

Two-silane chemical vapor deposition treatment of polymer (nylon) and oxide surfaces that yields hydrophobic (and superhydrophobic), abrasion-resistant thin films

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Two-silane chemical vapor deposition treatment of polymer (nylon) and oxide surfaces that yields hydrophobic (and superhydrophobic), abrasion-resistant thin films

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This article describes a two-silane, chemical vapor deposition (CVD) approach to creating hydrophobic (or even superhydrophobic), abrasion-resistant coatings on silicon oxide and polymer (nylon) substrates. This multistep approach employs only reagents delivered in the gas phase, as follows: (i) plasma cleaning/oxidation of the substrate, (ii) CVD of 3-isocyanatopropyltriethoxysilane, which is used as an adhesion promoter for the substrate, (iii) hydrolysis with water vapor, and (iv) CVD of (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane (the “R_f-Cl silane”). Surfaces are characterized by wetting, spectroscopic ellipsometry, x-ray photoelectron spectroscopy (XPS), and time-of-flight secondary ion mass spectrometry (ToF-SIMS). This work has the following unique features. First, the authors explore an all gas phase deposition of a new silane coating that is scientifically interesting and technologically useful. Second, the authors show that the presence of an adhesion promoter in the process leads to thinner films that are *more* robust in abrasion testing. Third, results obtained using plasma/deposition equipment that is relatively inexpensive and/or available in most laboratories are compared to those obtained with a much more sophisticated, commercially available plasma/CVD system (the YES-1224P). The entire deposition process can be completed in only ~1 h using the industrial equipment (the 1224P). It is of significance that the polymer surfaces modified using the 1224P are superhydrophobic. Fourth, the thickness of the R_f-Cl silane layer deposited by CVD correlates well with the thickness of the underlying spin coated nylon surface, suggesting that the nylon film acts as a reservoir of water for the hydrolysis and condensation of the R_f-Cl silane. © 2008 American Vacuum Society. [DOI: 10.1116/1.2953699]

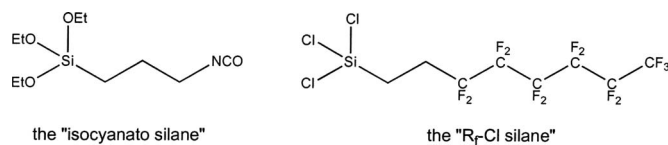
I. INTRODUCTION

In this article we describe a multistep chemical vapor deposition (CVD) process for coating polymer and silicon substrates with ultrathin silane coatings that have high hydrophobicity and good abrasion resistance. Silane coatings are inherently hybrid materials. They offer the flexibility and reactivity of a broad range of organic functional groups, while they also offer the strength and potential cross-linking of the inorganic Si–O–Si linkage between monomer units. Polymer surface modification is important because many polymers/plastics have extremely desirable bulk properties such as low density, low cost, good strength, and ease of processing that have allowed them to become integral components of countless consumer goods and devices. However, many plastics that have ideal bulk properties for certain applications are lacking in their surface properties, such as

abrasion resistance or wetting. As a result, it is often necessary to coat a polymer/plastic to modify its surface so that its favorable bulk properties can be exploited.

CVD of silanes is an effective, solvent-free method for the covalent attachment of these reagents to surfaces. In general, this method can be made more reproducible and robust than silane deposition from solution because it is often difficult to control the degree of hydrolysis and oligomer formation of silanes in solution.¹ In contrast, in the CVD of silanes it is unlikely that hydrolyzed or oligomerized species will reach the substrate because their volatility typically decreases significantly when they hydrolyze or condense with each other. In general, gas phase deposition of silanes is also much cleaner than the liquid phase approach because the surface is not exposed to impurities that may be in the solvent, and no surface rinsing or cleaning is required after adsorption. In addition, if no solvent is required during silane adsorption or in subsequent substrate cleaning, the gas phase approach will generally be more environmentally friendly

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SCHEME 1. Structures of 3-isocyanatopropyltriethoxysilane (the "isocyanato silane") and (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane (the "R_f-Cl silane").

and industrially viable. Silanes with a variety of terminal functionalities, including amino, vinyl, alkyl, perfluoro, glycidyl, isocyanato, Si-H, and polyethylene glycol, and with different numbers of reactive groups on Si, e.g., -Cl, -OMe, and -OEt, are commercially available, and have been deposited by CVD.¹⁻⁸ One of these reports showed alternating deposition of gaseous aminopropyltrimethoxysilane and water vapor on porous silica surfaces via atomic layer deposition.⁴ Another study showed the liquid phase deposition of 3-(mercaptopropyl)trimethoxysilane onto silver surfaces, followed by hydrolysis in aqueous 0.1M HCl, with subsequent treatment by gas phase deposition of octadecyltrichlorosilane or dimethylchlorooctadecylsilane.⁶ The sequential deposition of 3-aminopropyltriethoxysilane and (tridecafluoro-1,1,2,2-tetrahydrooctyl)dimethylchlorosilane onto polymer substrates has also been reported.⁹ However, the polymer substrates in this study were not plasma treated, as they are in this work, and all depositions were out of solution.

Reagent delivery and/or surface modification in this study takes place entirely in the gas phase and consists of (i) cleaning and/or oxidizing a polymer (nylon) or silicon surface with an air or oxygen plasma, (ii) vapor depositing 3-isocyanatopropyltriethoxysilane (denoted the "isocyanato silane" herein) onto these primed substrates, (iii) a hydrolysis step in which water vapor reacts with this surface, and (iv) vapor deposition of (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane¹⁰⁻¹² (denoted the "R_f-Cl silane" herein). Plasma cleaning of inorganic surfaces to remove organic contamination is a well known cleaning procedure.^{13,14} Plasma treatment of polymer surfaces is also a known and effective approach for oxidizing their surfaces.^{15,16} Plasma treatment of polymer surfaces should allow the silanes employed in this study to polymerize more readily on them (Scheme 1 shows their structures). To repeat, no reagents are delivered from solution, and no rinsing of the surface is necessary between, or after, the steps in the process. We have demonstrated this process with native oxide coated silicon, spin coated nylon 6,6 on silicon, and bulk, glass-reinforced nylon 6,6 substrates. It should be possible to coat virtually any polymer or organic material using this method, provided it has a surface that can be oxidized and/or provide reactive-OH groups. Almost all polymers meet these qualifications. Surface reactions are confirmed and followed by water and hexadecane contact angles, spectroscopic ellipsometry, x-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS),¹⁷ and abrasion testing.

JVST A - Vacuum, Surfaces, and Films

II. EXPERIMENT

A. Reagents

(Tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane ($\geq 97\%$, Aldrich), 3-isocyanatopropyltriethoxysilane (95%, Gelest, Morrisville, PA), *m*-cresol (97%, Aldrich), and nylon 6/6 pellets (Aldrich, Cat. No. 181129) were used as received. The "aqueous salt/acid" solution employed herein is a formulation for artificial sweat, which was 0.34M NaCl, 0.08M urea, 0.33M NH₄Cl, 0.04M CH₃COOH and 0.12M lactic acid. The solution was adjusted to pH 4.7 with 2M NaOH.

