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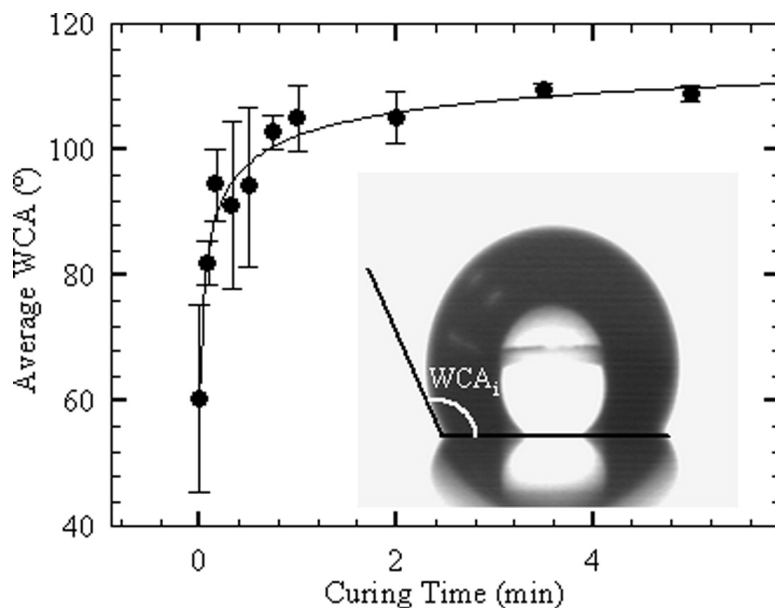
Hydrophobic Films by Atmospheric Plasma Curing of Spun-On Liquid Precursors

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Hydrophobic Films by Atmospheric Plasma Curing of Spun-On Liquid Precursors

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Hydrophobic coatings have been produced on glass and acrylic samples by using a low-temperature atmospheric pressure plasma to polymerize liquid fluoroalkylsilane precursors. The fluoroalkylsilane precursor was dissolved in isooctane and spun onto the substrate at 550 rpm. The sample was then exposed to the reactive species generated from a nitrogen plasma. The plasma was operated with 2.3 vol % N_2 in helium at 7.4 W/cm^2 at a radio frequency of 27.12 MHz. The total and polar component of the coating's surface energy was found to equal 11.0 and 1.2 dyn/cm, respectively. Average water contact angles of 110° and 106° were measured on the coated glass and acrylic surfaces, respectively. X-ray photoelectron spectroscopy revealed that, after treatment, the fluoroalkyl ligands remained intact on the Si atoms, with a F/C atomic ratio of 2.23.

1. Introduction

Hydrophobic surfaces are defined as having a water contact angle exceeding 90°. Coatings with such a property have a number of uses, for example, self-cleaning windows,[1] gas barrier coatings,[2] low stiction coatings in MEMS/NEMS devices,[3,4] and biomaterials which reduce cell adhesion.[5,6] Hydrophobic coatings exhibit a low surface energy, where the polar component is close to zero, as this is the driving force for a water droplet to increase its interfacial area with the substrate.

A number of fluoroalkylsilane precursors tailored to provide low surface energy materials have been investigated for this application. These precursors vary significantly in their specific structure but always include at least one fluorinated organic ligand connected to the silicon atom. The remaining ligands are methoxyl or ethoxyl groups, attached to the silicon via a bridging oxygen atom. Condensation of the precursor and cross-linking of the silicon atoms via oxygen atoms can be accomplished by gently heating the material in an inert atmosphere over a minimum of 1−2 h, yielding water contact angles of 100−112°.[7,8] It has been reported that these liquid precursors will form self-assembled monolayers on a carefully prepared substrate, with surface energies as low as 8 dyn/cm.[6−8]

