

Surface Functionalization and Imaging Using Monolayers and Surface-Grafted Polymer Layers

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Abstract: A method of surface functionalization of ceramics with monolayers and surface grafted polymer layers is described. A phenylsilane monolayer is created on the substrate's oxide surface by using phenyltrichlorosilane as the silane coupling agent. To control the formation of the monolayer and ensure the growth of a dense, homogeneous layer, the ceramic surface is first dried and then a controlled amount of water is adsorbed onto it, and a hindered organic base is added to the phenyltrichlorosilane solution to absorb acid generated in the reaction of the silane coupling agent with hydroxyl groups on the ceramic surface. This procedure results in dense homogeneous phenylsilane monolayers on a variety of surfaces, including silicon, Pt/PtO, and quartz. These layers can now be functionalized by addition of triflic acid, which removes the phenyl ring as benzene, and introduction of a nucleophile. Monolayers of $-\text{C}\equiv\text{CH}$, $-\text{OCH}_2\text{CF}_3$, $[(\text{OCH}_2\text{-CH}_2)_2\text{O}]$, $-\text{OCH}_2\text{CF}_2\text{CF}_3$, and $-\text{O}(\text{CH}_2)_6\text{NH}_2$ were generated in this fashion, all proving to be continuous and homogeneous. In addition, the cationic silyl triflate site generated by the removal of the phenyl ring is capable of initiating polymerization to form covalently bound polymer layers on the surface. Polymer layers of poly(methyl methacrylate), poly(propylene oxide), and poly(dimethylsiloxane) were generated in this manner; in the case of poly(dimethylsiloxane), layers up to 300 Å thick were formed. Anionic initiation of polymerization is also possible, using a bromopropyl trichlorosilane coupling agent to form the initial monolayer, followed by lithiation with lithium di-*tert*-butylbiphenyl. Acrylonitrile can be anionically polymerized to films of up to 2450 Å in thickness. The monolayers and polymer layers were characterized by XPS, AFM, contact angle measurements, and profilometry and were found to be continuous. The initial phenylsilane monolayer can be lithographically patterned by using 193 nm light to cleave the surface phenyl groups; the remaining groups can then be functionalized as discussed above to create surface-grafted patterned polymer layers.

Introduction

Modification of solid surfaces by the chemical attachment of monolayers has proven to be an effective and important method for altering the interaction of solids with their environments.¹ Monolayers have been used for the chemical modification of electrodes,^{1c,2} tailoring the chromatographic characteristics of solid supports,³ to act as boundary lubricants and anti-fouling coatings⁴ and to enhance the biocompatibility of a substrate surface.⁵ Further development of this method for the modification of surfaces has led to investigations exploring the use of monolayers as functionalized surfaces such as sensors⁶ or for the immobilization of catalysts and other chemically or optically active species.⁷ Patterned functionalized monolayers have also been produced on surfaces allowing for the ordered attachment of biologically active components.^{6a,8} Other methods for the production of patterned monolayers allow the generation of micron sized features by etching into the substrates⁹ or by the metallization on surfaces.¹⁰

Applications currently being investigated with use of monolayers could be enriched by the covalent attachment of grafted

polymers to surfaces in dense, homogeneous, and continuous arrays or patterns. The thicker polymeric layers would serve as better etch barriers for microlithographic applications, yield better mechanical and chemical protection and surface interactions, alter the chemical and electrical characteristics of the underlying substrates, and provide new pathways to functionalized surfaces for molecular recognition.

However, while both monolayers and grafted polymer layers provide access to improved and tailored properties of surfaces,

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a number of obstacles in producing these surface coverings have been encountered. Only a limited number of substrates are available to which current monolayers can be attached in a simple manner. Organosulfur adsorbates, for example, are only suitable for use with non-oxide transition metal surfaces: the formation of organosulfur SAMs on gold surfaces¹¹ is partially facilitated by the absence of a native oxide layer on the gold surface, which is an otherwise uncommon feature of many metals. Alkyl/aryl trichlorosilanes and trialkoxysilanes (RSiCl₃, RSi(OR')₃) have been shown to be excellent molecules for the formation of monolayers via condensation reactions with substrates that bear a surface layer of hydroxyl groups.¹² Due to the stability of complete monolayers of alkyl/aryl silanes, they are ideal for surface modification and for many applications.^{1a} However, formation of SAMs of organosilicon derivatives has in some cases presented difficulties that are impediments to their practical applications. These include irreproducibility, incomplete coverage of substrates, self-condensation of the silanes in solution, and difficulty in synthesis and purification of many functionalized silanes.^{1a,c,d} Graft polymerization from surfaces suffers from greater difficulties. The attachment of long preformed polymer chains to a surface¹³ is difficult because as the surface becomes covered it is less likely that large molecules can reach the remaining surface sites. Thus only limited coverage may be achieved.¹⁴ Growth of covalently attached polymer layers from a substrate that initiates the polymerization of monomers could overcome this problem, and accomplishments of such polymerizations have been reported.^{13,15} Methods

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for forming on surfaces patterned covalently bound graft-polymeric layers that can act as lithographic etch barriers would eliminate several difficulties encountered with advanced microlithographic techniques such as poor line-edge acuity stemming from the limiting molecular dimensions and compositional inhomogeneities inherent to solution-prepared polymers.