B. Substrates

Silicon wafers (test grade, *n*-type, <1-0-0> orientation, 2–6 Ω cm) were purchased from UniSil Corporation, California and cleaved into $\sim 1.5 \times 1.5$ cm² pieces. Reinforced nylon 6/6 surfaces were FDA grade and contained 35% chopped glass fiber by weight (1/8–3/16 in. long). This material contains FDA compliant additives, i.e., colorants, and no UV or high flow additives.

C. Surface cleaning

Prior to any surface chemistry, reinforced nylon surfaces were sonicated in an aqueous 2% sodium dodecyl sulfate (SDS) solution for 5 min. They were then sonicated in deionized water for 10 min. This water was changed three times during sonication. Bare Si wafers were also cleaned with SDS solution and water but without sonication. Spin coated nylon surfaces were heated to remove residual *m*-cresol (see below) and then plasma cleaned without any other cleaning.

D. Spin coating

Spin coating was performed with an instrument from Laurell Technologies Corporation model WS-400B-6NPP/LITE. Spin coated nylon surfaces were prepared by spin coating a solution of nylon 6/6 pellets in *m*-cresol onto native oxide coated silicon wafers using the following program: 1000 rpm (10 s) followed by 5000 rpm (90 s). The initial concentration of the nylon 6/6 solution was <3% (*w/w*), but this solution was diluted in *m*-cresol until these spin coating conditions gave a film thickness of approximately 170 Å.

E. Plasma cleaning/treatment (for depositions in the dessicator and vacuum oven)

Plasma cleaning was performed with a plasma cleaner model PDC-32G from Harrick Plasma (Ithaca, NY) at medium power (10.5 W applied to the rf coil) for 30 s.

F. Isocyanato silane deposition (for depositions in the vacuum oven)

After plasma cleaning, all of the surfaces were dehydrated at 100 °C at reduced pressure. The vacuum for this oven was provided by a rotary vane pump. The apparatus contained a dry ice/acetone-cooled glass trap that prevented both back-

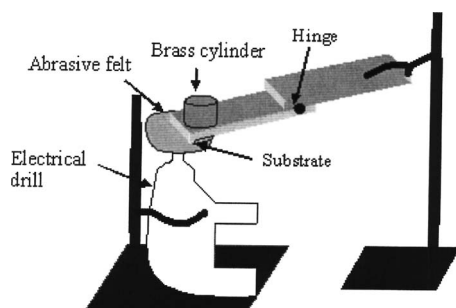


FIG. 1. Abrasion apparatus consisting of an automatic electric drill configured to move a piece of abrasive felt under a coated substrate. The weight of the brass cylinder was 164 g.

streaming of oil from the pump and solvents and/or reagents from entering the pump. The reinforced and spin coated nylon surfaces appear to be stable for extended periods of time at 100 °C. Aldrich gives the melting point of the nylon 6/6 they provided as 263 °C, and its glass transition temperature as 45 °C. After introducing the surfaces into the oven, the pump was turned on for ~3 min to attain a pressure of 15 Torr (–25 in.), and the valve to the pump was then closed. The surfaces were allowed to dehydrate under these conditions for 30 min. The pump was then turned on again for 3 min to pump off water vapors, and the valve to the pump was again closed. An aliquot of 250 μ l of (3-isocyanatopropyl triethoxysilane) was then injected into the vacuum oven through a septum, and it evaporated quickly. The surfaces were then allowed to react with the vapors of the NCO silane under these static conditions for 30 min. The valve to the vacuum pump was then opened to pump off any unreacted NCO silane. A Petri dish containing 5 ml of water was then introduced into the oven. The door to the oven was closed and the surfaces were allowed to hydrolyze at atmospheric pressure and at 100 °C for 30 min.

G. Testing the abrasion resistance of the films

An apparatus was built to test abrasion resistance (see Fig. 1). It consisted of an electrical drill (Craftsman, model No. 315.101160) that was clamped vertically. A commercially available polishing disk (Craftsman), which is designed to be used with an electric drill, was attached to the chuck of the drill, and a piece of abrasive felt (15 \times 14.7 cm²) was pasted onto it. Thus, when the drill was turned on, it caused the felt disk to rotate parallel to the bench top. A sample holder was made from two rectangular strips of plywood joined end to end with a steel hinge. The end of one of these pieces was clamped to a stand. The reinforced nylon sample was attached to the end of the other piece with double-sticky tape. The sample was then placed on the felt wheel 4.5 cm from its center, and allowed to ride on the wheel as it rotated. A brass cylinder weighing 164 g was placed directly above the sample on the wood strip. The rotational speed of the drill was controlled with a powerstat and the felt was also marked on its edge so as to count the number of cycles during the abrasion tests.

H. R_f-Cl silane deposition in a dessicator

The R_f-Cl silane was deposited onto hydrolyzed NCO silane coated surfaces by placing these surfaces in a dessicator along with an open vial of the R_f-Cl silane, for at least for 16 h.⁸ After this reaction, the surfaces were removed from the dessicator and cured in an oven at 80 °C for 1 h at atmospheric pressure.

I. Surface analytical instrumentation

ToF-SIMS was performed with an ION-TOF (TOF-SIMS IV) instrument with a two-lens, monoisotopic ⁶⁹Ga⁺ gun as a primary ion source. XPS was performed with an SSX-100 instrument from Surface Sciences using an Al K α source and a hemispherical analyzer. An electron flood gun was employed for charge compensation of the reinforced nylon samples, and this charge compensation was further enhanced by placing a fine Ni mesh ~0.5–1.0 mm above the surface of the glass reinforced polymer. No charge compensation was necessary for the silicon or spin coated nylon on silicon samples. Water contact angles were measured with a Ramé-Hart (model 100-00) contact angle goniometer. Spectroscopic ellipsometry was performed with an M-2000 instrument from the J.A. Woollam Co., Inc. The wavelength range was 190.5–989.4 nm, and the angle of incidence was fixed at 75°. Silicon oxide, hydrocarbon, deposited silane films, and spin coated nylon were modeled using the optical constants of silicon oxide that were found in the instrument software. This is a good approximation for such ultrathin films, and good fits to the data were obtained for all of the results reported in this work.

J. Commercially available CVD system

The results obtained using conventional and/or inexpensive equipment available in our laboratory were compared to those found using a commercially available, fully automated CVD system: the YES-1224P from Yield Engineering Systems (Livermore, CA). The YES-1224P Chemical Vapor Deposition System incorporates a plasma cleaning method into a heated vacuum deposition chamber. Reactant chemicals are vaporized in temperature controlled vessels and introduced via heated lines to the main chamber. The system allows precise control of chemical volume, reaction temperature, and exposure time. The plasma cleaning process prepares substrates for surface reactions.

III. RESULTS

Here we describe a two-silane functionalization of spin coated nylon, reinforced nylon, and native oxide coated silicon. The resulting thin films exhibit good hydrophobicity, abrasion resistance, and are invisible to the eye. In the first section of this document, we describe work that was performed with three pieces of equipment that are inexpensive and/or available to most researchers. In the second section we show that it is possible to significantly shorten the deposition procedure and also eliminate the use of one of the

TABLE I. Advancing water contact angles [$\theta_a(\text{H}_2\text{O})$] of substrates before and after plasma cleaning, and after treatment with the isocyanato silane. (Notes: A reported advancing water contact angle less than 15° implies that the surface is wet by water. The number in parentheses indicates the number of experiments that were performed to get the average and standard deviation reported in this table, where each experiment employed two to three surfaces, each of which was characterized.)