Alternatively, chemical vapor deposition (CVD) and plasma enhanced CVD (PECVD) have been used to produce hydrophobic coatings.[6,9−11] In this case, the precursor is vaporized into a carrier gas and fed to the reactor where it is transported to the substrate surface and decomposed. Atmospheric pressure CVD has been used to form hydrophobic coatings from fluoroalkylsilane with water contact angles of 112° after 1 h of processing at 150 °C.[7] Coatings with greater rms surface roughness, 30−100 nm compared with <0.1 nm, have shown increased hydrophobicity and even superhydrophobic properties and are obtained by a variety of methods including sol−gel mixtures[12,13] and plasma-assisted particulate deposition.[14]

This Article reports on the formation of hydrophobic coatings directly from liquid fluoroalkylsilane spun onto a substrate. This process is different from PECVD, since the plasma reacts directly with the liquid precursor distributed on the solid surface. In this case, the plasma is used instead of heat to convert the precursor into a solid film. Below, we demonstrate that the fluoroalkyl ligands remain intact on the Si−O−Si network, producing transparent coatings with water contact angles exceeding 105° on glass and plastic substrates.

2. Experimental Methods

Several different substrate materials were used in this work: Corning 1737 glass plates 1.5 in. × 1.5 in. × 0.02 in. thick were obtained from Precision Glass & Optics. Wafer-type borofloat glass substrates, 4.0 in. in diameter, were used for the transparency measurements and the long-term aging study. Cast acrylic poly-(methylmethacrylate) (PMMA) sheets 1/8 in. thick were obtained from McMaster-Carr, Inc. and were cut into 1.5 in. × 1.5 in. squares. All substrates were washed and cleaned with isopropyl alcohol and then baked on a hot plate in air at 65−80 °C for several minutes until dry.

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The substrates were pretreated with an atmospheric pressure plasma source.[15] The source produced a 2 in. wide reactive gas beam and was operated with 30.0 L/min helium, 0.40 L/min oxygen, and 150 W RF power at a frequency of 27.1 MHz. The gas temperature at the outlet of the source was below 85 °C. The plasma source was mounted on a robot and scanned over the surface at a rate of 50 mm/s, with a separation distance of 3.0 mm for glass and 7.0 mm for acrylic. This process was repeated four times on the 1.5 in. long substrates for a total of about 3 s of exposure, unless otherwise indicated.

All coatings were prepared by applying 1.2 ± 0.2 mL of a fluoroalkylsilane solution onto the substrate which was being spun at 550 ± 50 rpm. The fluoroalkylsilane (FAS) solution consisted of 50 ± 5 mM heptadeca-fluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane ($C_8F_{17}C_2H_2Si(OC_2H_5)_3$), obtained from Gelest, Inc., in 99.8% anhydrous isooctane (2,2,4-trimethylpentane) from Sigma-Aldrich. The atmospheric pressure plasma source used to convert the liquid coating consisted of a 2 in. diameter showerhead,[16] operated at 30.0 L/min helium, 0.70 L/min nitrogen, and 150 W RF power at 27.1 MHz. The samples were positioned 7 ± 1 mm below the plasma source. Because of the high reactivity of FAS with water, all coating and curing steps were performed in a sealed acrylic box which was purged with argon.

Contact angle measurements were performed with a Krüss EasyDrop goniometer, using distilled water, di-iodomethane, and glycerol. The values of the surface energy of these liquids are taken from Janczuk and Zdziennicka.[17] Each average contact angle was determined from 10 to 30 droplets per sample, and 50 to 100 automated measurements per droplet. The error in each average value is estimated by calculating the standard deviation of the measured data. Surface energy calculations were made using the data from the three fluids, and performing a linear regression in accordance with the Owens, Wendt, Rabel, and Kälble theory.[18,19] The data were plotted according to eq 1.

$$\frac{(1 + \cos \theta)\gamma_1}{2\sqrt{\gamma_1^D}} = \sqrt{\sigma_s^P}\frac{\sqrt{\gamma_1^P}}{\sqrt{\gamma_1^D}} + \sqrt{\sigma_s^D} \qquad (1)$$

In this equation, σ_s^P and σ_s^D represent the polar and dispersive components of the solid−air surface energy, γ_1^P and γ_1^D are that of the liquid−air surface energy, and θ is the contact angle of the test liquid with the substrate surface.

