Amino-Terminated Organic Monolayers on Hydrogen-Terminated Silicon Surfaces

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A new approach has been developed to prepare amino-terminated monolayers on hydrogen-terminated silicon surfaces. This two-step procedure is the first method that provides direct control over the surface density of the amino groups. First, a mixed monolayer of a protected ω-amino-1-alkene and a nonfunctional 1-alkene is prepared on a H-terminated Si surface, using either phthalimide or acetamide as NH_2-protecting groups. Subsequent removal of the protective groups generates the covalently attached NH_2-terminated monolayer, as evidenced from water contact angle measurements, IR spectroscopy, and X-ray photoelectron spectroscopy. Both protecting groups have their own advantages: use of the phthalimide moiety is synthetically very convenient; the relatively small acetamide moiety can be used to prepare monolayers with high densities (>50%) of amine groups. The reactivity of the amine groups has been confirmed by further modification of the monolayers.

Introduction

Functionalized organic monolayers on solid substrates provide new well-defined means to obtain direct information on biochemical phenomena such as cell adhesion[1] or to develop new types of (bio)sensors.[2] A particularly interesting system is formed by amino-terminated monolayers,[3] which have been used for the binding of biological material such as DNA[3−5] and proteins[6,7] to these monolayers.

Several different routes currently exist for the preparation of amino-functionalized monolayers. Extensive work has been reported on the physisorption of ω-amino thiols on gold surfaces.[6,8] This method has as an advantage that soft lithographic methods such as microcontact printing can be used to obtain precisely defined surfaces.[9] Disadvantages of the method are, however, that the noncovalent Au−S interactions that constitute these monolayers allow for slow but gradual cross-surface diffusion[10] and that these monolayers are relatively easily detached from the Au surface at elevated temperatures.[11] Therefore, there is a growing interest in covalently attached NH_2-terminated monolayers. The first published procedure to obtain such monolayers uses the reaction of ω-amino trialkoxysilanes with oxidized silicon surfaces.[12−14] Although these monolayers are more stable, the resulting Si−O−Si bonds that link the monolayer to the surface are thermally still rather labile[15] and susceptible to hydrolysis. In addition, if well-defined monolayers are to be prepared, the direct use of amino compounds is not possible, as the reactivity of the amino group with the alkoxy groups of the silane derivative results in disordered layers[12,13] or multilayers.[14] This latter problem has been circumvented by the interconversion of functionalized groups into amino groups.[16,17]

Strong covalent Si−C bonds form the basis of covalently bound monolayers of 1-alkenes on H-terminated Si surfaces. These monolayers have been investigated extensively both experimentally[18−26] and theoretically.[27]

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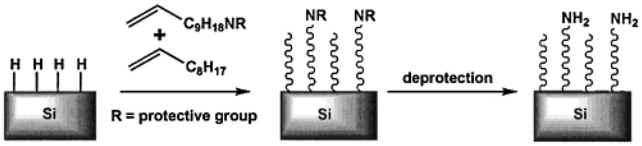

Figure 1. Schematic representation of the procedure developed for the preparation of the amino-terminated monolayers.

They display thermal stability in organic solvents at elevated temperatures,[18,19] do not easily hydrolyze under both acidic and slightly basic conditions (pH range of 0−10),[18,19,23,24] can be modified in both polar and nonpolar solvents using standard reactions from organic chemistry,[19,23,24] and can be prepared in nanometer-scale lines via a self-assembly procedure.[25] The preparation of such organic monolayers in which a fraction of the alkyl chains was terminated by an amino group has been reported.[3] In this procedure, the terminal methyl groups of an alkyl monolayer were chlorosulfonylated by the use of Cl_2 and SO_2, followed by a reaction with 1,2-diaminoethane. Although the resulting layer does contain amino groups that are capable of reacting selectively with DNA,[3] the relatively harsh reaction conditions and the difficulties involved in obtaining control over the precise composition of the monolayer (percent of NH_2 groups on the surface) stimulated the development of new procedures.