Substrates	Before plasma cleaning	After plasma cleaning	After NCO silane treatment
Bare Si/SiO ₂	40°	<15°	82 ± 6 ^a
Spin coated nylon	60 ± 3° (5)	34 ± 3° (6)	82 ± 7 ^b
Reinforced nylon	69 ± 2° (3)	32 ± 2° (5)	87 ± 3° (5)

^aThis value is the average and standard deviation of measurements made on seven different surface prepared in three separate experiments.

^bThis value is the average and standard deviation of measurements made on six different surfaces prepared in three separate experiments.

pieces of equipment. In the third section, we demonstrate the use of a single piece of highly automated equipment: a commercially available plasma/CVD system.

A. Silane deposition with conventional/inexpensive equipment

In this section, surfaces were first oxidized/cleaned in a small Harrick Plasma device. The isocyanato silane was then deposited in a vacuum oven, and the R_F-Cl silane was deposited at atmospheric pressure in a dessicator.

1. Plasma cleaning/treatment

All of the surfaces were cleaned with an air plasma. The air plasma should generate numerous oxygen atoms from O₂, which should effectively oxidize and etch the organic species at the surfaces. The small plasma system we employed was specifically designed not to have enough power to etch inorganic materials. As expected, Table I shows that the advancing water contact angles [$\theta_a(\text{H}_2\text{O})$] for the three different surfaces decrease noticeably after plasma cleaning. The moderately high water contact angle for the Si/SiO₂ surface prior to plasma cleaning is a reflection of adventitious hydrocarbon contamination on this surface, which is removed by plasma cleaning.

The expected surface oxidation of nylon by plasma cleaning is further confirmed by XPS. Figure 2 shows the XPS of

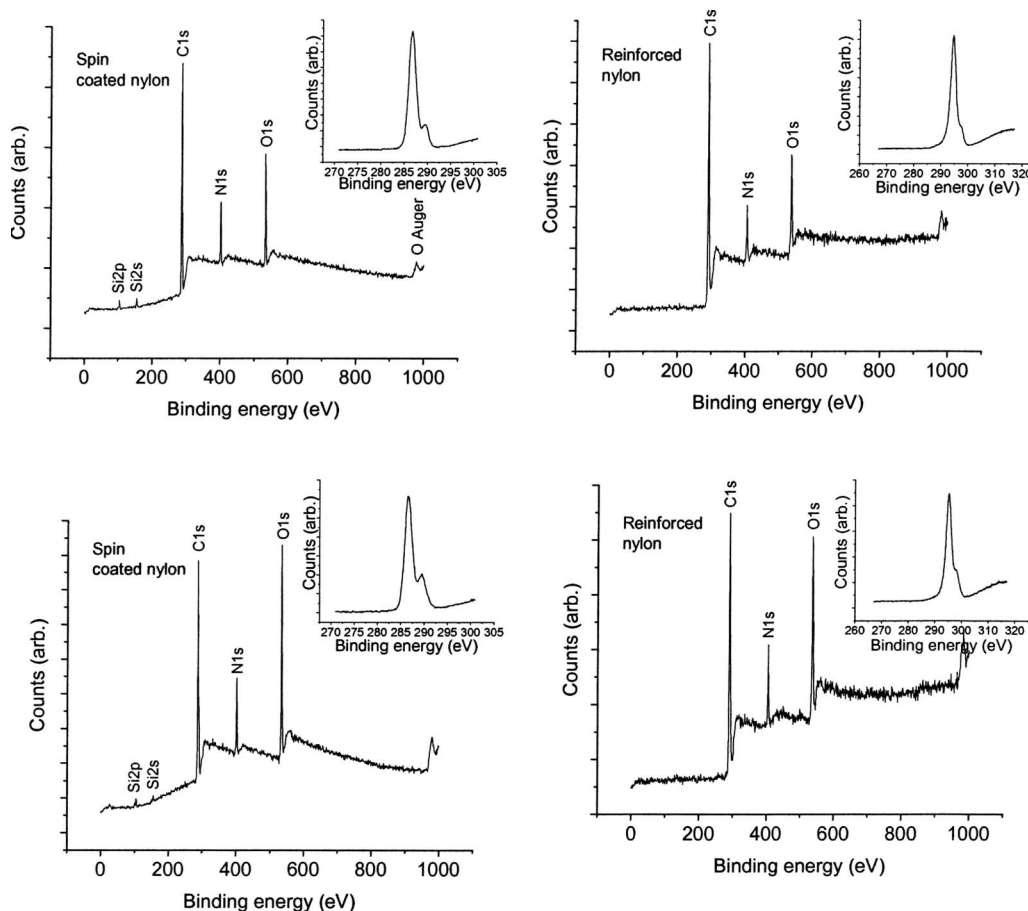


FIG. 2. XPS survey and C 1s narrow scans of spin coated nylon (left) and bulk reinforced nylon (right) before plasma treatment (top) and after plasma treatment (below).

spin coated and fiberglass reinforced nylon before and after plasma cleaning. Prior to plasma cleaning the XPS are dominated by signals from oxygen (O 1s), nitrogen (N 1s), and carbon (C 1s) (see Fig. 2). The same three peaks dominate the XPS after plasma cleaning (see again Fig. 2), and the nitrogen to carbon ratio is nearly the same in both spectra. However, the O 1s signal, as measured by the O 1s/C 1s peak ratio, increases significantly after plasma cleaning, going from, for example, 0.16 to 0.28 for a glass reinforced nylon sample and 0.18 to 0.35 for a spin coated nylon surface. The C 1s narrow scans also show a notable increase in oxidized (chemically shifted) carbon (see Fig. 2). The negative ion ToF-SIMS spectra of the glass reinforced and spin coated nylon surfaces also suggest an increase in the oxygen content of these surfaces after plasma cleaning. For example, the area ratios of the O⁻ to the C⁻ peaks on three different glass reinforced nylons and three different spin coated nylon surfaces in the negative ion spectra are 3.6 ± 0.2 and 4.7 ± 0.2 before plasma treatment and 9.2 ± 0.5 and 11.4 ± 1.3 , respectively, after plasma treatment, i.e., these results, like the XPS results, indicate that the amount of oxygen in the near surface region of the sample increases significantly.

Not only is surface oxidation after plasma cleaning observed, but the expected etching of organic material from the surfaces is also confirmed. Thus, the ellipsometric thicknesses of the "silicon oxide" layer on the as received silicon oxide terminated silicon wafers decreased after plasma cleaning. A typical example is a silicon/silicon oxide surface where the thickness of the layer on the silicon substrate decreases from 23.2 to 17.6 Å after plasma cleaning, demonstrating the removal of organic material. The spin coated nylon surfaces show an even larger decrease in thickness of the nylon layer after plasma treatment. For example, for a set of representative surfaces, the thicknesses of spin coated nylon films decreased from 135.2, 222.9, 133.6, 132.5, and 223.2 Å to 88.2, 139.5, 78.2, 74.2, and 165.6 Å after 30 s of plasma treatment, respectively, which corresponds to an average loss of 60 ± 14 Å of material. The variability in this removal may be due to somewhat different positions of the substrates in the plasma cleaner, and the difficulty associated with exact control of the plasma power and duration in the device.

