was attached to the PEI layer by allowing the amine-terminated surface to react with poly(octadecene-*alt*-maleic anhydride) (POMA, M_w 30 000) or poly(styrene-*alt*-maleic anhydride) (PSMA, M_w 350 000). This procedure (alternating reaction with PEI and POMA/PSMA) was repeated up to five times to increase the number of layers and the thickness of the patterned structure. The polymer multilayers were characterized using atomic force microscopy (AFM), ellipsometry, and polarized infrared external reflectance spectroscopy (PIERS). The stability of the films was demonstrated by using the patterned polymer multilayers as etch resists and by measuring their breakdown voltages.

Introduction

This paper describes the formation of patterned, covalently bonded polymer multilayers on self-assembled monolayers (SAMs) and the use of these structures as etch resists and dielectrics. Our approach is based on a sequence of reactions: (i) preparation of a surface presenting patterns of anhydride groups; (ii) grafting of poly(ethylene imine) (PEI) to that surface; (iii) further functionalization by reaction of the surface derivatized with PEI with polymers containing anhydride groups. The resulting polymer thin films are up to 20-nm thick. The initial edge roughness ($\sim 0.5 \mu\text{m}$)¹ of the patterned SAM generated by microcontact printing (μ CP) is retained during the growth cycle. The process used to prepare these systems combines techniques for the formation of polymer multilayers described by Crooks,² Grainger,³ and others,⁴ with techniques for generating patterned reactive SAMs described earlier.⁵

Techniques to fabricate and pattern polymer thin films are interesting for possible applications in corrosion-resistant coatings, in sensors, as resists, and as materials in microelectronic and microoptical devices. Several methodologies have been developed for obtaining unpatterned thin polymer films: spin-coating,⁶ grafting poly-

mers on surfaces,⁷ deposition of ionic polymers via electrostatic interactions,⁸ and growing multilayers via covalent interactions.⁹ Patterning of thin polymer films has been achieved, inter alia, by photolithography,¹⁰ phase separation in diblock copolymers on patterned surfaces,¹¹ and deposition on patterned surfaces.^{12,13} The approach described in this manuscript gives patterned films of controlled thickness and with lateral dimensions that are typically in the 1–10- μm range. The polymers in the films are highly cross-linked and firmly attached to the surface.¹⁴ Our main interest in these polymer films is to improve the etch resistance of SAMs patterned by microcontact printing.

Results and Discussion

Preparation of Patterned Surfaces Supporting Multilayer Polymer Films. Scheme 1 shows the pro-

