Stepwise Synthesis of a Well-Defined Silicon (Oxide)/ Polyimide Interface

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Self-assembly of 1-bromo-16-(trichlorosilyl)hexadecane leads to highly ordered bromide-terminated monolayer films on silicon (oxide) substrates. The bromides were converted to azides by treatment with sodium azide and then reduced to corresponding amines using lithium aluminum hydride. Protonation of these amine surfaces was difficult to reverse and rendered them unreactive toward electrophiles. The unprotonated form, however, reacted with molten phthalic anhydride to form the corresponding imide. These chemical transformations were characterized by ellipsometry, attenuated total reflectance infrared spectroscopy, contact angle goniometry, and X-ray photoelectron spectroscopy. Spin-coating of a polyamic acid, the precursor of poly-*N*,*N*-(4,4′-oxydiphenylene)pyromellitide, onto the pure amine-terminated surface, followed by curing (up to 350 °C), resulted in covalent linkages between the substrate and the polymeric coating. The success of this curing was confirmed by infrared spectroscopy. Adhesion test results showed that this amine-terminated monolayer enhanced the adhesion of polyimide films to these substrates.

Introduction

In studies focused on adhesion and delamination at silicon (oxide)/polymer interfaces, we have prepared a structurally well-defined system, modeled after the technologically important use of 3-aminopropyltrimethoxysilane (APS) as an adhesion promoter at these interfaces. Although APS has been used successfully in applications such as glass-fiber-reinforced composites,[1−3] polymer−metal adhesion,[4,5] and protection of microelectronics,[6] the mechanism by which it enhances adhesion has been a matter of debate because of the lack of well-defined structure in the siloxane networks derived from this difunctional reagent.[7,8] In principle, hydrolysis and condensation of the silyl group at one end of the molecule could form a quasi-two-dimensional network anchored to the surface of SiO_2 through siloxane linkages, and the amine group at the other end could provide covalent linkages to a polymeric coating. In addition to this mode of bonding, which has been demonstrated for polyimide and model compounds,[9,10] however, the basic amine group can also react with surface silanols by proton transfer and hydrogen bonding as well as participate in the condensation reactions that form the siloxane network and thereby lead to the formation of complex multilayers.[8] Mechanical interlocking, arising from diffusion of polymer chains from a coating into this three-dimensional siloxane network, has also been proposed as a mechanism for enhancing adhesion.[4,11]

Our approach to a well-defined model system involved first forming ordered self-assembled *mono*layers (SAMs) via the reaction of alkyltrichlorosilanes at the surface of a silicon wafer, followed by chemical derivatization of the outermost atoms of the monolayers to produce amine groups. These amine groups were then used to form covalent attachments to a polyimide coating.[9,10] Stepwise chemical synthesis to form amine groups at the surface of such SAMs has been demonstrated by others,[12−16] though preliminary experiments in our laboratories

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indicated that the amines produced by these methods were curiously unreactive toward electrophiles. The lack of reactivity of these SAMs prevented their use as effective coupling agents, so we conducted the present study to solve this problem as well as to provide a more detailed characterization of the surfaces involved than previously reported. Unlike coupling layers formed from APS, these SAMs provide a system free of ambiguity regarding whether adhesion results from interfacial contact and bonding or from mechanical interlocking.

Experimental Section

General. Hexadecane (Fisher Scientific, 99.4%) used in contact-angle measurements was purified by percolation twice through activated alumina. Chloroform (99.8%), *N*,*N*-dimethylformamide (99.94%), sulfuric acid, hydrogen peroxide (30% in water), and toluene (99.5%) were obtained from EM Science and used as received. Alumina (Fisher Scientific), hexanes (Pharmco, 98.5%), hydrochloric acid (J. T. Baker, 36.5%), and undec-10-enyl bromide (Lancaster, 98%) were used as received. 1,5-Dibromopentane (97%), dilithium tetrachlorocuprate (0.1 M solution in THF), hydrogen hexachloroplatinate(IV) hydrate (99.9%), lithium aluminum hydride, phthalic anhydride (99+%), silica gel (70−230 mesh, 60 Å), and $HSiCl_3$ (99%) were obtained from Aldrich and used as received. Diethyl ether (99+%) and tetrahydofuran (99.98%) were obtained from EM Science and were distilled from sodium-benzophenone ketyl before use. A syringe filter with a PTFE membrane, 0.25 μm, was obtained from VWR Scientific. Deuterated chloroform was obtained from Cambridge Isotope Laboratories and used as received. Pyralin PI-2545, 13.5% polyamic acid, pyromellitic dianhydride 4,4′-oxydianiline (PMDA-ODA) in *N*-methyl-2-pyrrolidone (NMP), and the thinner T9093 (NMP) were obtained from DuPont. Silicon wafers were manufactured by Wacker Siltronic and provided by WaferNet, Inc. These wafers were (100)-oriented, p-doped (boron), and 0.50−0.55 mm in thickness. Attenuated total reflectance IR (ATR-IR) crystals (50 mm × 20 mm × 1 mm, 45° silicon prism) were obtained from Spectra-Tech, Inc. All water used in this work was purified with a Milli-Pore Milli-Q system to a resistivity of at least 15 MΩ cm.

