Synthesis and Preparation of Ionically Bound Dendrimer Monolayers and Application toward Scanning Probe Lithography

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Received April 30, 1999. Revised Manuscript Received July 26, 1999

Dendrimer monolayers have been designed for use as positive resists for scanning probe lithography (SPL). Several new amphiphilic poly(benzyl ether) dendrimers with carboxylic acids at either the focal point or the "periphery" have been prepared. These can form ionically bound dendrimer monolayers that may serve as either positive or negative tone resists for SPL. The amphiphilic dendrimers self-assemble onto (3-aminopropyl)silanized Si(100) wafer surfaces to afford ultrathin films. The dendrimer monolayers were characterized by AFM, ellipsometry, and contact angle goniometry. Patterning a singly charged dendrimer monolayer results in the formation of positive tone holes ∼35 nm in width. Similarly, patterning a multiply charged dendrimer monolayer in a direct-write manner with the scanning probe microscope results in the formation of negative tone oxide features ∼80 nm in width.

Introduction

The drive toward the miniaturization of microelectronics is fueled by the demand for higher performance in both computing power and data storage. As the technologies for the manufacturing of silicon-based microelectronics move into the realm of nanotechnology, both new materials and instrumentation methods must be developed to meet the demand. Engineering nanostructures[1,2] from a materials perspective involves the utilization of organic, inorganic, and composite materials such as carbon nanotubes,[3] inorganic nanowires,[4] metal and semiconductor nanocrystals,[5] nanoparticles,[6] and polymeric materials. We have been investigating the use of functional linear, dendritic, and hybrid polymers as the building blocks for engineered nanostructures[2f] and nanodevices for future applications including microelectronic and information storage systems.

The solution properties of dendrimers have been well-characterized[7−9] and there have been a number of reports concerning the physical and chemical properties of dendrimers at interfaces.[10−13] The highly compact and globular shape, as well as the monodispersity of dendrimers, suggests that they may be ideal candidates to

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10.1021/cm990255f CCC: $18.00 © 1999 American Chemical Society
Published on Web 09/25/1999

serve as individual pixels in a hypothetical single-molecule data storage or nanolithography system. An external stimulus acting to chemically alter a single dendrimer on a surface would create a chemical or physical image with dimensions on the order of a single dendrimer molecule. We are currently exploring the possible use of dendrimer monolayers as resists for future high-resolution maskless lithography and high-density data storage systems.

Recently, we have shown that covalently bound monolayers of poly(benzyl ether) dendrons could effectively be used as resists for scanning probe lithography (SPL).[14] We are further investigating the fabrication and imaging properties of a variety of monolayer chemistries and ultrathin films of dendrimers on modified silicon (100) surfaces. We have chosen to work with poly(benzyl ether) dendrimers[8] for this study primarily because the convergent growth approach allows for control over peripheral group chemistry, while at the same time purification at each growth and activation step results in a uniformly monodisperse final product.

Results and Discussion

Synthesis. Poly(benzyl ether) dendrons terminated with benzyl ether,[8] *tert*-butyldiphenylsilyl ether,[15] and ethyl ester[16] groups at the periphery (Figure 1) were all synthesized according to their published procedures. To obtain ionically bound dendrimer monolayers we prepared several dendrimers containing carboxylic acids that could self-assemble onto an amino-functionalized silicon wafer surface. The benzyl ether protected third-generation [G-3]COOH dendron (**1**) was obtained in two steps (Scheme 1a) by alkylation of methyl 3,5-dihydroxybenzoate with the second-generation bromide dendron, [G-2]CH_2Br,[8] under standard conditions, followed by saponification of the methyl ester. A third-generation dendron protected at the periphery with *tert*-butyldiphenylsilyl ethers[15] was treated with succinic anhydride and *N*,*N*-dimethylaminopyridine (DMAP) to afford dendron (**2**) (Scheme 1b) which has a short carboxylic acid terminated chain extending from its focal point.

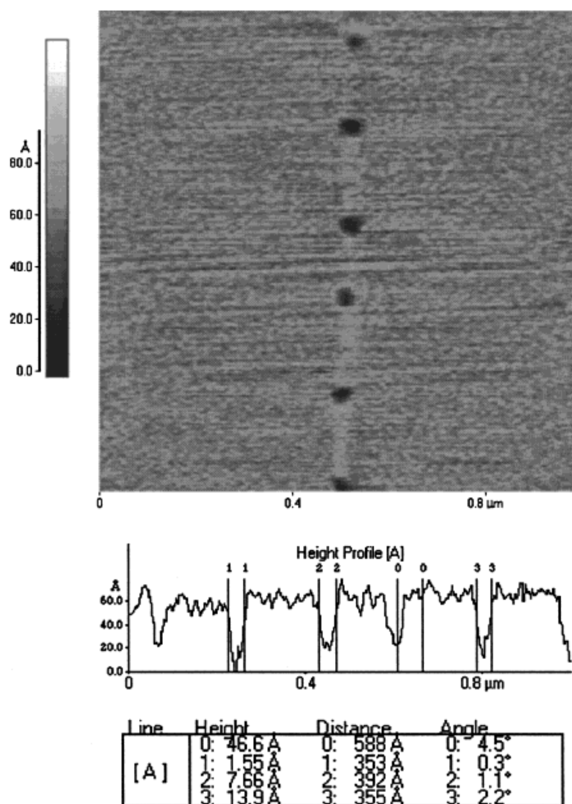

Figure 1. Two-dimensional AFM image of positive tone features formed from patterning film prepared from dendron **2**. Bias: +20V. Scan speed: 0.5 μm/s. Mean hole diameter: 35 nm. Mean hole depth: 4.5 nm. Mean hole spacing: 180 nm. Angle refers to the angle from horizontal for the intersection of two lines bearing the same number.

