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Photochemical Covalent Attachment of Alkene-Derived Monolayers onto Hydroxyl-Terminated Silica

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The functionalization of optically transparent substrates is of importance, for example, in the field of biosensing. In this article, a new method for modification of silica surfaces is presented that is based on a photochemical reaction of terminal alkenes with the surface. This yields highly hydrophobic surfaces, which are thermally stable up to at least 400 °C. The formed monolayer provides chemical passivation of the underlying surface, according to studies showing successful blocking of platinum atomic layer deposition (ALD). The reaction is photochemically initiated, requiring light with a wavelength below 275 nm. X-ray photoelectron spectroscopy and infrared spectroscopy studies show that the alkenes initially bind to the surface hydroxyl groups in Markovnikov fashion. At prolonged reaction times (> 5 h), however, oligomerization occurs, resulting in layer growth normal to the surface. The photochemical nature of the reaction enables the use of photolithography as a tool to constructively pattern silica surfaces. Atomic force microscopy shows that the features of the photomask are well transferred. The newly developed method can complement existing patterning methods on silica that are based on soft lithography.

Introduction

Silica glasses are an important class of materials because of their excellent optical properties. The specific properties of a silica glass depend on its composition and fabrication method.[1] Whereas silica glasses made from natural quartz show considerable absorption above 200 nm, synthetic fused silica is transparent at wavelengths down to 180 nm. Optical transparency is a desired property in the field of biosensing, where techniques of fluorescent labeling are well-developed.[2] For biosensing, the material of choice should also be easily functionalized. For silica, a number of functionalization methods have been developed. Esterification of silica surface hydroxyl groups with alcohols has been known since the 1950s;[3] however, the resulting monolayers are easily hydrolyzed.[4] The currently prevailing method makes use of organosilanes,[5] which can react with surface hydroxyl groups to yield a closely packed monolayer.[6,7] The modification is rapid and is usually performed in dilute solutions, and several functional groups are compatible with the procedure. Patterned functionalization of silica surfaces is possible, e.g., using soft lithographic techniques.[7]

However, the reaction is notoriously difficult to control due to the tendency of silanes to condense in solution.[8,9] In addition, the high reactivity of organotrichlorosilanes requires careful handling and limits their use in an industrial environment. Third, the monolayer is prone to hydrolysis under certain conditions. Finally, the excellent optical properties of silica are currently not exploited by using photolithography to locally absorb the monolayer.

In this paper, we demonstrate a novel and mild method for surface modification of silica surfaces, synthetic fused silica in particular, based on a photochemical reaction of terminal alkenes with the glass surface. A first indication for the occurrence of this reaction was given by Mischki et al., who reported that oxidized silicon surfaces that were immersed in 1-alkenes became slightly more hydrophobic upon illumination with UV light (> 300 nm).[10] They concluded that 1-alkenes can bind to the silicon oxide in a Markovnikov fashion, but the extent to which this reaction occurs under the applied conditions is small. Here, we show that monolayers of 1-alkenes can be formed photochemically on fused silica surfaces, resulting in very hydrophobic surfaces. We characterize the modified surfaces with water contact angle measurements, infrared spectroscopy, and X-ray photoelectron spectroscopy, and using thermogravimetric mass spectroscopy, we show that the modified surfaces are thermally stable. Atomic layer deposition (ALD) experiments are further used to show that the monolayers are chemically passivating, indicative of a well-packed layer. Finally, we demonstrate that silica surfaces can be constructively patterned with photolithography and characterize the resulting pattern with atomic force microscopy.

Materials and Methods

Materials. Glassware used for surface modification was cleaned with organic solvents and etched overnight in basic detergent solution. Prior to use, it was rinsed with ultrapure water

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and dried at 120 °C. 1-Hexadecene (98%, Sigma-Aldrich) was purified by column chromatography and vacuum distillation. 11-Fluoroundec-1-ene was synthesized as described elsewhere.[11] Solvents used were either of analytical grade or distilled prior to use.

Surface Modification. A specially designed quartz flask (see Supporting Information) was filled with 1-hexadecene (∼2 mL). This was degassed using three consecutive freeze−pump−thaw cycles. Liquid N_2 was used as cooling agent. Prior to sample immersion, the 1-hexadecene was frozen again by short immersion in liquid N_2, and the flask was filled with argon.

