

## Poly(ferrocenylsilanes) as Etch Barriers in Nano and Microlithographic Applications

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**Summary:** Thin films of organic-organometallic block copolymers are shown to be efficient self-assembled templates for nanolithography. Block copolymers composed of organic blocks such as polyisoprene or polystyrene and a poly(ferrocenylsilane) block microphase separate to form a monolayer of densely packed organometallic spheres in an organic matrix. The high resistance of the organometallic phase to reactive ion etching enables the nanoscale patterns to be transferred into silicon substrates, forming nanostructured surfaces. Electrostatic self-assembly of poly(ferrocenylsilane) polyanions and polycations is discussed as a means to form laterally structured organometallic multilayer thin films by area-selective adsorption onto chemically patterned substrates.

**Keywords:** block copolymers; nanolithography; organometallic polymers; polyelectrolytes; reactive ion etching

### Introduction

Macromolecules containing inorganic elements or organometallic units in the main chain combine potentially useful chemical, electrochemical, optical and other interesting characteristics with the properties and processability of polymers.<sup>[1]</sup> Poly(ferrocenylsilanes), composed of alternating ferrocenyl and alkylsilyl units in the main chain, belong to this class of organometallic polymers. With the discovery of the anionic ring-opening polymerization (ROP) of silicon bridged ferrocenophanes,<sup>[1]</sup> well-defined poly(ferrocenylsilanes) and block copolymers featuring corresponding organometallic blocks have become accessible.<sup>[2]</sup>

As we discovered that poly(ferrocenyldimethylsilane) was an effective resist in reactive ion etching processes,<sup>[3]</sup> it became of interest to employ this polymer in surface patterning of silicon substrates, which has relevance in the fabrication of *e.g.* electrooptical and magnetic storage devices, and sensors. Patterns on the (sub)micrometer scale can be introduced by soft lithography,

using poly(ferrocenylsilanes) as ink. Block copolymers featuring poly(ferrocenylsilane) blocks form nanoperiodic microdomain structures upon phase separation.<sup>[4]</sup> Thin films of such block copolymers, *e.g.* poly(ferrocenyldimethylsilane-*block*-isoprene), can serve as self-assembling templates, enabling nanometer-sized patterns to be transferred directly into silicon or silicon nitride substrates by reactive ion etching.<sup>[5]</sup> Ferrocenylsilane-styrene block copolymer thin films were successfully used as templates in the fabrication of arrays of nanometer-sized cobalt magnetic dots.<sup>[6]</sup>

Water soluble poly(ferrocenylsilane) polyions, belonging to the rare class of main chain organometallic polyelectrolytes, have recently been reported by us and others.<sup>[7-10]</sup> Polyelectrolytes can be employed in electrostatic self-assembly processes to form ultrathin multilayer films.<sup>[11,12]</sup> In this process, a substrate is immersed alternately in polyanion and polycation solutions, leading to the assembly of a multilayer thin film with controlled thickness and composition. We recently reported the synthesis of the first poly(ferrocenylsilane) polyanion.<sup>[13]</sup> This development enabled the fabrication of all-organometallic multilayers,<sup>[14,15]</sup> which are of interest *e.g.* due to their redox activity. In addition to forming continuous organometallic multilayer thin films, we explored the layer-by-layer deposition of poly(ferrocenylsilane) polyions onto hydrophilically/hydrophobically modified substrates with the aim of building two-dimensionally patterned organometallic multilayers.<sup>[14]</sup> Such films may be of interest as ultrathin resists in reactive ion etch processes.

