A Two-Silane Chemical Vapor Deposition (CVD) Treatment of Polymer (Nylon) and Oxide Surfaces that Yields Hydrophobic (and Superhydrophobic), Abrasion-Resistant Thin Films

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Abstract
This paper 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 multi-step approach employs only reagents delivered in the gas phase, as follows: i) plasma cleaning/oxidation of the substrate, ii) CVD of 3isocyanatopropyltriethoxysilane, 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 “Rf-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, we explore an all gas phase deposition of a new silane coating that is scientifically interesting and technologically useful. Second, we show that the presence of an adhesion promoter in our 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 ca. 1 hr 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 Rf-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 Rf-Cl silane.
Introduction

In this paper we describe a multi-step 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 crosslinking of the inorganic SiO-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. 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 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. One of these reports showed alternating deposition of gaseous aminopropyltrimethoxysilane and water vapor on porous silica surfaces via atomic layer deposition. Another study showed the liquid phase deposition of 3-(mercaptopropyl)trimethoxysilane onto silver surfaces, followed by hydrolysis in aqueous 0.1 M HCl, with subsequent treatment by gas phase deposition of octadecyltrichlorosilane or dimethylchlorooctadecylsilane. The sequential deposition of 3-aminopropyltriethoxysilane and (tridecafluoro-1,1,2,2-tetrahydrooctyl)dimethylchlorosilane onto polymer substrates has also been reported. 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)trichlorosilane (denoted the “Rf–Cl silane” herein). Plasma cleaning of inorganic surfaces to remove organic contamination is a well known
cleaning procedure.\textsuperscript{13,14} Plasma treatment of polymer surfaces is also a known and effective approach for oxidizing their surfaces.\textsuperscript{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 (ToFSIMS),\textsuperscript{17} and abrasion testing.

**Experimental**

**Reagents** (Tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane (\(\geq 97\%\), Aldrich), 3isocyanatopropyltriethoxysilane (95\%, Gelest, Morrisville, PA), triethoxy(1\(H\), 1\(H\), 2\(H\), 2\(H\)-perfluorooctyl)silane (98\%, Aldrich), \(m\)-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 0.34 M NaCl, 0.08 M urea, 0.33 M NH\(_4\)Cl, 0.04 M CH\(_3\)COOH and 0.12 M lactic acid. The solution was adjusted to pH 4.7 with 2 M NaOH.

**Substrates**

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

**Surface Cleaning**

Prior to any surface chemistry, reinforced nylon surfaces were sonicated in an aqueous 2\% sodium dodecyl sulfate (SDS) solution for 5 minutes. They were then sonicated in deionized water for 10 minutes. 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.

**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 seconds) followed by 5000 rpm (90 seconds). 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.
**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 seconds. 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 backstreaming 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 ca. 3 min. to attain a pressure of 15 Torr (-25 inches), and the valve to the pump was then closed. The surfaces were allowed to dehydrate under these conditions for 30 minutes. The pump was then turned on again for 3 minutes to pump off water vapors, and the valve to the pump was again closed. An aliquot of 250 μL 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 minutes. 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 minutes.

**Testing the Abrasion Resistance of the Films**

An apparatus was built to test abrasion resistance (see Figure 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 cm × 14.7 cm) 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.

**Rt–Cl Silane Deposition in a Dessicator**

The Rt–Cl silane was deposited onto hydrolyzed NCO silane coated surfaces by placing these surfaces in a dessicator along with an open vial of the Rt–Cl silane, for at least for 16 hours. After this reaction, the surface was removed from the desiccator and cured in an oven at 80°C for 1 hour at atmospheric pressure.

**Surface Analytical Instrumentation**

ToF-SIMS was performed with an ION-TOF (TOFSIMS IV) instrument with a two-lens, monoisotopic $^{69}$Ga$^+$ gun as a primary ion source. XPS was performed with an SSX-100 instrument from Surface Sciences using an Al Kα 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 ca. 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 M2000 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.

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.

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 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.

1. 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 Rf-Cl silane was deposited at atmospheric pressure in a dessicator.