Because a fairly large amount of polymer (tens of Ångströms) was removed from the polymer surfaces during plasma cleaning, it did not seem necessary to optimize this step in the procedure. That is, etching a little more or a little less of the polymer would not be expected to change the surface chemistry after plasma etching/oxidation. This decision was further confirmed by the optimization of the time for plasma etching reported in Sec. III C (*vide infra*).

2. Isocyanato silane treatment

After treatment of the plasma-cleaned surfaces with the isocyanato silane, the water contact angles of all of the surfaces increase substantially, as shown in Table I.¹⁸ XPS was also used to characterize these surfaces. For the bare silicon

TABLE II. Spectroscopic ellipsometric thicknesses of coatings on bare silicon and spin coated nylon surfaces at different stages of the deposition.

Substrates	After NCO silane treatment and hydrolysis	After R _f -Cl silane treatment
Bare Si ^a	29.1 ± 0.6 Å	78 ± 7 Å
Spin coated nylon	125.9, 138.8, 124.3, 136.4 Å	272.3, 192.1, 196.2, 202.7 Å

^aThe thicknesses of the films reported here include the thickness of the native oxide, which was 18.0 ± 0.5 Å.

surface, no N 1s signal could be observed before NCO silane treatment, but a small N 1s signal was present in the survey spectrum after this exposure. The thickness of this isocyanato layer is 9.5 Å by spectroscopic ellipsometry.

For the spin coated nylon surface, there is a small silicon peak in the survey spectrum (presumably from the substrate) prior to isocyanato silane deposition that increases after isocyanato silane deposition. For example, on one such surface, the Si/C ratio was 0.045 and 0.098 before and after-NCO silane treatment, respectively. It was difficult to observe an increase in thickness for spin coated nylon after isocyanato silane deposition, presumably because solvent loss during isocyanato silane deposition changed the thickness of the nylon layer.¹⁹ In one experiment, spin coated nylon surfaces were baked in a vacuum oven at 100 °C for 2 h at reduced pressure to drive off *m*-cresol. The film thickness increase after isocyanato silane deposition was observed to be 4.8 ± 0.6 Å.

3. Hydrolysis of the isocyanato silane treated surfaces

The isocyanato silane treated surfaces were hydrolyzed with water vapor for 30 min at 100 °C, and at atmospheric pressure. The ellipsometric thicknesses of the covalently attached isocyanatosilane layer on Si/SiO₂ and spin coated nylon substrates remained essentially constant after hydrolysis. As a representative example, for one Si/SiO₂ surface and one spin coated nylon surface, the total thicknesses (on top of the silicon substrate) before and after hydrolysis of the isocyanato layer were found to be 27.9 and 142.3 Å, and then 28.3 and 141.3 Å, respectively.

4. Reaction of the hydrolyzed surfaces with the R_f-Cl silane

After hydrolysis, the isocyanato silane treated surfaces were placed in a desiccator overnight (12–16 h) where they were exposed to the vapors from an open vessel of (tridecafluoro-1,1,2,2-tetrahydrooctyl) trichlorosilane, which we refer to herein as the R_f-Cl silane. Table II gives the ellipsometric thicknesses of the isocyanato silane treated bare silicon surface and spin coated nylon surfaces after hydrolysis and then after exposure to the R_f-Cl silane (the fiber reinforced nylon surfaces are not sufficiently flat for ellipsometry to be performed). It is clear that significant deposition of the R_f-Cl silane occurs, especially in the case of the

TABLE III. Advancing contact angles for different probe liquids (water, an artificial sweat formulation, and hexadecane) for different substrates that were plasma treated, treated with the isocyanato silane, hydrolyzed, and then treated with the R_F-Cl silane. Each of the experiments reported in these columns was performed once.

Substrates	$\theta_a(\text{H}_2\text{O})$	θ_a (artificial sweat)	θ_a (hexadecane)
Bare Si	126°	118°	75°
Spin coated nylon	127°	120°	72°
Reinforced nylon	132°	130°	71°
Average	128° ± 3°	123° ± 6°	73° ± 2°

spin coated nylon surface. These results suggest cross-linking of R_F-Cl silane molecules into a polymeric thin film on the substrates. We believe that these reactions are facilitated by water that diffuses out from underlying polymer layers. As expected, the advancing water contact angles, advancing contact angles for an artificial sweat formulation, and advancing hexadecane contact angles for these R_F-Cl silane treated surfaces are quite high, and consistent for a material with an extremely low surface free energy, such as a fluorocarbon (see Table III).²⁰ XPS and ToF-SIMS also confirm the presence of large amounts of fluorine after CVD of the R_F-Cl silane on the hydrolyzed isocyanato silane surface (*vide infra*).

5. Effect of the adhesion promoter on the thickness of the R_F-Cl silane coating

To determine the effect of the adhesion promoter, the isocyanato silane, on the thickness of the R_F-Cl silane coating, plasma treated (bare) Si/SiO₂ and nylon spin coated surfaces having no adhesion promoter coating were exposed to the R_F-Cl silane. These surfaces without the adhesion promoter, and the surfaces treated with the adhesion promoter were placed together in the oven during the hydrolysis step. After the hydrolysis, all the surfaces were allowed to react with the R_F-Cl silane as described previously. Table IV shows a comparison of the thickness of the R_F-Cl silane coating for bare Si/SiO₂ and nylon spin coated surfaces made with and without the adhesion promoter coating. Interestingly, the surfaces coated with the adhesion promoter (the isocyanato silane film) are considerably thinner than the surfaces that were not treated with the isocyanato silane. This may be because the

TABLE IV. Increase in ellipsometric thicknesses after treatment with the R_F-Cl silane.^{a,b}

Substrates	With adhesion promoter (Å)	Without adhesion promoter (Å)
Bare Si	48 ± 8	117 ± 13
Spin coated nylon	67 ± 11	233 ± 37 ^b

^aThese results are the average of three silicon surfaces and three spin coated nylon surfaces, each, that underwent the same exposure to the R_F-Cl silane as indicated in the table.

^bThe thickness of the native silicon oxide layer on silicon was subtracted from the total ellipsometric thicknesses to give the results in this table.

thin film of the isocyanato silane acts as a diffusion barrier to water at or near the surface of the substrate. In spite of the thinness of these films, it will be shown below that these thinner layers appear to have superior abrasion resistance over R_F-Cl silane deposited on surfaces that were not treated with the adhesion promoter (*vide infra*).

6. XPS analysis of surfaces treated with the R_F-Cl silane

XPS confirms the addition of the R_F-Cl silane to the isocyanato silane treated surfaces. For example, Fig. 3 shows XPS of the reinforced nylon surface after the coating process: plasma treatment, reaction with the isocyanato silane, hydrolysis, and exposure to the R_F-Cl silane. The dominant feature of this spectrum is the F 1s signal, with its accompanying F Auger peaks. The split carbon signal that is observed is due to (i) carbon bonded to carbon and/or hydrogen and/or mildly oxidized carbon at lower binding energy, and (ii) carbon in CF₂ groups at higher binding energy, where each F atom bonded to a C atom shifts the C 1s signal by 2.9 eV. It is significant that no N 1s signal from the substrate or the isocyanato silane layer can be observed. This indicates that the R_F-Cl silane film is free from pinhole defects, and/or that it is relatively thick in all places. A small oxygen signal is also present, which would be expected from Si-O linkages in the film.

