Molecular Transfer of Surfactant Bilayers: Widening the Range of Substrates

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Handling nanometer-thick films and nano-objects remains a challenge. Applying self-assembly properties of surfactants to nanomaterials manipulation may be the key to the fast, easy, cost-effective growth of 2D and 3D nanostructures. Newton black films (NBFs) are self-assembled bilayers of surfactant, well-organized, but fragile objects. To render such films amenable to practical applications, it is necessary to find ways to transfer them onto solid substrates. A method developed recently to transfer NBFs onto a solid substrate while preserving their molecular organization (Benattar, J.-J.; Nedyalkov, M.; Lee, F. K.; Tsui, O. K. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 4186) is broadened here to different surfaces. The method requires hydrophobic, planar, atomically smooth surfaces. This study presents the adhesion of a fluorinated NBF surfactant onto hydrophobically treated silica and silicon surfaces (with etching or silanization). The structures of the free-standing film, bare substrates, and transferred films are investigated using X-ray reflectivity. The homogeneity of the surfaces before and after bilayer deposition is examined by atomic force microscopy (AFM). Multiple transfers are tested and described for the future development of more complex architectures involving many surfactant layers and inserted nanosized objects.

1. Introduction

The self-assembly of nanoscale materials to form ordered structures promises new opportunities for developing miniaturized electronic, optoelectronic, and magnetic devices. Such devices require the control of molecular orientation and nanoscale organization because their function strongly depends on the local environment. Nanoparticles display fascinating electronic and optical properties as a consequence of their dimensions, and they may be easily prepared from a wide range of materials. The dimensions of these particles make them ideal candidates for the nanoengineering of surfaces and the fabrication of functional nanostructures. In the past few years, much effort has been expended with regard to their organization on surfaces for the construction of functional interfaces.

It is therefore highly desirable to develop methods for the controlled assembly of complex nanostructures. The self-organization properties of surfactants are widely used for ordering sufficiently small objects, employing the Langmuir–Blodgett or the Langmuir–Schaefer method, for example.[2] The resulting arrangements have a large range of applications. Combining the self-assembly of surfactants and nanomaterials may be the key to fast, easy, and cost-effective 2D and 3D nanostructures.

Surfactant thin films are typical 2D assemblies of amphiphiles, composed of a water layer sandwiched between two layers of surfactants that direct their hydrophobic tails outward. Films are called "black films" when their thickness is much smaller than the wavelength of visible light because they appear transparent to the human eye. The thickness of their water layer ranges from a few angstroms to a few nanometers. Common black films possess a rather large water core[3] whereas Newton black films are much thinner and contain only residual water of hydration in the core upon maximal drainage.[4]

Black films can be stabilized in different systems.[4–7] It was reported that the self-assembly properties of Newton black films can be used for the ordering of complex molecules such as cyclodextrins[8] and polymers.[9] Two different physical processes (diffusion and electrostatic attraction) leading to the insertion of dense protein monolayers into surfactant and phosopholipid Newton black films have been reported.[10,11] The driving forces, such as the diffusion of nanoparticles and electrostatic attractions between the inserted molecules and the surfactant walls, are independent of the nature of the objects being inserted. Nanoparticles, either water-soluble or made water-soluble by an appropriate surfactant, could be organized into 2D crystals using this process.

However, Newton black films are delicate to manipulate. Therefore, it is crucial both for applications and for physical

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studies to develop a reliable method allowing their transfer onto solid supports. We have recently described such a method of film transfer.[1] A "black bubble" is brought into contact with a hydrophobic silicon substrate, and the strong adhesion leads to a large transferred area where the molecular assembly of the films is preserved. The transferred films cover a large surface area (of up to several square centimeters). They are homogeneous, and their molecular structure is maintained during the transfer.

The present work reports an extension of this method to different types of hydrophobic substrates and the consequent effects on bilayer transfer. Using different substrates and different surface treatments increases the number of applications of our method. The physical, chemical, and optical properties of the substrate play important roles in possible applications. Surface requirements for the present method are a planar and even atomically flat surface that is hydrophobic and homogeneous all over the surface after treatment. NH$_4$F-etched silicon surfaces with (111) orientation[12–14] as well as silica surfaces silanized with octadecyltrichlorosilane[15,16] meet these requirements. The silica surfaces chosen are silicon wafers with a native oxide layer and glass slides. Etched silicon surfaces are widely used in the semiconductor industry. Widening our method to silanized substrates will allow a larger number of applications. Many surfaces can be silanized (silica and metallic oxides) and the design of the grafted silane can be finely chosen according to its practical use,[17] for example, creating biocompatible surfaces,[18] designing molecular sensors, and patterning substrates.[19] Employing a silanization treatment opens a number of possibilities for many applications; it is easily applied without the risks due to the use of HF or NH$_4$F and allows the use of cost-effective substrates such as glass. In addition, using chemical postmodification on grafted silane monolayers leads to a large range of chemical functionalities. The three different hydrophobic surfaces employed in this study may be considered to be typical surfaces. They have the same difficulties of bilayer transfer as do other conceivable surfaces.