1.1. 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 1 shows that the advancing water contact angles (θa(H2O)) 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 X-ray photoelectron spectroscopy (XPS). Figure 2 shows the XP spectra of spin coated and fiberglass reinforced nylon before and after plasma cleaning. Prior to plasma cleaning the XP spectra are dominated by signals from oxygen (O 1s), nitrogen (N 1s), and carbon (C 1s) (see Figure 2). The same three peaks dominate the XP spectra after plasma cleaning (see again Figure 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 Figure 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 nylon 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 Å 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 Ångstroms) 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 Section 3 (vide infra).

1.2. 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 1. XPS was also used to characterize these surfaces. For the bare silicon 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. In one experiment, spin coated nylon surfaces were baked in a vacuum oven at 100ºC for 2 hours at reduced pressure to drive off m-Cresol. The film thickness increase after isocyanato silane deposition was observed to be 4.8 Å ± 0.6 Å.

1.3. Hydrolysis of the Isocyanato Silane Treated Surfaces
The isocyanato silane treated surfaces were hydrolyzed with water vapor for 30 minutes at 100ºC, 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 Å and 142.3 Å, and then 28.3 Å and 141.3 Å, respectively.

1.4. Reaction of the Hydrolyzed Surfaces with the Rf−Cl Silane
After hydrolysis, the isocyanato silane treated surfaces were placed in a dessicator overnight (12-16 hours) 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 “Rf−Cl silane”. Table 2 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 Rf−Cl silane (the fiber reinforced nylon surfaces are not sufficiently flat for ellipsometry to be performed). It is clear that significant deposition of the Rf−Cl silane occurs, especially in the case of the spin coated nylon surface. These results suggest crosslinking of Rf−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 Rf−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 3). XPS and ToF-SIMS also confirm the presence of large amounts of fluorine after CVD of the Rf−Cl silane on the hydrolyzed isocyanato silane surface (vide infra).

1.5. Effect of the Adhesion Promoter on the Thickness of the Rf−Cl Silane Coating
To determine the effect of the adhesion promoter, the isocyanato silane, on the thickness of the Rf−Cl silane coating, plasma treated (bare) Si/SiO₂ and nylon spin coated surfaces having no adhesion promoter coating were exposed to the Rf−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 Rf−Cl silane as described.
previously. Table 4 shows a comparison of the thickness of the Rf-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 prometer (the isocyanato silane film) are considerably thinner than the surfaces that were not treated with the isocyanato silane. This may be because the 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 Rf-Cl silane deposited on surfaces that were not treated with the adhesion promoter (vide infra).

1.6. XPS Analysis of Surfaces Treated with the Rf-Cl Silane

XPS confirms the addition of the Rf–Cl silane to the isocyanato silane treated surfaces. For example, Figure 3 shows XPS of the reinforced nylon surface after the coating process: plasma treatment, reaction with the isocyanato silane, hydrolysis, and exposure to the Rf–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 C1s 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 Rf–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.

1.7. 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 Rf–Cl silane. ToFSIMS, which has an information depth of only about 2 nm, is more surface sensitive than XPS, 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 Rf-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 Figure 3) is also observed.

1.8. 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 Rf-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 fiber glass reinforced nylon coupons that had been plasma cleaned and then i) exposed to the isocyanato silane, hydrolyzed, and finally exposed to the Rf-Cl silane, or ii) only hydrolyzed and then exposed to the Rf-Cl silane. Figure 4 shows the effect of the isocyanato silane on the robustness of Rf-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 ca. 10° higher than the surfaces prepared without the isocyanato compound. To confirm these results, XPS was taken of two surfaces coated with the Rf-Cl silane after abrasion testing, one with the adhesion promoter and one without. The C1s / F1s 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.

2. 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 Section 1 of this paper 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 Rf-Cl silane deposition, where all of the experiments in Sections 2.1 and 2.2 were performed at ca. 100°C.