In this paper, the first two-step route is described that allows for variation of the surface density of amino groups in the NH_2-terminated monolayers. Mixed monolayers are prepared in a convenient fashion by the reaction of a mixture of a NH_2-protected ω-amino-1-alkene and an underivatized 1-alkene with H-terminated Si(100) surfaces, followed by deprotection reactions that generate the free amino groups (Figure 1). The use of NH_2-protecting groups is required to prevent the direct reaction of amino groups with the Si surface,[28] which results in disordered monolayers.[19] In this new approach, direct control over the density of the amino groups on the surface can be obtained, as demonstrated by the preparation of mixed monolayers of the amino-functionalized compound with 1-decene (**C10**). Two synthetic routes are explored. One route makes use of the Ing−Manske modification of the Gabriel synthesis of amines, i.e., a reaction of phthalimide groups with hydrazine.[29] Such a route has been attempted for monolayers of alkylsilanes; however, only disordered monolayers were obtained in that case.[13] The other route involves acidic hydrolysis of acetamide groups.

Experimental Section

General Information. C10 (>97%, Fluka) was distilled in vacuo and stored at −20 °C. *N*-(ω-Undecylenyl)phthalimide (**I**) was recrystallized from distilled methanol, and *N*-(ω-undecylenyl)acetamide (**II**) was used without further purification. The purified compounds **I** and **II** were stored at room temperature under vacuum. Mesitylene (Fluka, 99%) was distilled at atmospheric pressure and stored on $CaCl_2$. Hydrazine monohydrate[30] (99%) was obtained from Acros. Trifluoroacetic anhydride (99+%) was obtained from Aldrich. All glassware for distillations, recrystallizations, and monolayer preparations was cleaned with distilled solvents only. All other details have been described previously.[19,22,26]

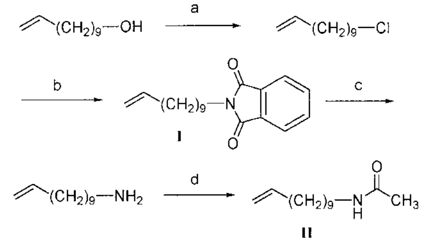

Figure 2. Synthesis of the protected amine derivatives **I** and **II**: (a) $(C_6H_5)_3P$, CCl_4, CH_3CN, reflux, 24 h; (b) potassium phthalimide, DMF, 90 °C, 24 h; (c) $NH_2NH_2{\cdot}H_2O$, ethanol, reflux, 3 h; (d) acetic anhydride, reflux, 10 min, followed by chromatography.

Synthesis of the Functionalized Alkenes. The protected 1-amino-10-undecene derivatives **I** and **II** were synthesized by the route depicted in Figure 2. Details of the syntheses, the analytical data, and the purification procedures for **I** and **II** are given in the Supporting Information.

Monolayer Preparation and Characterization. For the water contact angle measurements, the monolayers were prepared by the following procedure.[26] In a small, three-necked flask fitted with a nitrogen inlet, a thermometer, and a reflux condenser with a $CaCl_2$ tube was placed 10 mL of a solution of the mixture of the 1-alkenes in mesitylene. The total concentration of the 1-alkenes was 0.2 M. The solution was deoxygenated with dry nitrogen for at least 1 h. Subsequently, a piece of double-polished silicon was etched in 2.5% HF for 2 min and immediately placed in the solution. The flask was immersed in an oil bath of 210 °C and refluxed for 2 h, while maintaining a slow N_2 flow. Subsequently, the sample was removed from the solution and cleaned in petroleum ether (40−60 °C), methanol, and dichloromethane.