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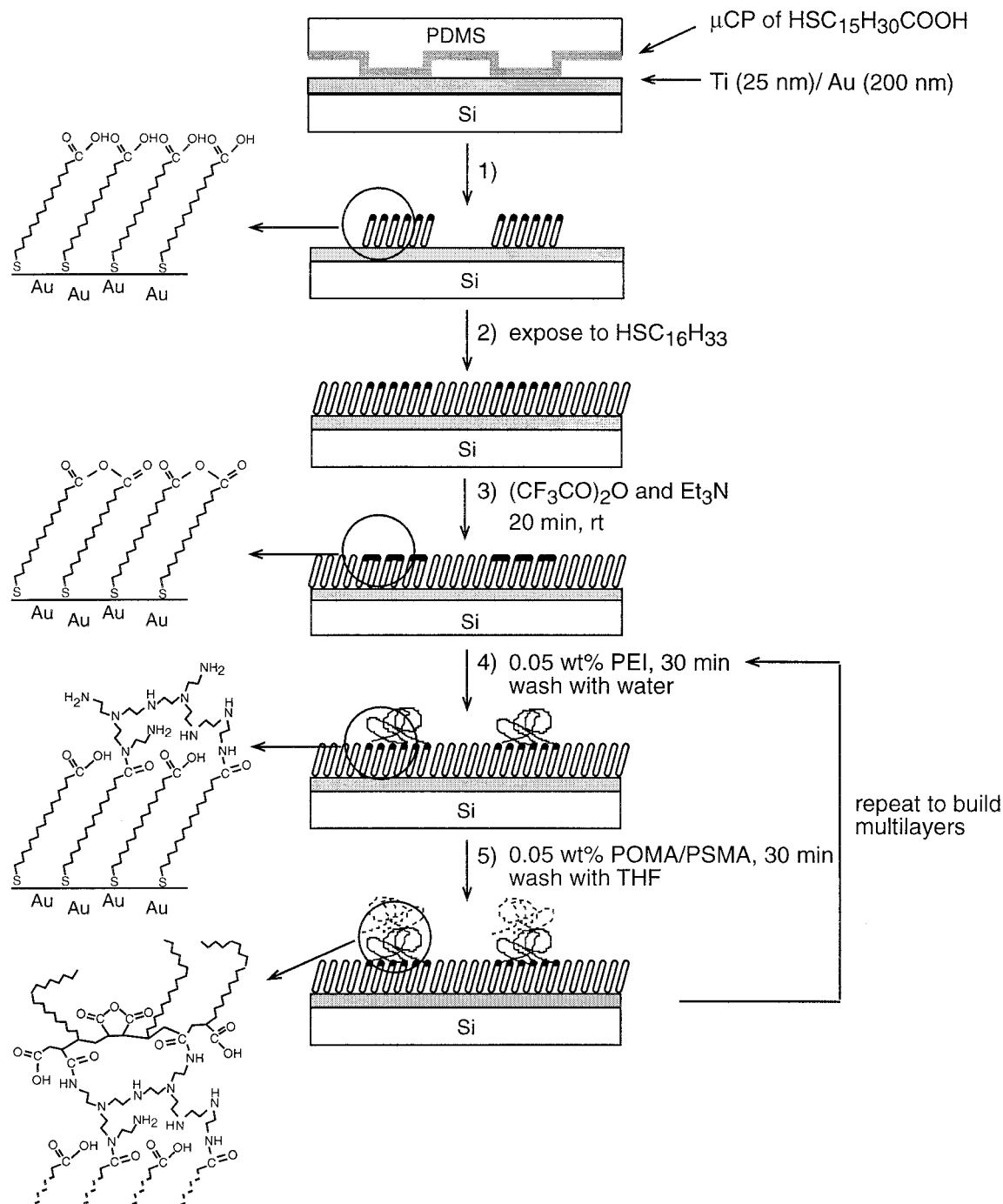
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Scheme 1. Schematic outline of the Procedure To Prepare Patterned Polymer Multilayers

cedure that was followed to pattern SAMs on Au or Ag and to grow polymer multilayers on these patterns. In detail, the procedure has *five* steps: (1) $\text{HS}(\text{CH}_2)_{15}\text{COOH}$ was patterned on gold or silver using microcontact printing (μCP)¹⁵ using a poly(dimethylsiloxane) (PDMS)¹⁵ stamp. (2) The patterned surface was placed in a solution containing $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ to form a methyl-terminated SAM on the remaining bare metal surface. (3) The patterned SAM was allowed to react with trifluoroacetic anhydride and triethylamine in DMF to convert the carboxylic acid groups into interchain anhydride groups.¹⁶ (4) The reactive substrate was placed in a 0.05 wt %

solution of PEI (branched, M_w 750 000) in 2-propanol for 20 min. Approximately 75% of the nitrogen atoms of the PEI are primary and secondary amine groups that can react with the anhydride groups on the surface. The surface was washed with water, briefly sonicated (<30 s),¹⁷ and dried under a stream of nitrogen. (5) The second polymer layer was attached by allowing the amine-terminated surface to react with a 0.05 wt % solution of poly(octadecene-*alt*-maleic anhydride) (POMA, M_w 30 000) or poly(styrene-*alt*-maleic anhydride) (PSMA, M_w 350 000) in THF. The excess polymer was removed by briefly sonicating (<30 s) the sample in THF. This procedure

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(17) We found that sonication is essential to remove all of the physisorbed polymer. AFM images of samples that were not sonicated showed considerable amounts of polymer adsorbed to the methyl-terminated SAM "background".

