

Preparation of Silica-on-Titania Patterns with a Wettability Contrast

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The preparation of patterned inorganic surfaces consisting of silica (SiO_2) and titania (TiO_2) is described. The approach is based on a combination of standard photolithography and plasma-enhanced chemical vapor deposition. Silicon wafers coated with a titania layer (40 nm) were patterned by use of a positive photoresist and then a thin silica layer (10–40 nm) was plasma-deposited. The photoresist was removed by decomposition at 800 °C. The inorganic patterned surfaces possessed excellent high-temperature resistance. Since the silica patches were effectively dehydroxylated during the thermal treatment, the patterns consisted of moderately hydrophobic (silica) and hydrophilic (titania) domains with a significant wettability contrast (40° for water). The surface was further hydrophobized with a self-assembled monolayer of fluoroalkylsilane (FAS) and exposed to UV light. The FAS layer was locally oxidized on the TiO_2 patches and the wettability contrast was maximized to 120° (the highest possible value on smooth surfaces).

Introduction

If the volume of liquid material that is transported or transformed is reduced, then efficiency generally increases and consumption decreases. As a consequence, miniaturization has always been a leading tendency in technology but it has gathered significant pace in more recent times. The science of miniaturization has become a topic in its own right.¹ From a colloid science point of view, miniaturization is related to a significant increase in the surface-to-bulk ratio, which in turn amplifies the importance of interfaces, including capillary phenomena and wetting, surface forces, interfacial properties, etc.² Surfaces with a pattern having the desired wettability contrast, for example, a relatively hydrophilic channel crossing a more hydrophobic matrix, are the building blocks of various microfluidic devices. It therefore seems timely to develop protocols for their fabrication and assess their properties in detail.

Most liquids will not spread completely on many surfaces. Their spreading will proceed until a finite contact angle is reached. From a macroscopic point of view, the contact angle reflects the balance between the forces of cohesion and adhesion.³ On a more hydrophobic solid, adhesion is lower and the contact angle is higher. There is a strong correlation between the chemical constitution of the solid surface (the type and packing of the terminal groups in the outermost layer of the solid) and the contact angle for a given liquid.⁴ The most hydrophobic surfaces are terminated by densely packed perfluoromethyl groups, and the water contact angle on such surfaces (when homogeneous and smooth) is 115–125°. ^{4,5}

Self-assembled monolayers (SAM) are a popular system due to their availability, versatile termination, and ease

of preparation.^{6–8} Alkanethiols on gold and organosilane on hydroxylated surfaces adsorb quickly, bond strongly, and form well-arranged monolayers. The surface free energy, and therefore the wettability of the modified surface, can be controlled by altering the terminal group of the SAM: from completely hydrophilic (e.g., -OH or -COOH) to very hydrophobic (e.g., -CH₃ or -CF₃).⁶ Thiol-based SAM can be easily removed after UV photooxidation and thus, by use of lithography, patterned surfaces can be prepared. This technique is widely used to fabricate model surfaces for wettability studies.^{7,9}

Our goal in this investigation is to prepare an oxide-on-oxide patterned surface. Oxide surfaces are very common as oxides are ubiquitous and extensively used in industry. Oxides have the advantage of being resistant to heat and aggressive solutions. Oxide surfaces almost always contain surface -OH groups,¹⁰ which can generate a surface charge in aqueous solutions or can be further derivatized under dry conditions.

There has been a recent surge of interest in silica–titania patterned surfaces^{11–13} as the different chemical affinities of the two oxides can be exploited to selectively adsorb (or in fact prevent adsorption of) proteins, which is therefore of enormous interest in biological applications.

We have recently investigated the different wettability of silica and titania after exposure to UV irradiation and heat treatment at elevated temperatures.¹⁴ Both silica and titania recontaminate after cleaning if left in the ambient atmosphere (the process on titania surfaces is

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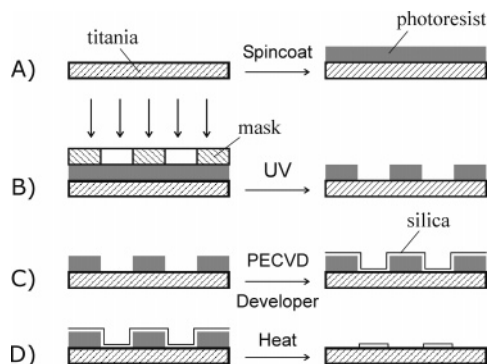