2. Experimental Section

2.1. Materials and Methods. *2.1.1. Newton Black Films.* Newton black films were prepared using the nonionic fluorinated sulfoxide surfactant with the chemical formula C$_6$F$_{13}$-CH$_2$-CH$_2$-SO-CH$_2$-CH$_2$-CO-NH-C(CH$_2$CH$_2$OH)$_3$, synthesized according to a procedure described elsewhere.[20] It will henceforth be referred as C$_6$F$_{13}$SOTHAM. Its concentration was kept constant at 0.5 g/L (about twice the C$_6$F$_{13}$SOTHAM cmc). We sometimes added 1 equiv of CaCl$_2$ (0.0008 mol/L). Calcium chloride (CaCl$_2$) was purchased from Sigma and used without further purification. All solutions were prepared in ultrapure water (18.2 M Ω, Milli-Q system). Adding calcium chloride, because of its hydration properties, rigidifies the surfactant layers, which makes film transfer easier.[21] The effect of this property on film transfer will be discussed later in the article.

Free-standing films are drawn from the surfactant solution using a rectangular steel frame (35 × 3 mm^2). All of the experiments are carried out in a sealed box to maintain a saturated vapor atmosphere; details can be found elsewhere.[4,7]

2.1.2. Hydrophobization of Substrates. The substrates used were 2-in.-diameter n-type Si (111) wafers (1−20 Ω cm), which were 280 μm thick, provided by Neyco SA (France) and 76 × 26 mm^2 glass slides, 1.1 mm thick, provided by FLD (France). Glass slides were then diamond cut to 50 × 26 mm^2 dimensions.

Silicon substrates were etched using a 40% NH$_4$F solution. For etching, substrates were first degreased using hot acetone and then rinsed with Milli-Q water. They were then cleaned in a mixture of concentrated sulfuric acid and 30% hydrogen peroxide solution (volume ratio 3:1) for 30 min to remove any organic contaminant. After being rinsed again with Milli-Q water, the wafers were rendered hydrophobic by placing them in a 40% NH$_4$F aqueous solution for 20 min and were quickly rinsed afterward with ultrapure water and then dried using nitrogen gas. This treatment produces atomically smooth Si (111) surfaces with silicon monohydride terminations oriented normal to the surface.[12,13] NH$_4$F (40%) in aqueous solution and hydrogen peroxide (30%) in aqueous solution were purchased from Sigma and used as received. Acetone is ACS grade and used as received.

Silicon substrates were silanized using octadecyltrichlorosilane (OTS), which was purchased from Sigma and used without further purification. The substrates were first degreased using acetone in an ultrasonic bath for 5 min and then rinsed thoroughly with ultrapure water. They were cleaned in a mixture of concentrated sulfuric acid and 33% hydrogen peroxide solution (ratio 3:1) for 30 to 40 min. After being rinsed again with ultrapure water, wafers and glass slides were immersed in a freshly prepared solution of 5 mmol/L OTS in 70% chloroform and 30% hexadecane. The beaker, silanized prior to the reaction, was placed in an ultrasonic bath, and the reaction took place for 6 min at $T = 20$ °C. After reaction, the treated substrates were rinsed thoroughly with chloroform and dried with nitrogen.

Glass substrates were silanized using octadecyltrichlorosilane (OTS). The procedure of silanization is similar to that used for silicon wafers except that toluene is used instead of hexadecane during the silanization reaction. Different solvents were used for different substrates, and they play an important role in the quality of the silanization.[16] The solvents used (acetone, chloroform, hexadecane, and toluene) were all ACS grade and used as received.

2.1.3. Transfer of Bilayers onto Hydrophobic Substrates. The experimental cell used for transferring the black films is described elsewhere.[1] We used a slightly different draining material (i.e., filter paper instead of a porous silica plate). Figure 1 is a simplified sketch showing the deposition method. A bubble is created using a plastic pipet from a surfactant solution. It is then carefully deposited onto a solution-soaked filter paper placed in a closed chamber containing the solid substrate to be used for film transfer. Using the filter paper is advantageous because it is disposable and can be used in the future for more complex solutions. (For example, solutions that contain nanoparticles cannot be easily rinsed after use.) The filter paper is cleaned thoroughly before use in boiling ultrapure water.

The bubble then drains until it becomes transparent at the top. Figure 2 shows the drainage of a C$_6$F$_{13}$SOTHAM-stabilized bubble. The drainage time depends mainly on the dampness of the filter paper. It should be wet enough for the bubble to be stable but not so wet that the drainage would not be too slow. Once the film becomes black, the hydrophobic substrate is brought into contact with the bubble, which transforms to a slightly deformed cylinder. The adhesion of the film to the substrate is immediate. The cylinder then breaks rapidly. The transferred film can be characterized by X-ray reflectivity and near-field microscopy. The area of the surfactant film in contact with the substrate is on the order of a few square centimeters and can be easily adjusted by injecting more air and forming a larger bubble.[1]