Some of the problems associated both with the formation of silane monolayers and with graft polymerization from solid surfaces are overcome by the surface modification method presented here: functionalization of well-defined phenylsilane monolayers. Phenylsilane monolayers produced under proper conditions yield homogeneous, reproducible, stable monolayers from commercially available, high purity reagents that do not undergo the unfavorable side reactions encountered with other more exotic silane monolayers.^{8a} The phenylsilane monolayers can be formed on a variety of commercially important substrate surfaces such as silicon, glass, metal oxides, and other ceramics, on which a hydroxyl surface layer can be generated. Furthermore, as demonstrated by Calvert and co-workers,^{8a} phenylsilane monolayers can be photopatterned with high resolution, allowing for their use in photolithographic processes. We have reported previously that dearylation of phenylsilyne groups in polysilyne network backbone polymers with trifluoromethanesulfonic acid (triflic acid; HOTf) results in the generation of reactive silyl cation sites on the polymer backbones. These sites react with nucleophiles and suitable monomers to form functionalized polysilynes or graft polymer side chains, respectively.¹⁶ We report here that functionalization of phenylsilane sites on surfaces can be accomplished in a similar manner, and that a variety of ceramic surfaces have been functionalized by this method. We also report growth of patterned graft polymer layers on silicon substrates.

Results and Discussion

Surface Functionalization Method. This approach to the functionalization of solid hydroxyl-terminated surfaces consists of three basic steps (Scheme 1): (1) the formation of a well-defined SAM of phenylsilane at the substrate surface; (2) the dephenylation of this monolayer by reaction with HOTf, which results in the formation of a highly reactive and dense population of Si–OTf surface sites; and (3) reaction of these sites with suitable nucleophiles or monomers to produce a desired monolayer or to initiate graft polymerization from the surface, respectively. By adapting the procedure outlined in Scheme 1, patterned arrays of polymer layers are produced. Irradiation of the phenylsilane monolayer at 193 nm with photolithographic techniques removes the phenyl surface groups leaving a silanol surface;¹⁷ selective functionalization can now be accomplished as outlined in Scheme 2.

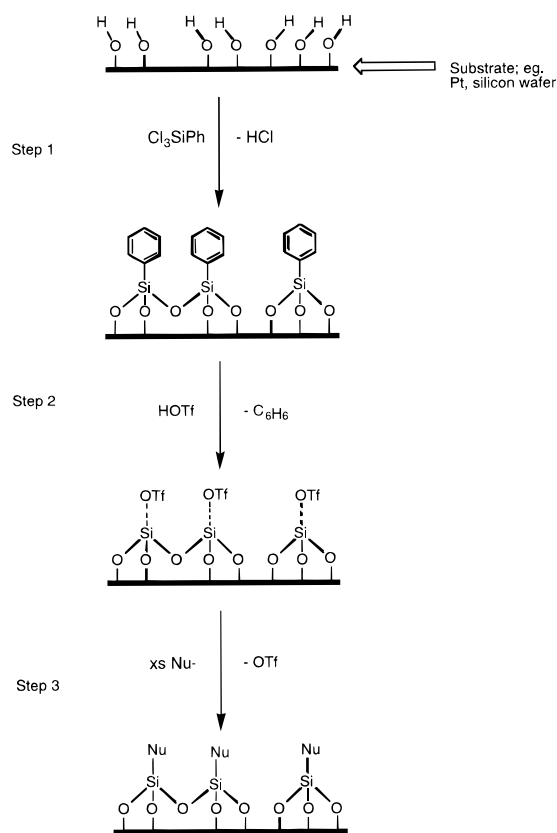
Synthesis and purification of reactive silanes that adhere to substrate surfaces (RSiCl₃ and RSi(OR')₃) are often challenging when R is chemically or electrochemically active, or particularly large. Moreover, functionalized silanes often self-condense, forming species inappropriate for deposition on surfaces.^{1c} Ensuring complete and uniform coverage by functionalized silanes on a substrate surface has proven difficult,^{10c} and

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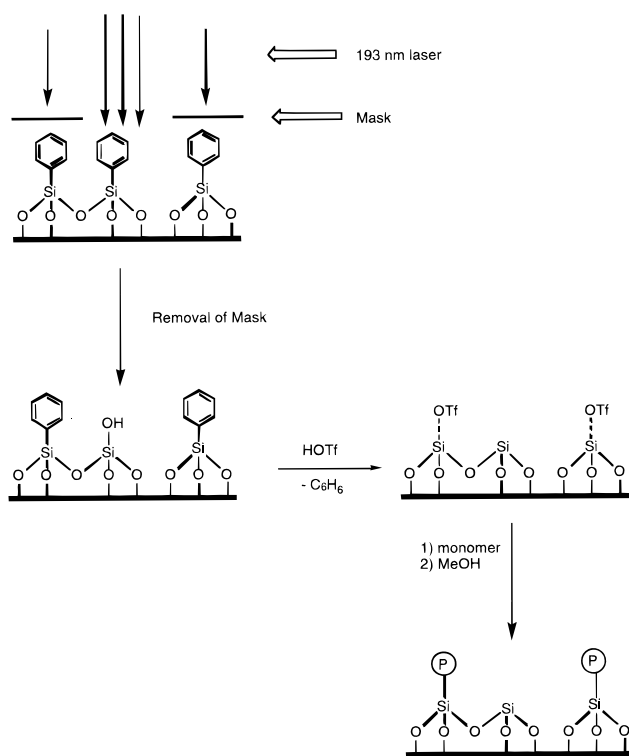
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Scheme 1