Advancing contact angles of water were measured using a Rame-Hart NRL model 100 goniometer. A minimum of six measurements on three independent drops were made for each sample. Infrared spectra were collected using a Perkin-Elmer FT-IR 1600 spectrometer, at a resolution of 2 cm^{-1}. In each case, 1024 scans were averaged to achieve a satisfactory signal-to-noise ratio. Ellipsometric measurements were made using an automatic null ellipsometer (Rudolph Auto-EL III) with a helium−neon laser ($\lambda = 632.8$ nm) set at an incident angle of 70°. Measurements were collected from at least four spots on the samples. Data were analyzed using the manufacturer's program, and calculations of film thickness assumed a refractive index of the monolayer of 1.5. The masses of sufficiently volatile (and hydrolytically stable) products were confirmed using a Hewlett-Packard 5890 Series II Gas Chromatograph, equipped with a Hewlett-Packard 5972 series Mass Selective detector. ^{1}H NMR spectra were acquired using a Bruker AMX 360 spectrometer, referenced to $CHCl_3$ at 7.24 ppm, and are reported in units of δ.

X-ray Photoelectron Spectroscopy (XPS). The XPS spectra in this paper were obtained using a Scienta ESCA-300 spectrometer, equipped with a rotating anode (Al Kα) source producing approximately 6.0 kW of X-ray power, a monochromator, and a 300-mm (diameter) hemispherical analyzer. Spectra were collected at various takeoff angles between the plane of the surface and the detector (as noted), with a slit width of 0.8 mm, and were referenced to the main C 1s peak set at 285.0 eV. The background pressure in the sample chamber was 2×10^{-9} Torr. Survey scans were collected with a pass energy of 75 eV and a step energy of 1.0 eV and took 19 min to complete. High-resolution spectra were collected with a pass energy of 150 eV and a step energy of 0.1 eV. For quantitative analysis, the sensitivity factors used to correct the number of counts under each peak (or envelope) were: C 1s, 1.000; N 1s, 1.620; Br 3d, 2.840. The sensitivity factors for carbon and nitrogen were determined by A. C. Miller with the Scienta ESCA-300 at Lehigh University; that for Br 3d photoemission is the Scofield value.[17]

Bromohexadec-15-ene. This compound was synthesized following a literature procedure[18] and was purified using flash chromatography (hexanes). ^{1}H NMR: $BrCH_2CH_2$, 1.83, (m, 2H); $BrCH_2CH_2(CH_2)_{11}$, 1.24−1.57, (m, 22H); $CH_2{=}CH{-}(CH_2)$, 2.00, (q, 2H); $BrCH_2$, 3.40, (t, $J = 7$ Hz, 2H); $CH{=}CH_2$, 4.88−5.02, (m, 2H); $CH{=}CH_2$, 5.79−5.92, (m, 1H). GC−MS: MW = 302.1 and 304.2 g/mol.

1-Bromo-16-(trichlorosilyl)hexadecane, 1. This silane was synthesized by hydrosilation of 1-bromo-15-hexadecene with trichlorosilane, catalyzed by hydrogen hexachloroplatinate(IV) hydrate, according to a literature procedure,[19] and was purified by Kugelrohr distillation at 150−165 °C and 0.1 Torr. ^{1}H NMR: $Cl_3Si(CH_2)_{14}$, 1.24−1.57, (m, 28H); $BrCH_2CH_2$, 1.83, (m, 2H); $BrCH_2$, 3.40 (t, $J = 7$ Hz, 2H).