Scanning electron microscopy (SEM) images were obtained using a Hitachi S4700 scanning electron microscope operated at 2.00 kV, 48.5 μA, and a working distance of 11.6 mm. Atomic force microscopy (AFM) data were acquired with a Veeco Dimension 3100 atomic force microscope in tapping mode at a scan rate of 1 Hz. Profilometry measurements were performed using a Veeco Dektak 8 surface profiler. Ultraviolet−visible spectroscopy measurements were taken with a Hitachi U-3410 spectrophotometer with tungsten halogen and deuterium lamps. Property measurements were obtained for fresh samples less than 1 week after processing, and older samples aged approximately 12 ± 1 months. The effect of short-term aging on the average water contact angle was also examined.

The compositions of two surfaces, a coated silicon wafer and a 0.5 mm thick poly(tetrafluoroethylene) (PTFE or Teflon) film, were analyzed by X-ray photoelectron spectroscopy (XPS). Core level photoemission spectra of the Si 2p, C 1s, O 1s, and F 1s lines were collected with a PHI 3057 XPS instrument using Mg Kα X-rays at 1286.6 eV. Each measurement was taken in small area mode with a 7° acceptance angle and 23.5 eV pass energy. The detection angle with respect to the surface normal was 25°. Two different references
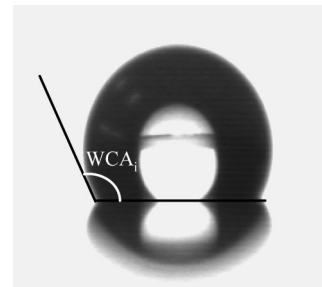

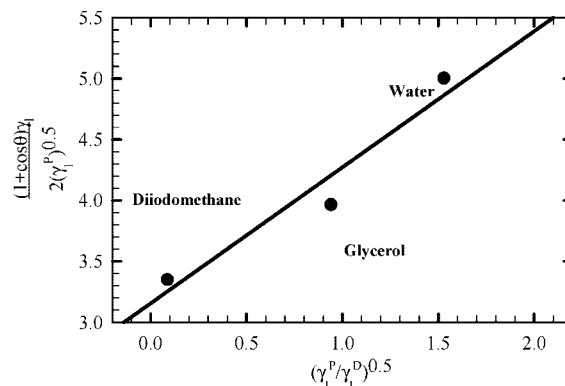**Figure 1.** Image of a water droplet on a coated glass substrate.

Figure 2. Surface energy plot for a coated 4 in. glass substrate aged 1 year (●).

were used to align the spectra to the correct binding energies. The Si 2p spectrum was referenced to the zero valence Si peak at 99.8 eV, while all other atomic lines were referenced to the C 1s peak of the fluorinated carbon atom ($-CF_2-$) at 292.4 eV.[20] The surface atomic percentages were determined from the integrated intensity of the Si 2p, C 1s, O 1s, and F 1s photoemission peaks, divided by their sensitivity factors, 0.34, 0.30, 0.71, and 1.00, respectively.[20,21]

3. Experimental Results

3.1. Contact Angle Measurements and Surface Energy. An image of a single droplet on a coated glass surface is shown in Figure 1. It can be clearly seen that the water contact angle (WCA) is greater than 90°. The average WCA on coated glass substrates was $110° \pm 3°$, while the average WCA on coated acrylic substrates was $106° \pm 5°$. Note that the uncoated glass and acrylic surfaces exhibited average WCA values of $70° \pm 3°$ and $76° \pm 3°$, respectively, before any plasma treatment. Coatings on glass obtained using a similar method, but without plasma, yielded an average WCA of $115° \pm 5°$.[22] Contact angles of water, di-iodomethane, and glycerol were measured in the goniometer, and used in combination with referenced physical properties of the fluids to generate the surface energy plot shown in Figure 2.[17,19] The polar component for this sample is equal to 1.2 dyn/cm, while the total surface energy is equal to 11 dyn/cm.