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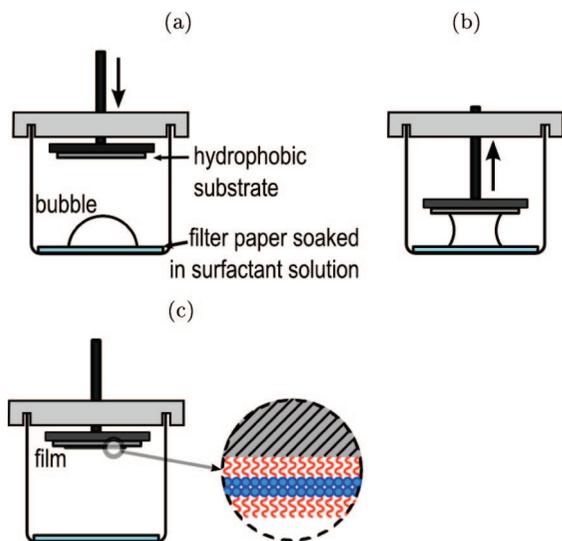
Figure 1. Simplified sketch of the apparatus used to transfer surfactant bilayers onto a hydrophobic substrate. (a) A sheet of clean filter paper is soaked in a surfactant solution. It is placed in a closed chamber of glass containing the treated solid substrate. A bubble is formed using a plastic pipet from a surfactant solution and is carefully placed onto the filter paper. It is then left to drain off the water. (b) When the bubble is black, the solid substrate is lowered until it touches the top surface of the bubble. Because of the adhesion to the solid substrate, a cylinder forms for a few seconds during the deposition. (c) The solid substrate is then removed from the chamber, and a bilayer of surfactant is deposited onto its surface.
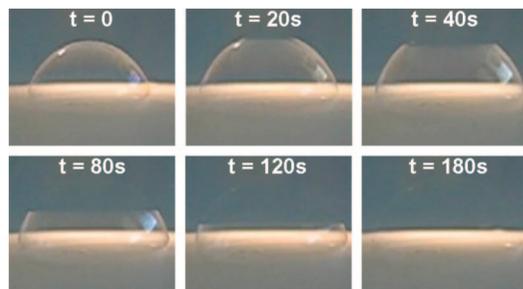
Figure 2. Drainage of a C_6F_{13}SOTHAM bubble at different times. After a few minutes, the bubble becomes black (i.e., transparent to the human eye).
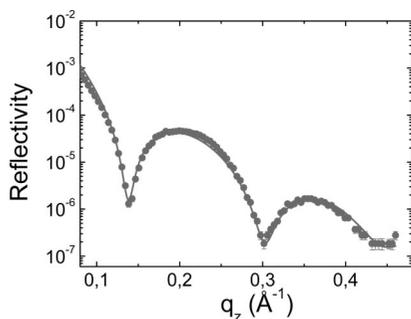
Figure 3. Plot of the reflectivity as a function of the wave vector q_z for a C_6F_{13}SOTHAM free-standing Newton black film. Grey circles with error bars are the experimental data points, and the solid gray curve is a least-squares fit to the X-ray data (see text). The thicknesses and electron densities of the layers as well as their interfacial roughnesses deduced from the fit are given in Table 1.

2.2. Characterization. X-ray reflectivity experiments were performed using a copper tube X-ray source ($\lambda = 1.5405$ Å Cu Kα 1 line) and a high-resolution diffractometer (Optix-Nonius) described elsewhere.[4,6] The reflectivity is defined as $R(q) = I(q)/I_0$, where $I(q)$
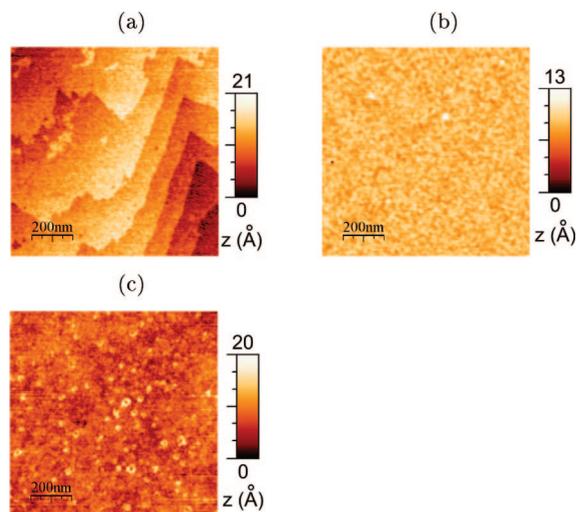
Figure 4. AFM topographic images of the hydrophobic substrates used in this study: (a) an etched Si(111) wafer, (b) an OTS-silanized Si wafer, and (c) an OTS-silanized glass slide. On b, the white dots are probably dust particles from the air. On c, the white rings are probably defects from the glass surface before silanization.

and I_0 are, respectively, the intensities of the reflected and incident beams and q is the scattering wave vector. The reflectivity profile provides access to the electron density profile normal to the film. In fitting the reflectivity curves, the entire films (transferred or free-standing films) in the normal direction are divided into a series of homogeneous slabs, and each slab is fitted for its thickness and interfacial roughness using an optical formalism taking into account multiple reflections.[22] The integration of the different parameters corresponds to a macroscopic surface area of 4 mm^2, which is the surface grazed by the X-ray beam at such angles of incidence. The goodness of the least-squares fit is determined by the minimization of χ^2.