Monolayer Preparation. Samples were cut from silicon wafers to an appropriate size (3 cm × 1 cm) and cleaned by heating in a solution of concentrated H_2SO_4 and 30% H_2O_2 (70:30 v/v) at 90 °C for 0.5 h. (*Caution*: *this "piranha" solution reacts violently with many organic materials and should be handled with extreme care*.) The substrates were then rinsed with deionized water and dried with a stream of N_2. Within 15 min of cleaning a wafer, monolayers were formed by immersion into a solution of 1-bromo-16-(trichlorosilyl)hexadecane and/or hexadecyltrichlorosilane in toluene (1 wt %) for 0.5 h at room temperature.[20] After this treatment, the substrates were rinsed with chloroform to remove any residual silane and dried with a stream of N_2.

Azide-Terminated Monolayer. A silicon substrate bearing a bromide-terminated monolayer was immersed in 10 mL of a stirred 0.12 M solution of sodium azide in DMF at room temperature for 48 h. The substrate was then rinsed with deionized water and chloroform and dried with a stream of N_2.

Amine-Terminated Monolayer. Two methods were used for the reduction of azide-terminated SAMs to give amines:[12]

1. A sample bearing an azide-terminated monolayer was placed into 15 mL of a stirred solution of 0.02 M $SnCl_2$ in methanol at room temperature for 4 h, after which it was dipped into 20 mL of 1.2 M aqueous HCl and then rinsed with deionized water and dried with a stream of N_2.

2. A sample bearing an azide-terminated monolayer was immersed in a stirred slurry of $LiAlH_4$ (0.05 M) in dry THF at room temperature for 5 h. The sample was then immersed in 15 mL of 0.5 M aqueous NaOH for 1 min, rinsed with deionized water, and dried with a stream of N_2.

Amidation of Amine-Terminated Monolayer. A silicon substrate bearing a 30% amine-terminated monolayer (70% methyl-terminated) was immersed in 30 mL of a 0.1 M solution of trifluoroacetic anhydride in toluene at room temperature for 16 h and then rinsed with acetone and dried with a stream of N_2.

Phthalimide-Terminated Monolayer. A sample bearing an amine-terminated monolayer was immersed in neat molten phthalic anhydride at 175 °C for 1 h. After cooling slightly (to 160 °C), the sample was removed from the still-molten phthalic anhydride, cooled to near room temperature, rinsed with acetone to remove any residual phthalic anhydride, and dried with a stream of N_2.

Spin-Coating of Polyamic Acid on Amine-Terminated Surfaces. A solution of polyamic acid (DuPont Pyralin PI-2545) in NMP was formed by diluting the original PI-2545 according to guidelines provided by the manufacturer with the thinner TI-9039 (PI-2545/TI-9039 = 8:1, v/v). The solution was filtered

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using 0.25-μm syringe filters to ensure that the solution was free of dust and microgel particles. The diluted PI-2545 was then spun onto an amine-terminated (100%) monolayer for 60 s at 5000 rpm. The coating was cured in a nitrogen atmosphere for the following sequence of temperatures and times: 100 °C/30 min, 150 °C/30 min, 200 °C/1 h, 300 °C/1 h, and 350 °C/15 min.[21] The rate of increase in temperature in each step was about 4−5 °C/min.

Results and Discussion

Synthesis and Characterization of Bromide-Terminated Monolayers. Bromide-terminated siloxane monolayers were prepared on clean silicon wafers (Si/SiO_2) by immersion of the substrate in a (1%, w/w) solution of 1-bromo-16-(trichlorosilyl)hexadecane (**1**) in toluene. The average thickness, determined by ellipsometry, of these monolayers was ~26 Å, consistent with the anticipated length of a *trans*-extended conformation of this absorbate as well as with results reported by others.[22] Attenuated total reflectance (ATR) infrared spectra of a monolayer formed on a silicon ATR crystal revealed C−H stretching bands at 2920 cm^{-1} (ν_a, CH_2) and 2851 cm^{-1} (ν_s, CH_2), indicative of crystalline-like order in the SAM.[23] The advancing contact angles of water on these SAMs, 81−85°, were also consistent with values reported by others.[12−16, 24]

Atomic force microscopic (AFM) images of this surface were generally featureless, with a root-mean-square roughness of 1.5 Å, in agreement with literature values for monolayers formed from *n*-octadecyltrichlorosilane[25] and thus consistent with monolayer formation.[26]

