

Communications to the Editor

Formation of Polymer Microstructures by Selective Deposition of Polyion Multilayers Using Patterned Self-Assembled Monolayers as a Template

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I. Introduction. Techniques for fabrication of ionic multilayers by self-assembly have been of great interest in the polymer science and organic thin films communities.^{1–4} These techniques take advantage of the ionic interactions of oppositely charged molecules or macromolecules to build thin films sequentially, one monolayer at a time;¹ the ability to control the architecture of these films and the relative versatility of the method (compared to LB film techniques) have contributed to the rapid incorporation of the method into materials research. Systems that have been prepared by this procedure include conducting polymers and electroluminescent films,⁵ and those that integrate layers of ceramic and metallic compounds.^{6–8}

We have previously described methods to pattern micron-sized features of a large variety of functionalized alkanethiolate self-assembled monolayers (SAMs) on gold using microcontact printing (μ CP).^{9,10} This method utilizes a poly(dimethylsiloxane) stamp molded from a photolithographic master to transfer an image using an alkanethiol “ink”, with feature sizes down to 100 nm. In the following communication, we have explored the use of patterned SAMs as a template for the selective deposition of ionically charged polymer multilayers. For this initial study, we used common polyelectrolytes: sulfonated polystyrene (SPS), poly(diallyldimethylammonium chloride) (PDAC), and poly(allylamine hydrochloride) (PAH).

II. Experimental Section. Gold substrates were prepared by electron beam evaporation of 50 Å of titanium as an adhesion-promoting layer, followed by 200 Å of gold, onto silicon wafers (Si/SiO₂) (Silicon Sense). Using μ CP, the gold surface was patterned with 2.5 μ m lines of hexadecanethiol CH₃(CH₂)₁₅SH (CH₃) or 16-mercaptohexadecanoic acid HS(CH₂)₁₅COOH (COOH), separated by 3.5 μ m spaces. For most cases, gold substrates were then dipped into a 5 mM solution of oligo(ethylene glycol)-terminated alkanethiol SH(CH₂)₁₁-(OCH₂CH₂)_nOH (EG_n, *n* = 2–7) for 10 s to cover the remaining gold regions and then rinsed with ethanol and heptane. The oligo(ethylene glycol)-terminated alkanethiol was used to prevent adsorption of the ionic polymers onto the regions of bare gold in the pattern; typically, EG₃ was used as a mask.

We used two polycation/polyanion systems for this work.

(1) *Poly(allylamine hydrochloride)/Sulfonated Polystyrene.* Molar concentrations of all polymer solutions are based on the molecular weight of the polymer repeat unit, M_u . A dilute aqueous polycation solution of 20 mM PAH (Aldrich, M_n = 8500–11 000) was prepared in Millipore ultrapure filtered DI water. PAH was synthesized by Aldrich suppliers using traditional free radical polymerization of allylamine hydrochloride, and polymer chain end groups are therefore expected to consist of vinyl and methylene amine hydrochloride groups and initiator fragments. To protonate the amine groups in solution, the pH was adjusted to 1.7 using hydrochloric acid. A 20 mM SPS (Aldrich, M_w = 70 000) solution was prepared from Millipore water, and the pH was adjusted to 2.5.

(2) *Poly(diallyldimethylammonium chloride)/Sulfonated Polystyrene.* A 20 mM solution of PDAC was prepared from a 20% solids solution (Polysciences, M_w = 240 000) by dilution with Millipore water. An 20 mM SPS solution was prepared by dilution of a 20% solids solution of sodium poly(styrene sulfonate) (M_w = 70 000). No pH adjustments were used for the PDAC/SPS system.

After patterning with SAMs, the substrates were placed in a dilute aqueous solution of polycation, allowed to soak for 20 min, and rinsed thoroughly with water. The substrates were placed in a dilute solution of polyanion for 20 min, to build a bilayer film. This procedure was repeated several times to build up polymer multilayers on the patterned surface.