The water contact angle measurements were measured as described previously.[26] All samples were prepared in triplicate. The samples for the X-ray photoelectron spectroscopy (XPS) measurements were prepared by the same procedure on pieces (~1 cm^2) of single-polished p-type Si(100) wafers (float zone quality, 1−2 Ω cm). The attenuated total reflection (ATR) crystals for the IR measurements were modified and investigated as described in ref 26.

The XPS measurements were performed in a VG-ESCALAB 200 system with a background pressure of 5×10^{-10} mbar using an aluminum anode (Al Kα = 1486.3 eV) operating at 510 W. All binding energies are referenced to metallic Si(2p) at 99.3 eV, and intensities are normalized to the total Si(2p) peak area. The takeoff angle was 45°.

Modification of the Monolayers. Monolayer modifications with hydrazine were performed in closed flasks. The samples were placed in a 5% solution (v/v) of hydrazine in distilled ethanol, and the solution was stirred at room temperature for 40−48 h. Subsequently, the samples were removed from the solution and cleaned as usual.

Monolayer modifications with 4 M HCl were carried out as described previously for the hydrolysis of the ester-terminated monolayers.[19] A reaction time of 20−24 h was used. After the reaction, the substrates were rinsed repeatedly in large portions of water. The same setup was used for the reactions with trifluoroacetic anhydride.

Results and Discussion

Water Contact Angle Measurements and IR Spectroscopy. Monolayers with different surface densities of the amino groups can be prepared by using mixtures of

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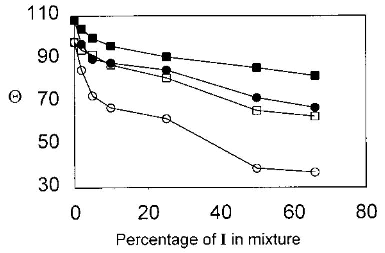

Figure 3. Advancing and receding water contact angles (Θ_a and Θ_r, respectively) of the mixed monolayers of **C10** and **I** before (closed symbols) and after (open symbols) reaction with hydrazine. Advancing angles, squares; receding angles, circles.

the protected amine derivative and an underivatized 1-alkene in the surface modification. As there will be no significant difference in the reactivity of the alkene moieties of the two compounds, both alkenes will react with the H-terminated Si surface. Consequently, it is expected that a monolayer will be formed in which both alkenes are incorporated.

The molar ratio of the two alkenes was varied from **C10/I** = 1:2 to 49:1.[31] The results of water contact angle measurements on the mixed monolayers are shown in Figure 3. From this figure, it is clear that the water contact angles of the monolayers are a function of this ratio: a decrease of the relative amount of **I**, which contains a polar, hydrophilic phthalimide group, results in an increase of the water contact angles, and at low concentrations of **I**, the water contact angles approach the values for a monolayer of neat **C10** ($\Theta_a = 108°$, $\Theta_r = 98°$). In addition, the hysteresis of these monolayers is small ($\leq$10°). This behavior has been found previously for mixed monolayers.[12,17] It clearly shows that both 1-alkenes react with the Si surface and that their ratio in the monolayer depends on the molar ratio in solution.

The incorporation of a higher percentage of **I** in the monolayer decreases the contact angles. An increase in the contact angle hysteresis is observed as well, especially for the monolayers with relatively large percentages of **I** (i.e., for the **C10/I** ratios of 1:2 and 1:1). This effect has previously been reported for similar mixed monolayers on oxidized silicon,[13] where it was attributed to the formation of less ordered monolayers upon increase of the relative amount of phthalimide groups. In the present investigations, it was found that for the monolayers with **C10/I** ratios of 1:1 and 1:2 the contact angles also decrease by several degrees ($\geq$4°) during the measurement, which indicates the adsorption of water on these monolayers with many relatively polar phthalimide groups. The contact angles of monolayers with relatively high **C10/I** ratios (from 3:1 up to 49:1) were stable. Water adsorption will lead to an increase in the polarity of the surface and, thus, to a decrease in the contact angles during the measurement. This means that it is not possible to draw any conclusion about the packing density of these monolayers with high percentages of **I** from the contact angle measurements.