XPS was used to determine the composition of pure and mixed (brominated and unbrominated) monolayers, as well as to follow subsequent functional-group transformations. Figure 1, for example, shows a plot of the mole fraction of bromoalkylsiloxane in pure and mixed monolayers formed by adsorption from solutions containing the bromoalkylsilane (**1**) and the corresponding unbrominated compound, hexadecyltrichlorosilane (**2**). The linearity of these data confirmed that the composition of mixed monolayers mirrored the composition of the solutions from which they were adsorbed, as found by one other group[15] but not by a second.[14] The wetting behavior of these mixed monolayers was roughly linearly related to the mole fractions of the two components on the surface, as predicted by the Cassie equation (eq 1),[27]

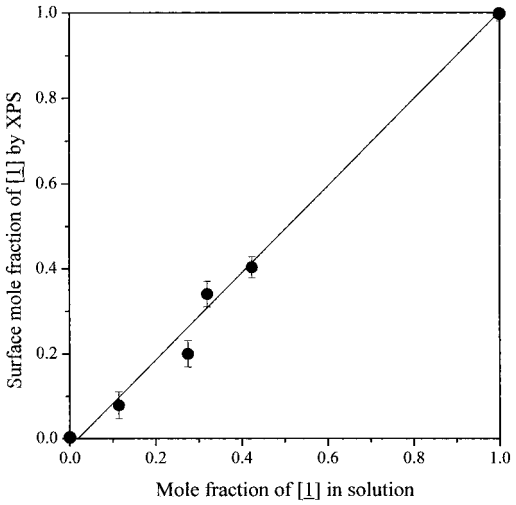

Figure 1. A plot of the mole fraction of brominated adsorbates in SAMs, prepared using pure and mixed solutions of 1-bromo-16-(trichlorosilyl)hexadecane (**1**) and hexadecyltrichlorochlorosilane, versus the mole fraction of brominated precursor in the solutions from which they were adsorbed. The XPS spectra were collected using a takeoff angle of 5°. The error bars indicate the estimated uncertainty in quantifying the bromide 3d photoemission.

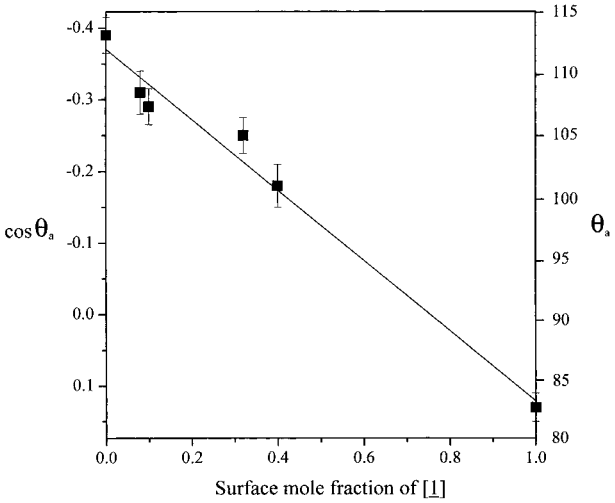

Figure 2. A plot of the cosine of the contact angle of water on mixed (brominated and unbrominated) monolayers versus the mole fraction of brominated silane on the surface, determined by XPS. The error bars indicate the range of values within one standard deviation of the average.

$$\cos\theta = \sum[f_i \cos\theta_i] \qquad (1)$$

where θ is the contact angle on the composite surface, θ_i is that on a pure surface of the ith component, and f_i is the mole fraction of ith component in the composite surface. Figure 2 shows a plot of cos θ versus f_i for the pure and mixed monolayers.

Chemical Derivatization of These Monolayers. A two-step synthetic approach, reported previously by others,[12] was used to convert these surface-bound bromides to the amine groups needed as coupling agents (Scheme 1). Bromide-terminated monolayers were immersed in a stirred 0.12 M solution of sodium azide in DMF for different periods of time and checked by XPS (5° takeoff angle) to assess the extent of conversion. Although this reaction was reported to be complete within 12 h,[12] we found by