Scheme 2



discrepancies within the literature as to the degree of substrate coverage, recently reviewed by Ulman, are common.^{1a,c} The deposition of a phenylsilane layer from PhSiCl_3 does not suffer from any of these difficulties; a dense, uniform, homogeneous monolayer can easily be formed.^{8a} Dearylation of this monolayer by HOTf generates a surface that has a high density of reactive cationic silyl triflate sites. These sites are substitutionally active

Table 1. Contact Angles^a

monolayer/polymer	substrate contact angles (degrees)		
	silicon wafer N (100)	platinum	quartz
native oxide (uncleaned substrate)	49.3	63.9	55.1
OH (after piranha solution treatment)	18.7	20.2	21.0
SiPh	79.0	77.2	80.1
SiCCH	53.4	54.4	55.8
SiOCH ₂ CF ₃	57.6	65.0	67.0
Si(OCH ₂ CH ₂) ₂ O	49.8		48.4
SiOCH ₂ CF ₂ CF ₃	89.5		
SiOCH(CH ₂) ₅ NH ₂	39.2		
Si(OCH ₂ CHCH ₃) _n	55.0–65.0 ^b		
Si(MMA) _n ^c	76.5		
Si(OSiMe ₂) _n	93.3		
Si(CH ₂ CHCN) _n	41.8		

^a All angles measured using distilled water. All values exhibited less than $\pm 5^\circ$ variation between at least five individual samples for each monolayer or polymer. ^b Varied widely between individual samples. ^c MMA = methyl methacrylate.

or serve as initiator sites for the graft polymerization of monomers. The use of this approach allows for the attachment of a wide variety of nucleophilic R groups, thus generating silane monolayers, including those previously inaccessible, without the use of synthetically challenging or unstable $\text{RSi}(\text{OR}')_3$ or RSiCl_3 silanes. Also, since the phenylsilane monolayer can be patterned⁸ leaving a surface that is inactive for initiation of polymerization, patterns of graft polymer layers can be formed.

To form well-defined, defect-free functionalized surfaces by the method outlined above, a dense and uniform phenylsilane monolayer must initially be generated by a reproducible procedure, and therefore a maximally hydroxylated surface must be produced prior to silanization. To this end our standardized hydroxylation procedure for all substrates begins with the oxidation of the substrate surfaces by exposure to boiling piranha solution ($\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$) for at least 30 min.^{5b,7a} Contact angles of surfaces so treated were consistent with uniform $\text{O}_{\text{substrate}}\text{-H}$ layers (Table 1). Significantly, all $\text{O}_{\text{substrate}}\text{-H}$ contact angles are similar to each other regardless of the substrate's identity, suggesting the outer surfaces of these monolayers are identical and that the substrates are therefore completely covered (contact angles: silicon 18.7° ; platinum 20.2° ; quartz 21.0°). Surfaces hydroxylated in this manner and then exposed to a phenyltrichlorosilane/toluene solution for no more than 3 h become covered with uniform and dense phenylsilane films. Both water drop contact angles (Table 1) and ellipsometry data were consistent with the formation of well-defined monolayers (Table 2). The increase in contact angle on silicon from 18.7° after hydroxylation to 79.0° after silanization demonstrates that the hydrophobic $\text{O}_{\text{substrate}}\text{-SiPh}$ layer has replaced the much more hydrophilic hydroxyl layer. That contact angles for the PhSi-layer on silicon varied less than $\pm 2^\circ$ between samples establishes the homogeneity of the monolayer;¹⁸ also, tapping mode AFM shows that the phenyl layers' RMS roughness is 1.7 \AA , indicating complete surface coverage. For the silanized surfaces as for the hydroxylated surfaces, all $\text{O}_{\text{substrate}}\text{-SiPh}$ contact angles for all substrates were similar (contact angles: platinum 77.2° ; quartz 80.1°), indicative of monolayer homogeneity. Analysis of the PhSi surfaces by XPS indicated that all of the substrates have only phenyl rings and no other chemical functionalities at the surfaces (Figure 1a).

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Table 2. Ellipsometry Data for Silicon Substrates^a

surface	thickness ($\pm 3 \text{ \AA}$)
SiO (native) ^b	35
SiOH	21
SiPh	28
SiCCH	12
SiOCH ₂ CF ₃	17
Si(OCH ₂ CH ₂) ₂ O	18
SiOCH ₂ CF ₂ CF ₃	21
SiOCH(CH ₂) ₅ NH ₂	38
Si(OCH ₂ CHCH ₃) _n	16–140 ^c
Si(MMA) _n	11–96 ^c
Si(OSiMe ₂) _n	325 ^d
Si(CH ₂ CHCN) _n	375–2450 ^{d,e}

^a All measurements assume refractive index of $n_D = 1.54$. ^b Untreated wafer. ^c Film thickness varied widely over the sample set. ^d Error estimated at $\pm 20 \text{ \AA}$ (profilometry). ^e 375 \AA thickness obtained from 26 h of reaction; 2450 \AA obtained from 8 days of reaction.