It was determined that a minimum plasma exposure time of 1 min was required to completely cure the FAS film (see below). Underexposed coatings appeared to react with the water droplets. In this case, the goniometer video camera recorded a change in refraction in regions within the droplet after it contacted the

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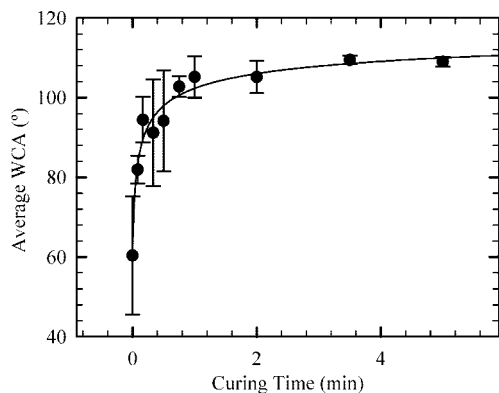
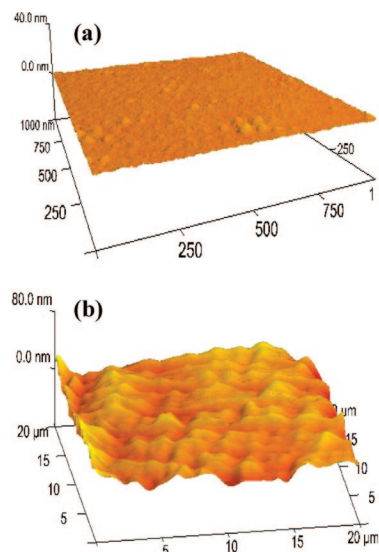**Figure 3.** Effect of plasma curing time on the average water contact angle of the FAS-coated glass sample.
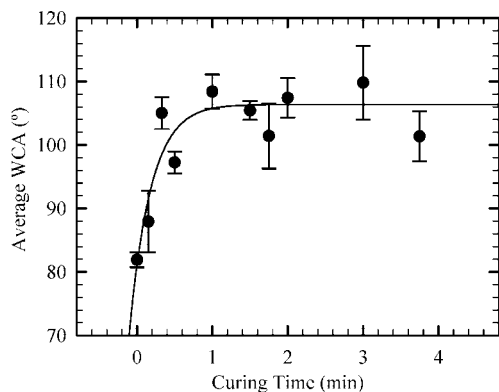
Figure 4. Effect of plasma curing time on the average water contact angle of the FAS-coated acrylic sample.

Figure 5. AFM images of (a) uncoated and (b) coated acrylic substrates.

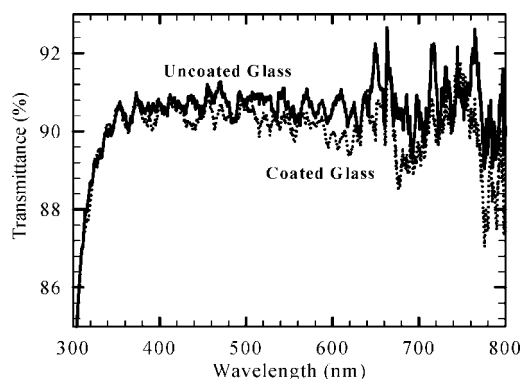**Figure 6.** UV–visible transmission spectrum for an uncoated and coated glass substrate.

surface. Furthermore, underexposed coatings could be partially removed by submerging them in deionized water in an ultrasonic bath for 5 min, whereas coatings cured for 1 min or more had WCA values which were unchanged by this procedure.