N-Alkylphthalimide derivatives can be converted into amines using the Ing−Manske modification of the Gabriel reaction (see step c in Figure 2).[32] Thus, the mixed monolayers were reacted with a 5% solution of hydrazine in ethanol at room temperature for 40−48 h.[33] This results in a decrease in the water contact angles (Figure 3), which indicates the removal of the phthalimide groups and the emergence of hydrophilic NH_2 groups.[17] In monolayers with a high **C10/I** ratio, this decrease is small as expected, whereas it is much larger if relatively large percentages of **I** are present. For these latter layers (percentage NH_2 groups = 50 or 66%), the contact angles approach those of monolayers that are fully terminated with NH_2 groups ($\Theta_a = 63−68°$, $\Theta_r = 42°$).[16,17] No changes in the water contact angles of the monolayers occurred if the mixed monolayers were placed in ethanol for the same period or when a monolayer of only **C10** was reacted with the hydrazine solution. This indicates that the covalent Si−C linking of the monolayers to the Si surface is not damaged under the reaction conditions and that the change in the contact angles is due to a reaction of the phthalimide groups of **I** with hydrazine. Longer reaction times (up to a week) did not result in a further decrease of the contact angles, which indicates that the reaction is apparently complete after 2 days. It also confirms that the monolayers are stable under the reaction conditions.

Further evidence for the conversion of the phthalimide groups into amino groups was obtained from IR spectroscopy. A 1:1 monolayer of **C10** and **I** was prepared on an ATR crystal and measured before and after the reaction with the hydrazine solution. The results are shown in Figure 4. The C=O vibration from the phthalimide groups is clearly visible at 1717 cm^{-1} in the spectrum of the as-prepared monolayer (Figure 4a). The maxima of the methylene C−H stretching vibrations are visible at 2925 and 2853 cm^{-1}, values that are somewhat higher than those of a monolayer of **C10** (2923 and 2853 cm^{-1}). This indicates that this 1:1 monolayer of **C10** and **I** is not as ordered as those of neat 1-alkenes,[18,19] which is most likely due to steric hindrance between the phthalimide groups, an effect that has previously been found for similar monolayers on oxidized silicon.[13] The monolayers with higher **C10/I** ratios all showed a better ordering according to IR spectroscopy (maxima at 2922 and 2852 cm^{-1}, respectively); however, in these layers, the C=O vibration is not clearly discernible.

After the monolayer reacted with the hydrazine solution, the C=O vibration disappeared completely (Figure 4b). This confirms that the phthalimide groups have been removed by conversion into amine groups. The peaks for the methylene vibrations did not change, which shows that the ordering in the monolayer is not significantly affected and that molecules are not removed from the surface. No changes in the C=O or the C−H vibrations occurred in any of the control experiments mentioned above. This shows that the reaction of these mixed monolayers of **C10** and **I** with the hydrazine solution generates amino-terminated monolayers.

A second method for the preparation of amino-terminated monolayers on Si surfaces involves the use of **II**. Mixed monolayers of this compound and **C10** were prepared (**C10/II** ratios of 9:1, 3:1, and 1:1), and the same relation between the water contact angles and the percentage of **II** was found as observed for mixed monolayers of **C10** and **I**. This was also confirmed by a Cassie plot, which is for both **I** and **II** linear from the 5% solutions onward, both before and after the hydrolysis reaction (see the Supporting Information).

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(31) Pure **I** was also tried but gave highly irreproducible results.

(32) March, J. *Advanced Organic Chemistry*, 4th ed.; J. Wiley and Sons: New York, 1992; pp 425−426.