AFM topographic imaging was done with a Seiko Instruments (Chiban, Japan) SPA300HV model AFM equipped with a platinum-coated silicon cantilever with a spring constant of 0.035 N/m and a tip radius of less than 32 nm (manufacturer specification from MikroMash, tip reference CSC37/Pt). The AFM was operated in tapping mode for Figures 4, 5b,c, 6, and 9b. The AFM was operated in contact force mode for Figure 7 with an applied normal force of approximately 50 pN. Using a platinum-coated tip allowed a reduction of the noise when compared with a noncoated silicon tip. Moreover, platinum-coated tips have smaller curvature and good wear resistance. It works as well in tapping mode as in contact force mode because its Q factor is well shaped in air. Its small spring constant is also advantageous for soft samples such as these measured. Results were analyzed with WSxM software.[23]

3. Structure of Free-Standing Films and Hydrophobicity of Substrates

3.1. Free-Standing Films of C_6F_{13}SOTHAM. Newton black films (NBFs) of C_6F_{13}SOTHAM are obtained at room temperature with high stability. Once formed, they can last for several days without breaking. Figure 3 shows the reflectivity curve of the C_6F_{13}SOTHAM free-standing NBF. It exhibits two distinct interference Kiessig fringes, indicating that the film is very homogeneous. The reflectivity curve is fitted using a three-layer model (described in the Experimental Section), allowing us to determine the film structure. The fitted results are summarized in Table 1, and the fitted curve is shown in Figure 3. The three-

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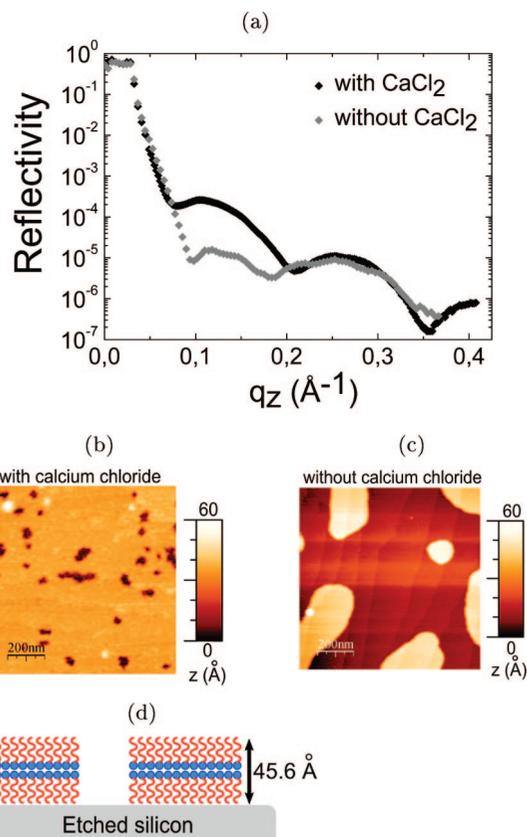
Figure 5. Fluorinated surfactant bilayer transferred onto an etched silicon wafer; calcium chloride is added to the solution to ease the transfer. (a) Plots of the X-ray reflectivity data. (b, c) AFM images of a bilayer transferred with and without calcium chloride added to the solution. (d) Sketch of the deposited bilayer with one defect.
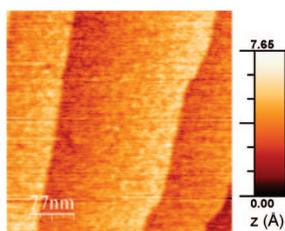
Figure 6. Transfer of a C_6F_{13}SOTHAM bilayer onto an etched silicon wafer. The surfactant bilayer follows the step features of the etched substrate (Figure 4).

layer model utilized for fitting the experimental data lacks some precision for precisely fitting the first Kiessig fringe but allows an adequate determination of the freestanding film structure.

The central layer (corresponding to the hydrophilic sulfoxide part of the C_6F_{13}SOTHAM molecule) is sandwiched between two identical layers formed by the fluorinated chains of the compound C_6F_{13}SOTHAM. According to the fit given in Table 1, the hydrophobic chain length is 12.8 ± 0.1 Å. The length of a fully extended $C_6F_{13}CH_2CH_2$ chain (all trans configuration) is given by $l_C = 1.3(m + 1) + 1.265(n + 2.58)$, where n is the number of CH_2 groups and m is the number of CF_2 groups.[24,25] For $n = 2$ and $m = 5$, the length l_C is 12.91 Å. Thus, in the free-standing film, the hydrophobic tails of the molecules are not very tilted, and the tilt angle is calculated to be 7.5°. The overall
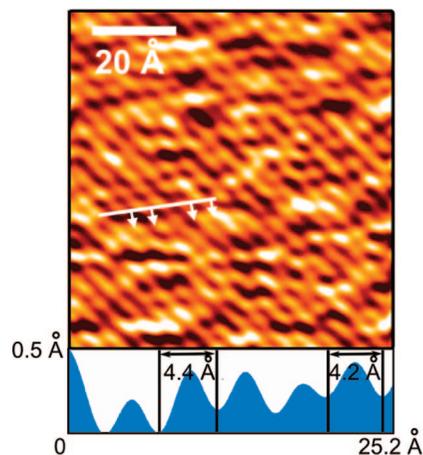
Figure 7. AFM topographic image of the transferred C_6F_{13}SOTHAM film with a scan size of 7×7 nm². The cross-sectional profile along a line drawn across the image is shown below the image. Distances between arrows in the image are 4.4 and 4.2 Å. High-frequency noise in the image is removed by Fourier filtering. During imaging, the AFM was operated in contact force mode with an applied normal force of approximately 50 pN.