3.2. Influence of Pretreatment and Curing Time. Shown in Figures 3 and 4 are the effects of plasma curing time on the average water contact angle for coated glass and acrylic substrates, respectively. The samples were submerged in an ultrasonic bath of deionized water for 5 min immediately after processing to remove any unreacted precursor and improve the accuracy of the goniometer measurements. One sees that the WCA rises rapidly with curing time and plateaus at a maximum value after about 1 min of exposure to the atmospheric nitrogen plasma. For coated glass, the contact angle levels out at $110° \pm 3°$, whereas for coated PMMA it plateaus at $106° \pm 5°$.

Oxygen plasma pretreatment of glass and acrylic substrates is essential in order to obtain a permanent hydrophobic coating. A single scan with the O_2 plasma decreases the WCA of the glass surface from 70° to <10°, while for acrylic it decreases from 75° to about 45°. Applying the FAS to these substrates and curing with nitrogen plasma leads to uniform coatings with average WCA values of $112° \pm 2°$ and $108° \pm 3°$, respectively. Glass and acrylic samples coated without pretreatment exhibit an average WCA of $71 \pm 14°$ and $80 \pm 6°$, respectively. There was no trend in the WCA for increasing the number of pretreatment scans (up to 20), as the WCA of all pretreated samples agree, within error, with the 106° and 110° values reported previously. These data reveal that, without pretreatment, the coating process provides for only a small increase of the WCA. The large error value associated with the WCA is due to widely varying contact angles measured at different positions on the surface, indicating some scattered presence of the coating on the surface.

3.3. Coating Thickness and Morphology. To measure thickness, the coating was scratched six times and each scratched region was analyzed by AFM. The scratch profiles gave a thickness of about 50 ± 10 nm. The scratched coating was again analyzed by physical profilometry for greater statistical accuracy. Sixty-five measurements of the six scratches were recorded and yielded an average thickness of 37 ± 6 nm.

Atomic force microscopy images of an uncoated and coated PMMA sample are presented in Figure 5. From these images, one can see that the coated substrate is much rougher than the uncoated substrate. The hydrophobic coatings on the glass and acrylic substrates exhibit rms roughnesses of 5.5 and 4.4 nm, respectively. Uncoated glass and acrylic substrates exhibit values of 1.1 and 2.9 nm, respectively.

3.4. Optical Transparency. The hydrophobic coatings are highly transparent to the naked eye, as coated substrates are indistinguishable from uncoated substrates. Transmission spectra were measured for the glass and acrylic substrates over the visible range, between 400 and 700 nm. These data are presented in Figures 6 and 7. For 1/8 in. thick PMMA, the hydrophobic coating reduces the average transmission from 92% to 90%. On the other hand, no significant change in the transmittance is seen for uncoated and coated glass. These yield average values of 90.7 and 90.2%, respectively.
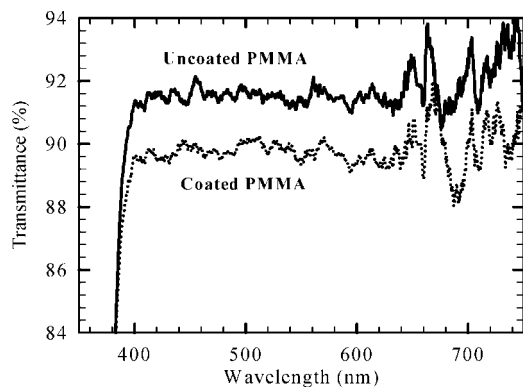
Figure 7. UV−visible transmission spectrum for an uncoated and coated acrylic substrate.
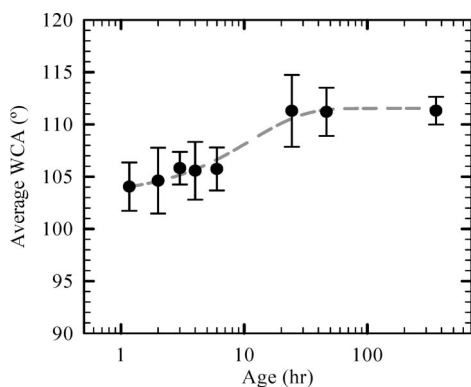

Figure 8. Effect of short-term aging on coated glass substrates.