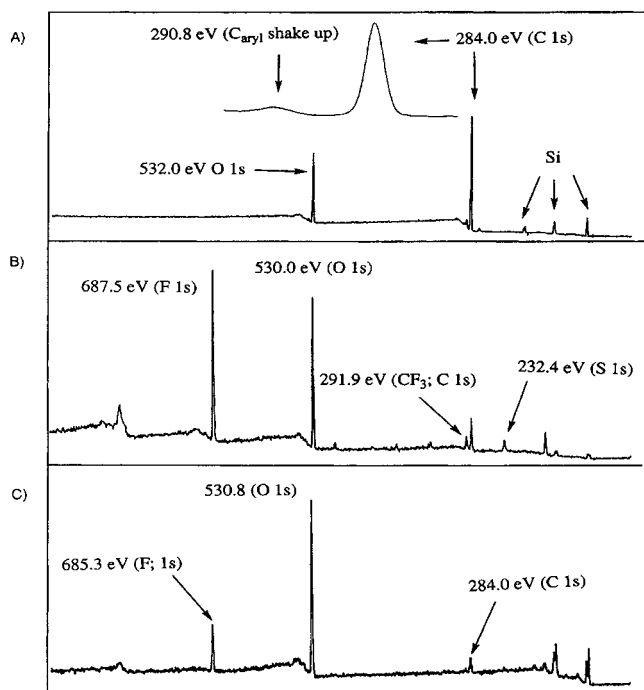


Figure 1. XPS spectra of silicon substrates with monolayers of (A) SiPh, (B) SiOTf, and (C) SiOCH₂CF₂CF₃. Silicon substrates used here all have a native carbon C 1s peak at 284.0 eV, which predictably varies in intensity dependent on which monolayer surface is examined.

Dephenylation of phenylsilane sites in polymers by triflic acid (HOTf) can be extended to phenylsilane monolayers on solid surfaces. After deposition of the PhSi monolayer, the substrates were immersed in 99% HOTf for at least 12 h. Examination by XPS showed only OTf groups on the surfaces, while no observable aryl carbon remained (Figure 1b). Only peaks attributable to Si, O, F, S, and aliphatic C are evident, and the absence of the C_{aryl} $\pi^*-\pi$ peaks previously present for the PhSi monolayer (Figure 1a) indicates that all phenyl groups have been removed. If the triflated surfaces are allowed to stand in air for 30 min and then reexamined, 35% decay of the XPS signal for fluorine is observed, which indicates the hydrolysis of the highly reactive silyl triflate surface sites.

Surface Functionalization with Monolayers. Since phenylsilyne polymers exhibit substitutional behavior with nucleophiles after treatment with HOTf,¹⁶ we studied the reactivity of the triflated ceramic substrates with similar reagents. Under inert atmosphere, reaction substrates bearing a TfOSi– monolayer were placed in rigorously dry solutions of various nucleophiles

(NaC≡CH, NaOCH₂CF₃, Na₂[(OCH₂CH₂)₂O], HOCH₂CF₂CF₃, HO(CH₂)₆NH₂) dissolved or slurried in toluene or THF. After several hours the substrates were rinsed with dry solvents, removed from inert atmosphere conditions, and sonicated in spectroscopic grade methanol. Examination of substrates with use of the sessile water drop contact angle method indicates in each case that contact angle values are consistent with the chemical identity of the proposed monolayer. For example, the diethylene glycol monolayer proved to be mildly hydrophilic (49.8°) while the fluorinated monolayers were more hydrophobic. The fluorinated surfaces on the silicon wafer substrates display differing results dependent on the degree of fluorination. The more C–F bonds closer to the outer surface of the monolayer, the greater the hydrophobicity of the surface. Thus, the pentafluoropropoxide monolayer (CF₃CF₂CH₂O) has a higher contact angle of 89.5° than the trifluoroethoxide monolayer (CF₃CH₂O), with a value of 57.6°. Uniform and dense monolayers were produced on all of the different substrates, since the contact angles of substrates with identical monolayers varied less than $\pm 5^\circ$ (Table 1). For example, all substrates bearing the CF₃CH₂OSi– monolayer have contact angles within 10° of each other, and AFM of these monolayers showed a RMS surface roughness of 5 \AA . In all cases, the XPS spectra show only peaks appropriate to the particular monolayer and indicate complete removal of the triflate ion (OTf). The XPS spectra of the CF₃CF₂CH₂OSi– monolayers (Figures 1c and 2a) display signals for aliphatic C, O, and F. The carbon 1s signal for the CF₃ of the triflate ion (291.9 eV) is gone, as is the sulfur 1s peak (232.4 eV), and new carbon 1s signals appear for CF₂ (286.5 eV) and CF₃ (290.0 eV) groups. These data indicate that, on all substrates, substitution of the surface-bound silyl triflates by the nucleophiles used is quantitative in each case.

The thicknesses of the monolayers deposited on silicon wafers were estimated with use of ellipsometry. Data generated by using ellipsometry are dependent on several parameters that are difficult to assess (e.g., refractive indexes and orientation of monolayers), but certain notable trends in the relative thicknesses can be elucidated.¹⁹ For example, on silicon, the acetylide monolayer at 12 \AA is markedly thinner than the trifluoroethoxide and the diethylene glycol monolayers, at 17 and 18 \AA , respectively²⁰ (Table 2). Also, the latter two monolayers are effectively the same thickness, which would be expected since both are extended the same number of bonds from the surface oxide (Table 2). Finally, the pentafluoropropoxide monolayer, which is slightly longer than the ethoxide and the glycol monolayers, also has a congruent increase in the measured film thickness at 21 \AA . Thus, while the absolute values of the thicknesses of the monolayers are difficult to determine, the increase in thicknesses with increasing chain length is clearly evident.