To measure film thickness after each bilayer was deposited, samples were dried with nitrogen and the film thickness was determined using ellipsometry. In all cases, the thickness obtained with the ellipsometer reflects an average of the film thicknesses in the patterned and unpatterned regions over an area with a 2–3 mm diameter. The refractive index of the film was assumed to be 1.45 in all cases, as most organic polymers have refractive indices of 1.4–1.5. Noncontact mode atomic force microscopy (AFM) was used to examine the degree of selectivity of the patterning, as well as the film morphology, uniformity, and edge resolution.

III. Results and Discussion. The principle of assembling ionic multilayers is the adsorption of polymers functionalized with ionic groups onto a surface of opposite charge. Sequential buildup of multilayers is achieved by alternating adsorption of two polyelectrolytes of opposite charge. In this study, we have patterned a gold substrate with a carboxylic acid-terminated alkanethiol and thus directed polyion deposition to the COO[–] regions of the surface. Figure 1 illustrates the technique. The gold substrate was patterned with a COOH/COO[–] monolayer, and the remaining gold areas were covered with an EG₃ SAM. The COOH-functionalized regions of the substrate were allowed to adsorb polymer from a dilute polycation solution. This adsorption was followed by rinsing and a subsequent

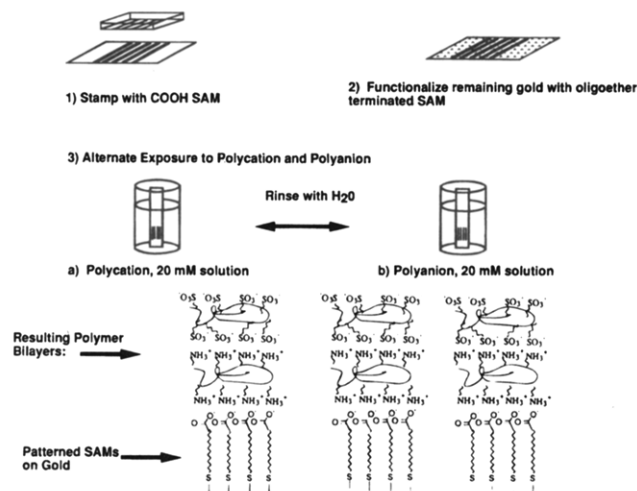


Figure 1. Schematic showing preparation of a patterned SAMs film with SPS/PDAC multilayers.

adsorption of anionic polymer onto the (now positively charged) surface. Multilayers were built up sequentially by repeatedly putting down polyion bilayers. Each ionic polymer monolayer can range in thickness from 3 to as much as 33 Å, as observed in the literature.¹¹ Larger thicknesses can be obtained when electrolytes such as sodium chloride are added to the aqueous polymer solutions.^{2,11}

Ellipsometry of bare gold stamped with carboxyhexadecanethiol indicated an averaged thickness of 14–15 Å for the SAM monolayer. When this value is adjusted to account for bare regions of gold present in the patterned sample, the estimated thickness of the SAM is 24 Å. This number is relatively close to the thickness of an ideal functionalized monolayer of 16-mercaptohexadecanoic acid (22 Å); the slight discrepancy may be due in part to the adsorption of adventitious organic matter onto the regions of “bare” gold. The presence of a SAM after stamping was verified by measuring the loss of the Au signal in XPS. After rinsing samples with the oligo(ethylene glycol)-terminated SAM, the thickness was increased by only a few angstroms.

For the systems described here, the thickness of each bilayer ranged from 5 to 10 Å, as measured using ellipsometry. The patterned regions were 3.5 μm lines with 2.5 μm spaces. When the ellipsometry measurement was adjusted to account for the fact that the film was patterned, these values corresponded to periodic increases of 8–16 Å per bilayer. These thicknesses are comparable to those observed by Decher et al.¹¹ for continuous multilayer films of poly(vinyl sulfate)/poly(allyl amine).