Figure 1. Schematic representation of the patterning process: (A) spin coating of the photoresist; (B) UV irradiation through a mask; (C) plasma-enhanced chemical vapor deposition of silica; (D) thermal lift-off of the photoresist.

faster). UV light is very effective in removing the accumulated organic contamination from the titania surface, essentially due to the strong photocatalytic properties of the TiO₂. The effect on silica is negligible. At high temperatures, both silica and titania become gradually dehydroxylated. While silica surfaces turn moderately hydrophobic (water contact angle $\sim 40^\circ$), titania surfaces remain hydrophilic, that is, fully water wet.¹⁴

This dissimilarity is now exploited to prepare patterned inorganic surfaces with a moderate wettability contrast. Flat titania surfaces are patterned with conventional photolithography.^{1,15} A thin layer of silica is deposited by plasma-enhanced chemical vapor deposition (PECVD) and the patterns are “developed” during a subsequent heat treatment. The patterned surfaces consist of hydrophobic silica patches embedded in a hydrophilic titania matrix. They can withstand temperatures in excess of 1000 °C and can be easily cleaned with UV irradiation. They can be further modified by targeted adsorption and localized oxidation.

Materials and Methods

Substrates and Reagents. Silicon wafers, P(100), were provided by Dr. M. Bjelopavlic (MEMC Electronic Materials). The RMS roughness of the wafers was 0.24 nm and the peak-to-valley height was 0.88 nm as obtained with atomic force microscopy (AFM) imaging over an area of 1 μm^2 . Silicon wafers covered with a thin layer of titanium dioxide were obtained from Philips Research Laboratories (Eindhoven, The Netherlands). Magnetron sputtering was used to deposit layers of pure stoichiometric TiO₂ (details can be found elsewhere¹⁶). The RMS roughness of the layers was 0.3 nm and the peak-to-valley height was 1.5 nm over an area of 1 μm^2 .

Tetraethoxysilane (TEOS), Si(C₂H₅O)₄, was obtained from Aldrich and used as a precursor in the PECVD.

A fluoroalkylsilane (FAS), CF₃(CF₂)₅(CH₂)₂Si(OCH₃)₃, was purchased from Apollo Scientific and used as received. Self-assembled monolayers (SAM) were formed by chemical vapor deposition. Pieces of wafer (10 × 10 mm²) were placed in a vial with 50 μL of FAS, heated to 100 °C, and kept at that temperature for 1 h. The FAS reacts with surface OH groups and forms SAM.¹⁷ After deposition, the samples were thoroughly rinsed with pure water.

Photolithography. The patterning of the surfaces was achieved by photolithography in four consecutive steps (Figure 1). A Waycoat photoresist (HPR-206, Fuji Hunt Electronics Technology) was spin-coated on the titania wafer (preheated at

100 °C for 60 s) with a spin-coater (EC101D, R485 Bowl Assembly, Headway Research,) at 5400 rpm for 20 s and subsequently baked at 80 °C for 60 s (Figure 1A). This procedure gives a photoresist layer thickness of 1.2–2.0 μm .¹⁵ Waycoat 206 has been designed for improved adhesion to silicon dioxide and metal surfaces and specifically formulated to minimize variations in coating thickness.

The photoresist was further exposed to UV light (436 nm, g-line of mercury) for 40 s through photomasks by use of a mask aligner (K&S 686) (Figure 1B). Photomasks (DSTO, South Australia) were used to create patterned surfaces. They consisted of chromium circles (10 μm in diameter, area fraction 30%) deposited on quartz. The photoresist undergoes a photoinduced rearrangement (known as Wolf's rearrangement¹⁸), which is characteristic for 2-diazo-1-naphthalenones. It was then developed with Waycoat MIF developer solution (1:1 dilution in water) for 180 s (Figure 1B). A layer of silica was deposited onto these photoresist-patterned surfaces by low-temperature PECVD (Figure 1C) and the photoresist was removed by heat treatment (Figure 1D).

Plasma-Enhanced Chemical Vapor Deposition of Silica. Plasma deposition was carried out in a Harrick plasma unit (model PDC-32G) operated at 100 W and frequency 13.56 MHz. The pressure in the plasma chamber during deposition was monitored by a vacuum gauge (Inficon, model PG3). Preconditioning of the reactor to remove products of previous reactions was carried out via a methanol wash followed by air discharge for 30 min. This procedure was shown to be effective (as assessed by X-ray photoelectron spectroscopy, XPS) in removing all contaminants. Samples were placed vertically on a microscope slide in the middle of the reactor by use of a spacer block. Flow of liquids was adjusted by three mass controllers (Mass-Flo Controllers, type 247, MKS Instruments).