## **Nanostructured Surfaces by a Combination of Block Copolymer Self-Assembly and Reactive Ion Etching**

Block copolymer self-assembly is an attractive method for introducing nanoperiodic patterns on substrates, due to the simplicity and low cost of the process. The domain size and domain spacing obtained by phase segregation can be controlled by tuning the chemistry, composition and molar mass of the diblock copolymer. As domains obtained by block copolymer phase separation typically have sub-100 nm dimensions, applications in electronic, optoelectronic and magnetic devices can be envisaged. The applicability of block copolymers in forming nanostructured surfaces increases significantly if the self-assembled pattern can act as a lithographic template,

enabling patterns to be transferred into substrates. Block copolymers featuring poly(ferrocenylsilane) (PFS) blocks have great potential as etch masks: the high resistance of the organometallic phase to reactive ion etching compared to the organic phase enables one to form nanopatterned surfaces in a one-step etching process.

Various approaches have been employed to enhance the etch selectivity in thin block copolymer films. A common feature of these approaches is to selectively load one of the phases with suitable inorganic components. Park *et al.*<sup>[16]</sup> used an OsO<sub>4</sub>-stained microphase-separated thin film of poly(styrene-*block*-butadiene), PS-*b*-PB, which produced holes upon RIE in silicon nitride substrates, resulting in an etch selectivity of 2:1. Möller *et al.* in a series of papers discussed the use of poly(styrene-*block*-2-vinylpyridine), PS-*b*-P2VP, to prepare masks for nanolithography either by loading the P2VP domains with gold particles<sup>[17]</sup> or by selective growth of Ti on top of PS domains.<sup>[18]</sup> These approaches achieve etching contrast by selective introduction of inorganic components in one of the phases.

The advantage of our approach is that the inorganic components are inherently present in the block copolymer, thus eliminating the need for a loading step by a metal and allowing for simple one-step lithography.<sup>[19,20]</sup>

A thin film (approximately 30 nm) of isoprene-*block*-ferrocenylsilane copolymer (IF 36/12, 36 kg/mol PI -*block*- 12 kg/mol PFS) forms lateral patterns when cast on silicon substrates.<sup>[5]</sup> At suitable volume fractions and film thicknesses it is possible to obtain a regular morphology, which consists of hexagonally packed organometallic domains (see Figure 1). After spin-casting, the entire silicon wafer is covered by this regular morphology, without the need for subsequent annealing.

Atomic concentrations of carbon (1s), oxygen (1s), silicon (2p), and iron (2p), obtained by XPS for a PI-*b*-PFS diblock and PFS homopolymer before and after oxygen reactive ion etching (O<sub>2</sub>-RIE), provide information on the etching process. For the unetched PFS homopolymer we find atomic concentration ratios for C:Si:Fe of 12:0.86:0.97 which is close to the theoretical relative amounts of 12:1:1 (C<sub>12</sub>H<sub>14</sub>SiFe for a repeat unit). After O<sub>2</sub>-RIE the oxygen concentration increased significantly, accompanied by a decrease in the carbon concentration. A large amount

of carbon is removed by RIE compared to the relative amounts of silicon and iron. Upon etching the PFS homopolymer, the Si/C ratio increased from 0.07 to 0.24. At the same time the Fe/C ratio increased from 0.08 to 0.51. It is interesting to see that following O<sub>2</sub>-RIE, the relative amount of Fe with respect to Si increased. This suggests that Fe is more stable towards O<sub>2</sub>-RIE treatments than Si. XPS further shows that both the Si2p and Fe2p binding energies increase following the oxygen plasma treatment, indicating the conversion of Si and Fe into a complex oxide.<sup>[3]</sup> These results demonstrate that poly(ferrocenylsilane) forms an etch barrier when exposed to an oxygen plasma due to the formation of an oxide layer at the surface of the polymer. This leads to a very low etch rate of the organometallic material compared to organic polymers such as polyisoprene,