The method presented for fabricating perhaps otherwise inaccessible monolayers on a variety of substrates is therefore quite general and useful for producing functionalized monolayer surfaces that are chemically homogeneous and physically uniform. Several disadvantages of current methods for producing functionalized monolayers are eliminated, and this method therefore could improve the properties and reliability of the surface characteristics of electrodes, glasses, solid chromatography supports, or other ceramics.²¹ Since a phenylsilyne

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(20) The diethylene glycol monolayer formed from dianion sodium salt, Na₂[(OCH₂CH₂)₂O] would be bound to the surface twice. This surface, which should show increased biocompatibility, should also provide an extra level of structural integrity since each surface molecule is attached twice as opposed to once for the other monolayers.

monolayer can also be generated on metallic surfaces by the deposition of PhSiH_3 ,²² the procedure outlined here could possibly be adapted to tailor surfaces of metals without oxide layers, allowing access to an even wider range of property manipulation.

Surface Functionalization with Grafted Polymer Layers.

Jordan and Ulman have shown that surface-initiated living cationic polymerization can produce dense, homogeneous polymer layers grafted to gold surfaces.^{15c} As was observed with polysilyne network backbone polymers,¹⁶ cationic silyl triflate sites on solid substrates can also initiate polymerization of monomers, generating covalently attached polymer layers grafted to the surfaces. Under inert atmosphere, silicon substrates bearing a TfOSi- monolayer were placed in rigorously dry solutions of various monomers (propylene oxide, methyl methacrylate, hexamethylcyclotrisiloxane [D_3]) dissolved in toluene or THF. After standing for up to 10 days the substrates were rinsed with dry solvents, removed from inert atmosphere conditions, and sonicated in spectroscopic grade methanol. Contact angle measurements indicate that in each case values are consistent with the chemical identity of the proposed polymer layer (Table 1). The poly(dimethylsiloxane) layer is highly hydrophobic (93.3°), while the poly(propylene glycol) layer is less hydrophilic ($55.0\text{--}65.0^\circ$) than the glycol monolayer, consistent with the presence of methyl side groups on the polymer. The range of contact angles found for the poly(propylene glycol) layer arises from the wide range of polymer film thicknesses evolved (see below); poly(methyl methacrylate) contact angles showed similar variation ($76.5\text{--}81.0^\circ$). Contact angles for these polymer layers are consistent with those determined for the bulk polymers.¹⁸

Ellipsometry was again used to estimate thicknesses of the polymer layers grafted on silicon. In all cases, film thicknesses indicated that a grafted polymer layer had formed (Table 2). SIMS of the poly(propylene glycol) layers on silicon confirmed the polymeric nature of the films by the observation of only fragments characteristic for poly(propylene glycol) of up to sixteen repeat units in length.²³ The XPS spectra of these polymer layers exhibited peaks only assignable to C and O (Figure 2b). No peaks characteristic of the substrate were observed, indicating complete coverage of the substrate by a polymer layer of at least 50 \AA thickness. The poly(propylene glycol) and poly(methyl methacrylate) layers showed great variation in film thickness from sample to sample ($16\text{--}140$ and $11\text{--}96 \text{ \AA}$, respectively). This can be attributed to chain-transfer reactions in the case of methyl methacrylate^{15a} confirmed by the formation of free poly(methyl methacrylate) in the reaction solution. Graft polymerization of both organic monomers was found to be very sensitive to trace impurities such as water, and variations in thickness resulted from minimal variations in reaction conditions and reagent purities. However, the graft polymerization of D_3 proved less sensitive to reaction conditions, especially to trace amounts of water, as has been seen in the solution cationic polymerization of D_3 initiated by either triflic acid or trimethylsilyl triflate.²⁴ The graft polymerization of this monomer routinely produced uniform polymer layers (with no

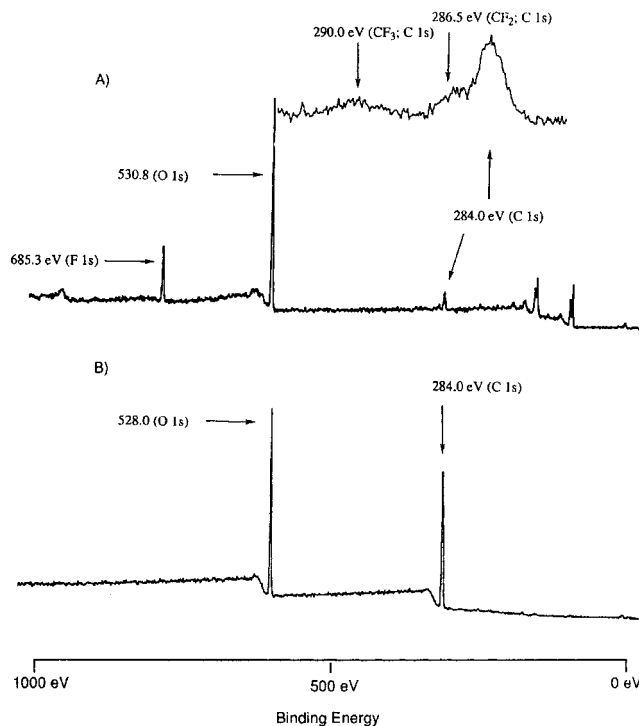


Figure 2. XPS spectra of silicon substrates with monolayers of (A) $\text{SiOCH}_2\text{CF}_2\text{CF}_3$ and (B) $\text{Si}(\text{OCH}_2\text{CHCH}_3)_n$; note the lack of Si substrate peaks in the spectra of the poly(propylene glycol) layer.

significant variance in contact angle) of up to 400 \AA in thickness²⁵ with film thickness increasing with longer reaction time. X-ray photoelectron spectroscopy and contact angle measurements indicate that the polymer films cannot be removed from the substrate by Scotch tape or by prolonged exposure to water, demonstrating stable covalent binding to the surface.