A synthetic fused silica slide (15 × 25 mm, Praezisions Glas & Optik, Iserlohn, Germany) was cleaned by sonication in acetone for 5 min. After drying with argon, the slide was immersed in a freshly made 1:1 (v:v) mixture of hydrochloric acid (37%, analytical grade, Acros) and methanol for at least 30 min. The slide was rinsed with ultrapure water, dried with argon, and inserted into the flask containing frozen 1-alkene. Vacuum was applied again until the 1-alkene was molten completely and the slide was immersed, after which the flask was filled with argon and kept under a slight overpressure. Two low-pressure mercury lamps (6.0 mW/cm^2, Jelight, Irvine, CA, USA) were placed at a fixed distance (∼0.5 cm) from the fused silica slide. For some experiments, a long-pass filter (cut-on wavelength 275 nm, Asahi Spectra, Torrance, CA, USA) was placed in between the lamps and the flask. The setup was packed in aluminum foil, and the slide was illuminated for a specified time. After illumination, the slide was removed from the flask, rinsed with petroleum ether 40/60 and ethanol, sonicated in ethanol and dichloromethane for 5 min per solvent, rinsed with dichloromethane, and finally dried with argon.

Photolithography. Photolithography was performed with cleaned slides and degassed 1-hexadecene in a glovebox. An electron microscope grid (T2000-Cu or SEM F1 (Au), Gilder Grids) was placed on top of the fused silica slide, onto which the 1-alkene was dropped. A fused quartz microscope slide (Alfa Aesar) was used as a cover, onto which a mercury capillary lamp (Jelight) was pointed. Samples were irradiated for 10 h, then removed from the glovebox and cleaned as described above.

Water Contact Angle Measurements. Static contact angles were measured using a Krüss DSA-100 goniometer. Droplets of 3 μL were dispensed on the surface, and contact angles were measured with a CCD camera using a tangential method. The reported value is the average of at least 5 droplets and has an error of ±1°.

Infrared Reflection Absorption Spectroscopy. IRRA spectra were obtained with a Bruker Tensor 27 FT-IR spectrometer, using a commercial variable-angle reflection unit (Auto Seagull, Harrick Scientific). A Harrick grid polarizer was installed in front of the detector and was used for measuring spectra with s-polarized radiation with respect to the plane of incidence at the sample surface. Single channel transmittance spectra were collected at an angle of 75° using a spectral resolution of 4 cm^{-1} and 2048 scans in each measurement. The raw data were divided by the data recorded on a freshly cleaned reference fused silica slide, after which a baseline correction was applied to give the reported spectra.

X-ray Photoelectron Spectroscopy. XPS analyses of the substrates following reaction with the alkene were performed using a JPS-9200 photoelectron spectrometer (JEOL).

The spectra were obtained under ultrahigh-vacuum (UHV) conditions using monochromatic Al Kα X-ray radiation at 12 kV and 25 mA, with an analyzer pass energy of 30 eV. The X-ray incidence angle and the electron acceptance angle were 80° and 10° with respect to the surface normal, respectively. To prevent surface charging during measurements, samples were irradiated with electrons with a kinetic energy of 3.8 eV. Post-ALD XPS analyses were performed using a PHI Versa Probe Scanning XPS. The C_{1s} peak at 285.0 eV was used as a reference for both systems. Spectra were corrected using a linear background subtraction before quantification and any peak deconvolution.

Determination of Attenuation Lengths. Electron attenuation lengths (EALs) were determined using the NIST Electron Effective-Attenuation-Length database.[12] In this program, electron inelastic mean free paths (IMFPs) were determined using the TPP-2 M equation.[13] This required input of the density as well as the bandgap of the 1-hexadecene adlayer. For both parameters, the values of (low-density) polyethylene, 0.92 g/cm^3 and 8.8 eV, respectively, were used. The uncertainty in the attenuation length is mainly dependent on the uncertainties in the calculated IMFP, the transport mean free path and the transport approximation,[12] and amounts to ca. 20%.