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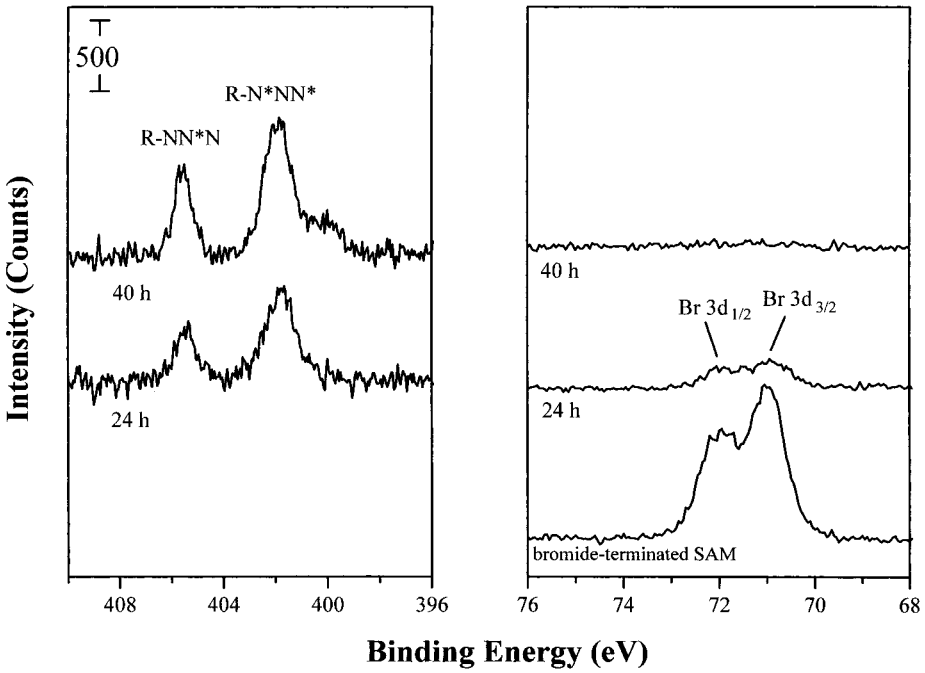
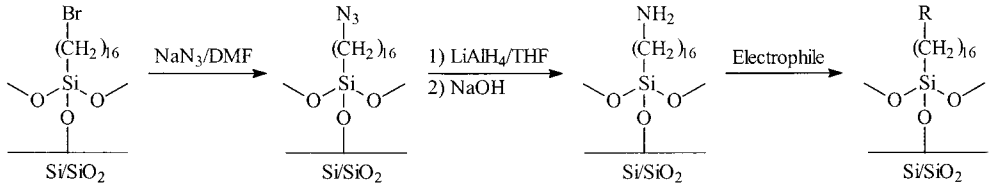


Figure 3. X-ray photoelectron spectra (N 1s, left; Br 3d, right) of a mixed (brominated and unbrominated, 1:2) monolayer treated for 24 and 40 h with NaN_3. A spectrum of the unreacted bromide-terminated monolayer is added for comparison.

Scheme 1. Surface Modification by In Situ Chemistry on Self-Assembled Monolayers



R = phthalimide, trifluoroacetamide, or PMDA-ODA

XPS that a longer time was required. A 40-h immersion resulted in quantitative conversion of the bromide to the corresponding azide by XPS (Figure 3).[16] The appearance of N (1s) photoemission at 402.1 and 405.0 eV and the disappearance of the Br (3d) peak at 71.0 eV confirmed the azidation. The fully azide-terminated monolayer had a contact angle of water of 75−79°. The bromide- and azide-terminated monolayers were very susceptible to X-ray-induced damage during these measurements.[15,28] For example, the intensity of the Br (3d) photoemission decreased by approximately 10% and the N(1s) peaks of the azide-terminated monolayer almost disappeared after a single high-resolution scan. To maximize the reliability of XPS data from these surfaces, the survey and high-resolution scans were collected at different spots on the sample.

Infrared spectroscopy confirmed that the azidation reaction had occurred and that the azide-terminated monolayer was ordered. An ATR-IR spectrum of the product contained a band at 2097 cm^{-1}, assigned to the N_3 asymmetric stretching mode.[29] In addition, the positions and relative intensities of the peaks in the C−H stretching region were the same as those found for the starting monolayer, indicating that the chemical transformation did not disrupt the order of the SAM.