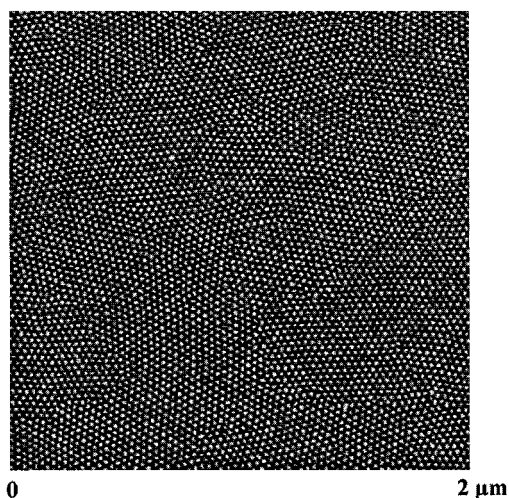


Figure 1. Tapping mode AFM phase image of 30 nm thin spin cast film of IF 36/12. The film consists of laterally separated poly(ferrocenylsilane) domains in an organic matrix.

since the oxide protects the underlying polymer from the plasma. Under the conditions employed here, we observed an etch selectivity for PI:PFS of approximately 40:1, as determined from the corresponding homopolymer etch rates (ca. 7.3 nm/s and 0.18 nm/s for PI and PFS respectively).

Figure 2 shows a representative AFM height image of a thin film (~30 nm) of IF 36/12 (Figure 1) after O<sub>2</sub>-RIE for 10 s. The organometallic domains, which were converted into an oxide by O<sub>2</sub>-RIE, are still arranged in their original hexagonal structure. The height contrast in the

AFM image increased significantly upon etching, due to the removal of the organic matrix. The line scan in Figure 2 (top right) indicates a domain height of approximately 7 nm. According to the Fourier transform of the AFM image (bottom right in Figure), no change in domain spacing occurred upon etching. This simple one-step etching process results in a nanostructured surface with an area density of approximately  $1.2 \cdot 10^{11}$  dots/cm<sup>2</sup>. After etching, the nanostructured surface is stable when stored at room temperature or rinsed with common organic solvents, in contrast to the thin diblock copolymer film.

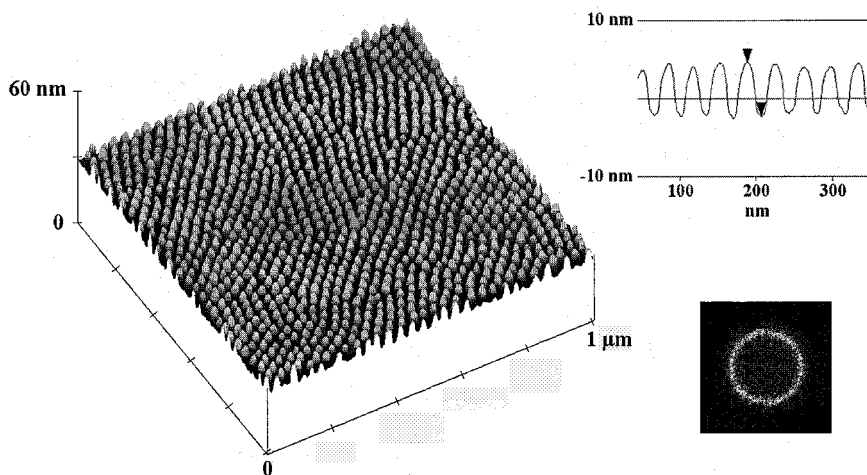


Figure 2. Tapping mode AFM height image (left) of a 30 nm thin film of IF 36/12 after O<sub>2</sub>-RIE. A single line scan (top right) and the 2D Fourier transform (bottom right) demonstrate the regularity of the structure. Reproduced with permission from ref. 5, © 2000 ACS.

The aspect ratio of the domains, however, is limited. Due to the removal of material from the organometallic phase, the features shrink which leads to somewhat flatter domains. To obtain a good visualization of the domains, a cross-sectional transmission electron micrograph is shown in Figure 3. Since the cross-section contains more than one row of domains, the sample had to be tilted so that the corresponding rows were aligned. The dots are regularly spaced which confirms the AFM observations. Furthermore, selected area diffraction indicated that the inorganic nanodomains were essentially amorphous.