X-ray Reflectivity. X-ray reflectivity measurements were performed on a Panalytical X'Pert Pro diffractometer using nickel-filtered Cu Kα radiation (tube settings 40 kV and 50 mA). The data were collected using a fixed divergence slit of 1/32° and a parallel plate collimator on the diffracted beam side. The layer thickness is calculated from the interference fringes.

Fluorescence Spectroscopy. Steady-state fluorescence excitation and emission measurements were performed on a time-correlating single photon counting F900 spectrometer (Edinburgh Instruments). For emission measurements, λ_{exc} = 254 nm; for fluorescence excitation measurements, λ_{em} = 387 nm. To allow for comparison, the measured spectra have been normalized.

Thermogravimetric-Mass Spectrometry. TG-MS analyses were carried out in a TGA/SDTA851e instrument (Mettler-Toledo GmbH, Switzerland), coupled to a Thermostar GSD 301 T2 quadrupole mass spectrometer (Pfeiffer Vacuum GMBH, Asslar). Samples were weighed into 100 μL aluminum crucibles and sealed. The seals were pinholed, and the crucibles were heated in the TGA from 25 to 400 at 10 °C min^{-1}. Dry N_2 gas was used for purging. The detection limit of the MS for release gases was 10^{-14} mbar. A multiple ion detection (MID) measurement was performed with a channeltron voltage of 950 V. The scan measurements were performed over the mass range 0−130 amu.

Atomic Force Microscopy. AFM images (512 × 512 pixels) were obtained with an MFP3D AFM (Asylum Research, Santa Barbara, CA). The imaging was performed in contact mode in air using NP silicon nitride cantilevers with a stiffness of 0.58 N/m (Veeco Metrology, Santa Barbara, CA) at a scan speed of 18.75 μm/s. The scan angle was 90° with respect to the cantilever axis, which allowed the simultaneous recording of lateral force images. Images were flattened with a zeroth-order flattening procedure using the MFP3D software.

Atomic Layer Deposition. ALD of Pt was carried out in a custom-built reactor. The ALD process consisted of 2 s pulses

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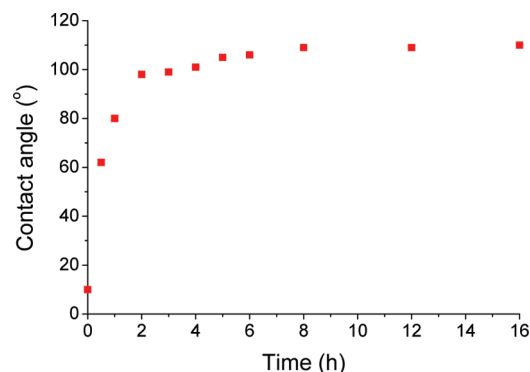(13) Tanuma, S.; Powell, C. J.; Penn, D. R. *Surf. Interface Anal.* **1994**, *21*, 165–176.

Figure 1. Static water contact angle of fused silica slides modified with 1-hexadecene after different modification times.

of high-purity methylcyclopentadienyl trimethyl platinum [CH$_3$C$_5$H$_4$Pt(CH$_3$)$_3$] and dry air, each separated by 30 s nitrogen purges, carried out for 100 cycles with the substrate at 300 °C.

Results and Discussion

Cleaned synthetic fused silica slides were modified with 1-hexadecene by illumination with a low-pressure mercury lamp under an argon atmosphere. After cleaning, the degree of modification was initially assessed by determining the surface wettability with static contact angle measurements. Figure 1 shows the influence of the modification time on the surface wettability. The contact angle increases steadily with modification time, reaching a maximum value of 109 ± 1° after 8 h. As the surface wettability does not change upon sonication in organic solvents, this shows that a tightly bound hydrophobic layer is formed on the surface.