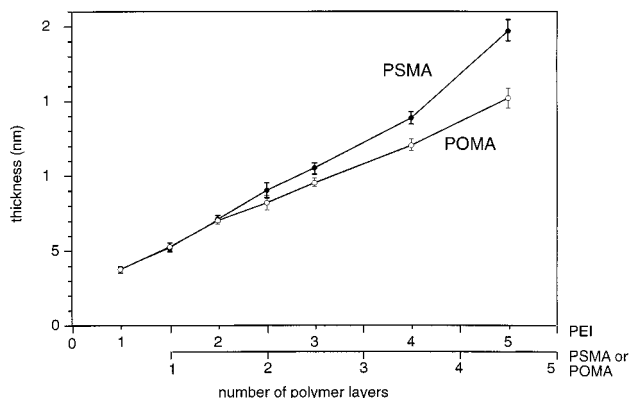


Figure 1. Ellipsometry data on unpatterned polymer multilayers. Odd layers correspond to poly(ethylene imine) (PEI) and even numbers to poly(styrene-*alt*-maleic anhydride) (PSMA) or poly(octadecene-*alt*-maleic anhydride) (POMA). Error bars indicate the standard deviation from at least six different measurements.

(alternating reaction with PEI and POMA/PSMA) was repeated up to five times to increase the number of layers and the thickness of the film.

Characterization. Unpatterned films were prepared to measure the thickness of the multilayers by ellipsometry. The thickness of the first PEI layer was dependent on the concentration of the polymer solution. Below concentrations of 1 wt %, the thickness was approximately constant between 1 and 1.5 nm. Between 1 and 10 wt % PEI solution, the thickness gradually increased to 2–3 nm. The reaction of the amine groups of the PEI with the anhydrides is rapid and irreversible. Above 10 wt %, the thickness rises rapidly, probably because of physisorption or entanglement of the polymer. To avoid fluctuations in thickness, we used dilute (0.05 wt %) solutions of polymer to grow multilayers. Figure 1 shows the increase in thickness of the layers after deposition of the different polymers. Odd numbers are layers of PEI and even numbers correspond to layers of PSMA or POMA. The thickness of the SAM of the carboxylic-acid-terminated thiol is 2 nm. The average increment is approximately 2.8 nm for every PEI/POMA bilayer and 3.8 nm for every PEI/PSMA bilayer. The difference might reflect the difference in molecular weight between the two polymeric anhydrides.

IR spectroscopy on homogeneous PEI films covalently bonded to SAMs confirmed the formation of amide bonds (Figure 2a). Table 1 lists the key absorption bands of these samples. The appearance of an absorption band around 2800 cm^{-1} indicates the presence of PEI on carboxylic-acid-terminated as well as anhydride-terminated SAMs. We attribute the signals at 1654 and 1550 cm^{-1} to amide I and II vibrations, respectively. A PEI film that was physisorbed to a carboxylic-acid-terminated SAM did not show these characteristic absorptions. In the IR spectrum of POMA/PEI multilayers (four layers, Figure 2c), the signals at 1655 and 1558 cm^{-1} are assigned to amide vibrations. These spectral signatures are evidence that the polymers films are covalently attached to the surface and to each other, rather than physisorbed.

We also characterized the patterned polymer multilayers by AFM. Figure 3a–c shows contact mode AFM images of patterned polymer multilayers of one, two, and four POMA/PEI bilayers, respectively. The pattern in Figure 3a is approximately 2.5-nm thick; this value corresponds reasonably well to ellipsometry measurements, where one POMA/PEI bilayer gave a value of roughly 3 nm. The line scans in Figure 3a–d show that

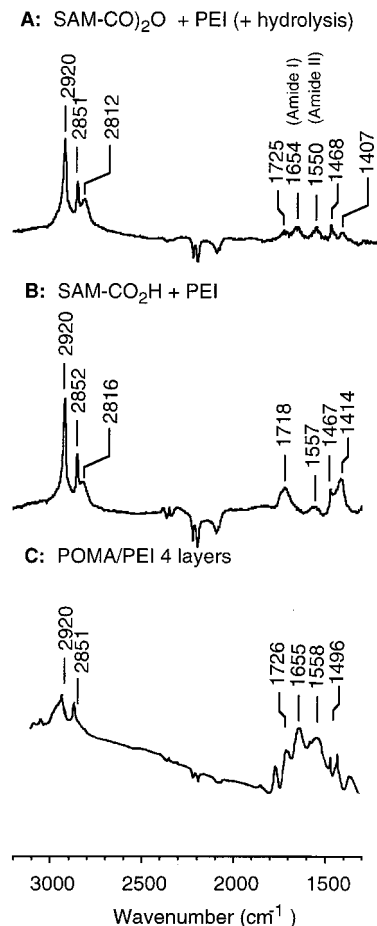


Figure 2. PIERS spectra of (a) PEI covalently attached to an anhydride SAM. (b) PEI physisorbed on a carboxylic acid SAM. (c) Covalently bonded POMA/PEI multilayers (four layers).