Figure 2 is a plot of the increase in thickness of the patterned polyion film as measured by ellipsometry versus the number of bilayers added. The laser spot used in the ellipsometer was a few millimeters in diameter and averaged the film thickness of the polymer over the patterned surface. For this figure, two measurements were taken at different regions of the sample and both data were plotted. Upon adding the first layer of polycation, a thin (3–5 Å) thickness increase was observed with ellipsometry. Adsorption of SPS led to an additional increase of 3–5 Å. The linear increase in thickness observed for the PDAC/SPS system after the deposition of several bilayers indicates that the buildup of multilayers is stepwise and periodic. There is some scatter in the data; this scatter may reflect uneven adsorption across the sample. No increase in

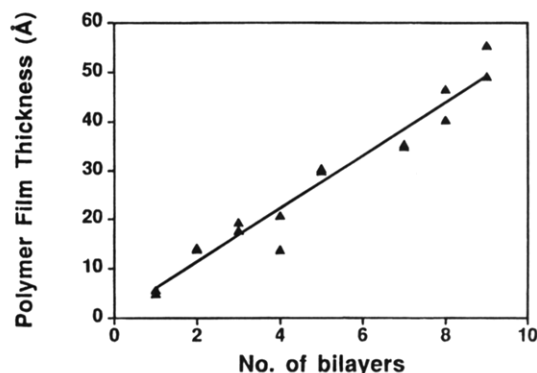


Figure 2. Ellipsometry measurements, thickness vs number of bilayers, for a patterned film.

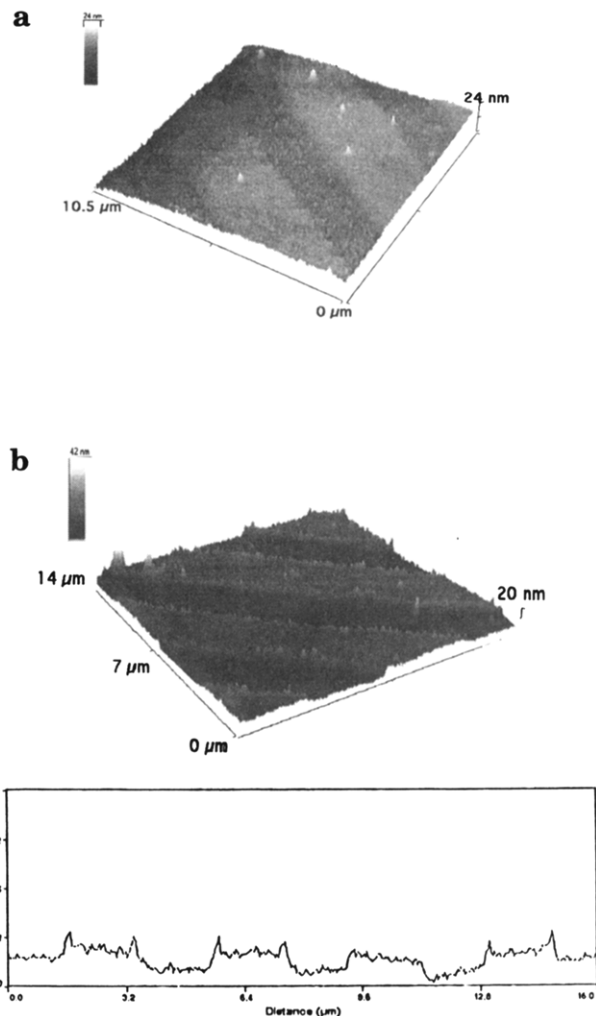


Figure 3. AFM of PDAC/SPS films (a) on gold patterned with COOH alone and (b) on COOH/EG.

thickness was observed between the third and fourth bilayers, as seen in Figure 2. The fourth bilayer was deposited after the sample had been stored for 24 h. Similar observations have been made by other researchers, and this phenomenon may be due to a need to reactivate the surface after several hours of storage in the atmosphere.