To confirm the presence of a hydrophobic layer, the samples were studied with infrared reflection–absorption spectroscopy (IRRAS). The obtained spectra display an increased intensity of the C–H stretching vibrations with modification time (Figure 2a). This implies that the absorbed layer is steadily growing, even after 8 h of modification, after which no further change in the contact angle is observed. After 8 h of illumination, the positions of the symmetric and antisymmetric methylene stretching peaks are at 2854 and 2924 cm^{-1}, respectively, and do not shift upon prolonged modification. This indicates that the adsorbed layer is disordered.[14] These observations contrast with the monolayer formation of thiols on gold, silanes on silicon oxide, and alkenes on silicon, where the position of the methylene stretching peaks shifts to lower values with increasing packing density.[15–18] The increased peak intensity at prolonged modification times is therefore likely to be caused by ongoing growth normal to the surface.

Another feature in the IRRA spectra is the sharp negative peak at the Christiansen frequency (1374 cm^{-1}), named the substrate band,[19,20] which becomes more negative with prolonged modification time (Figure 2b). At this frequency, the refractive index of fused silica passes from a value above 1.0 to a value below 1.0. Because its absorbance coefficient is also very small, fused silica optically resembles air at the Christiansen frequency. The substrate with adsorbed film can therefore be modeled as a freestanding film.[21] Figure 2b shows that the intensity of the peak at 1374 cm^{-1} correlates well with the intensity of the C–H stretching peaks. This is in accordance with previous reports, where it was shown that the peak intensity at the Christiansen frequency is very sensitive to layer thickness.[20]

Compared to the unmodified sample, all modified samples show decreased absorptions in the OH region. The two main features have maximum intensities at 3720 and 3550 cm^{-1}, which can be attributed to free and hydrogen-bonded Si–OH, respectively.[6,22] In addition, loss of physisorbed water is also contributing to the signal. The intensity of these peaks is similar for all modified samples.

XPS analysis of the modified samples shows the presence of three elements only: Si, O, and C. Figure 3 shows that the C atomic ratio increases with modification time. By plotting atomic ratios, two effects are combined: the increase of the C$_{1s}$ signal and the decrease of the Si$_{2p}$ and O$_{1s}$ signals. Both effects are the result of growth of the adsorbed hydrocarbon layer.

From Figure 3, it can be seen that the increase in C atomic ratio is gradual for small modification times, but after 5 h, the relative C signal rises rapidly, giving rise to a sigmoidal curve. At high modification times, the absolute O$_{1s}$ and Si$_{2p}$ signals are < 20% of those of the unmodified samples, measured under the same conditions. The thickness of the growing hydrocarbon layer can be calculated using

$$I_{Si} = I_{Si}^{\infty} \exp\left(\frac{-d}{\lambda_{Si,C} \cos\theta}\right) \qquad (1)$$

with I_{Si} the absolute silicon peak intensity, I_{Si}^{∞} the absolute silicon peak intensity of unmodified, cleaned fused silica, d the thickness of the adsorbed layer, $\lambda_{Si,C}$ the attenuation length of Si$_{2p}$ electrons in the hydrocarbon layer, and θ the electron takeoff angle. $\lambda_{Si,C}$ was calculated to be 4.9 nm using the NIST Electron Effective-Attenuation-Length database.[12] Similarly, the adlayer thickness can be calculated from the oxygen peak intensities using the attenuation length of O$_{1s}$ electrons in the hydrocarbon layer (3.6 nm). Using both these methods, the thickness of the hydrocarbon layer was, after 5 h of modification, calculated to be 1.7 nm. This is slightly less than the length of a 1-hexadecene molecule (1.9 nm, as determined with *Chem3D*), indicating that the layer formed is still a monolayer, most likely with tilted alkyl chains. After 16 h of modification, the layer thickness was calculated to be 10 nm for various samples (estimated experimental uncertainty: ~2 nm, due to assumptions). This evidence shows that after long modification times the attached coating layer is significantly thicker than a monolayer.

To evaluate the accuracy of these calculations, X-ray reflectivity was performed. With this method, the thickness of the adsorbed layer can be directly determined, provided that it is larger than 2 nm. Reflectivity measurements on a sample modified for 5 h did not result in any interference fringes, indicating that the layer thickness is indeed below 2 nm. Conversely, an adsorbed layer thickness of 9.9 ± 0.2 nm was derived from measurements on a sample after 16 h of modification (Figure 4). This agrees well with the XPS-derived value and thus shows the validity of XPS attenuation length calculations for such layer thickness estimations.