An amphiphilic dendrimer made from two different dendrons was also synthesized (Scheme 2) to investigate the effect of multiple points of attachment on the stability and patterning characteristics of the film. Bisphenol A was first monoalkylated with a benzyl ether terminated [G-3]CH_2Br dendron,[8] affording dendron (**3**). The unsubstituted phenolic focal point was then alkylated with an ethyl ester terminated $(EtOOC)_8$[G-2]CH_2-Br dendron,[16] to give dendrimer (**4**). The eight ethyl esters of the resulting dendrimer were then saponified to afford the desired unsymmetrical amphiphilic dendrimer (**5**).

Film Preparation. An amino-functionalized silicon surface was prepared by treating freshly cleaned Si(100) wafers with (3-aminopropyl)triethoxysilane under standard conditions.[17] Self-assembled monolayers of dendrons **1** and **2** were prepared by immersing a freshly prepared amino-functionalized wafer into a ~0.5 mM solution of the dendron with carboxylic acid focal substituent in 5% 2-propanol/hexanes for several hours.

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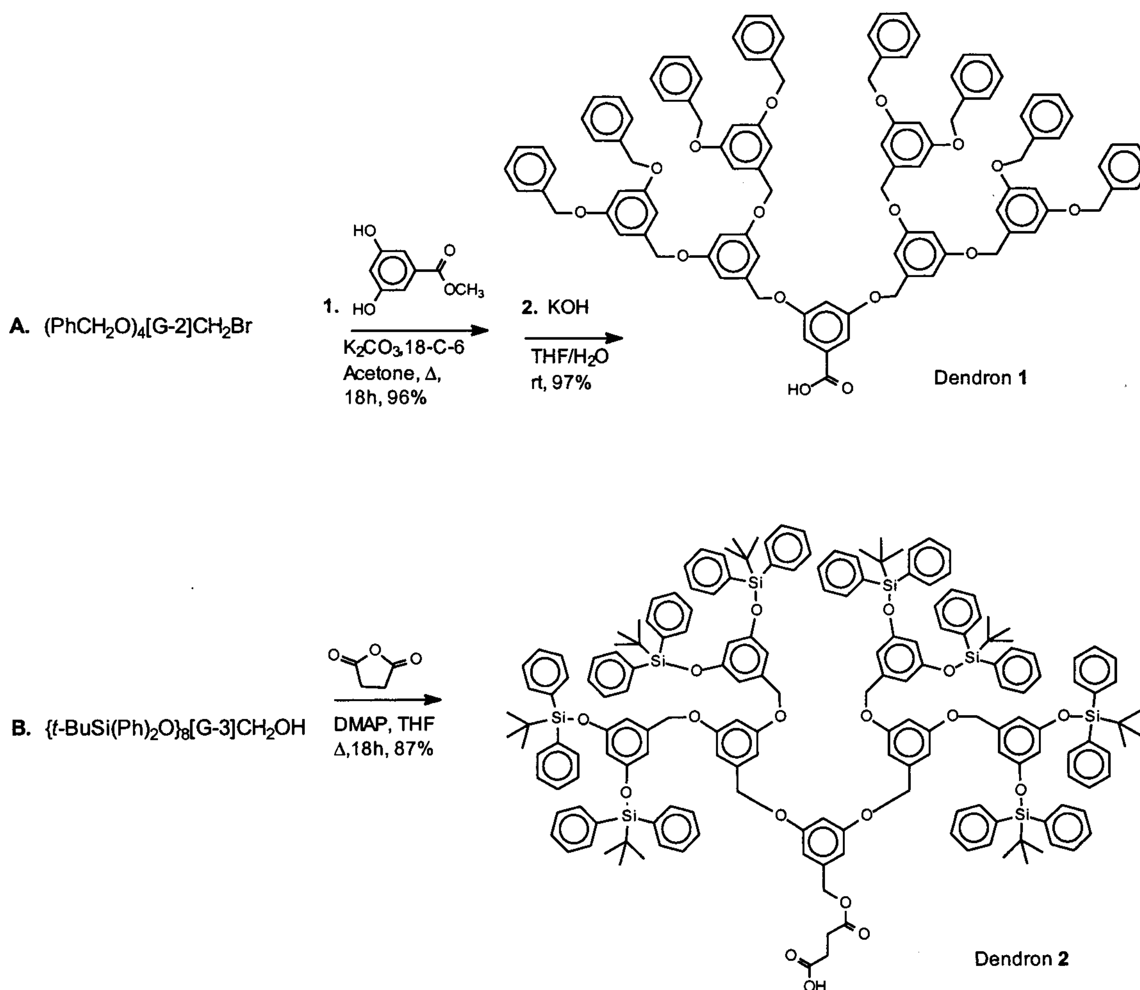
Scheme 1