Anionic initiation of polymerization has also been accomplished by generating a lithium di-*tert*-butyl biphenyl or 3-bromopropylsilane monolayer on the substrate in place of the phenylsilane monolayer. This layer is then lithiated with lithium di-*tert*-butylbiphenyl, and subsequent introduction of monomer to this system leads to its anionic polymerization (Scheme 3). The monomer that has initially been investigated is acrylonitrile. Similar to the poly(dimethylsiloxane) cationically initiated system, a dependence of the poly(acrylonitrile) film thicknesses upon the reaction time is seen. If left to react 26 h, visible films of 375 \AA are produced. If left for 8 days, surface-grafted poly(acrylonitrile) films of 2450 \AA are formed, as determined by profilometry. Contact angle data (41.8°) and XPS spectra are consistent with those expected for bulk poly(acrylonitrile).

Because of the wide variety of surfaces that can be silanized by this method, and the wide range of monomers that can be graft polymerized by cationic and anionic initiation, this method should prove very useful in modification of surfaces by grafted polymer films for use in all the applications currently being investigated for monolayers, as discussed above.

Surface Imaging with Grafted Polymers. The extension of conventional photolithographic technology into the nanometer regime has brought with it concerns that fundamental limits of polymer-based resists may soon be reached. Already, studies have shown that polymer dispersivity, molecular weight, and

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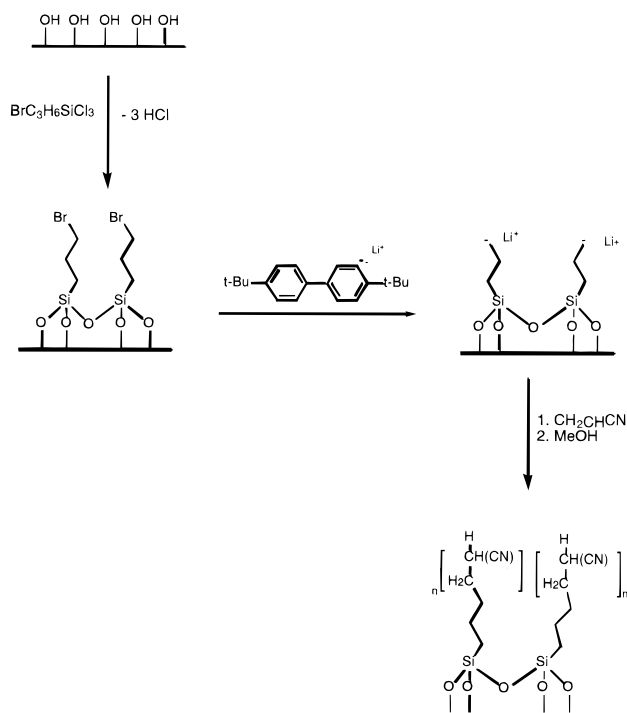
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(25) This value is an underestimate since the refractive index of poly(dimethylsiloxane) is lower ($n = 1.43$) than the value used for ellipsometry measurements ($n = 1.54$). Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; John Wiley and Sons: New York, 1989.

Scheme 3



component interdiffusion²⁶ as well as the actual processing conditions²⁷ effect the edge acuity of the patterned features, often leaving the resultant resist pattern incapable of proper replication of the circuit pattern. This has led to both the investigation of novel polymeric architectures such as calixarenes²⁸ for resist applications and entirely new patterning strategies employing manipulation of self-assembled monolayers.²⁹ In either instance, the goal has been to develop a replication method where spatial control of the latent image is limited to less than a few nanometers. Use of surface-grafted polymers offers another possibility to address this issue, with the added benefits of a richer range of available chemistry (i.e., silicon for added etch resistance and thicker layers up to 30 nm) than available with SAMs.

As seen in Scheme 2, one lithographic application of surface-grafted polymers, selective area growth, begins by patterning a phenylsilane monolayer with 193-nm light through a lithographic mask. Calvert and co-workers have shown that this is an efficient way to cleave Si–R bonds at surfaces, generating an SiOH group.^{8a} In this case, the Si–phenyl bonds are removed in the irradiated areas, leaving a monolayer of reactive Si–phenyl groups in the unexposed regions. Reaction with triflic acid and exposure to a variety of monomers results in growth of grafted polymers in a pattern that is a negative of the lithographic mask. SIMS of such patterned polymer features are shown in Figure 3. This surface imaging procedure could