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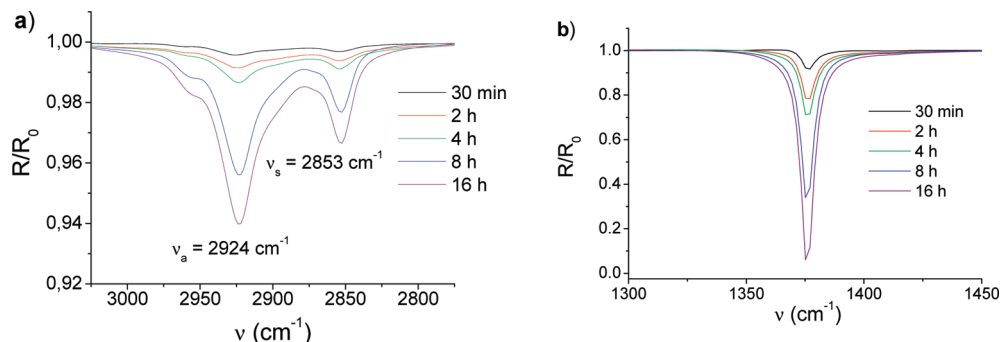
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Figure 2. IRRA spectra of fused silica modified with 1-hexadecene for different modification times: (a) methylene stretching region, (b) substrate band region.
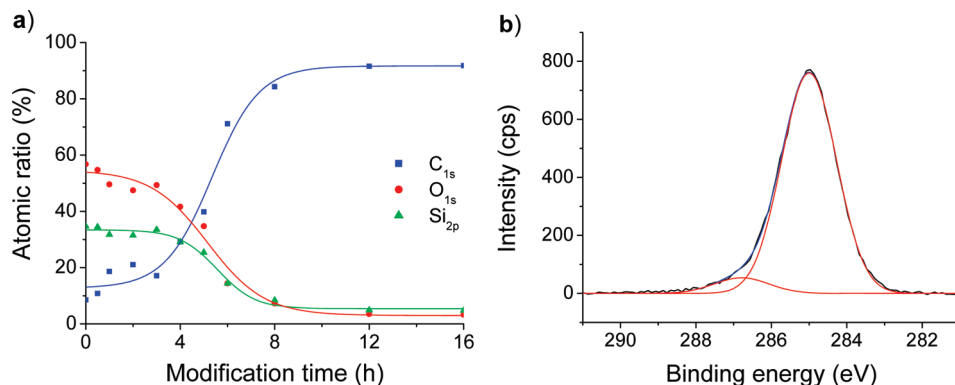

Figure 3. (a) Ratios of elements present on the surface of fused silica plotted against modification time. Ratios were determined by integrating the XPS C_{1s}, O_{1s}, and Si_{2p} signals. Lines were added as a guide to the eye. (b) C_{1s} spectrum with curve fitting for fused silica modified with 1-hexadecene for 5 h.
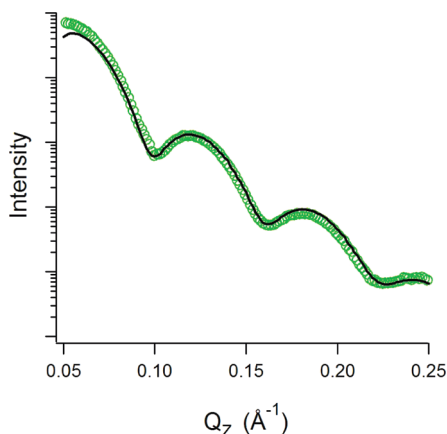

Figure 4. X-ray reflectivity profile of fused silica that was modified for 16 h with 1-hexadecene (green circles) and the calculated profile for a layer of 9.9 nm thickness (—).