This leads to a stable film via formation of an ammonium salt of the functionalized dendrimer. After removal from the deposition solution, the wafers were gently rinsed by dipping in a fresh solution of 5% 2-propanol/hexanes, followed by drying under a gentle stream of nitrogen. The monolayer made from amphiphilic dendrimer **5** was prepared by immersing a freshly prepared amino-functionalized wafer into a ~0.5 mM solution of dendrimer **5** in 5% THF/$CHCl_3$ for several hours. The wafers were then gently rinsed with 5%THF/$CHCl_3$ and dried with nitrogen upon removal from the deposition solution.

Film Characterization. Dendrimer film formation was confirmed by contact angle goniometry, optical ellipsometry, and atomic force microscopy (AFM). These three characterization methods provide evidence that film formation is nearly complete within minutes; however, to enable the formation of a more complete and homogeneous film, the wafers are typically left submerged in the deposition solution for several hours. The relatively hydrophilic (3-aminopropyl)silanized wafers exhibit a water contact angle of $47 \pm 3°$. Following the deposition of dendrons **1** and **2**, the water contact angles nearly doubled to $90 \pm 3°$ (Table 1), indicating the presence of a hydrophobic film. Similarly the hydrophobic film prepared from dendrimer **5** exhibited a contact angle of $80 \pm 2°$.

The thickness of the dendrimer films as estimated by optical ellipsometry are presented in Table 1. The average thickness of the (3-aminopropyl)silane films was measured to be 9 ± 2 Å, increasing by a factor of about 5 after the deposition of dendrimers **1** and **2**. The films prepared from dendrimer **5** had a thickness of about 39 Å, slightly less than the thickness of the monolayers formed from dendrons **1** and **2**, which only possess a single carboxylic acid at their focal points. Contact mode AFM was used to determine the root-mean-square (rms) roughness of the dendrimer films, and these values are also listed in Table 1.

The formation of each of the three films was reversible, as the monolayers could be removed by rinsing the wafer in an appropriate solvent. Reintroduction of a recently rinsed wafer into a deposition solution resulted in the formation of a dendrimer monolayer with properties identical to the film first formed on a fresh wafer. The films formed from dendrons **1** and **2** could easily be removed by rinsing the wafers in a more polar solvent such as acetone or THF. As a result of the presence of multiple binding sites, the films formed from amphiphilic dendrimer **5** were much more robust. Rinsing the wafer with copious amounts of THF, acetone, ethanol, or methanol did not result in any change in either contact angle or film thickness. Removal of the monolayer could be achieved by rinsing the wafer with a solution of dilute H_2SO_4 in THF/water (1:1). Under such acidic conditions, the carboxylate moieties at the periphery of the dendrimer are protonated, thereby allowing desorption of the amphiphilic dendrimer from