Table 1. C_6F_{13}SOTHAM Free-Standing Film, Including Fitted Thickness, Electron Density, and Roughness Using the Three-Layer Model[a]

components	thickness (Å)	electron density δ	roughness σ (Å)
fluorinated chains	12.8 ± 0.1	$3.8 \pm 0.1 \times 10^{-6}$	2.5 ± 0.2
hydrophilic core	16.9 ± 0.2	$2.8 \pm 0.1 \times 10^{-6}$	2.5 ± 0.2

[a] The film is symmetric. The electron density δ is the real part of the refractive index $\delta = \lambda^2 r_e \rho / 2\pi$, where $\lambda = 1.5405$ Å is the X-ray wavelength, r_e is the classical electron radius, and ρ is the mean electron density. The least-squares fitting parameter χ^2 is less than 10^{-2}, and errors are determined when χ^2 is changed by 10%.

thickness of the C_6F_{13}SOTHAM Newton black film is found to be 42.5 ± 0.4 Å, which is in agreement with the value that was previously found.[7]

The addition of calcium chloride to the solution (1 equiv, i.e., 0.0008 mol/L) decreases the thickness of the hydrophilic core of the NBF by 1 Å (data not shown), which is explained by a screening of the residual charges that might be present in the film.

3.2. Substrate Characterization. Because the hydrophobic part of the surfactants faces the air in Newton black films, adhesion of the film can occur only on similarly hydrophobic substrates, with a water contact angle equal to or larger than 90°. Moreover, to preserve the bilayer organization, the substrate should be smooth and atomically flat. Two methods of hydrophobization are selected: wet chemical etching using an NH₄F aqueous solution and alkylsilane grafting, which is also called silanization or silanation.

Etching Si(111) wafers using an NH₄F aqueous solution has been proven to provide ideally terminated monohydride surfaces. These atomically flat surfaces are extremely well ordered and exhibit terraces that extend to hundreds of nanometers.[12–14] After being etched, the surfaces were characterized by measurements of the X-ray reflectivity and AFM. The roughness deduced from the X-ray reflectivity data is very low, and its average on 17 different etched wafers is 3.9 ± 1.1 Å. Fitted values of the electron density and the interfacial roughness of the etched silicon are given in Table 2. AFM characterization confirms previous observations.[26,27] Indeed, many steps of approximately 2 Å

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Table 2. Results of the Fit to the X-ray Reflectivity Data for Three Different Hydrophobic Substrates: A (111)-Oriented Silicon Wafer Chemically Etched Using NH₄F, a Silanized Silicon Wafer, and a Silanized Glass Slide[a]

substrates	components	thickness (Å)	electron density δ	roughness σ (Å)
etched Si(111)	Si		7.4×10^{-6}	3.9 ± 1.1
silanized Si	OTS	24.8 ± 1.2	3.5×10^{-6}	3.6 ± 0.3
	Si		7.4×10^{-6}	3.6 ± 0.5
silanized glass	OTS	22.6 ± 1.9	3.5×10^{-6}	4.7 ± 1.2
	SiO₂		7.2×10^{-6}	5.3 ± 1.2

[a] Values of the fitted thickness, electron density, and interfacial roughness are averaged on 17 fits corresponding to 17 different samples for etched Si, 4 fits corresponding to 4 different silanized Si wafers, and 12 fits corresponding to 12 different silanized glass slides. The fitting procedure is described in the Experimental Section. Errors are determined from different fits on many samples (see text).

between terraces of 100 to 300 nm in size can be observed in Figure 4a.

Grafting alkyl chain onto a surface is also a widely used technique to obtain tunable surfaces. Octadecyltrichlorosilane (OTS) is routinely grafted onto silica surfaces, such as glass or native silicon. Our experimental method provides homogeneous, smooth, hydrophobic surfaces. X-ray reflectivity data showed a dense layer of thickness 24.8 ± 1.2 Å (respectively, 22.7 ± 1.9 Å) for a silanized silicon wafer (respectively, a silanized glass slide). These values are in good agreement with the fully extended aliphatic chain length.[25] Such a result implies that the hydrophobic chains are perpendicular to the wafer. The OTS layer thickness and roughness, as well as the substrate roughness, were deduced from the X-ray reflectivity data; their averages were taken on 4 different silanized wafers and on 12 different silanized glass slides. The thickness of the alkyl layer for silanized glass is smaller than for silanized silicon, which could be explained by a slight tilt of the alkyl chains depending on the substrate. The roughness of the air−layer interface is about 3.6 ± 0.3 Å (respectively, 4.7 ± 1.2 Å) for a silanized silicon wafer (respectively, a silanized glass slide) which is similar to or slightly smaller than that of the bare substrate (3.6 ± 0.5 and 5.3 ± 1.2 Å, respectively). Average values of the fitted thickness, electron density, and interfacial roughness are given in Table 2. The values for silanized glass deviated more than the results for silanized silicon wafers. This is expected because the glass slides are not as uniform as the silicon wafers. The results in Table 2 are in good agreement with values previously reported in the literature.[15,16]

AFM measurements shown in Figure 4b confirm that the silanized silicon surface is very homogeneous without any defect and is also very smooth. The calculated rms roughness over a surface of $1 \mu m^2$ is 0.75 Å. According to the AFM measurements shown in Figure 4c, the silanized glass substrate is also very smooth, and the calculated rms roughness (over a surface of $1 \mu m^2$) is 2 Å. The difference between interfacial roughnesses given by the X-ray data fit and the AFM technique is explained by the difference in the integration surfaces, one being microscopic and the other being macroscopic as mentioned in Table 2. A few yellow rings are visible on this image, which are probably defects from the glass substrate.