The process of preparation of silica film consists of three steps. In the first step, air plasma was used for surface cleaning; then in the second step, silicon species were introduced into the plasma (flow of air/TEOS). In the final step, H₂O₂ was introduced into the plasma reactor and provided a final hydroxylation of the silica surface. Full details are described elsewhere.¹⁹

Atomic Force Microscopy. Surface imaging was performed with an atomic force microscope (NanoScope III, Digital Instruments) in tapping mode. Silicon NT-MDT cantilevers (spring constant of 11.5 N/m) were used to collect detailed topographic information. RMS roughness and peak-to-valley height were obtained with the AFM running software.

Scanning Electron Microscopy. A scanning electron microscope (CamScan Model CS44FE) equipped with a field emission gun operated at an accelerating voltage of 20 kV was used. The samples were mounted on a stub with double-sided conductive tape and coated with carbon to avoid surface charging, which affects the secondary electron imaging. The images were recorded in both secondary electron image (SEI) and backscatter electron image (BEI) modes.

X-ray Photoelectron Spectroscopy. XPS analysis was performed on a Physical Electronics PHI Model 5600 hemispheric electron spectrometer employing a nonmonochromatic Mg K α source (1253.6 eV) operated at 300 W. A fixed pass energy of 93.9 eV was used for survey scans and 29.35 eV for multiplex scans. All XPS measurements were acquired at a takeoff angle of 45° to the surface. During analysis, the base pressure remained below 3 × 10^{−8} mbar. All peaks were referenced to the C(1s) (hydrocarbon C–C, C–H) contribution at 284.8 eV. The XPS signal was calibrated with the silver 3d_{5/2} and copper 2p_{3/2} photoelectron peaks obtained after sputtering the Ag and Cu surfaces with an argon ion beam for 2 min in order to remove the surface contamination.

Time-of-Flight Secondary Ion Mass Spectrometry. Secondary ion mass spectra were recorded on a PHI TRIFT 2100 time-of-flight secondary ion mass spectrometer in the mass range 0–200 *m/z*. ToF–SIMS imaging was carried out with a gallium liquid-metal ion gun at a current of 600 pA. For imaging purposes,

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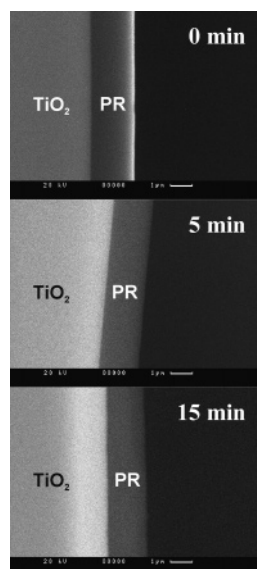


Figure 2. SEM images of the photoresist (PR) layer on a titania wafer after exposure to air plasma for 0, 5, and 15 min (plasma parameters are identical to those used in the PECVD of silica).

the gun was operated at 25 keV, at a pulse width of 15 ns. Surfaces of $60 \times 60 \mu\text{m}^2$ area were scanned with a ~ 120 nm ion beam. No charge compensation was necessary for acquisition.

UV Irradiation. Silica and titania samples were irradiated in ambient atmosphere with ultraviolet light of fixed wavelength ($\lambda = 250$ nm) from an UV eraser (Lawtronics ME15).

Contact Angle Measurement. Advancing water contact angles were measured with the sessile drop method. Digital images of the drop profile (624×580 pixels, 8-bit monochrome) were captured with a progressive scan CCD camera (JAI CV-M10BX). The contact angle was determined by numerically drawing a tangent close to the edge of the droplet. All measurements were performed with high-purity water at pH = 5.6 (resistivity $18 \text{ M}\Omega\cdot\text{cm}$ and surface tension 72.8 mJ/m^2 at 20°C).

Results and Discussion

The bare titania substrate was imaged before and after extended heat treatment (15 h at 800°C in air) with tapping-mode AFM. The original substrate is uniform and very smooth; the RMS roughness is only 0.3 nm over an area of $1 \mu\text{m}^2$. After the heat treatment, the surface of the sample is still uniform but the RMS roughness and peak-to-valley height have significantly increased: 6.8 and 20 nm, respectively. Most probably the increased roughness is due to the mismatch between the thermal expansion coefficients of silica ($0.5 \times 10^{-6} \text{ K}^{-1}$)²⁰ and titania ($7.1 \times 10^{-6} \text{ K}^{-1}$).²¹

The behavior of the photoresist during plasma deposition as well as through the removal step is crucial to the patterning process and was studied in some detail. Samples of the photoresist spin-coated on titania were exposed to air plasma for different periods of time and examined by SEM and XPS. It appears from the SEM images, shown in Figure 2, that the overall integrity of the layer has not been compromised.