Scheme 2

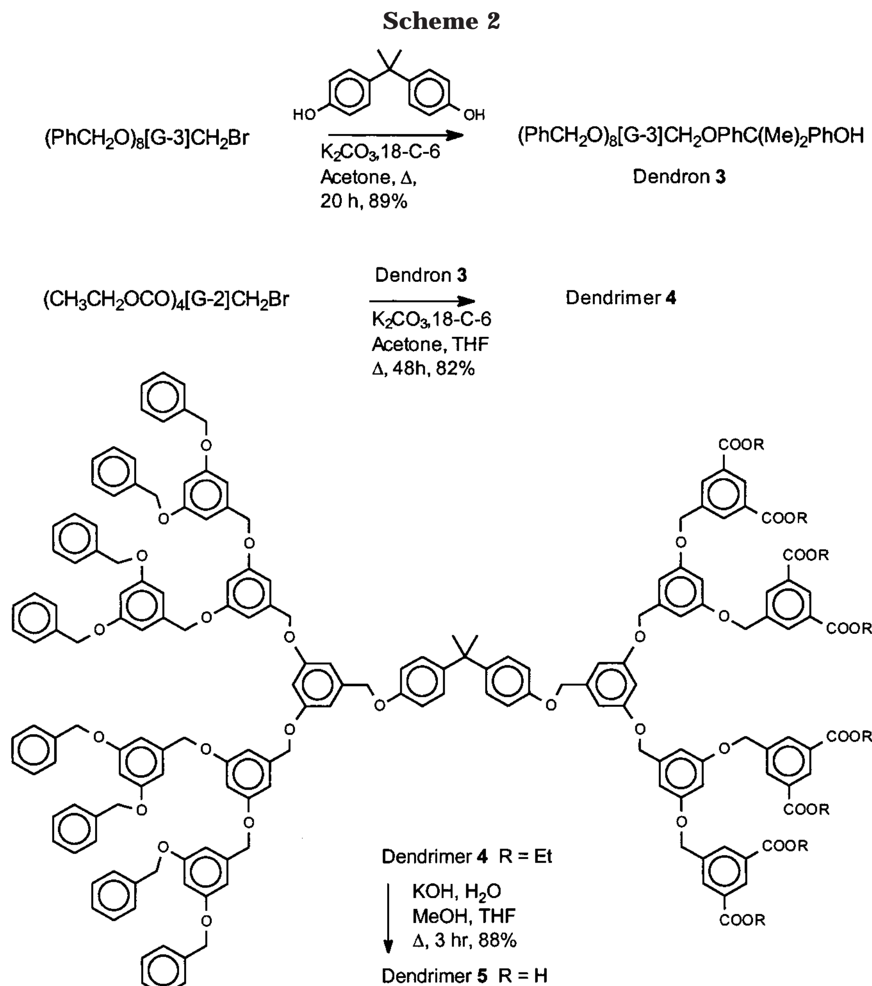


Table 1

monolayer	contact angle, deg	thickness, Å	rms roughness, Å
3-AMPS	47 ± 3	9 ± 2	4.9
dendron **1**	90 ± 3	48 ± 5	7.6
dendron **2**	90 ± 3	53 ± 5	8.7
dendrimer **5**	80 ± 2	34 ± 2	5.8

the surface. Following removal of the film of dendrimer **5** with the use of the H_2SO_4/THF/water mixture (including subsequent rinses with water and ethanol), the ellipsometric film thickness decreased to 11 ± 2 Å. In addition, the silicon wafers exhibited a contact angle of 32 ± 2°, which may be indicative of the presence of an ionically charged, hydrophilic ammonium sulfate layer. The observation that the monolayer formed from dendrimer **5** exhibits slightly lower contact angles and ellipsometric thicknesses than monodendrons **1** and **2** may be due to the fact that dendrimer **5**, with its eight carboxylic acids is more strongly bound to the amino-functionalized surface. The higher binding affinity of the latter dendrimer for the ammonium surface likely leads to a slight flattening of the dendrimer on the wafer surface.[13a]

Finally, ionically bound dendrimer films formed from **1**, **2**, and **5** all showed similar stability, or etch resistance, toward 1 M hydrofluoric acid (50:1). Contact angles and ellipsometric thicknesses remained unchanged for each of the three films following immersion of the wafers in 1 M HF for 3 min.

Scanning Probe Lithography. Having recently demonstrated that covalently bound dendrimers may effectively be used as resists for SPL,[14] we sought to investigate whether ionically bound dendrimer monolayers could also be patterned using the scanning probe microscope (SPM). The SPM can be used as a direct-write lithography tool to pattern a variety of different surface chemistries according to several different patterning mechanisms. Self-assembled monolayers of small organic molecules on gold[18-21] and silicon,[22-25] thin polymer films,[26-29] and passivated metal sur-

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faces[30–35] have all been successfully patterned by SPL. When a voltage bias is applied between the SPM tip and the wafer, an intense electric field is created directly under the tip, resulting in the formation of patterns on the surface. The mechanism of pattern formation on the surface is considered to result from one or more of the following: electric field[30–34] enhanced oxidation, electron impact[33,36] enhanced oxidation, or electrochemical anodization[25,37] of the surface. Since patterning is performed under ambient conditions, an organic monolayer may be oxidatively decomposed,[22–24] resulting in the formation of positive tone images in the monolayer. This process is useful for lithography, since the remaining unexposed regions of the film may serve as an etch mask, allowing for pattern transfer into the underlying silicon substrate. Alternatively, depending on the ambient conditions and the wafer surface chemistry the underlying silicon wafer can also be oxidized. This leads to the production of negative tone relief features resulting from the incorporation of oxygen into the silicon crystal lattice.[30–35] The voltage dependence and resulting feature sizes are influenced by the particular surface chemistry involved in the patterning, including for example the presence of an oxide layer and its thickness, or the presence of an organic film and its thickness. Pattern transfer under these circumstances may be accomplished by choosing an etchant which is either selective against the silicon oxide or the organic film.[14]

Singly Charged Dendrimer Films. We initially attempted to pattern a wafer using the singly charged ionically bound monolayers formed from dendrons **1** and **2** using conditions similar to those that were used previously[14] to pattern the covalently bound dendrimer monolayers. To our surprise, under those conditions we were unable to produce any negative tone oxide features with the singly charged dendrimer films. However, increasing the bias to +20 V resulted in successful image formation. Although rather than forming the expected negative tone images, we were able to create patterns through the formation of positive tone images in the singly charged dendrimer monolayer. Figure 1 shows an AFM image of patterns created in a film formed from dendron **2**. In this example, a series of six holes with a spacing of ~180 nm were formed in the organic film. Each hole has an average diameter of 35 nm, and a depth of ~45 Å. The hole depths measured using the AFM are very close to the original film thicknesses measured by ellipsometry. Therefore, it may be reasonable to assume that the holes arise either from the removal, or perhaps more likely, the oxidative decomposition[22–24] of the dendrimer monolayer. Such positive tone latent images may then be transferred into the underlying silicon substrate by choosing an etchant which is selective against the dendrimer film. Since these ionically bound dendrimer films are stable toward aqueous HF, pattern transfer could be accomplished in a manner analogous to the example previously demonstrated for covalently bound dendrimer films.[14]

The stark contrast in behavior of the singly charged dendrimer monolayers from the covalently bound dendrimer films under similar lithography conditions was unexpected. We routinely monitor the current during the lithography, and in doing so we observe that in the case of the covalently bound dendrimer films, the current is typically constant in the range of 200–500 picoamps (pA).[14] By comparison, while patterning the singly charged monolayers, the current was sporadic on the order of hundreds of nanoamps (nA). We speculate that this may arise from a capacitance-related charging during the lithography process which only occurs when the singly charged monolayer is used as the resist material.