4. Results and Discussion

A promising area of application of this method is to construct complex architectures, such as bilayers and multiple bilayers containing nano-objects. Different physical processes (diffusion or electrostatic attraction) were reported for the insertion of a dense protein monolayer into surfactant and phospholipid Newton black films.[10,11] The molecules constituting black films are highly organized. For this reason, it is not unreasonable to expect that nanosized molecules confined within an NBF may exhibit a

tendency to form 2D crystals. Because the diffusion of nano-objects and attractive electrostatic forces between nano-objects and surfactant walls is independent of the details of the objects being inserted, nanoparticles that are or can be made soluble in water (by an appropriate surfactant) would be suitable candidates for this process. Work in progress involves the insertion of various types of nanoparticles in the polar part of the surfactant bilayer. Therefore, the improvement of the transfer method using different substrates and chemical additives is profitable. Preserving the molecular order of the free-standing film, achieving a high bilayer coverage on the substrate, and avoiding macroscopic defects, such as holes or aggregation in the bilayer, during transfer are necessary to producing the desired complex structures.

4.1. Transfer of Bilayers onto Etched Silicon Surfaces. The adhesion of a free-standing C12E6 film onto an etched Si(111) surface has been shown previously to be homogeneous and in-plane-ordered.[1] In this study, the adhesion of a free-standing C₆F₁₃SOTHAM film onto etched (111) silicon surfaces was found to be incomplete, probably because of the low adhesion energy of fluoroalkyl chains on monohydride Si−H-terminated surfaces.

4.1.1. Adding Calcium Ions Improves Transfer. To increase the surface coverage of the transferred bilayer, calcium ions were added to the surfactant solution. The calcium chloride concentration was chosen to be 1 equiv with respect to the surfactant concentration (i.e., 0.0008 mol/L). Calcium ions act as a "molecular zip" with which the free-standing film stiffens, and then the transfer is more complete.[21] X-ray reflectivity curves presented in Figure 5a compare the differences between the transfers with and without the addition of calcium chloride to the surfactant solution used to create the bubble. When calcium is added, the Kiessig fringes are better defined and have a higher contrast, indicating a low interfacial roughness and a high homogeneity for the transferred film. Fitting parameters of the X-ray reflectivity curve obtained on a transferred bilayer containing calcium ions are given in Table 3.

A four-layer model is utilized to fit the data, and the final results are found to be close to the free-standing film results (Table 1). The total thickness of the film is 45.6 ± 0.8 Å, which is only 3.1 Å larger than the free-standing film thickness. This increase in film thickness is attributed to a change in the hydrophilic part of the film as a result of a different environment. According to the fit, the thickness of the hydrophilic part is increased from 16.8 to 19.8 Å. The hydration of the hydrophilic part of the film changes when the film is transferred. The interfacial roughness also increases slightly, probably because of the presence of a few defects in the transferred bilayer.

The higher quality observed for the film transfer when calcium ions are present is attributed to the interlinking of neighboring surfactant molecules (amide or tris groups) through the complexation of calcium ions. The Ca²⁺ ions are assumed to position themselves between the hydrophilic heads of the surfactant molecules. AFM images shown in Figure 5b,c depict a higher sample homogeneity when calcium is added, with fewer

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Table 3. Fitted Thickness, Electron Density, and Interfacial Roughness for Different Layers of the Deposited C$_6$F$_{13}$SOTHAM Bilayer onto Etched Si(111)[a]

substrate	components	thickness (Å)	electron density δ	roughness σ (Å)
etched silicon wafer	fluorinated chains	12.9 ± 0.3	$3.8 \pm 0.1 \times 10^{-6}$	2.4 ± 0.2
	hydrophilic part	19.8 ± 0.3	$2.2 \pm 0.2 \times 10^{-6}$	1.3 ± 0.9
	fluorinated chains	12.9 ± 0.2	$4 \pm 0.2 \times 10^{-6}$	5.9 ± 0.9
	silicon substrate		7.4×10^{-6}	2.8

[a] Calcium chloride is added to the surfactant solution, and then a film is transferred onto the etched silicon surface according to the procedure described in the Experimental Section. A preliminary X-ray scan of the bare substrate is made, giving the values for the silicon substrate electron density and roughness. The least-square fitting parameter χ^2 is less than 10^{-2}, and errors are determined when χ^2 is changed by 10%.

macroscopic defects such as holes in the bilayer. The holes correspond to parts of the bilayer that did not stick to the treated Si−H surface. Figure 5b provides us with an internal calibration because one can observe monatomic steps on the Si(111)-etched surface. The height of this step is known to be 3.1 Å. The height of the holes is thus calculated to be 45.5 ± 2.5 Å from averages deduced from 10 different profiles arbitrarily drawn across such holes in both images. This height corresponds to the height of the surfactant bilayer, as determined by the X-ray reflectivity. Figure 5d depicts the structure of the transferred film with one hole.