Plasma, however, strongly reduces the solubility of the photoresist in acetone, which is the standard washing procedure. Once the Waycoat layer has been exposed to plasma it cannot be removed. The XPS data, shown in Figure 3, explicitly confirm that sonication in acetone decreases the amount of detected sulfur (representative of the Waycoat resist) but only slightly.

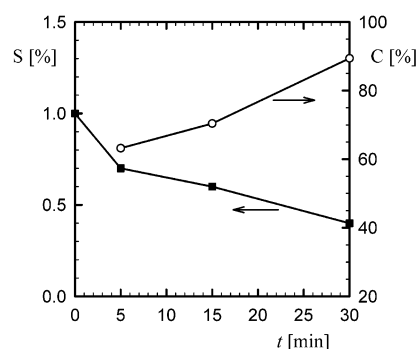


Figure 3. Sulfur and carbon concentrations as determined by XPS on a titania wafer coated with Waycoat photoresist versus time of exposure to air plasma.

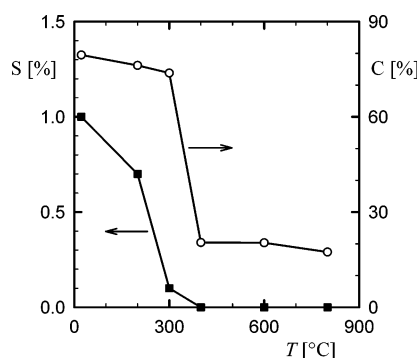


Figure 4. Sulfur and carbon concentrations as determined by XPS on a titania wafer coated with Waycoat photoresist versus temperature of heat treatment in air (duration is always 15 h).

Thermal decomposition, however, is very effective in removing the Waycoat layer. Samples of the photoresist spin-coated on titania were treated at different temperatures and analyzed with XPS. The amounts of detected carbon and sulfur are plotted in Figure 4. The simultaneous decrease in the amount of both elements reveals that the photoresist is gradually decomposed and entirely removed after baking of the sample at temperatures above 400°C . Additional tests with samples that were additionally exposed to plasma showed a trend similar to that seen in Figure 4. The carbon found after high-temperature treatment may be ascribed to adventitious contamination. This hypothesis is supported by contact angle and ToF-SIMS measurements: water contact angle was 0 and no photoresist pattern could be discerned after heat treatment. For these reasons the thermal liftoff of the photoresist was adopted as a standard procedure.

The quality of the silica layer deposited by CVD was assessed. XPS detected only silicon and oxygen in a 1:2 ratio, which indicates that full coverage with a silica layer has been achieved. The absence of titanium, even after heating of the sample at 800°C , confirmed that the silica coating is stable and can be dehydroxylated without exposure of the underlying titania. The silica layer deposited on a smooth titania wafer is also very smooth: the RMS roughness is 0.3 nm only. Interestingly, subsequent heat treatment (15 h at 800°C in air) increases the roughness only marginally, to 0.5 nm. Additional experiments have shown that the increase in surface roughness after extended heat treatment decreases as the thickness of the silica layer increases.

By carrying out the four steps outlined in Figure 1 we obtain well-defined silica-on-titania patterns. These can be seen with an optical microscope due to the different colors of the heat-treated silica (pale yellow) and titania