Table 1. Assignment of Selected Absorption Bands in the Infrared Spectra of Physisorbed PEI, Chemisorbed PEI, and POMA/PEI Multilayers^a

wavenumber (cm^{-1})			
SAM- CO_2O + PEI (+ hydrolysis) ^b	SAM- CO_2H + PEI ^b	POMA/PEI four layers	assignment
2920	2920	2920	$\nu_{\text{as}}(\text{CH}_2)$
2851	2852	2851	$\nu_{\text{s}}(\text{CH}_2)$
2812	2816		$\nu(\text{N}-\text{H}^+)$ or $\nu(\text{C}-\text{H})$
1725	1718	1726	$\nu(\text{C}=\text{O})$ for acid
1654		1655	amide I or amide stretch
1550	1557	1558	$\delta(\text{N}-\text{H}^+)$ or amide II

^a Assignments taken from ref 16 and from Dolphin, D.; Wick, A. *Tabulation of Infrared Spectral Data*; John Wiley & Sons: New York, 1977. ^b Data taken from ref 16.

the films are continuous, and without obvious holes (close-up AFM data, taken with smaller scan areas, corroborate this observation; data not shown). These experiments would, we believe, have detected holes greater than 100 nm in size. The roughness of the area covered by polymeric film is comparable to the roughness of the methyl-terminated SAM in the regions between the polymer films. In both cases, the roughness probably reflects the roughness of the gold substrate.¹⁸ The multilayers in Figure 3b,c are 5–6- and ~9–10-nm thick, respectively. Again,

(18) The gold substrate was not annealed after formation, but used as evaporated.

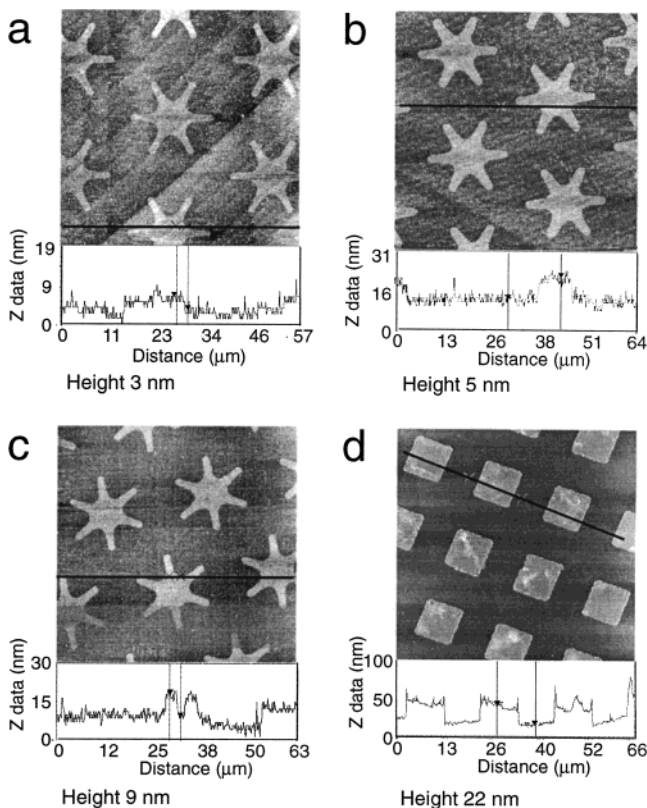


Figure 3. AFM images of polymer multilayers. (a) One bilayer of PEI-POMA (The diagonal lines in the image are artifacts that result from the procedure used to flatten the image); (b) two bilayers of PEI-POMA; (c) four bilayers of PEI-POMA; (d) five bilayers of PEI-PSMA.

these values are in agreement with ellipsometric data (6 and 10 nm, respectively). Exact measurements of height by AFM are difficult because the details of the interaction of the tip of the AFM with the substrate are not known for these polymers. The general trends observed by AFM agree, however, with those obtained by ellipsometry.