The thermal stability of the modified samples was studied using thermogravimetry−mass spectroscopy (TG-MS). No hydrocarbon fragments could be detected by MS when modified samples were heated up to 400 °C in a nitrogen atmosphere. This contrasts with the unmodified samples, which showed desorption of physically adsorbed hydrocarbon fragments between 70 and 160 °C. The absence of physisorbed material on the modified surface may be explained by its lower surface energy compared to cleaned fused silica.[23] In addition to the TG-MS measurements, samples were heated to 200 °C in an argon-purged vacuum oven and cooled down again. Because of the slow heating and cooling rate of the oven, the samples were exposed to a temperature of at least 185 °C for more than 60 min. Prior to and after this thermal treatment, XPS spectra were taken. No significant changes (> 2% in relative C_{1s} intensities) could be observed. This is in agreement with the TG-MS results, supporting the conclusion that the modified surfaces are thermally stable.

ALD of Pt was used to test the quality of the 1-hexadecene monolayer and its ability to passivate the underlying substrate. It has been shown that high-quality organic monolayers (such as highly hydrophobic organosilane self-assembled monolayers on silica) can resist ALD growth, whereas less well-packed mono-layers lead to deposition by ALD.[24,25] Fused silica samples with and without the 1-hexadecene monolayer were subjected to Pt ALD and then characterized by XPS. Figure 5 shows that, after 100 cycles of Pt ALD carried out 300 °C, all Pt XPS peaks were completely absent on the modified silica sample, compared to significant Pt (22.8 at %) for the unmodified sample. The ability to block the Pt ALD reactions indicates that the monolayers are dense and hydrophobic, and confirms their stability at these elevated temperatures.

It has recently been reported that illumination of silicon oxide-covered silicon in the presence of 1-decene with 300 nm light yielded a water contact angle of 59°.[10] Low-pressure mercury lamps mainly emit at 254 nm, but spectral lines are also present at 296 and 312 nm. When the emission at 254 nm

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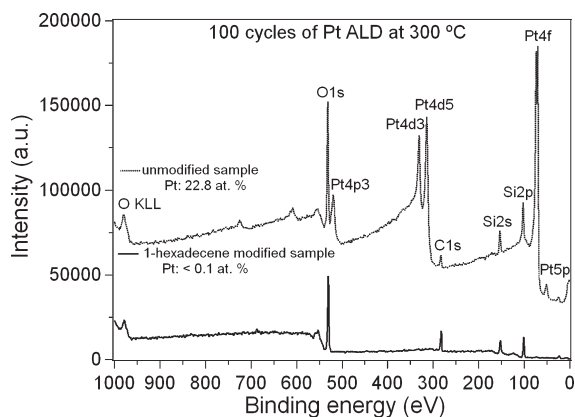
Figure 5. XP spectra of fused silica with and without a 1-hexadecene monolayer after 100 cycles of Pt ALD.

Figure 6. Excitation and emission spectra of fused silica. Emission was measured upon irradiation at 254 nm, while excitation was measured by monitoring the emission at 387 nm.

Figure 7. IRRA spectrum of a sample modified with 11-fluoro-undec-1-ene. The peak at 2960 cm^{-1} is attributed to the asymmetric methyl stretch vibration; this CH_3 group is introduced by the surface reaction.

was blocked using a 275 nm long-pass filter, prolonged illumination of fused silica indeed yielded a contact angle of only 60°. Using a phosphor-coated low-pressure mercury lamp, designed to emit at 285 nm, in combination with the 275 nm long-pass filter, similarly low contact angles were measured. This implies that the additional modification is caused by the 254 nm radiation.

To investigate the origin of the reaction, the absorption and emission spectra of fused silica were measured. UV/vis absorption spectroscopy is excluded, due to the very limited absorptivity of fused silica at the relevant wavelengths. Interestingly, exciting a fused silica slide at 254 nm in a fluorescence spectrometer gives rise to an emission at 387 nm (Figure 6). The corresponding fluorescence excitation spectrum shows a weak but distinct absorption peak at 253 nm. The origin of these photophysical properties lies in the presence of a small fraction of defects.[26] It has been reported that photoluminescent bands observed in silica around 400 nm are caused by oxygen-deficient Ge and Sn impurities (at levels too low to be detected by XPS).[27,28] These bands could be excited at 248 nm. The same bands were also found in oxygen-deficient high-purity silica and attributed to an oxygen deficiency-associated defect center.[29] In addition to the emission at 387 nm, a very weak emission at 452 nm is observed. This emission can be attributed to dicoordinated silicon, another oxygen deficiency-related defect center.[26]