3.5. Coating Stability and Durability. Hydrophobic coatings that have the ability to maintain consistent surface properties over a long period of time are desirable for many applications. The dependence of the average water contact angle on the aging time under ambient conditions (21 °C and ∼60% relative humidity) is depicted in Figure 8 for coated glass substrates. Note that the FAS coatings on these samples were cured for 2 min by atmospheric plasma. It is evident that the WCA of the coated glass increases from about 105° ± 4° to 110° ± 4° over 1 day's time. Further aging in ambient conditions for up to 12 months yielded a final WCA value of 111° ± 3° for the coated glass substrate, which agrees with the prior reported measurements, within error.

3.6. Chemical Composition. The chemical composition of the coated silicon substrate was determined by X-ray photoelectron spectroscopy and compared to that obtained for a PTFE surface, since this fluoropolymer demonstrates similar surface energy and hydrophobic properties. The survey spectra for these two materials are provided in Figure 9. This figure clearly identifies the presence of Si, C, O, and F atoms in the coating.

The multiplex spectra of the four elements identified on the coated sample are presented in Figure 10, while the binding energies and surface composition measured from these spectra are listed below in Table 1. Note that the surface compositions have been rounded to the nearest percent, because the accuracy of the measurement is estimated to be ±2.0%. The O 1s and F 1s spectra for the coated silicon wafer were recorded at 538.0 and 699.9 eV, respectively. The Si 2p spectrum observed on the coated silicon sample is resolved into two peaks: one for oxidized Si^{4+} at 103.7 eV and one for Si^0 at 99.8 eV.[20] The presence of the latter feature indicates that photoelectrons from the silicon substrate are being detected by the spectrometer. Examination
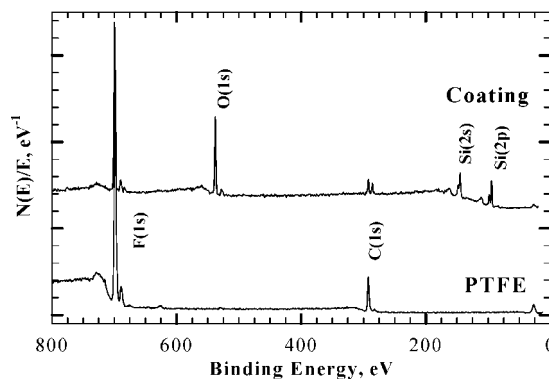
Figure 9. X-ray photoemission spectra of the PTFE film and the FAS-coated silicon substrate.

of the C 1s region reveals a peak at 292.4 eV and a shoulder at 294.8 eV, which may be assigned to CF_2 and CF_3 groups.[23] These species account for 53% and 6% of the total surface carbon, respectively. In addition, one sees a band at 286.1 eV due to "alkane" carbon that is bound to other C atoms and to hydrogen.[20] This latter species represents 41% of the total surface carbon. The error in these calculated values is approximately ±5%.

The calculated ratio of fluorine to carbon atoms for the coated substrate is 2.23. The F/C ratio for the fluoroalkyl ligand ($C_8F_{17}C_2H_2$) is 1.7, which is lower than that recorded by XPS. Nevertheless, the ratio of fluorine to carbon atoms for the PTFE film is 2.35, compared to a theoretical value of 2.0. Evidently, the sensitivity factors used in the calculation of the atomic concentrations overestimates the amount of fluorine on the surface. Applying a correction factor from the PTFE data to the coating yields an F/C ratio of 1.9 which, to within the experimental error of the measurement, agrees with the stoichiometry of the ligand.