Multiply Charged Dendrimer Films. To further explore the lithographic properties of ionically charged organic films, we proceeded to synthesize a dendrimer capable of supporting multiple ionic charges at the periphery of the molecule (vide supra). Patterning experiments performed on a monolayer of multiply charged dendrimer **5** led to patterns similar to those obtained from the covalently bound dendrimers.[14] Patterning was accomplished by applying a positive bias of 15 V to the wafer, with a tip scan speed of 0.5 μm/s. Contrary to the singly charged dendrimer films, the current here was not sporadic, but relatively constant on the order of hundreds of picoamps. Figure 2a is a two-dimensional AFM image of a grid pattern of raised oxide lines formed on a wafer coated with dendrimer **5**. The line width averages 80 nm, and the line height averages 11 Å above the surface of the unexposed regions of the dendrimer film. The latent negative tone patterns can be subjected to an image reversal by etching with HF as we have shown in an earlier example.[14] Alternatively, the dendrimer film could serve as a negative tone imaging system, since the unexposed regions of the film may be removed to reveal an enhanced aspect ratio for the exposed oxide lines. Figure 2b is an AFM image of the same grid pattern following removal of the dendrimer film. The line width still averages 80 nm, but the line height averages 28 Å presumably above the underlying (3-aminopropyl)-silanized wafer surface. This value for the dendrimer film thickness measured by AFM agrees with the value obtained by ellipsometric measurements.

Conclusion

We have shown earlier that the densely packed hydrophobic dendrimer monolayer provides a stable etch mask toward an aqueous hydrofluoric acid etch;[14] hence, treatment of a wafer to the prescribed etch conditions

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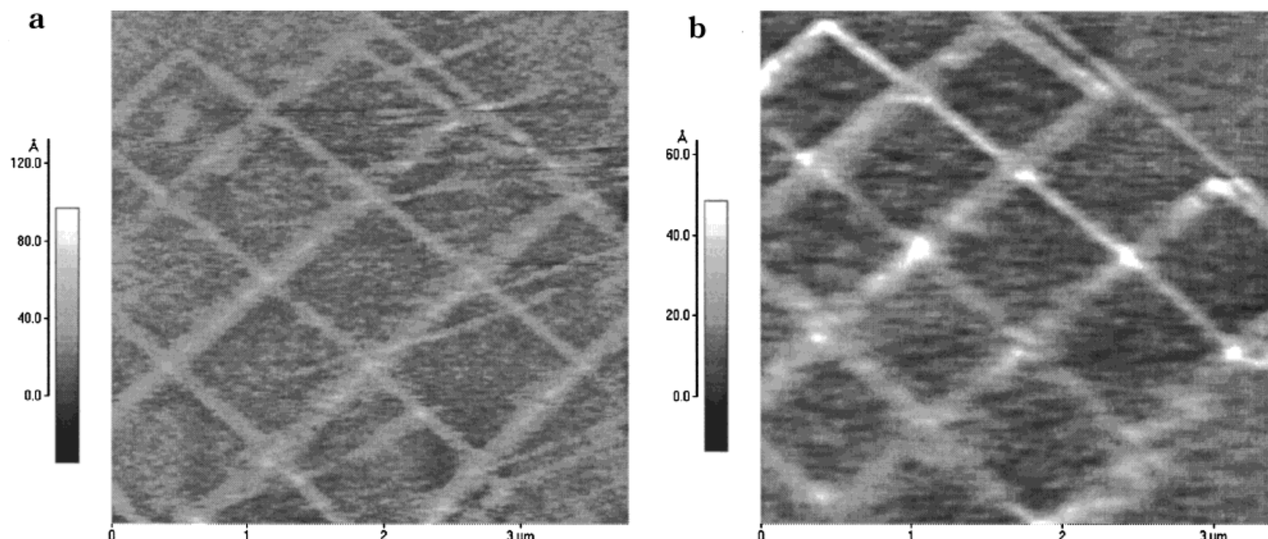

Figure 2. (a) Two-dimensional AFM image of negative tone features made by patterning film prepared from dendrimer **5**. Bias: +15 V. Scan speed: 0.5 μm/s. Pitch: 1.0 μm. Average line width: 80 nm. Average line height: 11 Å. (b) Two-dimensional AFM image following removal of dendrimer **5** from unpatterned regions. Average line width: 80 nm. Average line height: 28 Å.

should transfer these positive tone images into the underlying silicon. A lithographic technique that provides the ability to predictably pattern nanometer scale holes on a surface might prove useful as the basis for a hypothetical ultrahigh-resolution archival data storage system. We are continuing this work by exploring these and other dendrimers and hyperbranched polymers for their potential use as nanopatterning materials for scanning probe and other future maskless lithography technologies.