7. ToF-SIMS analysis

ToF-SIMS in both the negative and positive ion modes was performed on silicon oxide, spin coated nylon, and reinforced nylon samples after treatment with the isocyanato silane and again after treatment with the R_F-Cl silane. ToF-SIMS, which has an information depth of only about 2 nm, is more surface sensitive than XPS,¹⁷ which probes at least 10 nm into a material. Positive ion ToF-SIMS spectra of the silicon oxide, spin coated nylon, and glass reinforced nylon surfaces after the complete process, which culminated in the deposition of the R_F-Cl silane, shows a series of peaks that are characteristic of a perfluorinated hydrocarbon. The two largest peaks in these spectra are identified as the CF⁺ and CF₃⁺ peaks. The negative ion spectra from these same surfaces are dominated by a single peak: F⁻. The F₂⁻ ion, which is generally less than 5% intense as the F⁻ signal, (see Fig. 3) is also observed.

8. Abrasion tests

A goal of this research was to create a surface that would have a high degree of hydrophobicity, along with excellent resistance to abrasion. It was believed that the combination of the perfluorinated tails of the silane compound with the strong inorganic Si-O-Si linkages between the condensed R_F-Cl silane molecules would produce a thin film with these properties. To better understand the abrasion resistance of our thin films, we tested identical pairs of fiberglass reinforced nylon coupons that had been plasma cleaned and then (i) exposed to the isocyanato silane, hydrolyzed, and finally exposed to the R_F-Cl silane, or (ii) only hydrolyzed and then

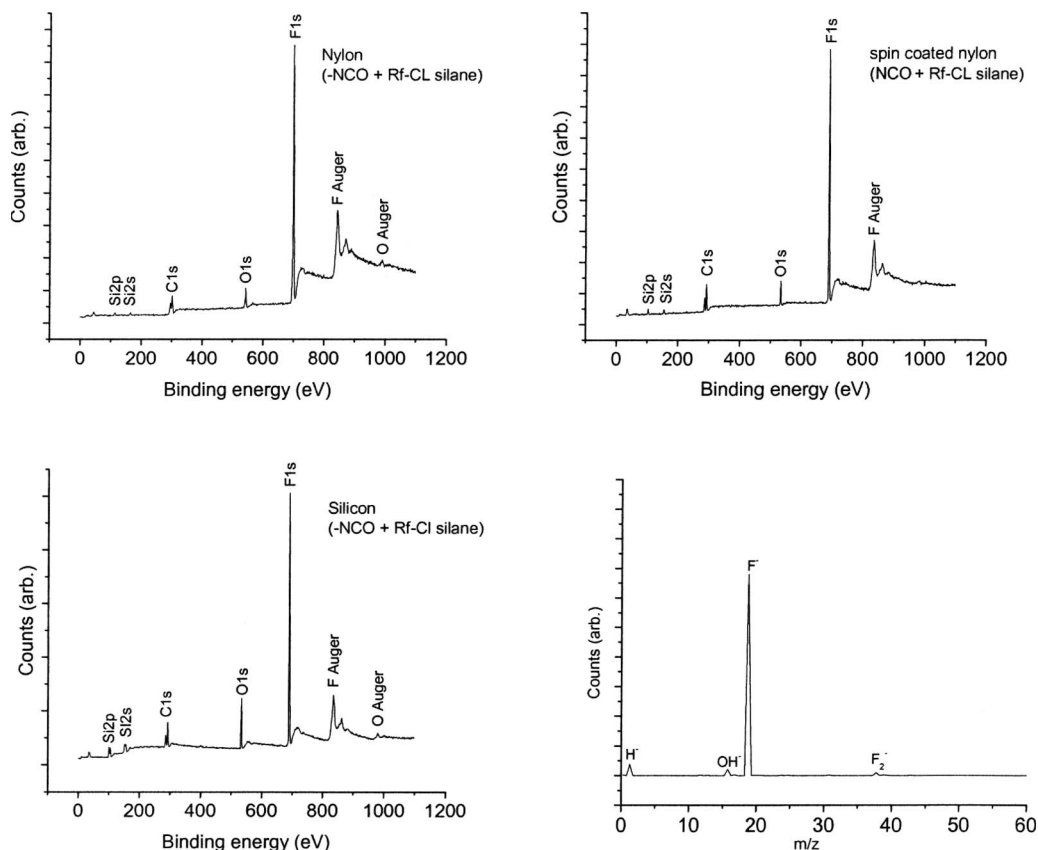


FIG. 3. XPS after deposition of the R_f -Cl silane on reinforced nylon (“nylon”), spin coated nylon, and bare Si/SiO₂. Lower right: negative ion ToF-SIMS after applying the silane multilayer film to the reinforced nylon substrate.

exposed to the R_f -Cl silane. Figure 4 shows the effect of the isocyanato silane on the robustness of R_f -Cl coating. That is, after 920, 160, and 430 cycles on three different pairs of coupons of different colors in a homebuilt abrasion testing apparatus, the water contact angle of the surfaces with the isocyanato silane adhesion promoting layer is $\sim 10^\circ$ higher than the surfaces prepared without the isocyanato compound. To confirm these results, XPS was taken of two surfaces coated with the R_f -Cl silane after abrasion testing, one with the adhesion promoter and one without. The C 1s/F 1s ratio after the abrasion test for the surface with the adhesion promoter was 43:57, while for the surface having no adhesion promoter coating, it was found to be 49:51. The higher level of fluorine is consistent with the higher water contact angles found for the surfaces made with the adhesion promoter.

B. Comparison of results obtained with conventional laboratory equipment to results obtained with a commercially available Plasma/CVD system

While the data we have shown clearly demonstrate that our procedure for coating polymers and inorganic substrates with durable hydrophobic films is viable, and that the adhesion promoter improves the durability of the final film, this procedure, as implemented in our laboratory, has some sources of error in it. Multiple pieces of equipment must be used (the plasma cleaner, a vacuum oven, and a dessicator), and the samples must be transported between these pieces of

equipment during the procedure. Each piece of equipment introduces some uncertainty into the procedure. For example, in practice, we find it somewhat challenging to control the nature of the plasma and its exact duration in the Harrick plasma cleaner. The vacuum oven is difficult to clean, and in spite of our best efforts, a small amount of carryover between runs or small amounts of contamination originating from other uses of the instrument seems unavoidable. The dessicator was opened to the air each time it was used. The relative humidity in the laboratory would vary from day to day and therefore have some influence on the results. We repeat that these possible sources of error did not seem to prevent us from reproducibly verifying the validity of our procedure, and that the results in Sec. III A of this article are important because they were obtained with inexpensive equipment and/or equipment that is available in most laboratories. However, we wondered if it would not be possible to improve the implementation of our procedure. As a first effort in this direction, we shortened the procedure and eliminated one of the pieces of equipment necessary for the process (the dessicator) by performing both silane depositions in our vacuum oven. We studied various deposition conditions to optimize the CVD process. In addition, we raised the temperature of the R_f -Cl silane deposition, where all of the experiments in Secs. III B 1 and III B 2 were performed at $\sim 100^\circ\text{C}$.