We used two methods previously reported to reduce azide-terminated monolayers to the corresponding amine-terminated monolayers.[12] In our laboratories, treatment with $SnCl_2$ in methanol at room temperature for 4 h gave only partial reduction, as indicated by the continued presence of an azide band in the infrared spectrum of the product. Immersion in $SnCl_2$/methanol for 24 h resulted in partial desorption of the siloxane monolayer, evidenced by decreased peak intensities due to methylene stretching modes and a shift of these peaks to higher frequencies (2923 cm^{-1},ν_a; 2853 cm^{-1}, ν_s), though a weak azide band was still present. An alternative method,[12] using lithium aluminum hydride ($LiAlH_4$) as the reductant, successfully produced the amine surface. The azide-terminated monolayers were immersed in a slurry of $LiAlH_4$ (0.05 M) in dry THF overnight at room temperature, followed by an acidic workup (1.2 M HCl). The substrate was then immersed in triethylamine for 5 h at room temperature in an attempt to deprotonate any ammonium groups at the surface.[12] The near disappearance of the N_3 stretching band in the infrared spectrum indicated that the reduction was successful, and X-ray photoelectron spectra of the product also confirmed the near-quantitative reduction.

(28) For damage to SAMs due to reduction by secondary electrons, see: (a) Tidswell, I. M.; Ocko, B. M.; Pershan, P. S.; Wasserman, S. R.; Whitesides, G. M.; Axe, J. D. *Phys. Rev. B*: *Condens. Matter* **1990**, *41*, 1111−1128. (b) Laibinis, P. E.; Graham, R. L.; Biebuyck, H. A.; Whitesides, G. M. *Science* **1991**, *254*, 981−983. (c) Tidswell, I. M.; Rabedeau, T. A.; Pershan, P. S.; Kosowsky, S. D.; Folkers, J. P.; Whitesides, G. M. *J. Phys. Chem.* **1991**, *95*, 2854−2861. (d) Graham, R. L.; Bain, C. D.; Biebuyck, H. A.; Laibinis, P. E.; Whitesides, G. M. *J. Phys. Chem.* **1993,** *97*, 9456−9464. (e) Rieke, P. C.; Baer, D. R.; Fryxell, G. E.; Engelhard, M. H.; Porter, M. S. *J. Vac. Sci. Technol., A* **1993**, *11*, 2292−2297. (f) Frydman, E.; Cohen, H.; Maoz, R.; Sagiv, J. *Langmuir* **1997**, *13*, 5089−5106.

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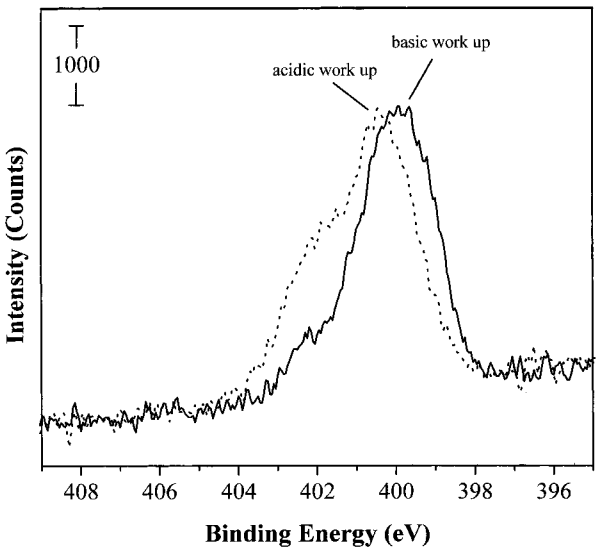

Figure 4. X-ray photoelectron spectra of the N 1s region for mixed monolayers (azide and methyl, 1:2) that had been reduced with $LiAlH_4$ followed by an acidic workup (10% HCl) or by a basic workup (0.5 M NaOH).

The amine-terminated surface produced in this way, however, was surprisingly unreactive toward electrophilies: acetic anhydride, phthalic anhydride, and even trifluoroacetic anhydride.[9,30] For example, treatment of the amine-terminated monolayer with neat acetic anhydride at room temperature overnight, followed by rinsing with acetone and drying with a stream of N_2,[31] did not produce the corresponding acetamide-terminated monolayer, as determined by ATR-IR. Likewise, treatment of the amine surface with a 0.1 M solution of trifluoroacetic anhydride in toluene for 12 h did not produce the corresponding trifluoroacetamide surface.[32]