Figure 6 shows an AFM image of a transferred bilayer onto the etched silicon. The lateral scale is smaller than the scale in Figure 5b but corresponds to the same deposition. The terraces are clearly visible, even after the transfer. The transferred bilayer copies the step feature created by the terraces of the etched silicon substrate. Hence this method applies to patterned substrates.

4.1.2. In-Plane Order of the Transferred Bilayer. The in-plane order of the transferred bilayer is examined using AFM, and results are presented in Figure 7. The image shows a close-packing structure of surfactant molecules with a periodicity of approximately 4.4 Å, reflecting an organized 2D structure of the deposited Newton black film. Therefore, the transfer preserves the arrangement of the surfactant molecules. The periodicity of the fluoroalkyl chains is very small, especially when compared with the periodicity of alkyl chains (6 Å).[1] This is in good agreement with the X-ray reflectivity data showing that the fluoroalkyl chains must be compressed during the transfer, achieving a higher packing density when deposited onto an etched Si(111) surface compared to that of their free-standing form.

4.1.3. Deposition of Multiple Bilayers onto the Etched Silicon Surfaces. Similar to Langmuir−Blodgett or Langmuir−Schaefer methods, the present method can be used to deposit successive layers. A solution with calcium chloride was used because it greatly diminishes transfer defects. First, a bubble was created and transferred after drainage onto an etched silicon substrate. X-ray reflectivity measurements were then carried out on this sample to check the evenness and homogeneity of the transferred bilayer. Then a second surfactant bilayer was deposited on top of the first transferred bilayer and characterized using X-ray reflectivity. Experimental results are presented in Figure 8.

The reproducibility of the transfer method is demonstrated by the corresponding curves presented in Figures 5 and 8. The total thickness of the first deposited film is deduced to be 45.9 Å from the X-ray reflectivity data (Figure 8a). After the second deposition, the X-ray reflectivity curve exhibits five fringes with reduced definition. The loss of contrast is explained by the increasing number of defects after the two transfers. Sketch 8b shows how disorder is introduced by two successive depositions. Higher interfacial roughnesses and lower definition are observed. Because of these complications, precise fitting of the curves could not be achieved, and only the total roughness of the two successive depositions could be measured. The thickness of the second transfer was deduced to be 40.2 Å, which is only a few angstroms
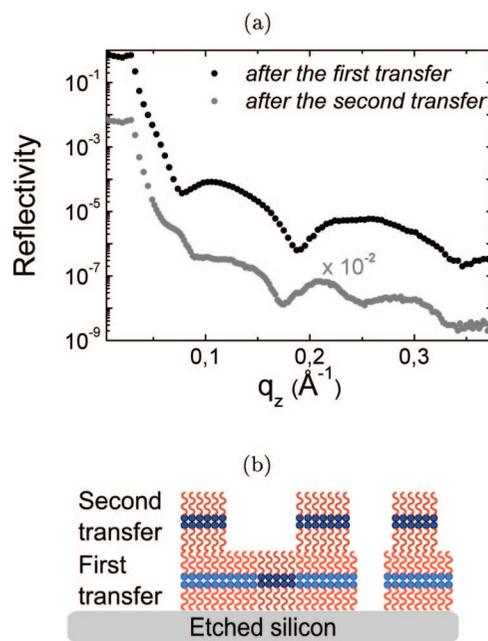
Figure 8. (a) Plots of the X-ray reflectivity as a function of the wave vector q_z for two successive transfers of the C$_6$F$_{13}$SOTHAM films. The upper curve shows the data points obtained after the first transfer, and the lower curve shows the data points after the second film deposition. For clarity, the reflectivity values after the second transfer (lower curve) are divided by 100, as indicated. (b) Sketch of the double transfer. The bilayer that is transferred first (pale colors) may present a few defects (holes). During the second transfer (dark colors), some defects may be filled with surfactant, creating a defect in the top bilayer. Other defects may stay, and some defects are created only in the second bilayer transfer. More disorder is introduced by the two transfers compared with that of only one transfer.

less than the expected value of 45.6 ± 0.8 Å. This decrease is also attributed to a larger number of holes present at the surface, which should be doubled for two successive transfers.

4.2. Transfer of Surfactant Black Films onto Silanized Silica Surfaces. The silanization of oxide surfaces has been well studied because of its potential utility for wetting, adhesion, and patterning purposes. Using trichloroalkylsilane or trimethoxyalkylsilane, a wide range of substrates (silica, metallic oxides, mica, gold)[17] may be silanized, allowing the control of hydrophobicity while lowering the roughness of the surface. The process has been well studied[15–17,33] and can be reproducibly applied. The properties of the substrate as well as the grafted silane may be chosen according to the prospective applications.[17]