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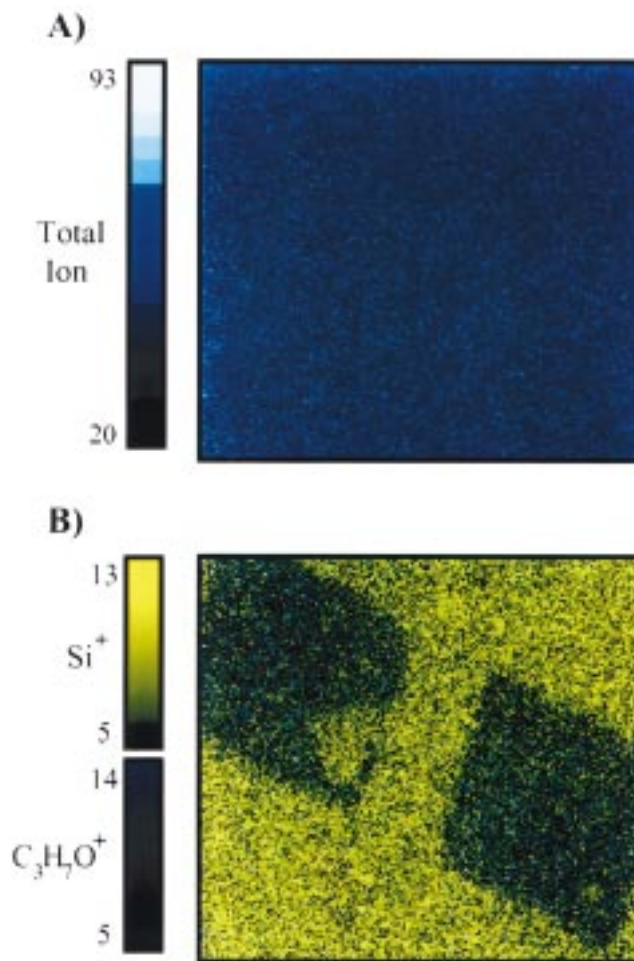


Figure 3. Molecular image of patterned poly(propylene glycol) covalently grafted on silicon. (A) Total positive-ion image of the patterned silicon wafer. (B) Molecular-specific contrast image of silicon at m/z 28 and poly(propylene glycol) base peak at m/z 59. The field of view in both cases is ~ 140 nm.

be thought of as “growing” the already patterned polymer etch barrier off of the surface without the need for a photoresist or a development step. Growth of such patterned polymer layers in good enough thickness would provide good etch barrier characteristics, especially in the case of inorganic-backbone polymers such as polysiloxanes and polymetalloacylsilanes. The ultimate resolution of features that can be obtained with this type of surface imaging and their characteristics as etch barriers remains to be seen. However, this method might have many potential advantages in producing sub-10-nm features. The need for a polymer that displays photoreactivity and sensitivity in the desired wavelength range is eliminated, as is the development step associated with polymeric resists. The polymer that is grafted can be chosen solely on the basis of its etch characteristics and the resolution that it can produce in the etching process and not on its photoreactivity.

Currently, we are investigating the fabrication of features using this surface imaging method, with the goal of determining the limit of resolution it can produce. Theoretically, precisely defined nanostructures could be so constructed, since the surface-imaged polymer features may provide detailing, and therefore resolution, on a molecular scale, not in bulk, as is seen with conventional resists. This possible advantage might make this surface imaging method valuable in ultradeep UV and vacuum UV photolithography, and in electron beam work, where nanometer size features are theoretically obtainable.

Experimental Section

General Procedures. Solvents were distilled from appropriate drying agents under an inert atmosphere. Silicon wafers (N(100) type), platinum, and quartz substrates were cut into approximately 1×1 or 1×3 cm squares. Phenyltrichlorosilane, 30% H_2O_2 , H_2SO_4 , trifluoromethanesulfonic acid, 2,6-di-*tert*-butyl-4-methylpyridine (DBMP), and anhydrous grade methanol were obtained from Aldrich and used as received. Propylene oxide (99+%, Aldrich) and methyl methacrylate (99%, Aldrich) were dried over and distilled from calcium hydride. Toluene, THF, and pentane (Baker-analyzed, VWR) were distilled from sodium/benzophenone ketyl, and toluene was further dried over calcium hydride in the glovebox. Acrylonitrile (99+%, Aldrich) was dried over molecular sieves and distilled prior to use. XPS was carried out with a Hewlett-Packard 5950A ESCA spectrometer. The energy scale was corrected by referencing the C 1s peak associated with a methyl group to 284.0 eV. Ellipsometric thicknesses were measured by using a Gaertner dual-wavelength ellipsometer with a two-wavelength in situ (2GC4A) program. The refractive index used for all monomer and polymer layers was $n = 1.54$. Contact angles were measured with 0.2 mL of distilled water using a Ramé-Hart Inc. NRL C.A. goniometer fitted with an environmental chamber. Ellipsometric thicknesses and contact angles were measured on a minimum of five individual samples for each monolayer or polymer layer. Each individual sample had multiple (3 to 5) measurements done, all of which were within the noted error. Atomic force microscopy was done on a Digital Instruments NanoScope III Atomic Force Microscope instrument in the tapping mode with a silicon tipped probe by Advanced Surface Microscopy Inc. of Indianapolis, Indiana.

The photolithographic exposures were performed with a research-grade ArF excimer laser operating at a wavelength of 193 nm. The fluence was approximately 1 mJ/cm^2 per pulse and the total exposure dose was 200 pulses. The exposure ambient was laboratory air. Under these conditions, no surface heating occurs and only negligible levels of ozone (<1 ppm) are formed, indicating that the transformations occurring on the wafer surface are purely photochemical in origin.

Cleaning of Substrates and Production of Hydroxide Layers. Substrates were cut into squares approximately $1 \text{ cm} \times 1 \text{ cm}$ and $1 \text{ cm} \times 3 \text{ cm}$. Each was then individually soaked in soap and distilled water for 10 min followed by sonication in a Braun 1200 bath for an additional 10 min. Each was then rinsed 3 times with deionized water. The substrates were then immersed in piranha solution (3 parts 30% H_2O_2 :7 parts concentrated H_2SO_4 ; 30 mL total volume) and boiled for at least 30 min and not longer than 1 h. *Note: Piranha solution can explode on contact with organic material and can cause serious injury. All proper precautions should be exercised when using this reagent.* After cooling, the substrates were rinsed two times with 18 M Ω deionized water and then sonicated in spectroscopic grade methanol for 5 min. Substrates were then rinsed three times with spectroscopic grade methanol and dried in an oven at 100°C for 2 h.