X-ray photoelectron spectroscopy provided insight into the reason for the lack of reactivity of this surface. A high-resolution spectrum in the N (1s) region of the amine surface revealed an asymmetric envelope containing at least two peaks, at approximately 400.4 eV (assigned as free amine) and 402.2 eV (assigned as protonated amine) in a ratio of about 2:1 (Figure 4).[33] The breadth and position of this photoemission suggested that several different species, such as free amine, hydrogen-bonded amine, and various protonated species, could exist on the surface. Protonation to give ammonium groups could explain the lack of reactivity of these surfaces toward electrophiles. The inability of triethylamine to deprotonate the surface indicates that the amine-terminated SAM behaves like a bi- or polydentate Brønsted base, with corresponding ammonium ions having pK_a values much higher than that of the triethylammonium ion. To avoid the problem of surface protonation, we quenched our $LiAlH_4$ reductions with 0.5 M aqueous NaOH (1 min) instead of 10% HCl. The resulting N (1S) peak in the XPS spectrum of the product was much narrower and at a lower binding energy than that for the acid-treated surface, indicating a much higher concentration of free amine (~90%).

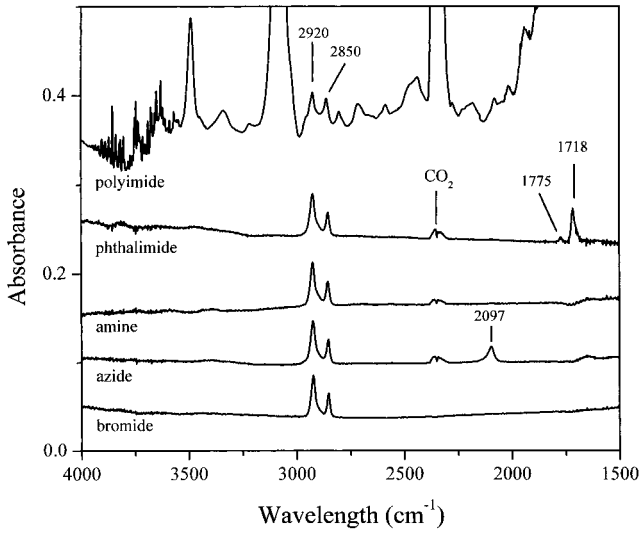

Figure 5. Attenuated total reflectance infrared spectra: (i) a monolayer formed by adsorption of $BrC_{16}H_{32}SiCl_3$, (ii) the same monolayer after azidation, (iii) the monolayer after $LiAlH_4$ reduction of the azide followed by a basic workup, (iv) a phthalimide-terminated monolayer formed by imidation of an amine-terminated monolayer with phthalic anhydride, and (v) a monolayer bearing a polyimide coating.

Consistent with the presence of unprotonated amine on surfaces prepared in this way, the infrared spectrum of a monolayer initially comprising approximately 30% terminal amine and 70% terminal methyl groups and treated with trifluoroacetic anhydride contained a peak at 1685 cm^{-1}, which we attribute to the conversion of the amines to trifluoroacetamide groups.[34] As a model for the type of imidation reaction to be used to attach polyimide chains to the surface, we also examined the reactivity of the surface amines toward phthalic anhydride. The amine-terminated (100% amine) SAM reacted with neat molten phthalic anhydride (170 °C) to form the corresponding imide, though it failed to react under less rigorous conditions (i.e., 0.1 M in acetone at room temperature for 30 min or at 60 °C for 18 h).[10] The conversion of phthalic anhydride to surface-bound phthalimide was confirmed by the appearance of new C═O stretching bands at 1718 cm^{-1} (ν(C═O) antisymmetric) and 1775 cm^{-1} (ν(C═O) symmetric) in the ATR-IR spectrum of the product (Figure 5).[9,10,35] The C−H stretching bands due to methylene groups (2922 cm^{-1}, ν_a; 2853 cm^{-1}, ν_s) shifted to slightly higher frequencies relative to those of the amine precursor, and the intensities of these bands remained unchanged, indicating that though somewhat less ordered, the monolayer remained intact after having been subjected to molten phthalic anhydride (170 °C). The XPS data in Figure 6 also confirmed the success of this imidation reaction; the N (1s) photoemission shifted from 400.0 eV (amine) to 401.1 eV, which is in accordance with the literature value for an imide nitrogen,[21,36] and an ad-