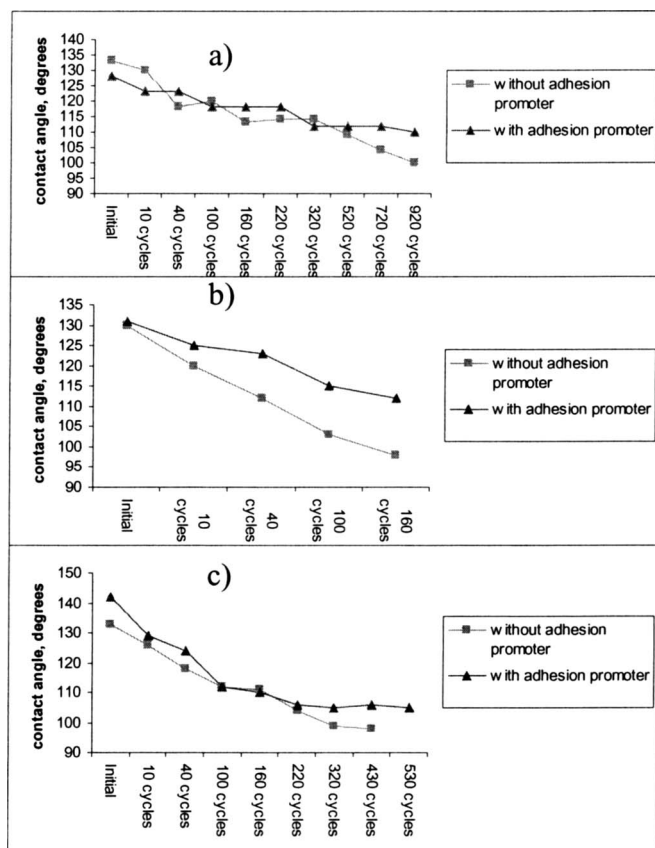


Fig. 4. Results from abrasion tests (advancing water contact angles vs number of cycles in the abrasion tester) of surfaces silanized with the $R_f\text{-Cl}$ silane, with and without the adhesion promoter (isocyanato silane).

1. Deposition of the adhesion promoter

The experiments described in this section were performed under the same conditions as those described in Sec. III A 2. Plasma cleaned silicon wafers were first placed in the vacuum oven. They were then dehydrated as described in Sec. II and finally exposed to the isocyanato silane. Three different experiments were performed to optimize this process. In the first, two injections of the isocyanato silane ($250\ \mu\text{l}$ and then $200\ \mu\text{l}$) were made ~ 30 min apart into the vacuum oven. The material from the first injection was not pumped off before injecting the second aliquot of the compound. This ~ 1 h exposure of the surface to the isocyanato compound led to an increase in film thickness of $10.3 \pm 0.7\ \text{\AA}$ (the average of four measurements from four surfaces in two separate experiments). This experiment was then repeated, except the total exposure time was ~ 30 min (the two injections of the silane ($250\ \mu\text{l}$ and then $200\ \mu\text{l}$) were about 15 min apart). The increase in film thickness after this experiment was $10.3 \pm 1.4\ \text{\AA}$ (the average of three measurements from three surfaces in three separate experiments). In a final experiment, the surfaces were exposed to the vapors from a single injection of $250\ \mu\text{l}$ of the isocyanato silane for 30 min. The resulting film thicknesses were $9.5 \pm 0.4\ \text{\AA}$ (the average of five measurements from five surfaces in four different experiments). To within experimental error, we find no significant difference between the results of

these three experiments. This suggests that any of these reaction conditions is adequate to saturate the silicon surface with the isocyanato silane.

These same three experiments, which were performed on silicon, were also performed on spin coated nylon, which had been plasma treated (oxidized) and dehydrated. Unlike the reproducible results obtained on silicon/silicon oxide, the experiments on spin coated nylon were ambiguous. That is, the resulting thickness changes were often a few \AA positive or even a few \AA negative. We attribute the lower thicknesses we obtained in general (usually $1\text{--}3\ \text{\AA}$), as well as negative thicknesses (usually 0 to $-4\ \text{\AA}$, but in two cases -16 and $-27\ \text{\AA}$), to solvent (*m*-cresol, with the additional possibility of water) diffusing out of the polymer. Such solvent is difficult to remove. In spite of these ambiguous results, the increase in water contact angle that was observed when the isocyanato silane deposited on spin coated nylon (*vide supra*) provides solid evidence for the deposition of this compound.

2. Deposition of the $R_f\text{-Cl}$ silane

For deposition of the $R_f\text{-Cl}$ silane onto isocyanato silane coated silicon, increases in film thickness were relatively modest, and appeared to depend on the reaction time and hydrolysis conditions. For example, for three isocyanato silane coated silicon surfaces in two separate experiments that were hydrolyzed with water vapor for 60–62 min at $100\text{--}107\ ^\circ\text{C}$, and then exposed to the vapors of the $R_f\text{-Cl}$ silane for 60–65 min at $100\text{--}106\ ^\circ\text{C}$, the increase in film thickness was $31 \pm 3\ \text{\AA}$. In contrast, for six isocyanato silane surfaces on silicon/silicon oxide in five separate experiments, which were hydrolyzed with water vapors for 30–31 min at $100\text{--}106\ ^\circ\text{C}$, and then exposed to the vapors of the $R_f\text{-Cl}$ silane for 45–46 min at $104\text{--}107\ ^\circ\text{C}$, the increase in film thickness was $14 \pm 5\ \text{\AA}$. These results are to be compared to the thicker films ($48\ \text{\AA}$, *vide supra*) found in Sec. III A of this article in which $R_f\text{-Cl}$ silane deposition onto adhesion promoter coated silicon took place in a dessicator. Under those conditions, the surfaces were not dehydrated, except by the slow, natural action of the dessicator, and the reaction time was much longer (12–16 h).

In contrast, the increase in film thickness for $R_f\text{-Cl}$ silane deposition onto adhesion promoter coated, spin coated nylon, was much lower when deposition occurred in the dessicator ($67\ \text{\AA}$, *vide supra*). For deposition of the $R_f\text{-Cl}$ silane in the vacuum oven, we observed a strong correlation between the thickness of the spin coated nylon after plasma treatment and the thickness of the subsequent $R_f\text{-Cl}$ silane coating (Fig. 5). We attribute this correlation to the polymer film acting as an increasingly thick (large) reservoir of water, which can cause hydrolysis and condensation of the $R_f\text{-Cl}$ silane at the surface.