(33) Shorter reaction times (16 and 24 h) gave smaller changes in the water contact angles, which suggests that there were still phthalimide groups present, as they are more hydrophobic than amino groups. The 16 h sample indeed still showed a small C=O peak in the IR spectrum. Much longer reaction times (up to 7 days) did not give a further decrease in the contact angles. These results indicate that this reaction time of 40−48 h is required for complete removal of the phthalimide groups. Heating the solution, to speed up the reaction, seemed to cause some damage to the edges of the Si substrate. At room temperature, no damage to these edges occurs.

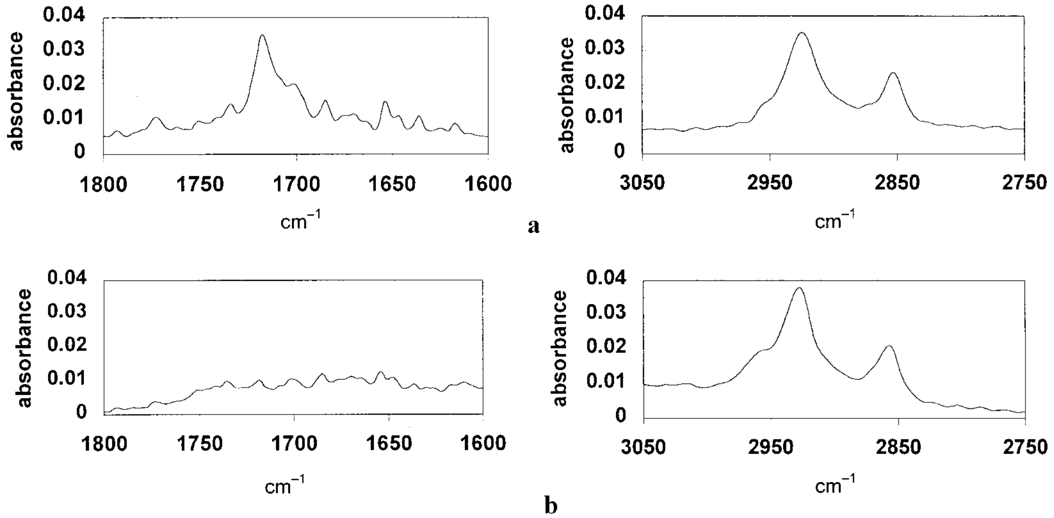

Figure 4. IR spectra (C=O and C−H regions) of a 1:1 monolayer of **C10** and **I** before (a) and after (b) reaction with hydrazine.

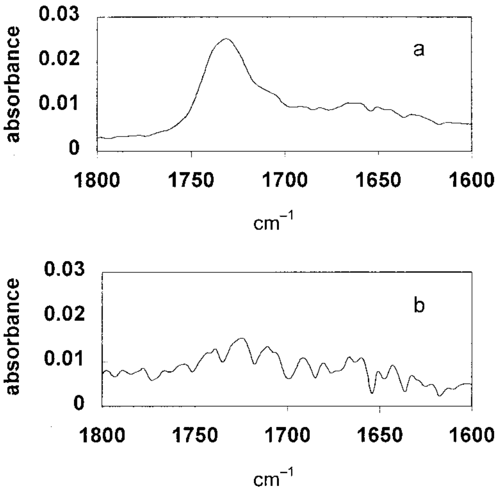

Figure 5. IR spectra (C=O regions) of a 1:1 monolayer of **C10** and **II** before (a) and after (b) acidic hydrolysis.

Reaction of the **C10/II** monolayers (9:1 and 3:1 ratios only) with refluxing 4 M HCl for 20 h resulted in a considerable decrease of the water contact angles.[34] The 9:1 monolayer gave a change from $\Theta_a/\Theta_r = 93/70°$ to 85/55°; for the 3:1 monolayer, the change was even larger, from $\Theta_a/\Theta_r = 87/62°$ to 58/27°. Amide groups can be hydrolyzed under strongly acidic conditions, which generates a monolayer with NH_3^+ groups on the surface. These groups are more polar than NH_2 groups, and thus, these NH_3^+-terminated monolayers give lower water contact angles.[16] Control experiments showed that monolayers of **C10** are not affected in any noticeable way (contact angle measurements and IR spectroscopy) under these conditions.