Production of Phenyl Monolayers. In an inert atmosphere of nitrogen, each substrate sample individually had 1.6 mL of toluene added along with between 2 and 4 μL of water, and the substrates were allowed to stand at room temperature overnight. The next day, 0.4 mL of phenyltrichlorosilane was added and left to react for between 2.5 and 3 h. Substrates were then rinsed 3 times with toluene, removed from the inert atmosphere, rinsed in spectroscopic grade methanol, and then sonicated in methanol for 1 min. Substrates were dried in the oven at 100°C for a further 2 h and returned to an inert atmosphere.

Triflation Procedure and General Functionalization Procedure. In an atmosphere of nitrogen, each substrate sample was immersed in 99% trifluoromethanesulfonic acid and allowed to stand for up to 4 days. Each was then individually rinsed once in toluene and twice in pentanes and placed into a new vial containing a solution or slurry of the desired nucleophile or monomer in a suitable solvent. After a suitable reaction time, substrates were rinsed with dry THF or toluene, removed from the inert atmosphere, and sonicated for 1 min in methanol and then dried in air.

Si(C \equiv CH) Monolayers. A slurry of $\text{NaC}\equiv\text{CH}$ in THF was added to a triflated substrate generated by the triflation procedure described above. The reaction solution was allowed to stand at room temperature for 24 h, and then rinsed with solvent and sonicated as described in the general functionalization procedure.

SiOCH $_2$ CF $_3$ Monolayers. A 1.5 M solution of $\text{NaOCH}_2\text{CF}_3$ in THF, produced by the reaction of HOCH_2CF_3 with Na metal in THF, was added to a triflated substrate generated by the triflation procedure described above. The reaction solution was allowed to stand at room temperature for 24 h, and then rinsed with solvent and sonicated as described in the general functionalization procedure.

Si(OCH $_2$ CH $_2$) $_2$ O Monolayers. A slurry of $\text{Na}_2[(\text{OCH}_2\text{CH}_2)_2\text{O}]$ in THF was added to a triflated substrate generated by the triflation procedure described above. The reaction solution was allowed to stand at room temperature for 24 h, and then rinsed with solvent and sonicated as described in the general functionalization procedure.

SiOCH $_2$ CF $_2$ CF $_3$ Monolayers. A 1.5 M solution of $\text{HOCH}_2\text{CF}_2\text{CF}_3$ in toluene with 0.0021 mol of di-*tert*-butylmethylpyridine (DBMP) was added to a triflated substrate generated by the triflation procedure described above. The reaction solution was allowed to stand at room temperature for 24 h, and then rinsed with solvent and sonicated as described in the general functionalization procedure.

SiO(CH $_2$) $_6$ NH $_2$ Monolayers. A 2.0 M solution of $\text{HO}(\text{CH}_2)_6\text{NH}_2$ in THF with an equimolar amount of di-*tert*-butylmethylpyridine (DBMP) was added to a triflated substrate generated by the triflation procedure described above. The reaction solution was allowed to stand at room temperature for 24 h, and then rinsed with solvent and sonicated as described in the general functionalization procedure.

Poly(propylene glycol) Layers. Ten milliliters of the 99+% propylene oxide in 5 mL of toluene was added to the triflated substrate generated by the triflation procedure described above. The reaction was allowed to stand at room temperature for 10 days, and then rinsed with solvent and sonicated as described in the general functionalization procedure.

Poly(methyl methacrylate) Layers. Ten milliliters of the 99% methyl methacrylate in 5 mL of toluene was added to triflated substrate generated by the triflation procedure described above. The reaction was allowed to stand at room temperature for 10 days, and then rinsed with solvent and sonicated as described in the general functionalization procedure.

Poly(dimethylsiloxane) Layers. Five milliliters of a 2 M solution of hexamethylcyclotrisiloxane in toluene was added to a triflated substrate generated by the triflation procedure described above. The reaction was left to stand at room temperature for 10 days, rinsed with solvent, and then sonicated as described in the general functionalization procedure.

Poly(acrylonitrile) Layers Produced by Anionic Initiation. The silicon substrates were cleaned, hydroxylated, and dried as stated above. In an inert atmosphere of nitrogen, 1.6 mL of toluene was added to each substrate sample with between 2 and 4 μL of water. After the mixture was left overnight at room temperature, 0.4 mL of 3-bromopropyltrichlorosilane was added, and the substrates were left to react for 2 h. The samples were then rinsed 3 times with toluene, removed from the inert atmosphere, dried in an oven at 100°C for 2 h, and returned to the inert atmosphere. Each sample was immersed in ~ 5 mL of lithium di-*tert*-butyl biphenyl, which was freshly prepared according to the published synthesis.³⁰ The vials were sealed, removed from the inert atmosphere, and immersed in an ice-bath overnight. The next day, the vials were dried and taken back into the inert atmosphere, where the substrate samples were rinsed three times with THF. The samples were placed into fresh vials containing ~ 5 mL of acrylonitrile and 1 drop of 1,4,7,10-tetraoxacyclododecane (12-crown-4). The reaction solutions were allowed to stand for between 1 and 8 days. The substrates were rinsed 3 times with ether and not sonicated.

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