Experimental Section

General Methods. All reagents and starting materials were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification unless otherwise noted. 3,5-Dihydroxybenzyl alcohol was recrystallized twice from acetonitrile. Tetrahydrofuran was distilled from sodium/benzophenone, and acetonitrile was distilled from calcium hydride immediately prior to use. NMR spectra were acquired on either a Bruker AMX-300 or a Bruker AMX-400 and were obtained using $CDCl_3$ as solvent unless otherwise noted. Matrix-assisted laser desorption ionization-time-of-flight (MALDI-TOF) mass spectrometry was performed on a Perseptive Biosystems Voyager-DE spectrometer using delayed extraction mode with an acceleration voltage of 20 keV. Samples were prepared by using a 1:20 ratio of analyte (5 mg/mL in THF) to matrix solution (*trans*-indoleacrylic acid, 10 mg/mL in THF). Infrared spectra were collected on a Mattson Genesis II FT-IR with a diffuse reflectance (DRIFT) accessory (Pike), and the samples were prepared by dispersing in powdered KBr.

Synthesis. *$(PhCH_2O)_8$-[G-3]-CO_2H (Dendron 1).* Methyl 3,5-dihydroxybenzoate (0.16 g, 0.94 mmol) was allowed to react with $(PhCH_2O)_4$[G-2]CH_2Br[7b] (1.51 g, 1.9 mmol), K_2CO_3 (0.63 g, 4.6 mmol), and a catalytic amount of 18-crown-6 in 3 mL of acetone and 0.7 mL of acetonitrile. The reaction mixture was stirred vigorously and heated to 55 °C for 24 h under a dry nitrogen atmosphere. Solvent was removed in vacuo, and the methyl ester was purified by column chromatography (silica gel, neat CH_2Cl_2) resulting in 1.46 g (0.90 mmol, 96%) of the desired material. ^{1}H NMR (300 MHz): δ 7.41−7.30 (m, 40H), 7.28 (d, 2H, J = 2 Hz), 6.78 (t, 1H, J = 2 Hz), 6.66 (d, 8H, J = 2 Hz), 6.65 (d, 4H, J = 2 Hz), 6.56 (t, 4H, J = 2 Hz), 6.54 (t, 2H, J = 2 Hz), 5.01 (s, 16H), 4.98 (s, 4H), 4.96 (s, 8H), 3.87 (s, 3H). ^{13}C NMR (100 MHz): 166.51, 160.03, 159.95, 159.57, 139.10, 138.78, 136.66, 131.96, 128.44, 127.85, 127.42, 108.28, 106.97, 106.30, 106.24, 101.67, 101.47, 69.88, 69.81, 52.10. MALDI-TOF MS (m/z): calcd for $[M + Na]^+$ 1644, found 1645; calcd for $[M + K]^+$ 1660, found 1661. IR (cm^{-1}): 1716, 1595, 1454, 1376, 1297, 1156.

$(PhCH_2O)_8$[G-3]COOMe (0.72 g, 0.44 mmol) was dissolved in 4.5 mL of THF. KOH (0.031 g, 0.55 mmol) and 0.25 mL of H_2O were added, and the reaction mixture was stirred overnight at room temperature. The reaction mixture was then acidified to pH 3−4 with 5% $NaHSO_4$ (aq) and concentrated. The residue was taken up in EtOAc, washed with brine (2 × 50 mL), and concentrated. The product was purified by column chromatography eluting on a gradient from 1:19 EtOAc/CH_2Cl_2 to 1:9 EtOAc/CH_2Cl_2, affording 0.69 g (0.43 mmol, 97%) pure product. ^{1}H NMR (300 MHz): δ ppm 7.51−7.22 (m, 40H + 2H), 6.82 (bs, 1H), 6.66 (bs, 8H + 4H), 6.55 (bs, 4H + 2H), 5.02 (s, 16H), 4.99 (s, 4H), 4.97 (s, 8H). ^{13}C NMR (100 MHz): δ ppm 171.42, 160.04, 169.98, 159.64, 139.11, 138.69, 136.67, 131.07, 129.45, 127.86, 127.43, 108.81, 107.93, 106.40, 106.27, 101.65, 101.50, 69.93, 69.85. MALDI-TOF MS (m/z): calcd for $[M + Na]^+$ 1631, found 1631; calcd for $[M + K]^+$ 1647, found 1647. IR (cm^{-1}): 3032, 1682, 1595, 1446, 1372, 1055.