4. Discussion

Oxygen plasma treatment of the substrates is important for obtaining a uniform hydrophobic film. Without it, the fluoroalkylsilane does not adhere well to the sample surface, so that after curing the coating covers only a fraction of the surface. The O_2 and He plasma activates the surface as evidenced by the large drop in water contact angle: from 70° to <10° for glass and from 75° to 40° for acrylic. Researchers have observed analogous changes in the WCA of other polymers following atmospheric plasma treatment.[24−28] For example, Gonzalez et al.[15,29] observed a drop in the WCA of poly(ethylene terephthalate) (PET) from 85° to 35° after a few seconds of exposure to the same O_2 and He plasma used in this study. In addition, they found that surface activation increased the bond strength of acrylic adhesive to the PET by 7-fold.

It has been shown that an increase in the polarity of the substrate enhances the bonding between the surface and polar molecules,

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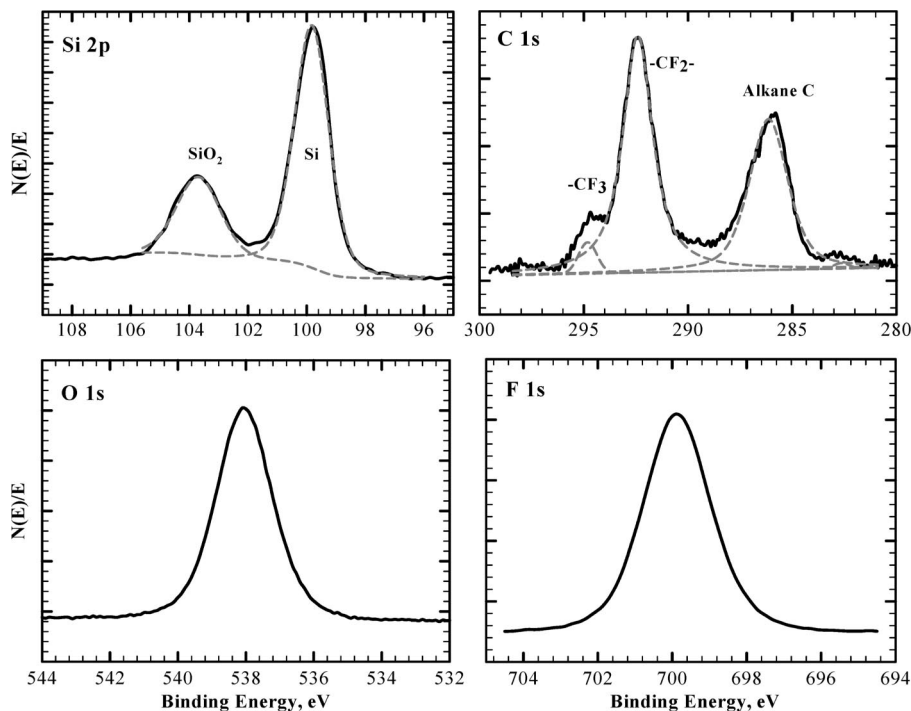(25) Schulz, U.; Munzert, P.; Kaiser, N. *Surf. Coat. Technol.* **2001**, *142−144*, 507–511.
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Figure 10. X-ray photoemission spectra of the (a) Si 2p, (b) C 1s, (c) O 1s, and (d) F 1s lines for the FAS-coated silicon sample.