Figure 3. Cross sectional TEM of a thin film of IF 36/12 after  $O_2$ -RIE treatment. The Fe-Si-oxide domains appear dark in the TEM, as does the silicon oxide layer at the surface of the silicon substrate.

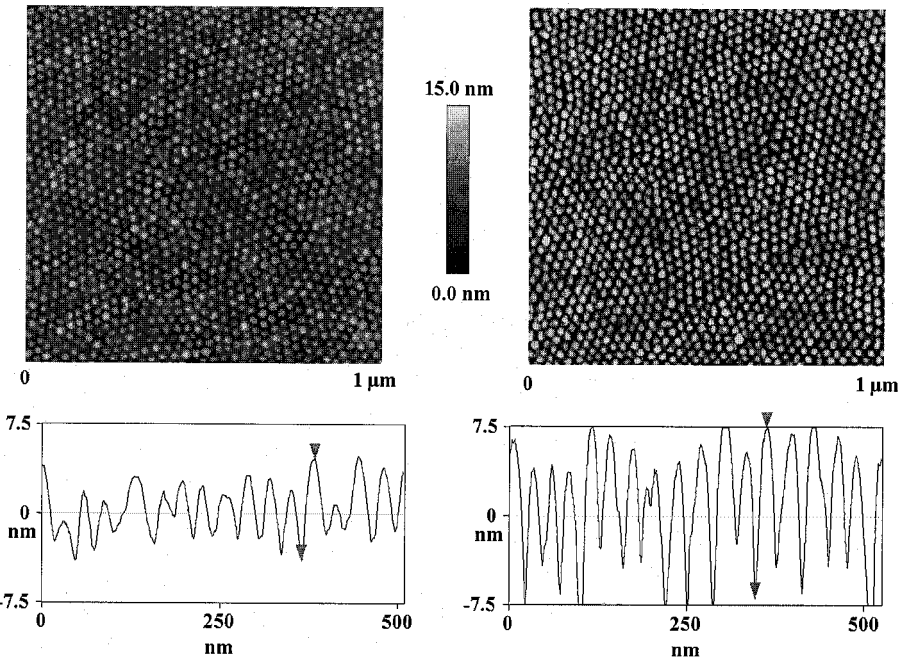


Figure 4. AFM height images of a thin IF 36/12 film on a silicon nitride substrate. The left image was taken after  $O_2$ -RIE of the film. The film displayed on the right was subsequently treated for 30 seconds with a  $CF_4/O_2$  plasma. The line scans below each image clearly demonstrate the increase in aspect ratio of the domains.

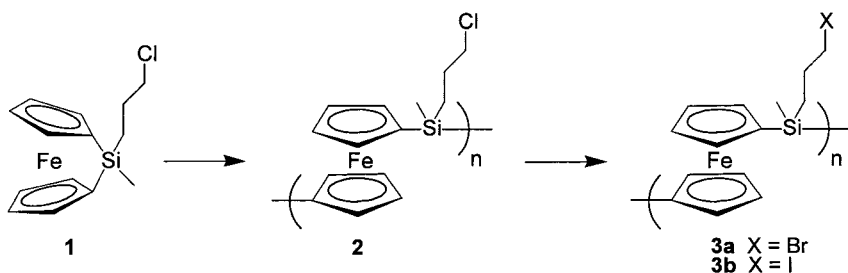
Due to the presence of iron in the inorganic domains, the pattern can be transferred into the underlying substrate by the action of  $\text{CF}_4/\text{O}_2$  reactive ion etching. Figure 4 shows the AFM images of a thin IF 36/12 film after  $\text{O}_2$ -RIE treatment (left) followed by a  $\text{CF}_4/\text{O}_2$ -RIE treatment (right). As can be concluded from the image scale and the line scans, the height of the features has increased upon the etching treatment. This is a result of the removal of the substrate in between the domains combined with the high etch resistance of the inorganic domains.