The surface of the polymer films in Figure 3d is not smooth. These squares consist of five bilayers of PSMA/PEI and are 22-nm thick. Ridges (height approximately 30 nm) can be seen at the edge of the squares and also in the centers. Hammond has reported this ridging previously for ionic multilayers.^{12,19} It may be due to retraction of a thin film of either PEI or PSMA from the hydrophobic alkanethiol surface during assembly or washing. The effect is only seen in thicker films. In some instances in which we did not wash the surface carefully after each reaction step, we observed physisorbed polymer films in the ostensibly unreactive part of the pattern. The lower molecular weight POMA polymers do not show this effect.

Dielectric Properties of Multilayer Films. Polymer thin films are commonly used as dielectric materials in film capacitors.²⁰ Commercial polymer films used in capacitors are relatively thick (~1 μm) and have breakdown voltages in the order of 1000 V. We wished to measure the breakdown voltages of these multilayer films.

We have recently described measurements of the electrical breakdown of SAMs of long-chain aliphatic thiols

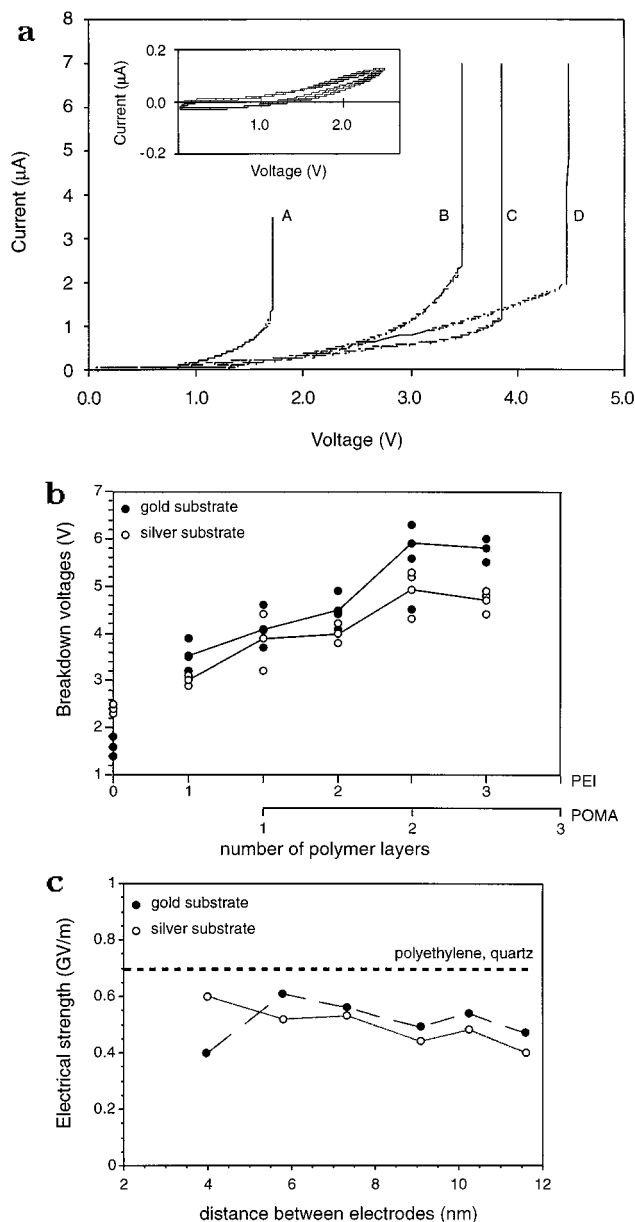


Figure 4. (a) Representative I-V curves for the electrical breakdown of Hg-hexadecanethiol/polymer-Au junctions. The individual I-V curves are (A) HO₂C-(CH₂)₁₅-S-Au (no cross-linking polymer); (B) one polymer layer (PEI); (C) two polymer layers (PEI/POMA); (D) three polymer layers (PEI/POMA/PEI). The inset shows 10 cycles for I-V measurements from 0 to 2.5 V at a sweep rate of 50 mV/s using two polymer layers (note different scales). (b) Breakdown voltages as a function of the number of polymer layers on gold and silver. (c) Breakdown voltages as a function of distance between the two electrodes. Error bars are omitted for clarity. For the breakdown voltage, we used average values taken from Figure 4b.