Table 1. Binding Energies and Surface Composition for the PTFE Film and the FAS-Coated Silicon Substrate

atom	bond state	binding energy (eV)	atomic % PTFE	atomic % coated
silicon	Si	99.8		114
	SiO2	103.7		6
oxygen		538.0		27
carbon	(alkane)	286.1		7
	CF2	292.4	30	9
	CF3	294.8		1
fluorine		699.9	70	37
F/C Ratio			2.35	2.23

or the polar ends of long-chained molecules.[15,29−31] Evidently, this mechanism is responsible for the enhanced coating density of the fluoroalkylsilane to the plasma-treated glass and acrylic substrates. The FAS molecule has one long, nonpolar ligand and three polar ethoxy ligands attached to the central silicon atom. During plasma curing, the ethoxy ligands decompose and form strong bridging oxygen bonds between the Si atoms as well as to the hydroxylated sites on the sample surface. The fluoroalkyl ligands, on the other hand, remain intact as evidenced by the XPS data, which show the presence of CF2 and CF3 groups in the C 1s spectrum, and an F/C atomic ratio of 2.23. A similar mechanism has been reported in the formation of self-assembled monolayers (SAMs) using FAS precursors. In these studies, it was necessary to pretreat the silicon substrate, either by plasma oxidation or by photochemical methods. This treatment terminates the surface with polar −OH groups which then anchor the FAS monolayer to the substrate.[7,8,32,33]

The hydrophobic coatings prepared by curing the spun-on liquid FAS with the atmospheric nitrogen plasma have a surface energy of 11.0 dyn/cm, with the polar component being equal to 1.2 dyn/cm. In comparison, PTFE and poly(ethylene) have total surface energies of 14.5 and 32.0 dyn/cm, with polar components of 1.0 and 1.1 dyn/cm, respectively.[19] Thus, the surface energy and the polarity of the hydrophobic coating is approximately the same as that of PTFE and lower than that of PE. It should be pointed out that the average WCA of a smooth PTFE surface is 95° to 105°, which is close to that recorded for the hydrophobic film.

The XPS spectra in Figure 10 reveal the presence of zero valent Si at 99.8 eV. This photoemission arises from the Si atoms beneath the native oxide layer on the silicon substrate. Note that the escape depth of the photoelectrons is ∼3.0 nm for a layer of SiO2 on Si.[34] This appears to contradict the measured thickness of the hydrophobic coating of 37 ± 6 nm. It is possible that the coating forms a somewhat porous network on the substrate surface, such that the Si substrate is "visible" to the XPS detector. Alternatively, the thickness of the coating may be less than that indicated by the AFM measurements of the scratched film. Further experiments are underway to identify the source of this discrepancy.

It is well established that the hydrophobic properties of a surface are determined by both its chemical composition and its morphology.[1,7,20,35,36] The effects of morphology on the water contact angle, however, can be difficult to characterize as recent studies into superhydrophobic structures seem to indicate. The Cassie−Baxter equation, established to account for the effects of surface morphology, relies on the ratio of the actual surface area to the projected surface area. This value increases with greater roughness but also depends strongly on the geometry of the surface

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features.[37] It is nevertheless a guide that indicates there is a minimum roughness below which the morphology does not affect the water contact angle. Feng et al.[35] demonstrated through fractal theory analysis of the lotus leaf structure that a surface roughness ≥ 100 nm is necessary to obtain superhydrophobicity, that is, a WCA $\geq 150°$. Additionally, Suzuki et al.[36] found that increasing the surface roughness of cured FAS coatings from 0.1 to 20 nm resulted in only a $3° \pm 1°$ increase in WCA. Since the rms roughness of the coatings prepared in this study ranged between 4.4 and 5.5 nm, it may be concluded that the hydrophobic properties of the surfaces are derived solely from their chemical composition and that morphology does not play a significant role.

5. Conclusions

Hydrophobic coatings have been obtained by atmospheric plasma curing of spun-on liquid fluoroalkylsilane precursors. The films exhibit a total surface energy of 11 dyn/cm with only 10% polarity, and average water contact angles ranging from 106° to 110°. Oxygen plasma activation was necessary in order to achieve strong adhesion of the FAS molecules to the glass and acrylic surfaces. Analysis of the film composition by XPS reveals that the fluoroalkyl ligands remain bonded to the Si atoms after conversion. The coatings are transparent and stable, and they maintain their hydrophobic properties for over 1 year.