IR spectroscopy confirmed that the expected modification had indeed occurred. Figure 5a shows the C=O region of a 1:1 monolayer of **C10** and **II**. The C=O vibration from the amide group is visible at 1734 cm^{-1}. After the hydrolysis, this peak has disappeared completely (Figure 5b), which indicates that all acetamide groups have been converted to NH_3^+ groups (themselves not discernible due to low intensity and water absorption). The vibrations from the methylene groups showed maxima at 2923 and 2853 cm^{-1}, which suggest that this monolayer is more ordered than the corresponding mixed monolayer of **C10** and **I**. Acetamide groups are smaller than phthalimide groups, and thus, the formation of ω-amino-protected monolayers with a higher degree of ordering is easier at high concentrations of the functionalized 1-alkene than in the case of phthalimide-protected NH_2 groups. In agreement with this, ordered monolayers terminated with acetate groups, a functional group that has similar dimensions as an acetamide group, have already been reported.[19] No significant changes in either the position or the intensity of the methylene vibrations were observed after the reaction. Thus, mixed monolayers of **C10** and **II** can be prepared and the acetamide groups in these monolayers can be converted into amine groups by a reaction with boiling HCl.

XPS Measurements. Direct detection of the amino groups in the monolayers is troublesome with IR spectroscopy because of hydrogen bonding to adsorbed water and slight ice formation on the liquid nitrogen-cooled mercury cadmium telluride detector. Therefore, the monolayers were investigated with XPS[2,18,35,36] to prove the presence of the NH_2 groups in these monolayers.

The phthalimide monolayers with a **C10/I** ratio of 1:1 were used for this purpose. In these substrates, small amounts of silicon dioxide are always observed with XPS because this monolayer is not densely packed, due to the high concentration of the relatively bulky protecting groups (vide supra). Therefore, the monolayer will have defects, which means that the oxidation of the underlying silicon surface is not well-inhibited. The wide scan spectra of the various monolayers show clear peaks from Si, C, and O. In general, the peaks from nitrogen are small due to the still relatively low concentration of this element at the surface, but the spectra with longer accumulation time clearly show the presence of nitrogen in these **C10/I** = 1:1 monolayers.

No nitrogen is detectable in the spectrum of a monolayer prepared analogously from neat **C10** (Figure 6a), which means that any nitrogen atoms detected in the mixed

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(34) Reaction times of only a few (2−5) hours seemed insufficient to completely remove the acetamide groups (contact angle measurements). A reaction time of 40 h gave contact angles that were comparable to the 20 h samples: they differed by only 1−2°, which is within the experimental error. Only minor changes in the water contact angles of the acetamide-terminated monolayers (decrease of ~5°) were observed if 1 M HCl was used.

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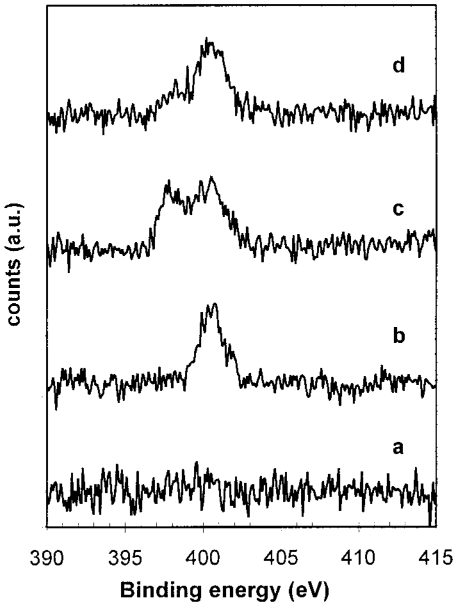