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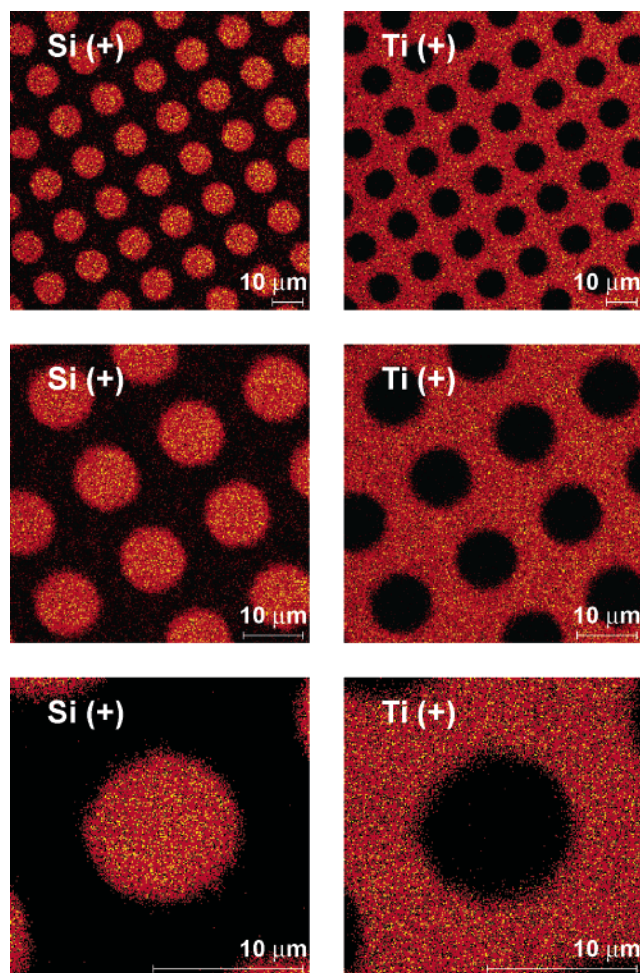


Figure 5. Chemical composition of the patterned surface (silica circles on a titania base) as determined by ToF-SIMS: positive ion maps of Si⁺ ($m/z = 28$) and Ti⁺ ($m/z = 47$).

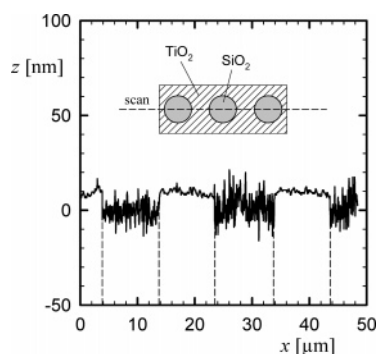


Figure 6. Topography of the patterned surface (silica circles on a titania matrix) as determined by AFM tapping-mode scan.

(bluish-grey). Because of the thermal hydrophobization of the silica (water contact angle $\sim 40^\circ$), the patterned surface exhibits a wettability contrast, which can demonstrated with selective water vapor condensation on the hydrophilic titania patches (water contact angle 0).

The chemical difference between the islands (SiO₂) and the matrix (TiO₂) is best seen in the positive SIMS image (Figure 5). The Si⁺ and Ti⁺ ion maps are complementary to each other, and the thickness of the transition edge between silica and titania is about 0.4 μm .

The topography of the patterned surface was investigated and an AFM height profile is given in Figure 6. The two types of patches are clearly distinguished. The RMS roughness is different and characteristic of the two

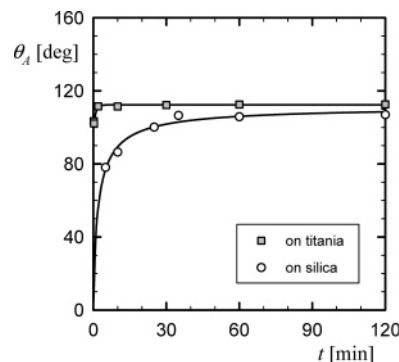


Figure 7. Water contact angle versus time of exposure of the clean silica or titania surface to FAS vapors.

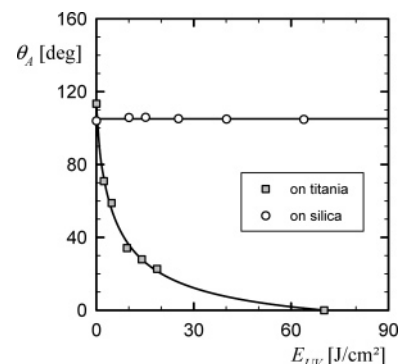


Figure 8. Water contact angle on FAS-coated silica or titania surfaces versus dose of UV exposure ($\lambda = 250 \text{ nm}$).

materials after high-temperature treatment. The average thickness of the silica layer is about 10 nm.

The patterned silica-on-titania surface is very robust: it can sustain high temperature (at least up to 1050 $^\circ\text{C}$), UV irradiation, or aggressive solutions. Various applications can be envisaged, as the properties of SiO₂ and TiO₂ are very different. Thermal dehydroxylation is part of the above preparation protocol and the surface has hydrophilic (TiO₂) and moderately hydrophobic (SiO₂) patches. The difference has been investigated in detail elsewhere.¹⁴ Another significant difference between the two oxides is that titania, unlike silica, has strong photocatalytic properties. This is a powerful tool for the preparation of patterns with enhanced wettability contrast.