C. Deposition using a commercially available CVD system

Fortunately, after completing the results in Secs. III A and III B we obtained access to a commercially available CVD

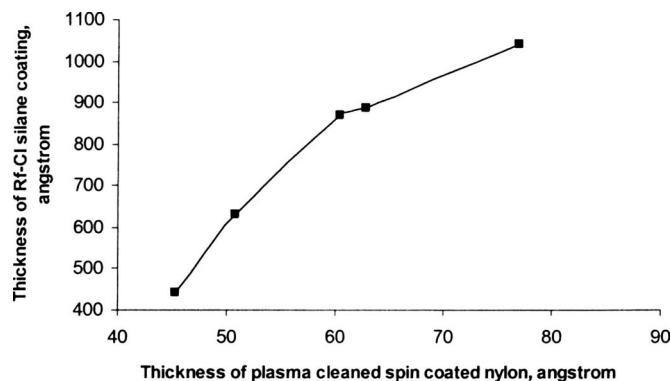


FIG. 5. Thickness of the R_f -Cl silane coating as a function of the thickness of the underlying plasma treated nylon surface. In general, thicker spin coated nylon surfaces than those reported in this figure yielded R_f -Cl silane coatings that could not be analyzed using the same ellipsometric model that was employed for the thinner coatings, i.e., they appear to be too thick. (Hydrolysis time: 30 min, hydrolysis temperature: 100–106 °C, temperature for the R_f -Cl silane reaction: 105–106 °C, time for the reaction: 45 min.)

system that was specifically designed for silane deposition, and that also contains built in plasma cleaning capabilities. We expect better precision and reproducibility from this equipment because this single tool replaces two or three other pieces of equipment. In addition, the plasma capabilities of the YES-1224P allow the deposition chamber to be more rigorously cleaned on a regular basis than the vacuum oven we had employed to this point in our research. While we only had limited access to this equipment, the experiments we were able to perform suggest that this method of depositing our multilayer films is superior to our previous approaches. Indeed, using the YES-1224P we were able to shorten the deposition time for the complete process to ~ 1 h, which makes our procedure industrially viable. In addition, the nylon surfaces treated with this equipment exhibit superhydrophobicity.

1. Plasma cleaning/treatment

Because of the change in the equipment, it was necessary to reoptimize some of the deposition parameters for our coating. Accordingly glass reinforced nylon surfaces were treated with an oxygen plasma in the YES-1224P for 1, 2.5, 5, and 7.5 min. As shown in Table V, the advancing water contact angle decreases steadily as the oxidation time increases. Based on these numbers (compare to Table I), we felt that a

TABLE V. Advancing water contact angles for glass fiber reinforced nylon after oxygen plasma treatment. The number in parenthesis indicates the number of surfaces used for the contact angle measurements.

Plasma treatment time (minutes)	$\theta_a(\text{H}_2\text{O})$
1	47 ± 0 (3)
2.5	45 ± 0 (3)
5	37 ± 0 (3)
7.5	34 ± 0 (3)

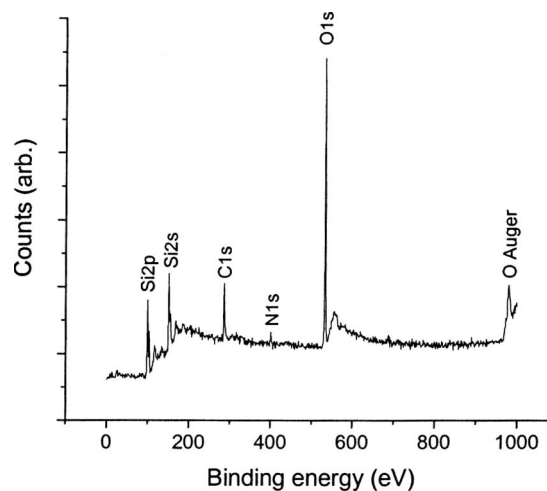


FIG. 6. XPS survey spectrum of isocyanato silane treated silicon dioxide.

6 min oxygen plasma clean would be adequate to oxidize the surface so that deposition of the adhesion promoter silane would be possible. Unfortunately, this plasma clean completely removes the spin coated nylon film so it was not possible to obtain ellipsometric thicknesses from these substrates.

2. Isocyanato silane treatment

After 6 min of plasma cleaning, 5 ml of isocyanato silane was introduced into the oven, and the surfaces were exposed to the vapors of this silane for 10 min. The temperature of the oven was maintained at 100 °C. Spectroscopic ellipsometry was done on the silicon oxide surface after this reaction, and the thickness of the adhesion promoter coating was observed to be 11.8 ± 1.8 Å. Figure 6 shows the XPS survey spectrum of a native oxide coated silicon surface after isocyanato silane treatment, which shows the expected N 1s signal.

3. Hydrolysis of the isocyanato silane treated surface

After the isocyanato silane treatment, 3 ml of water was introduced into the chamber, and the surfaces were exposed to these water vapors for 30 min at 100 °C.

4. Reaction of the hydrolyzed surfaces with the R_f -Cl silane

Finally, 5 ml of R_f -Cl silane was introduced into the oven, and the surfaces were exposed to vapors of this compound for 15 min. The temperature of the oven was maintained at 100 °C. Advancing water contact angles for silicon oxide and reinforced nylon surfaces after R_f -Cl silane treatment were 125° and $155 \pm 3^\circ$, respectively. The final thickness of the coating on the bare Si surface after R_f -Cl silane treatment was 173 ± 7 Å, which includes the thickness of the native oxide and isocyanato silane layers. Figure 7 shows the XPS survey spectrum after this R_f -Cl silane treatment.

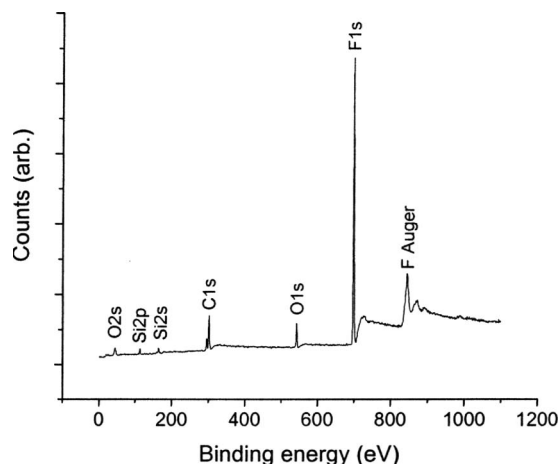


FIG. 7. XPS survey spectrum of a silicon/silicon dioxide surface that was (a) plasma cleaned, (b) exposed to the isocyanato silane, (c) hydrolyzed, and (d) treated with the R_f -Cl silane, all in the YES-1224P tool.

5. Scanning electron microscopy characterization of coated surfaces

In Sec. III A of this article, advancing water contact angles of $128^\circ \pm 3^\circ$ were reported after R_f -Cl silane deposition on reinforced nylon (overnight deposition in a desiccator at room temperature). These water contact angles rose substantially to $155 \pm 3^\circ$ after the two-silane deposition was performed at higher temperature in the YES-1224P. These much higher water contact angles indicate that a superhydrophobic surface is being created, and superhydrophobicity is often a result of surface roughness.²¹ To investigate the possibility of surface roughening, reinforced nylon coupons were examined by scanning electron microscopy (SEM) before and after treatment with the two-silane process in the YES-1224P, as outlined in this section. Figure 8 shows SEM micrographs of reinforced nylon surfaces before and after silane deposition. It is clear from these micrographs that the surfaces have become rougher after the two-silane treatment, developing a cauliflowerlike structure. This increase in surface roughness is attributed to HCl produced during R_f -Cl silane condensation leading to etching of the surface. Indeed, we observed that reinforced nylon parts dissolve slowly in concentrated, aqueous hydrochloric acid.