Recently, it was demonstrated that the organic-organometallic block copolymer domain patterns described here can be ordered over large areas by using sidewall constraints.<sup>[21]</sup> This development is of particular importance with regard to applications where long-range positional order of the domains is required.

### Water-Soluble Poly(ferrocenylsilanes), Synthesis and Directed Self-Assembly

Any route to high molar mass poly(ferrocenylsilanes) incorporates a ring-opening polymerization step of a strained silicon-bridged ferrocenophane.<sup>[1]</sup> Such ferrocenophanes are obtained by treating 1,1'-dilithioferrocene with a dichlorosilane of choice. Many functionalities, however, do not tolerate the highly basic dilithioferrocene or the reactive chlorosilane moieties, are incompatible with the reactive strained monomer itself, or hinder monomer purification. Therefore, functionalization after polymerization by side-group modification reactions will be required if polar or even ionic moieties are to be introduced.

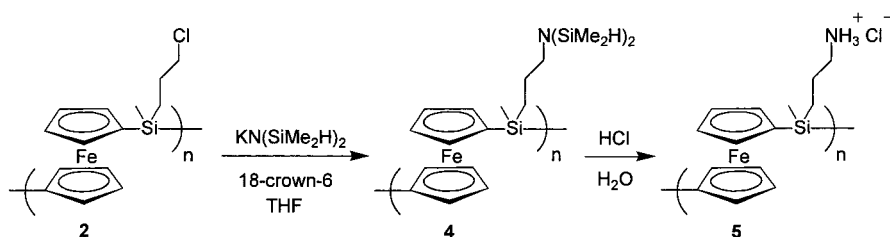
We introduced and employed a poly(ferrocenylsilane), featuring chloropropylmethylsilane repeat units, as an organometallic main chain which already has reactive pendant groups in place for further functionalization by nucleophilic substitution, see Scheme 1.<sup>[10]</sup>



Scheme 1. Poly(ferrocenylsilanes) featuring haloalkyl side groups.

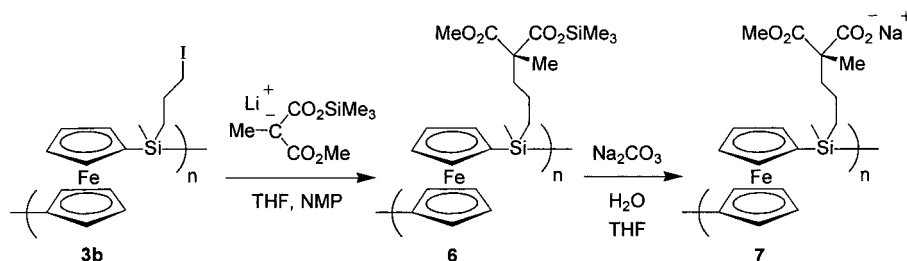
Poly(ferrocenyl(3-chloropropyl)methylsilane) **2** was readily accessible by transition-metal catalyzed ring-opening polymerization<sup>[22]</sup> of the corresponding (3-chloropropyl)methylsilyl[1]ferrocenophane **1**.<sup>[10]</sup> The chloropropyl groups are linked to silicon by Si-C bonds, which are stable to hydrolytic cleavage, as opposed to groups linked by e.g. Si-O bonds. By means of halogen exchange,<sup>[23]</sup> **2** can be converted quantitatively into its bromopropyl (**3a**) or iodopropyl analogues (**3b**),<sup>[13]</sup> which are particularly suitable for functionalization by nucleophilic substitution. Thus, a wider range of nucleophiles can be employed to prepare functional poly(ferrocenylsilanes).

As an example, reaction of **2** with potassium 1,1,3,3-tetramethyldisilazide<sup>[24]</sup> and dicyclohexano-18-crown-6 in THF afforded a N,N-bis(dimethylsilyl)-protected poly(ferrocenyl(3-aminopropyl)methylsilane) **4**, which was hydrolyzed to the desired polycation **5** in aqueous acid,<sup>[10]</sup> see Scheme 2.