Figure 6. (a) XPS spectrum (nitrogen region) of a monolayer of **C10**. (b) XPS spectrum (nitrogen region) of a monolayer of **C10/I** (ratio 1:1). (c) XPS spectrum (nitrogen region) of a monolayer of **C10/I** (ratio 1:1), after reaction with hydrazine. (d) XPS spectrum (nitrogen region) of a monolayer of **C10/I** (ratio 1:1), after storage in HCl.

monolayers must come from the protected amine derivative. The spectrum of the as-prepared monolayer is shown in Figure 6b. A clear peak from nitrogen is visible at ~400.6 eV, which shows that the nitrogen-containing molecules of **I** have been incorporated in the monolayer. The measured N(1s) core level binding energy is in excellent agreement with a reference value of ~400.5 eV found for imides.[37] After reaction with hydrazine, nitrogen remains in the monolayer (Figure 6c), resulting in two peaks at ~398.2 and ~400.7 eV. The relative intensity of the high energy component is almost the same (>90%) as the 400.6 eV peak in spectrum 6b. The intensity of the low energy peak is about 65% of the high energy peak, but the relative intensity of this peak showed considerable variation from sample to sample.

Most nitrogen-containing functional groups in organic compounds give very similar N(1s) binding energies in the range of 399.0−400.0 eV,[37] including amine, amide, nitrile, urea, and nitrogen in aromatic rings. Thus, both peaks in Figure 6c are observed outside the typical N(1s) binding energies of nitrogen in organic compounds. The observed disappearance of the C=O vibration (see Figure 4) confirms that the phthalimide groups have been converted, while the XPS measurements show that nitrogen remains in the organic layer. Consequently, it seems reasonable to assume that the phthalimide groups have been converted into amino groups by reaction with hydrazine. Therefore, the peak at 400.7 eV is assigned to nitrogen in the amino groups. The comparatively high binding energy could indicate partially positively charged quaternary nitrogen, as $-NH_3^+$ is reported in a range of ~401.5−402.5 eV.[37] The unusually low binding energy of the peak at 398.2 eV must then be related to an unknown nitrogen-containing byproduct or contamination left on the sample surface under the applied reaction conditions. This interpretation is assisted by observations in the spectrum of a monolayer that was stored in 1 M HCl for 1 h sample (Figure 6d). This results in a pronounced decrease of the 398.2 eV peak, while the intensity of the 400.6 eV peak remains unaffected, evidence of the removal of the unknown nitrogen species upon this treatment. The intensity of the 400.6 eV peak is again comparable to that of nitrogen in the phthalimide-protected monolayer of Figure 6b. This provides further evidence for the stability of the monolayers under the reaction conditions used for the conversion of the phthalimide groups into amino groups, because otherwise the peak arising from nitrogen in the monolayer would no longer be visible or would have considerably decreased in intensity.