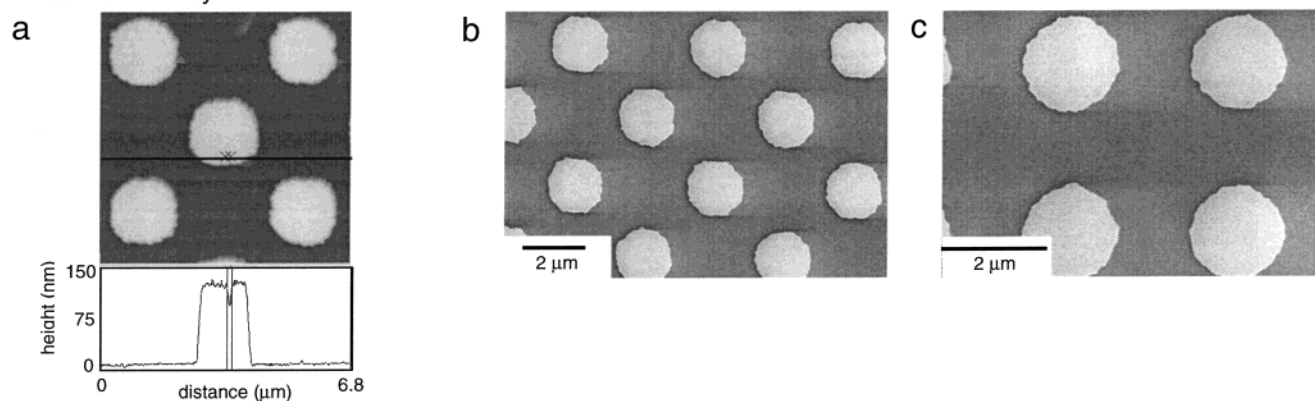
(C₇-C₂₆) using a mercury-SAM/SAM-metal junction.²¹ The compliance of the liquid mercury surface makes it possible to bring the two metal-SAM surfaces into contact without damage, and to assemble unshorted Hg-SAM/SAM-metal junctions. Here, we formed a hexadecanethiol (HDT) SAM on a hanging mercury drop electrode and brought this SAM into contact with the polymer surface (supported by silver or gold). The breakdown voltages were measured by increasing the electrical field between the two electrodes until the junction shorted (Figure 4a). Figure 4b indicates that the dependence of the breakdown voltages on the number of polymer layers supported on gold and silver was approximately linear. The breakdown

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1 PEI/POMA bilayer



2 PEI/POMA bilayers

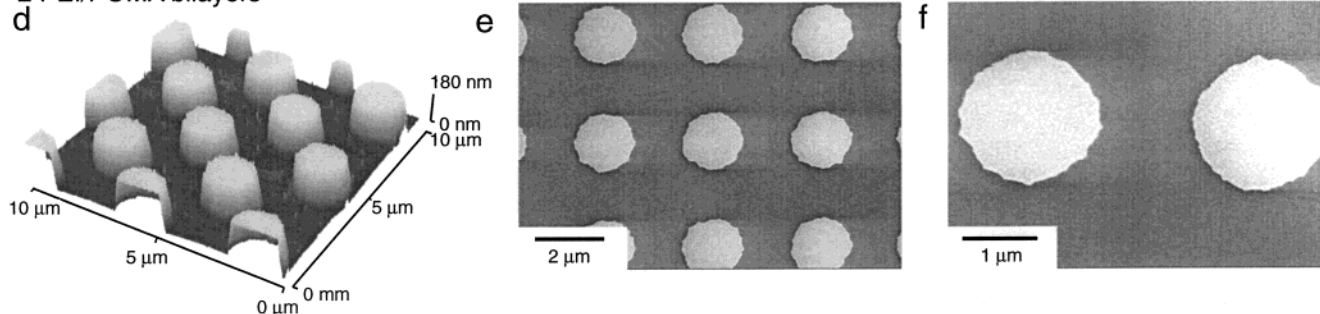


Figure 5. AFM and SEM images of 100-nm gold film, patterned using the procedure summarized in Scheme 1, and etched with 25% aqueous solution of KI-based commercial gold etchant. (a) AFM image, one PEI/POMA bilayer (The line scan shows a ~ 100 -nm-wide hole); (b–c) SEM image, one PEI/POMA bilayer; (d) AFM image, two PEI/POMA bilayers; (e–f) SEM image, two PEI/POMA bilayers.