Scheme 2. Synthesis of a poly(ferrocenylsilane) polycation.

The more reactive poly(ferrocenyl(3-bromopropyl)methylsilane) **3a** can be converted into polycation **5** using lithium 1,1,3,3-tetramethyldisilazide, without the aid of a crown ether.



Scheme 3. Synthesis of a poly(ferrocenylsilane) polyanion.

In case of functionalization by carbon nucleophiles, poly(ferrocenyl(3-iodopropyl)methylsilane) **3b** is a suitable starting material. Malonic ester enolates such as dimethyl methylmalonate anion or dibenzyl methylmalonate anion smoothly react to produce the corresponding polyesters with quantitative conversions. By using hydrolytically labile ester enolates, such as methyl trimethylsilyl methylmalonate anion,<sup>[25]</sup> one can easily convert the corresponding pendant ester groups into carboxylate salts, thus forming a polyanion<sup>[13]</sup> (Scheme 3). This polyelectrolyte is, to our knowledge, the first reported organometallic polyanion. The material is highly water soluble: it could be dissolved to concentrations exceeding 100 mg/mL.

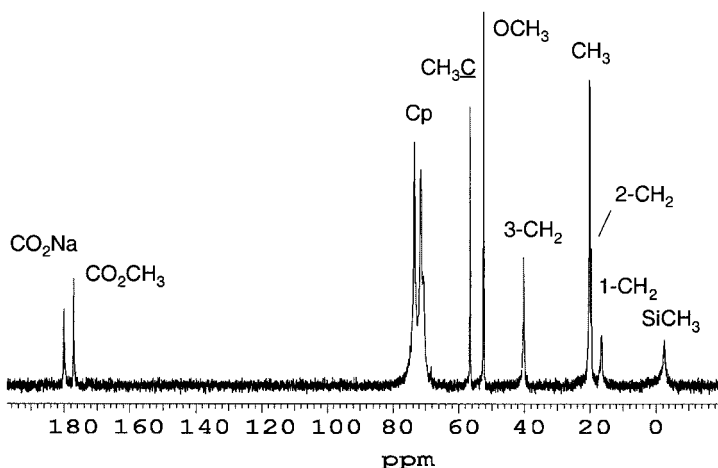


Figure 5.  $^{13}\text{C}$  NMR spectrum of the poly(ferrocenylsilane) polyanion **7** in  $\text{D}_2\text{O}$ . Reproduced with permission from ref. 13, © 2002 ACS.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy support the high efficiency of the side-group modifications. As an example, the  $^{13}\text{C}$  NMR spectrum of **7** is shown in Figure 5. No signals associated with residual iodopropyl moieties could be identified in the spectrum. In addition, elemental analysis of all polymers had excellent agreement between the expected and measured compositions. Polymers **2**, **3a** and **3b** were characterized using Gel Permeation Chromatography (GPC) in THF, using polystyrene standards, to ensure that no molar mass decline had occurred during the halogen exchange reaction. Based on GPC, poly(ferrocenylsilanes) **2** and **3a,b** have a degree of polymerization  $\text{DP}_n = 80$  and a polydispersity of  $\text{Mw}/\text{Mn} = 1.8\text{--}1.9$ . GPC measurements on

polycation **5** and polyanion **7** had to be carried out in water, precluding a direct comparison with their precursors, but the corresponding GPC traces showed a single maximum, indicating that the organometallic main chain had remained intact.