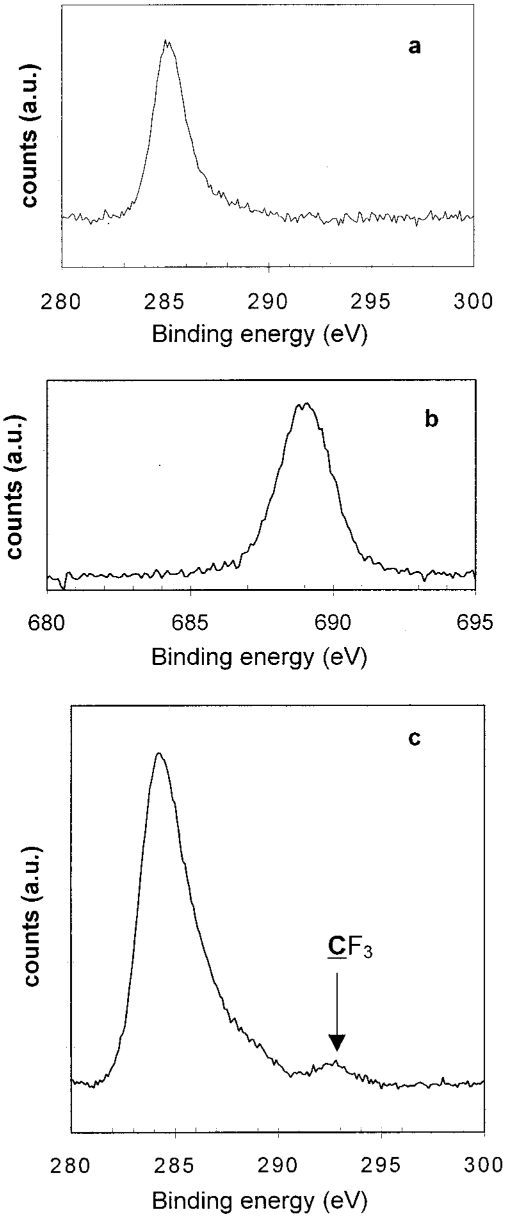

Figure 7. (a) XPS spectrum (carbon region) of an amino-terminated monolayer (from Figure 6c). (b) XPS spectrum (fluorine region) of the trifluroacetamide-terminated monolayer. (c) Same as panel b, the carbon region, showing the appearance of the CF_3 group.

Further modification of the amino-functionalized monolayer is interesting for the development of, for example, (bio)sensors, as was already discussed in the Introduction. The reactivity of the resulting amino group was demonstrated using a subsequent acetylation reaction with trifluoroacetic anhydride (reflux conditions). The resulting CF_3 groups in the monolayer can easily be detected by XPS. In the C(1s) region of the amino-terminated mono-

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[37] Briggs, D. *Surface Analyses of Polymers by XPS and Static SIMS*; Cambridge University Press: Cambridge, 1998; pp 47−73.

layer, there are no peaks above 290 eV. (Figure 7a). In Figure 7b,c, the results are shown of the XPS measurements on a monolayer that was reacted with trifluoroacetic anhydride for 20 h. A clear peak from fluorine is visible in the XPS spectrum at 689.1 eV (F(1s); Figure 7b), and a small peak at about 293 eV has appeared in the C(1s) region (Figure 7c), which arises from the CF_3 groups in the monolayer. These results show that our procedure indeed generates amino-terminated monolayers that can also be further modified.

The availability of such NH_2-terminated covalent monolayers opens up the possibility to attach bioactive materials to an accurately specifiable degree to these monolayers.[38] It would specifically be interesting to investigate the use of other combinations of alkenes, e.g., combinations that will allow for the immobilization of DNA or proteins at specific sites while hampering aspecific adsorption at the rest of the monolayer,[1] or to further develop thermal[25] and photochemical[39] routes that can be used in surface patterning. Such investigations are currently underway in our laboratories.

Conclusions

Two new routes have been developed for the preparation of amino-functionalized monolayers on H-terminated Si surfaces. Both routes are based on a two-step procedure in which a mixed monolayer is prepared of a protected ω-amino-1-alkene and a nonfunctional 1-alkene is prepared. Subsequent removal of the protective groups then generates the covalently attached NH_2-terminated monolayer without damaging the underlying Si surface or the monolayer composition, as evidenced from water contact angle measurements, IR spectroscopy, and XPS. As protecting groups, phthalimide groups and acetamide groups have been used. The phthalimide groups were removed by a reaction with hydrazine, and the acetamide groups were removed by hydrolysis under strongly acidic conditions. Both protecting groups have their own advantages: use of the phthalimide moiety is synthetically very convenient; the relatively small acetamide moiety can be used to prepare monolayers with high densities (>50%) of amine groups. The reactivity of the amine groups has been confirmed by further modification of the monolayers.

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Supporting Information Available: Details of the syntheses, analytical data, and purification procedures of compounds **I** and **II**. Cassie plot of the binary surfaces of **I** and **II** with **C10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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