{t-Bu(Ph)$_2$SiO}$_8$[G-3]$CH_2OCO(CH_2)_2COOH$ (Dendron 2). Succinic anhydride (40 mg, 0.40 mmol) was added with stirring to a solution of {*t*-Bu(Ph)$_2$SiO}$_8$[G-3]CH_2OH[15] (0.88 g, 0.36 mmol) and (*N,N*-dimethylamino)pyridine (49 mg, 0.40 mmol) in THF (2.0 mL) under a dry nitrogen atmosphere. The solution was heated to 60 °C and stirred overnight. Upon cooling to room temperature, ether (50 mL) was added, and the solution was washed with water (2 × 50 mL), 5% aqueous acetic acid (2 × 50 mL), and water (2 × 50 mL) and then dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude material was chromatographed over silica gel using CH_2Cl_2 as eluent affording 0.92 g (0.32 mmol, 87%) of the desired product. ^{1}H NMR (300 MHz) δ ppm 7.53 (m, 32H), 7.36−7.30 (m, 16H), 7.23 (m, 32H), 6.59 (m, 2H + 1H), 6.47 (d, 4H, J = 2 Hz), 6.42 (d, 8H, J = 2.2 Hz), 6.22 (t, 2H, J = 2.1 Hz), 6.13 (t, 4H, J = 2 Hz), 5.09 (s, 2H), 4.88 (s, 4H), 4.66(s, 8H), 2.66 (m, 2H + 2H), 0.99 (s, 72H). ^{13}C NMR (100 MHz) δ ppm 176.81, 171.87, 160.15, 159.89, 156.36, 138.60, 138.42, 138.02, 135.39, 132.71, 129.72, 127.62, 111.89, 111.03, 106.96, 106.48, 101.70, 101.37, 70.12, 69.51, 66.47, 28.80, 28.62, 26.52, 19.39. FTIR (cm^{-1}) 1959, 1890, 1820, 1740, 1712, 1591. MS (MALDI-TOF): $[M + Na]^+$ calcd 2903; found 2907.

$(PhCH_2O)_8$-[G-3]$CH_2OPhC(Me)_2PhOH$ (Dendron 3). A 50-mL round-bottom flask was charged with a magnetic stir-bar, dry acetone (21 mL), K_2CO_3 (0.83 g, 6.0 mmol), **[G-3]-Br** (0.31 g, 0.19 mmol), bisphenol A (1.27 g, 5.6 mmol), and 18-crown-6 (0.30 g, 1.1 mmol) added in that order. The reaction mixture was stirred and heated at 55 °C under a nitrogen atmosphere.

After 20 h, the reaction mixture was cooled and precipitated into CH_2Cl_2. The excess bisphenol A and potassium salts were filtered off, the filtrate was concentrated, and the crude product was purified by flash chromatography in 1:9 hexane/CH_2Cl_2 to afford 0.30 g (0.17 mmol, 89%) of the desired material. ^{1}H NMR (300 MHz): δ ppm 7.41−7.32 (m, 40 H, phenyl,), 7.07 (m, 4H), 6.83 (m, 2H) 6.70−6.66 (m, 8H + 4H + 2H + 2H), 6.56−6.53 (m, 4H + 2H + 1H), 5.01 (s, 16H), 4.95 (broad s, 8H + 4H), 4.90 (s, 2H), 1.6 (s, 6H); ^{13}C NMR (100 MHz) δ ppm 160.07, 159.97, 156.45, 153.41, 143.40, 142.88, 139.70, 139.16, 136.69, 128.49, 127.91, 127.78, 127.66, 127.48, 114.63, 114.14, 106.32, 101.55, 70.00, 69.89, 41.56, 30.90. FTIR (cm^{-1}): 3544, 3031, 2930, 2871, 1595, 1450. MS (MALDI-TOF): $[M + Na]^+$ calcd 1826; found 1829; $[M + K]^+$ calcd 1842; found 1845.

Dendrimer 4. A 25-mL round-bottom flask was charged with a magnetic stir-bar, acetone (2.5 mL), THF (2.5 mL), and K_2CO_3 (0.12 g, 0.87 mmol). The stirred mixture was heated to 55 °C under a nitrogen atmosphere and dendron **3** (0.26 g, 0.14 mmol), $(CO_2Et)_8$-[G-2]-Br[16] (0.20 g, 0.14 mmol), and 18-crown-6 (0.008 g, 0.03 mmol) were added in that order. After 48 h, the reaction mixture was cooled, and excess potassium salts were removed by filtration. The filtrate was removed in vacuo, and the crude product was purified by flash chromatography using neat CH_2Cl_2 to 2% EtOAc/CH_2Cl_2, affording 0.37 g (0.12 mmol, 82%) of the desired product. ^{1}H NMR (300 MHz): δ ppm 6.63, (t, 4H, J = 1.5 Hz), 8.29 (d, 8H, J = 1.5 Hz), 7.4−7.29 (m, 40 H, phenyl), 7.13 (d, 2H), 7.11 (d, 2H), 6.85 (m, 4H), 6.72−6.53 (m, 30 H, aromatic CH), 5.11 (s, 8H), 5.00−4.86 (m, 36H, benzylic CH_2), 4.40 (q, 16H, J = 7.2 Hz), 1.60 (s, 6H), 1.40 (t, 24H, J = 7.2 Hz). ^{13}C NMR (100 MHz): δ ppm 165.47, 160.07, 159.97, 159.73, 156.51, 143.37, 143.30, 139.70, 139.50, 139.15, 137.64, 136.70, 132.46, 131.25, 130.13, 128.48, 128.16, 127.89, 127.67, 127.45, 114.11, 106.53, 106.37, 106.28, 101.52, 101.38, 69.98, 69.88, 69.80, 69.00, 61.37, 41.62, 30.97, 14.25. FTIR (cm^{-1}): 3031, 2977, 2872, 1721, 1595, 1449. MS (MALDI-TOF): $[M + Na]^+$ calcd 3130; found 3126; $[M + K]^+$ calcd 3146; found 3143.