## Patterned Multilayer Thin Films

The availability of poly(ferrocenylsilane) polyanions and polycations enabled us to fabricate fully organometallic multilayer thin films on substrates such as quartz, silicon wafers and gold.<sup>[14]</sup> In addition, we were interested in forming patterned organometallic multilayer structures, i.e. to confine the deposition of the poly(ferrocenylsilane) polyelectrolytes to selected areas on substrates, as this would broaden the applicability of such multilayers. The selective deposition of polyelectrolytes on hydrophilically/hydrophobically patterned gold substrates has been described.<sup>[26,27]</sup> In this case, patterned self-assembled monolayers consisting of e.g. methyl-terminated and oligo(ethyleneglycol)-terminated alkanethiols were introduced on gold substrates, using microcontact printing.<sup>[28]</sup> Areas covered with oligo(ethyleneglycol)-terminated alkanethiols were found to prevent adsorption of polyelectrolytes. Here, as a demonstration, a gold substrate was patterned with 5  $\mu\text{m}$  wide methyl-terminated alkanethiol lines, separated by 3  $\mu\text{m}$ , by microcontact printing of 1-octadecanethiol. The uncovered areas were subsequently filled in with 11-mercapto-1-undecanol, resulting in a hydrophilically/hydrophobically patterned substrate. AFM height and friction force images of these patterned self-assembled monolayers (Figure 6, top images) show minimal height contrast but a large contrast in friction force, with the hydroxyl-terminated lines corresponding to the high friction areas.

The patterned substrate was then coated with 12 bilayers of organometallic polyions (**5/7**) and again examined by contact mode AFM. Clearly, after deposition, the height contrast increased and the contrast in friction force was reversed, which shows that the multilayers grow selectively on the broad, methyl-terminated stripes (Figure 6, lower images).<sup>[14]</sup>

The resistivity of the hydroxyl-terminated areas to polyion deposition was demonstrated by forming a monolayer of 11-mercapto-1-undecanol on a gold substrate, which was then processed similarly as the patterned substrates, and subsequently analyzed by XPS. Fe 2p signals, indicating

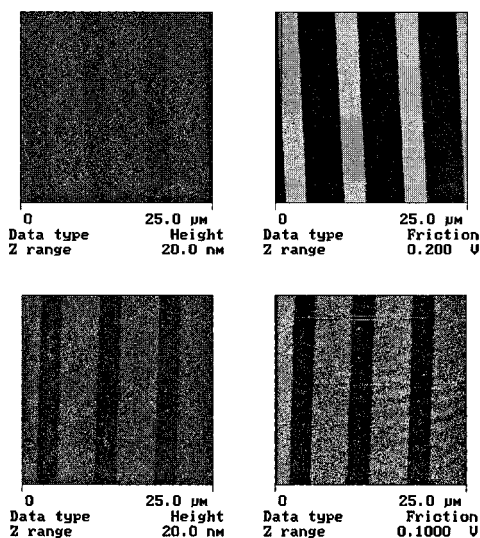


Figure 6. Multilayer deposition on a hydrophilically/hydrophobically patterned gold substrate. Upper AFM images: height (left) and friction force (right) images of patterned methyl- and hydroxyl- alkanethiol self-assembled monolayers. Adsorption of poly(ferrocenylsilane) polyions (5/7, 12 bilayers) occurs selectively on the broad methyl-terminated stripes (lower AFM images). Reproduced with permission from ref. 14, © 2002 ACS.

adsorbed polyions, were absent in the survey scan. The selective adsorption of the polyions on the methyl-terminated regions of the surface is most likely driven by favorable hydrophobic interactions between these areas and the hydrophobic poly(ferrocenylsilane) backbone. Such favorable secondary interactions<sup>[29]</sup> with the hydrophilic regions are excluded. Furthermore, the charged segments of the polyions cannot compete with water in forming hydrogen bonds with the hydroxyl-terminated regions, which are hydrated under the processing conditions.<sup>[30]</sup> Thus, deposition occurs selectively on the methyl-terminated domains.

Further support for the role of hydrophobic interactions in the area-selective adsorption was obtained by reversing the dipping sequence. A single bilayer was adsorbed on a methyl- and hydroxyl-terminated stripe pattern (10 and 5 μm, respectively), in one case starting with the polycation, in the other case with first adsorbing the polyanion. In both cases the bilayer had been deposited selectively on the methyl-terminated areas.

## Acknowledgement

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