When bare gold samples were stamped with COOH-terminated SAM and used directly, the polyions tended to deposit on the bare gold regions as well. Figure 3a is an atomic force micrograph of a five-bilayer PDAC/SPS patterned film on a substrate with COOH and “bare” gold regions (i.e. regions not covered with EG₃

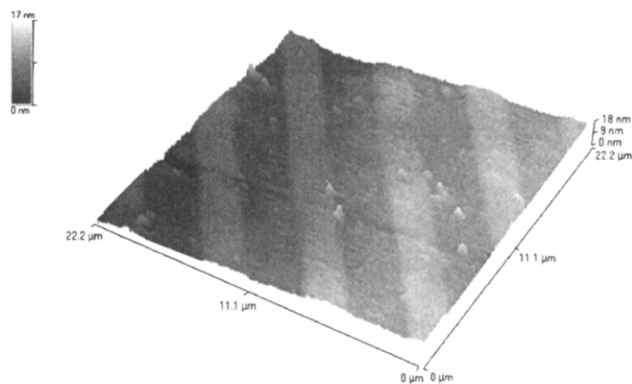


Figure 4. AFM of two bilayers of PAH/SPS on a CH₃/EG surface.

SAM). It is clear that the polymer has deposited on the gold as well as the SAM. The selectivity of the process was enhanced by the functionalization of the bare regions with EG₃ SAM. Figure 3b is an AFM micrograph of a PDAC/SPS five-bilayer film on a COOH/EG₃ patterned substrate; the EG₃ regions are relatively bare. In this case, the thickness of the polymer film regions is approximately 60 Å, as determined by AFM. The polyion multilayered film should account for approximately 30–35 Å, according to ellipsometry measurements. If the remainder of the film thickness is attributed to the underlying COOH monolayer, the overall maximum film thickness should be 55 Å; thus there is a reasonable agreement between the thickness obtained from ellipsometry and the AFM.

The surface of the patterned film region is nonuniform, with thin ridges bordering the edges of the pattern and relatively smooth middle regions. An AFM cross-section is shown in the inset. We believe this phenomenon may be due to the retraction of high molecular weight polymer film bridging two acid- or polyion-functionalized regions of the surface during the adsorption process. The polymer film may bridge these regions because the polycation cannot adsorb to the oligoethylene-functionalized surface; the net result is a ridge of additional polymer along the edges of the pattern. Actual webbed polymer films have been observed in some samples; the phenomenon may be due in part to shearing forces experienced by the patterned film upon withdrawal of the substrate from solution. Note that ridges due to webbing are not observed in the case of the COOH/bare gold functionalized surface shown in Figure 3a.

Polymer ridging has only been observed with high molecular weight samples thus far. When we used a low molecular weight polyamine (PAH) we found that the ridges were no longer present. A thin, two-bilayer patterned film of PAH/SPS is shown in Figure 4. In this particular sample, we used a methyl-terminated self-assembled monolayer of hexadecanethiol (CH₃) as

the polyion adsorption region in a CH₃/EG functionalized gold surface. The average thickness of the deposited film is approximately 30 Å, as determined by AFM; this number is consistent with a bilayer thickness of 10 Å and a SAM thickness of 20 Å. Similar results are observed with the COOH/EG-functionalized surface. With the lower molecular weight PAH/SPS system, the overall film surface roughness appeared to be greater, although the ridging was eliminated. It is likely that higher molecular weight polymers form smoother films.

IV. Conclusions. In this study, we have demonstrated that by patterning of regions of the surface with SAMs of a given functionality, we can direct the deposition of polymer multilayer films to form polymeric microstructures. Work in progress includes the patterning of polyions onto glass surfaces using trichlorosilanes patterned with μ CP.¹² We are also studying polymer/dye systems and systems containing electrochromic polymers as the basis for new diffractive sensor systems. Applications for organic thin films and organic/inorganic hybrids include optical waveguides, sensors, LEDs, and other electro-optical or photoresponsive systems. The applicability of these thin films to optical devices would be increased significantly by the ability to put these materials down in specific regions using a simple patterning technique.

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