The oxygen deficiency of the surface can be determined by calculating the XPS O_{1s}/Si_{2p} ratio. For cleaned unmodified silica, this ratio was found to be 1.7 ± 0.1 (rather than 2.0, expected for SiO_2), thereby implicitly confirming the presence of oxygen-deficient centers. To investigate whether these defects play a role in the photochemical reaction on the surface, the XPS C_{1s} spectrum of a modified sample was further examined. Deconvolution of the high-resolution C_{1s} spectrum for a sample that was modified for 5 h shows two contributions (Figure 3b). The major contribution is from C atoms solely bound to C or H atoms, which was set to 285.0 eV. The other contribution is found at 286.8 eV. A similar shift was observed for long-chain alcohols absorbed on glass and was attributed to the carbon atoms bound to oxygen in a C−O bond.[30] The ratio of the peak area at 286.8 eV to the total carbon peak area is 1 to 15.2, which would correspond to one C−O bond per molecule of 1-hexadecene. Thus, we can
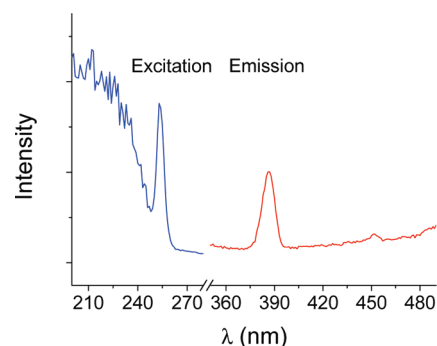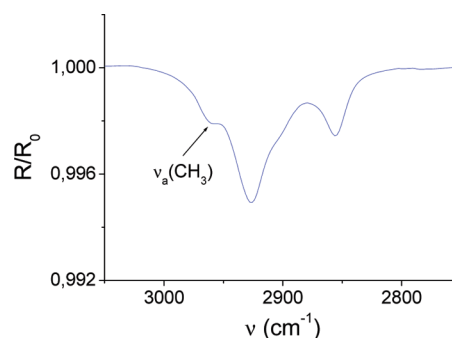
conclude that 1-hexadecene binds covalently to the surface hydroxyl groups. Oxygen-deficient surface defects therefore do not necessarily play a stoichiometric role in the reaction. Deconvolution of XPS spectra of samples that were modified for more than 5 h show a reduced contribution of oxygen-bound C atoms to a level where they become indiscernible, indicating that at prolonged reaction times another mechanism comes into play. This is in agreement with Figure 3, which shows a sharp increase of the C_{1s} signal after 5 h of modification.

The reaction of 1-decene with surface hydroxyl groups of oxidized silicon upon irradiation with 300 nm light was proposed to proceed via Markovnikov addition.[10] The same type of addition was also found when 1-alkenes were thermally[31] or photochemically[32] reacted with hydroxyl-terminated silicon carbide. To check the mechanism of the photochemical attachment of alkenes onto silica at $\lambda = 254$ nm, samples were modified with 11-fluoro-undecene, and studied with IRRAS. The attachment of this molecule via Markovnikov addition should introduce a methyl group to the surface that is not present in the alkene. The presence of a methyl stretching signal was indeed confirmed in the IRRA spectrum (Figure 7), thereby confirming Markovnikov addition. This type of addition also explains why the monolayers remain disordered, since the presence of a methyl group close to the surface does not allow the hydrocarbon chains to closely pack together.

The exact nature of the photochemical reaction is still unclear. Modification may be caused by direct excitation of the 1-alkene.

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Even though the absorption maximum of, e.g., 1-hexadecene lies around 193 nm in dilute solutions, the absorption edge of the pure compound stretches out to over 260 nm. The excited alkene may then be prone to addition to surface hydroxyl groups. On the other hand, excited surface defects may initiate a radical surface reaction, which then propagates laterally over the surface until a certain surface coverage is reached. Further studies are necessary to get a better understanding of the reaction mechanism.