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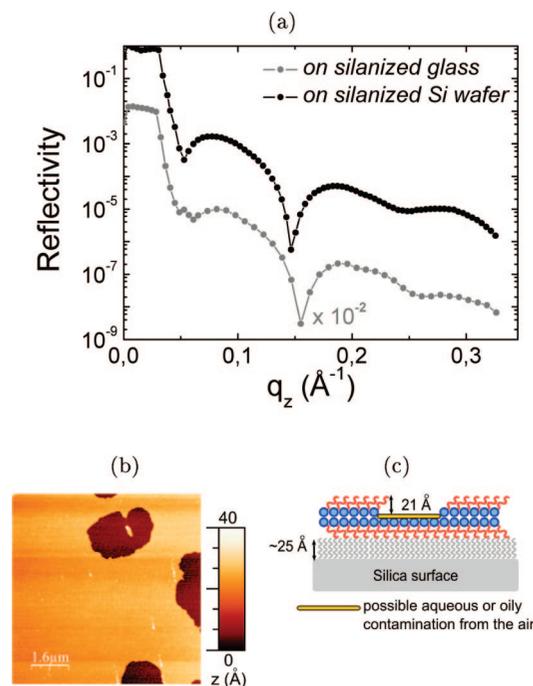
Figure 9. Fluorinated surfactant bilayer transferred onto a silanized silicon wafer and a silanized glass slide (a) X-ray reflectivity plots as a function of the normal wave vector q_z for the C_6F_{13}SOTHAM Newton black films transferred onto two silanized surfaces. For clarity, the reflectivity values for the glass slide (lower curve) are divided by 100, as indicated. (b) AFM topographic image of a bilayer transferred onto the silanized silicon wafer. (c) Sketch of a deposited bilayer with a defect in the bilayer. The exact configurations of the surfactant molecules in the layer below the defect remain unknown and therefore might not be drawn accurately.

The adhesion of a fluorinated surfactant bilayer onto silanized silica or glass is more complete than adhesion onto etched silicon. Adding calcium chloride is not necessary in this case. The interfacial energy of the silanized surface is low, 20.5 ± 5 mN/m,[33] and according to our experiment, fluorinated surfactants stick well to such surfaces. Figure 9a shows the reflectivity curves of the C_6F_{13}SOTHAM films transferred on a silanized 2 in. silicon wafer and a silanized 26×26 mm^2 glass slide. Both reflectivity curves exhibit distinct fringes with high contrast. Thus, we can measure the overall thickness of the transferred films directly from the position of the interference fringes position. It is 40 ± 1.5 Å on silanized Si and 39.3 ± 1 Å on silanized glass. Our slab model (described in the Experimental Section) is not detailed enough and thus does not allow us to obtained fitted values for the electron density or the interfacial roughness of the films.

The differencees in thickness compared to that of the freestanding film (2.5 and 3.2 Å for silanized Si and glass, respectively) may be explained either by a change in the conformation of the chain (a slight difference in the angle of tilt of the fluoroalkyl chains) or by an increase in disorder during transfer. The first hypothesis is favored because the fringes are well defined in the X-ray reflectivity curves which implies a low interfacial roughness. This is also supported by the fact that AFM images show a very low density of defects as shown on figure 9b.

The surface coverage is indeed very high and almost without macroscopic defects; only a few imperfections in the bilayer are observed on the AFM image in Figure 9b. The height of these imperfections is uniform and equals 21 ± 2 Å, which corresponds roughly to the height of a surfactant monolayer. This value is given by an average on 10 different profiles taken arbitrarily across the defects on the AFM image. Silanized substrates do not give us an internal calibration, such as NH_4F-etched Si(111) wafers. Therefore, this value is less quantitative than the value given for defects on transferred films on etched Si(111) wafers. Sketch c in Figure 9 depicts the structure of the transferred film with one defect. The hydrophilic heads of the first surfactant layer exposed to the air in the few defects may attract some water and oily contaminants from the atmosphere because the deposition is not done in vacuum or a cleanroom environment. The exact configuration of the layer of surfactants in the defects remains unknown and could not be determined by X-ray reflectivity or AFM measurements.

This is consistent with the previous observations of an easy adsorption of the bilayer onto the silanized surface. The mechanism of adsorption is clearly different between the silanized substrates and the etched silicon substrates. Free-standing films of fluorinated surfactants stick more easily and preferentially to the silanized surfaces than to the etched substrates. Sketch c in Figure 9 depicts the structure of the transferred film with one defect. This is consistent with the previous observations of easy adsorption of the bilayer onto the silanized surface. The mechanism of adsorption is clearly different between the silanized substrates and the etched silicon substrates. Free-standing films of fluorinated surfactants stick more easily and preferentially to the silanized surfaces than to the etched substrates.

5. Conclusions

A method for transferring Newton black films onto solid substrates while preserving their molecular organization is broadened here to different kinds of substrates. A fluorinated surfactant bilayer is deposited onto three different surfaces: an etched silicon surface, a silanized silicon wafer, and silanized glass slides. These surfaces are all very hydrophobic, smooth, and planar. The treated substrates and the transferred films are characterized using AFM and X-ray reflectivity, which are complementary techniques allowing a better description of the 2D structure of the transferred films. The bilayer organization of the film and its self-assembly properties are preserved after its deposition onto the solid surfaces. Noticeably, the transferred bilayers can copy the surface structure of the substrates, indicating that the method can be applied to patterned substrates. Such a transfer process can be utilized for the construction of 2D or 3D organization of small objects, such as proteins and nanoparticles. As an example, using this method we successfully carried out two successive transfers of bilayers onto an etched silicon substrate. The transferred bilayers have slightly different configurations depending on the chosen substrate. On silanized silica, the bilayers adhere easily whereas the transfer is slightly more difficult on etched silicon. In that case, adding calcium chloride to stiffen the bilayer improves the surface coverage. Being able to choose a suitable substrate for film transfer is a considerable advantage because it broadens the applications in the fields of material science and nanotechnology.