voltages increase by 0.3–0.4 V/polymer layer. When plotted normalized against the distance between the two electrodes (Figure 4c), it appears that the higher breakdown voltages are mostly a result of an increase in the distance between the electrodes. The distance between the two electrodes is the multilayer film thickness plus the thickness of the SAMs covering the metal surfaces. The breakdown electrical field strengths decrease from 0.6 GV/m for hexadecane thiol SAMs on silver to 0.48 GV/m for two PEI/POMA bilayers on silver. The values for the polymer multilayers on gold are slightly higher than those for Ag (0.54 GV/m for two PEI/POMA bilayers). Multilayer films with the hydrophobic POMA top layers have higher breakdown voltages than the films with hydrophilic PEI on top. All values are in the 0.4–0.6 GV/m range. This range is similar to (although slightly lower than) the values reported for commercial, but thicker (1 μm), polyethylene films.²²

Etch Masks. SAMs are efficient resists for certain types of wet etchants.^{23,24} Microcontact printing has been exploited to pattern surfaces with 100-nm features.²⁵ The density of defects in patterns of gold that are fabricated by using SAMs as resists is too high, however, to be of industrial use for fabricating high-resolution electronic devices.²⁶ The defects probably originate from the domain structures of the SAMs or from intrinsic defects (pinholes)

in the SAMs.²³ The polymer multilayers described here are highly cross-linked and much thicker than a single SAM. We hoped that the number of defects would therefore be lower, and that the polymer multilayers would be more stable under etching conditions than SAMs of *n*-alkanethiols. We patterned 100-nm thick gold with 1.5- μm diameter dots of carboxylic-acid-terminated SAMs. Polymer multilayers containing PEI and POMA were built up in the same way as described earlier. We found that etching the substrates with diluted (25%) KI-based commercial gold etch²⁷ gave the best results. Figure 5a–f shows AFM and SEM images of 1.5- μm dots etched in gold using polymer multilayers as resists. The images show that areas protected by the polymer are not etched by this etchant. The AFM images show that the height difference between etched and nonetched areas is ~ 130 nm, indicating complete etching of the gold in the nonprotected areas. Figure 5a–c shows that one polymer bilayer is already a very effective etch resist. We found very few defects in the polymer-covered regions. The line scan shows a ~ 100 -nm wide etch pit. Increasing the thickness to two PEI/POMA bilayers (Figure 5d–f) eliminated all defects that we could detect by AFM and SEM. The gold was etched completely in areas covered only by a hexadecanethiol SAM. The edge resolution reproduces the edge resolution of the stamp used for μCP .

Conclusion

We have described the synthesis and characterization of patterned polymer multilayers. Sequential deposition of up to five bilayers of PEI and POMA or PSMA was shown to give smooth, defect-free films, of a maximum

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(27) Gold Etchant Type TFA, Transene Company, Inc., Rowley, MA.

thickness of approximately 20 nm. The breakdown voltages of these polymer multilayers were found to be comparable to commercially used polyethylene films, when accounting for the differences in thickness. The breakdown voltages are nevertheless higher than those obtained for SAMs because SAMs cannot form such thick layers. The patterned films were tested as corrosion-resistant coatings. They showed a very small number of defects and good stability under the etching conditions used. The possibility of combining μ CP with polymer multilayers as etch resists enhances the possibility of fabricating electronic devices with pattern transfer accomplished by μ CP.

Experimental Section

General Methods. Absolute ethanol (Pharmcoproducts, Inc.), anhydrous dimethylformamide (DMF), triethylamine, trifluoroacetic anhydride (Aldrich), hexadecanethiol (Aldrich), and THF and CH_2Cl_2 (VWR) were used as received. 16-Mercaptohexadecanoic acid was prepared according to literature procedures.²⁸ Poly(ethylene imine) (PEI, M_w 750 000, 50 wt % in water, Aldrich) was dissolved in 2-propanol and passed through a 0.2- μm filter prior to use. Poly(styrene-*alt*-maleic anhydride) (PSMA, M_w 350 000, Aldrich) and poly(octadecene-*alt*-maleic anhydride) (POMA, M_w 30 000, Aldrich) were dissolved in THF.