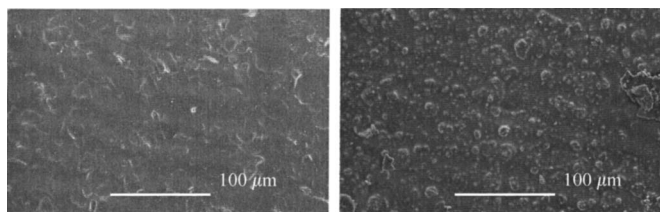
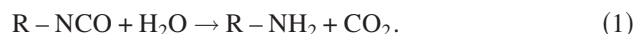


FIG. 8. Representative SEM micrographs of a reinforced nylon coupon (left) before silane deposition and (right) after the two-silane deposition in the YES-1224P.

IV. DISCUSSION

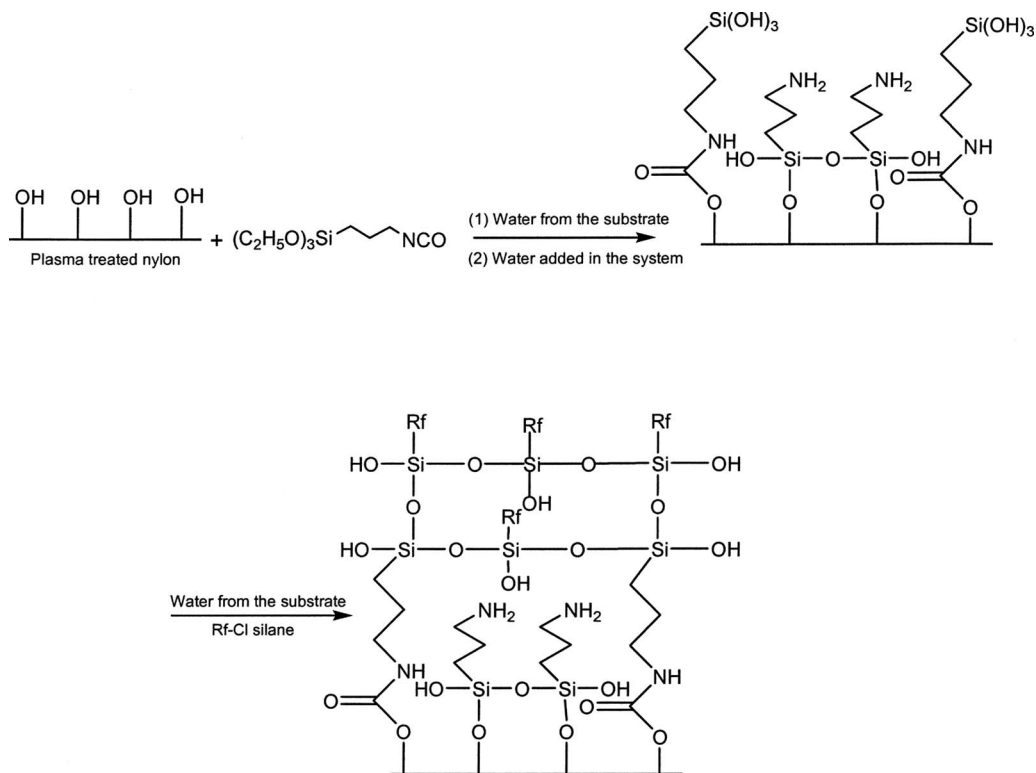
Based on the results in this article, and standard organic and surface chemistry, we propose the following. For the silane deposition in our study, we propose that the isocyanato silane reacts with the cleaned silicon oxide surface by condensation to form Si–O–Si linkages, which tethers the molecule to the surface. It is likely that some cross-linking/polymerization of these molecules also occurs. The isocyanato silane should react, at least in part, with C–OH groups on the plasma treated nylon surfaces to form urethane linkages and this film should act as an adhesion promoter for deposition of the next silane (see Scheme 2). Abrasion tests of the complete films indicate that this silane does perform this function. Some reaction of the surface C–OH groups with the isocyanato silane to form C–O–Si bonds may also occur. Water vapor will hydrolyze silanes and lead to condensation between monomer units to form robust Si–O–Si bonds, or create Si–OH sites that allow future reactions to take place. Water vapor should also facilitate hydrolysis of unreacted isocyanate groups to form amines as follows:



The resulting amines are Brønsted-Lowry bases that should accept protons and form ionic bonds with carboxyl groups at the surface of the polymer (created by plasma cleaning of the surface), and surface²² and bulk silanol groups in subsequent silane layers, which are also acidic. Upon heating, the amino groups that are ionically bonded to carboxyl groups (as $-\text{NH}_3^+ \text{ } ^-\text{OOC}-$) may form strong amide linkages ($-\text{NH}-\text{C}(\text{O})-$) with evolution of water.²³ These interactions should help stabilize films of these materials. In the final step of our chemistry, the R_f -Cl silane should chemisorb onto the isocyanato silane coated surface to form a network of strong Si–O–Si linkages, which will be covalently bonded to the silicon or polymer substrate through the isocyanato silane linking layer. The isocyanato silane layer and the substrate appear to act as a water reservoir to facilitate this condensation (see Fig. 5).

V. CONCLUSION

We have shown a two-silane, CVD approach to creating hydrophobic, abrasion-resistant coatings on silicon oxide and polymer (nylon) substrates. This coating is applied using three different arrangements of scientific equipment. Surfaces at each stage in the process are characterized by XPS, ToF-SIMS, wetting, and spectroscopic ellipsometry. This work has a number of unique features. First, it represents an all gas phase deposition of a new silane coating that is scientifically interesting and technologically useful. Second, the presence of an adhesion promoter in the process leads to thinner films that are *more* robust in abrasion testing. Third, results obtained using plasma/deposition equipment that is relatively inexpensive and/or available in most laboratories are compared to those obtained with a much more sophisticated, commercially available plasma/CVD system (the YES-1224P). The entire deposition process can be completed in only ~ 1 h using industrial equipment (the YES-1224P),

SCHEME 2. Reaction of plasma treated nylon with the isocyanato and R_f-Cl silanes.

and the polymer surfaces modified using the 1224P are superhydrophobic. Fourth, the thickness of the R_f-Cl silane layer deposited by CVD correlates well with the thickness of the underlying spin coated nylon surface, suggesting that the nylon film acts as a reservoir of water for the hydrolysis and condensation of the R_f-Cl silane. See Ref. 24 for supporting information.

ACKNOWLEDGMENT

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¹⁷*ToF-SIMS, Surface Analysis by Mass Spectrometry* (IM, Huddersfield, UK, 2001).

¹⁸The water contact angle for the reinforced nylon is higher than the contact angles for the other materials. The plaques of reinforced nylon that were used in this study appear to be somewhat rougher than the spin coated surfaces, which would raise the observed water contact angles. In addition, throughout our study we observe that our results vary somewhat between the reinforced nylon samples that have different colors. This underscores the importance of the use of spin coated nylon surfaces, which are not pigmented and appear to be much more representative of the true polymer. The reinforced nylon surfaces are important because they show that our process is applicable to an industrially viable material.

¹⁹While a change in water contact angle could always be observed after deposition of the isocyanato silane, we did not always observe a change in thickness by optical ellipsometry. We attribute the difficulty in seeing this change in thickness to diffusion of the solvent used in spin coating out of the nylon film, which would make the film thinner, during deposition of the isocyanato silane.

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²⁴See EPAPS Document No. E-JVTAD6-26-008805 for XPS of surfaces after plasma oxidation and after deposition of the isocyanato silane. For more information on EPAPS, see <http://www.aip.org/pubservs/epaps.html>.