The oligomerization we observed at prolonged reaction times may be initiated by the excitation of the alkene into its triplet state. The importance of the triplet excited state in the photopolymerization of ethylene has been pointed out by Hagiwara et al.[33] For ethylene, the transition from the singlet ground state to the triplet excited state occurs upon absorption of UV light in the range 260−350 nm, and it is promoted by oxygen.[34] The corresponding absorption coefficient of $\sim 10^{-4}$ shows that this transition occurs with very low probability.[35] As oxygen is involved in the initiation, the oxygen concentration strongly influences the rate of reaction, with an optimum concentration of around 100 ppm.[33] In our case, the oxygen level was minimized by extensive degassing, but this was limited by an oxygen contamination (< 5 ppm) in the argon that was used. Therefore, photopolymerization at prolonged reaction times cannot be excluded and is indeed observed on the surface.

As the reaction of 1-hexadecene with fused silica is clearly photochemical in nature, photolithography can be used to constructively create a pattern on fused silica surfaces. Photolithography was performed using contact masks in the inert atmosphere of a glovebox. After illumination, the sample was cleaned and exposed to water vapor. Condensation of water on the surface led to visualization of the pattern (Figure 8). The droplets formed on the illuminated, hydrophobic parts of the surface are small and appear colored, while droplets formed on the masked area are bigger and appear dark. The different appearance is caused by differences in hydrophilicity, introduced by the photochemical reaction.

AFM was used to study modified samples with smaller feature sizes (obtained using a 2000 mesh electron microscope grid). Contact mode measurements clearly reveal $7.5 \times 7.5 \, \mu m^2$ squares with a spacing of 5 μm, both in topography and in lateral mode (Figure 8). The underlying texture of the polished slides can also be distinguished. The height difference between the patterned and unpatterned area is at least 3 nm (not corrected for differences in elasticity). This value is bigger than the maximum chain length of 1-hexadecene (1.9 nm), again confirming the growth of an oligomeric multilayer. The data in Figure 8 provide the first examples of photolithography onto glass and reveal the power of this mild method of surface modification. The local modification of the inside of microchannels with DNA oligomers provides an
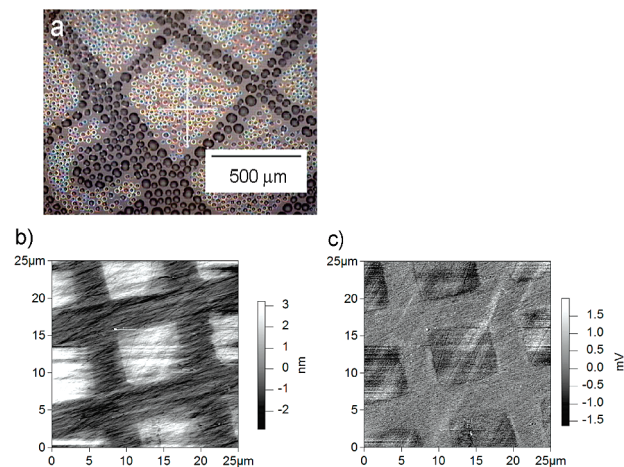

Figure 8. (a) Micrograph of a hydrophobically patterned sample exposed to water vapor. (b) Topography of a patterned sample, measured with contact-mode AFM. (c) Corresponding lateral force image.

example of the extension that this reaction yields over other surface modification reactions.[36]

Conclusions

We have developed a mild, room-temperature photochemical procedure by which 1-alkenes can bind covalently to the surface of hydroxyl-terminated fused silica. The resulting functionalized surfaces can be prepared reproducibly, are highly hydrophobic but disordered, and are thermally stable up to at least 400 °C. The 1-hexadecene monolayer was shown to act as a resist against Pt ALD, which indicates its high quality. The grafting reaction is photochemically initiated, requiring light with a wavelength below 275 nm, and occurs via Markovnikov addition of surface hydroxyl groups to the double bond of the alkene. However, after 5 h of modification, oligomerization normal to the surface is also observed. Using photolithography, it was possible to constructively pattern the fused silica surface with 1-hexadecene. This can complement currently existing (soft lithographic) patterning methods, specifically since without the light source none of the reactants involved displays any significant reactivity.

Supporting Information Available: A technical drawing of the specially designed reaction flask. This material is available free of charge via the Internet at http://pubs.acs.org.

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