Preparation of the Patterned, Anhydride-Terminated SAMs. A PDMS stamp having specific features was prepared according to previously published procedures.²⁹ The PDMS stamp was inked with a 2 mM ethanolic solution of 16-mercaptohexadecanoic acid and dried with nitrogen.³⁰ The stamp was placed in contact on a freshly evaporated metal substrate—200 nm of gold or silver onto test grade, $\langle 100 \rangle$ single-crystal silicon wafers, primed with 5 nm of titanium—for 30 s. The stamp was carefully peeled off and the substrate was immersed in a 2mM ethanolic solution of hexadecanethiol for 10 min. The anhydride surface was prepared following literature procedures.¹⁶

Deposition of Polymers on the Surface. The reactive, anhydride-containing SAM was allowed to react with a 0.05 wt % solution of PEI in ethanol for 30 min. To remove physisorbed PEI, the substrate was briefly sonicated in water for 30 s, rinsed with water and ethanol, and dried under a stream of nitrogen. The substrate was placed in a 0.05 wt % solution of PSMA or POMA in THF and allowed to react for 30 min. Excess polymer was removed by briefly sonicating the samples for 30 s in THF, after which the substrate was washed with THF and CH_2Cl_2 and dried under a stream of nitrogen.

Characterization. AFM measurements were carried out on a Topometrix TMX 2010 instrument. All images were obtained in contact mode under ambient conditions. The maximum surface area scanned was $70 \times 70 \mu\text{m}^2$ with a 100 $\mu\text{m/s}$ scan rate. Force conversion of the triangular cantilever (Topometrix) was ~ 0.16

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nN/Å. PIERS spectra were obtained in single reflection mode using a Digital Fourier transform infrared spectrometer (Biorad, Cambridge, MA). The p-polarized light was incident at 80° relative to the surface normal, and a mercury–cadmium–telluride (MCT) detector was used to detect the light. A spectrum of a SAM of *n*-hexadecanethiolate- d_{33} on gold was taken as a reference.³¹ Typically, 1024 scans were averaged to yield spectra with excellent signal-to-noise ratios. Ellipsometric measurements were made on a Rudolph Research Type 43603-200E ellipsometer using a He–Ne laser ($\lambda = 632.8 \text{ nm}$) at an incident angle of 70.0° relative to the surface normal of the substrate. At least three separate spots were measured on each of three individually prepared substrates and the readings were averaged. We used a refractive index of 1.45 to estimate the thickness of the PEI films, using a program written by Wasserman.³² The exact value of the refractive index for the polymer multilayers is not known. Varying the value between 1.45 and 1.54 did not, however, significantly influence the thickness of the layers.

Measurement of Breakdown Voltages. All measurements were performed with a two-electrode junction: Hg–SAM/polymer–metal (Ag, Au).²¹ A hanging mercury drop electrode was used to generate the one-metal surface of the junction. Mercury (electronic grade, 99.9998%) was purchased from Alpha. Before touching the second surface, the diameter of the Hg drop was $\sim 1 \text{ mm}$. The hexadecanethiol monolayer on the hanging mercury drop was formed on a fresh mercury surface and then dipped in the hexadecanethiol solution (10 mM in ethanol) for 5 min. The metal–polymer surfaces containing the polymer multilayers on gold or silver were formed as described above. The Hg–SAM/polymer–metal junction was assembled using a micromanipulator to bring the hanging mercury drop (Hg–SAM) into contact with the solid metal–polymer surface.

The junction was connected to a computer-controlled potentiostat (Pine, Biopotentiostat AFCBP1, Grove City, PA) and the voltage was swept from 0 to 10 V at a rate of 1 V/s. The breakdown voltage of the respective junction was determined from the sharp rise in the current/voltage diagram. All measurements were repeated three to five times for each junction. For better reproducibility and less sensitivity to vibration, all breakdown voltage measurements were performed immersed in a 1 mM solution of hexadecanethiol in ethanol.

Etching of Gold. After formation of the patterned polymer multilayers, the substrates were submerged in an 25% aqueous solution of commercial, KI-based gold etchant.²⁷ Etching times for 100-nm Au were typically 45 s. The etching was conducted under air. After etching was complete, substrates were removed from the solution, rinsed with deionized water, rinsed with absolute ethanol, and dried under a stream of nitrogen.

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