Dendrimer 5. The procedure of Leon et al.[16] was followed using dendrimer **4** (0.15 g, 0.05 mmol), KOH (0.14 g, 2.5 mmol), THF (6 mL), H_2O (4 mL), and MeOH (2 mL). Upon cooling to room temperature, the reaction mixture was precipitated into a solution of 0.25 M HCl, stirred for 30 min, and allowed to settle overnight. The precipitate was decanted, washed with water, and centrifugated. This process was repeated until the pH remained steady. Next, the product was suspended in acetone and concentrated, and the process was repeated twice. The product was dried under vacuum at 50 °C overnight to afford 0.12 g (0.04 mmol, 88%) of the desired material. ^{1}H NMR (DMSO-d_6, 300 MHz): δ ppm 11.73 (broad s, 8H), 8.42 (t, 4H, J = 1.5 Hz), 8.23 (d, 8H, J = 1.5 Hz), 7.40−7.27 (m, 40H, phenyl), 7.02 (m, 4H), 6.76−6.60 (m, 30H, aromatic CH), 5.24 (s, 8H) 5.03−4.94 (m, 36H, benzylic CH_2), 1.50 (s, 6H). ^{13}C NMR (100 MHz): δ ppm 176.65, 159.70, 159.63, 159.52, 156.51, 144.06, 142.93, 139.74, 139.48, 138.48, 137.01, 133.99, 132.23, 131.70, 129.58, 128.49, 127.92, 127.79, 127.50, 114.23, 107.15, 106.89, 106.56, 101.20, 69.44, 69.29, 41.34, 30.74. FTIR (cm^{-1}) 2923, 1709, 1596, 1509, 1450. MS (MALDI-TOF): $[M + Na]^+$ calcd 2906; found 2899.

Substrate Preparation. Silicon (100) wafers, n-type, phosphorus-doped (Addison Engineering, San Jose, CA) were cleaned prior to use according to the following procedure: The wafers were first rinsed with chloroform, ethanol, and water (18 MΩ cm) and then placed in a "piranha" bath (7:3 H_2SO_4/30% H_2O_2) (*Caution: powerful oxidant!*) at 120 °C for 20 min. The wafers were then rinsed by first placing them into boiling water (18 MΩ cm, EASYpure RF, Barnstead) for 2 min, followed by rinsing with additional EASYpure water, ethanol, and then blown dry with nitrogen. The silicon wafers were used immediately following the cleaning procedure.

Preparation of Dendrimer Monolayers. Freshly cleaned wafers were first functionalized by treatment with (3-aminopropyl)triethoxysilane (Gelest, Inc., Tullytown, PA) under standard conditions.[17]

Singly Charged Dendrimer Monolayer. A freshly prepared aminopropylsilane functionalized wafer was placed into a dilute solution (~0.5 mM) of dendron **1** or **2** in 5% 2-propanol/hexanes for several hours. Upon removal, the wafer was rinsed with by gently dipping into a fresh solution of 5% 2-propanol/hexanes followed by drying with a very gentle stream of nitrogen.

Multiply Charged Dendrimer Monolayer. A freshly prepared aminopropylsilane functionalized wafer was placed into a dilute solution (~0.5 mM) of dendrimer **5** in 5% THF/$CHCl_3$. After several hours, the wafer was rinsed by dipping gently into a fresh solution of 5% THF/$CHCl_3$, followed by drying under a gentle stream of nitrogen.

Monolayer Characterization. Contact angles were determined on a Krüss Model G10 goniometer at room temperature and ambient relative humidity using 18 MΩ cm according to the sessile drop method.[38] Monolayer thicknesses were determined using a Gaertner L116A optical ellipsometer equipped with a 632.8-nm He−Ne laser with an angle of incidence of 70 °C, and n_f = 1.46. Data presented are averages of at least 10 different measurements on three different areas of the wafer. Film roughness was determined in contact mode AFM and calculated using PSI ProScan software.

Scanning Probe Instrumentation. Lithography was performed under ambient conditions (class 100 clean room) using a PSI Autoprobe M5 (Park Scientific Instruments) operating in the contact AFM mode. A current preamplifier (Ithaco) was connected to the tip and used to monitor the tip−sample current during patterning. High-aspect-ratio silicon tips (p-type, boron-doped, PSI Ultralevers) were mounted on conductive holders and grounded through the current preamplifier. A positive voltage was applied to the sample with a metal clip resulting in a negative bias between the tip and the sample. PSI lithography and LabView data acquisition software were used to specify the path and speed of the tip and to monitor the current, respectively.

Acknowledgment. This work was supported by the Semiconductor Research Corporation (SRC contract 96-LC-460) and the Defense Advanced Research Projects Agency (DARPA contract MDA972-97-1-0010 and DARPA/ETO contract F306602).

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