As an example, we have fabricated a surface with a maximum wettability contrast. Our approach was inspired by previous work on photocatalytic lithography.^{22,23} In the first step the patterned surface was exposed to the vapors of FAS. The silane adsorbs on both silica and titania and forms a self-assembled monolayer. In the second step the FAS-coated surface was exposed to UV light and the silane layer was oxidized on the titania patches only. The adsorption of FAS on clean silica and titania can be followed by contact angle measurements (Figure 7).

The increase of the advancing contact angle of water reflects the increased area fraction covered with the silane. The adsorption proceeds faster on the titania surface (which has a higher surface free energy) and the plateau values are 113° on TiO₂ and 107° on SiO₂. These values are very close to values typically observed on fully fluorinated surfaces, and therefore we conclude that full surface coverage was attained. When exposed to UV irradiation, the FAS layer is gradually oxidized (though

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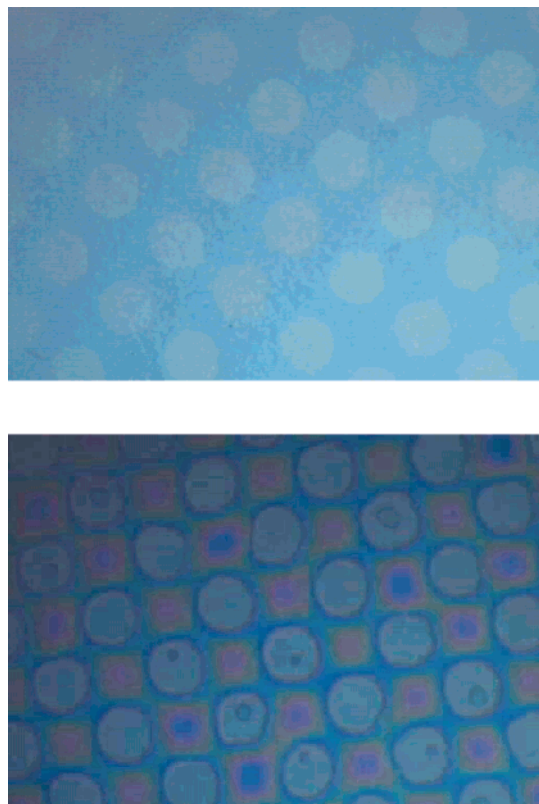


Figure 9. Microphotographs of the FAS patterned surface: (A) dry and (B) water condensation figures.

much more slowly than other organic layers) and titania becomes hydrophilic (Figure 8). On silica the FAS layer is perfectly stable (Figure 8). The decomposition of the FAS was confirmed with XPS measurements. The F(1s) peak completely disappeared on titania after UV irradiation but was perfectly stable on silica.

We accept that the same processes take place on the individual patches of the patterned surface and high contact angle difference is achieved. This dissimilar

wettability is illustrated in Figure 9. It should be noted that surfaces covered with densely packed perfluorinated methyl groups are the most hydrophobic ones. On the other hand, complete wetting of the titania is achieved with UV light. We have therefore developed a surface with the maximum wetting contrast achievable on a smooth surface.

Conclusion

We have described a technique for the preparation of patterned inorganic surfaces consisting of silica and titania. The method is based on well-established techniques, namely, photolithography and plasma-enhanced chemical vapor deposition. The thermal liftoff of the photoresist and the dehydroxylation of the silica patches are carried out in one step. The surface consists of silica (moderately hydrophobic) and titania (hydrophilic) patches. The size of the patterns is limited by the resolution of the lithography. Due to the different wetting behavior of SiO_2 and TiO_2 after high-temperature treatment, the patterned surface exhibits a wettability contrast of about 40° . Due to the photocatalytic activity of the TiO_2 , various coatings, initially deposited on the whole surface, can be locally oxidized and removed. As an example, we have prepared a surface consisting of hydrophilic ($-\text{OH}$) and hydrophobic ($-\text{CF}_3$) patches. Such a surface not only combines the highest ($\sim 115^\circ$)^{4,5} and the lowest (0°) contact angles achievable on smooth surfaces but also is easy to regenerate after contamination (by exposure to UV light). Other modifications are also possible, and targeted adsorption has been demonstrated. The inorganic patterned surfaces possess excellent high-temperature resistance.

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