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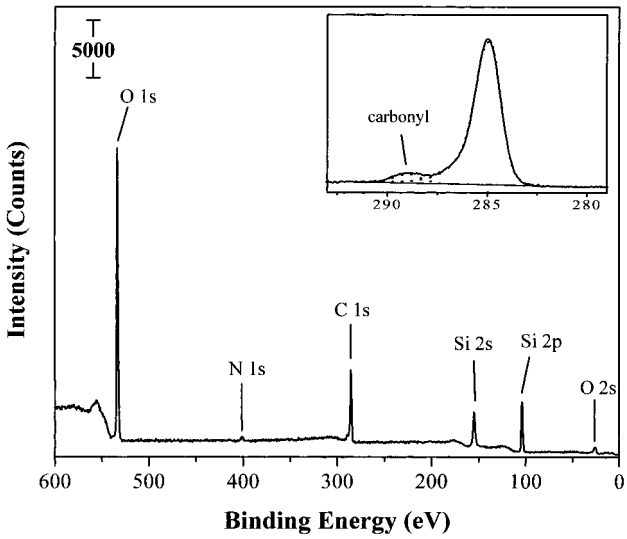

Figure 6. Survey XPS spectrum of a phthalimide-terminated monolayer on Si/SiO_2. The inset shows the high-resolution spectrum of this phthalimide-terminated monolayer in the carbon 1s region.

ditional C (1s) peak appeared at 289.4 eV, consistent with the presence of the carbonyl groups of the imide.[21,36] The yield of phthalimide was high, 85%, based on the ratio of carbonyl C (1s) to N (1s) photoemission.

To extend these studies to adhesion of polyimide, we used spin-coating to treat a 30% amine-terminated (70% methyl-terminated) surface with a solution of a polyamic acid (DuPont Pyralin resins PI-2545 in NMP, 11.1% w/w). The low surface energy of methyl groups on this surface, however, prevented the solution from wetting the monolayer. This solution did, however, wet the 100% amine-terminated surface when treated in the same way. The polyamic acid coating on this surface was cured (up to 350 °C) to produce a thin film of poly-*N*′,*N*′(4,4′-oxydiphenylene)pyromellitimide.[21,36] Upon curing, a new absorption band at 1780 cm^{-1} appeared in the infrared spectrum, consistent with the presence of imide groups (Figure 5).[35] This spectrum also contained a band at 1720 cm^{-1}, consistent with imide groups, though this band is less informative because the polyamic acid also absorbed in this region. Interestingly, this spectrum also contained methylene stretching bands at 2920 and 2850 cm^{-1} (Figure 5), indicating that the monolayer remained intact and ordered.

As a preliminary test of the adhesion in this system, a cured polyimide film prepared in this way was placed into boiling water and monitored for delamination. A second cured polyimide film, supported on a bare silicon wafer, was treated in the same way for comparison. The polyimide film on bare Si/SiO_2 started to delaminate at one corner within 10 h of immersion and completely detached after 12 h. The polyimide film on the monolayer-coated surface remained unchanged after 3 days, and ~70% of the film still remained on the surface after 7 days. The imide linkages between the coating and the monolayer thus appeared to give rise to significantly enhanced adhesion. In a separate experiment, Scotch tape did not remove the polyimide from either type of sample and thus did not differentiate between them.

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Conclusions

We have demonstrated a stepwise synthesis of a well-defined silicon (oxide)/polyimide interface that should prove useful in model studies of adhesion and de-adhesion in this technologically relevant system. A bromide-terminated siloxane monolayer on Si/SiO_2 was first prepared by treatment of the cleaned substrate with 1-bromo-16-(trichlorosilyl)hexadecane, or a mixture containing it, in toluene. Contact-angle measurements and X-ray photoelectron spectroscopy indicated that the surface composition of SAMs adsorbed from mixed solutions of brominated and unbrominated starting materials mirrored their solution compositions.

Bromide-terminated monolayers were converted to azide-terminated SAMs by immersion in a solution of NaN_3 in DMF for 48 h. Reduction of these azides with $LiAlH_4$ produced the desired amine-terminated SAMs. The workup of the reduction reaction was a critical step because protonation of amine groups was difficult to reverse and inhibited subsequent reactivity toward electrophiles. A basic workup yielded a free-amine-terminated monolayer that was reactive toward amidation and imidation; however, vigorous conditions were required for imidation with phthalic anhydride. Nonetheless, imidation with molten phthalic anhydride formed the corresponding imide-terminated surface in high yield without destroying the SAM. The amine-terminated monolayer also allowed covalent attachment to polyimide, by reaction with a polyamic acid followed by curing. Preliminary adhesion testing confirmed the improved adhesion between the polymeric coating and the silicon substrate.

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