2.1. Deposition of the Adhesion Promoter

The experiments described in this section (2.1) were performed under the same conditions as those described in Section 1.2. Plasma cleaned silicon wafers were first placed in the vacuum oven. They were then dehydrated as described in the Experimental 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 μL and then 200 μL) were made ca. 30 minutes apart into the vacuum oven. The material from the first injection was not pumped off before injecting the second aliquot of the compound. This ca. 1 hr exposure of the surface to the isocyanato compound led to an increase in film thickness of 10.3 ± 0.7 Å (the average of four measurements from four surfaces in two separate
This experiment was then repeated, except the total exposure time was ca. 30 minutes (the two injections of the silane (250 \( \mu \)L and then 200 \( \mu \)L) were about 15 minutes apart). The increase in film thickness after this experiment was 10.3 \( \pm \) 1.4 Å (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 \( \mu \)L of the isocyanato silane for 30 minutes. The resulting film thicknesses were 9.5 \( \pm \) 0.4 Å (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 Ångstroms positive or even a few Ångstroms negative. We attribute the lower thicknesses we obtained in general (usually 1 – 3 Å), as well as negative thicknesses (usually 0 – -4 Å, but in two cases -16 Å and -27 Å), obtained in this experiment 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.

### 2.2 Deposition of the \( R_f \)-Cl silane

For deposition of the \( R_f \)-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 minutes at 100 - 107°C, and then exposed to the vapors of the \( R_f \)Cl silane for 60 - 65 minutes at 100 - 106°C, the increase in film thickness was 31 \( \pm \) 3 Å. In contrast, for six isocyanato silane surfaces on silicon/silicon oxide in five separate experiments, which were hydrolyzed with water vapors for 30 – 31 minutes at 100 - 106°C, and then exposed to the vapors of the \( R_f \)-Cl silane for 45 - 46 minutes at 104 - 107°C, the increase in film thickness was 14 \( \pm \) 5 Å. These results are to be compared to the thicker films (48 Å, vide supra) found in Section 1 of this paper in which \( R_f \)-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 hours).

In contrast, the increase in film thickness for \( R_f \)-Cl silane deposition onto adhesion promoter coated, spin coated nylon, was much lower when deposition occurred in the dessicator (67 Å, vide supra). For deposition of the \( R_f \)-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 \( R_f \)-Cl silane coating (Figure 5). We attribute this correlation to the polymer film acting as an increasingly thick
A large reservoir of water, which can cause hydrolysis and condensation of the Rf–Cl silane at the surface.

3. Deposition using a commercially available CVD system

Fortunately, after completing the results in Sections 1 and 2 we obtained access to a commercially available CVD 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 ca. 1 hr, which makes our procedure industrially viable. In addition, the nylon surfaces treated with this equipment exhibit superhydrophobicity.

3.1 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 minutes. As shown in Table 5, the advancing water contact angle decreases steadily as the oxidation time increases. Based on these numbers (compare to Table 1), we felt that a six minute 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.

3.2 Isocyanato silane treatment

After 6 minutes 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 minutes. The temperature of the oven was maintained at 100ºC. 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 N1s signal.

3.3 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 minutes at 100ºC.

3.4 Reaction of the Hydrolyzed Surfaces with the Rf–Cl Silane
Finally, 5 ml of Rf-Cl silane was introduced into the oven, and the surfaces were exposed to vapors of this compound for 15 minutes. The temperature of the oven was maintained at 100°C. Advancing water contact angles for silicon oxide and reinforced nylon surfaces after Rf-Cl silane treatment were 125º and 155 ± 3º respectively. The final thickness of the coating on the bare Si surface after Rf-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 Rf-Cl silane treatment.

3.5 SEM Characterization of Coated Surfaces.

In Section 1 of this paper, advancing water contact angles of 128º ± 3º were reported after Rf-Cl silane deposition on reinforced nylon (overnight deposition in a dessicator at room temperature). These water contact angles rose substantially to 155 ± 3º 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. To investigate the possibility of surface roughening, reinforced nylon coupons were examined by 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 cauliflower-like structure. This increase in surface roughness is attributed to HCl produced during Rf-Cl silane condensation leading to etching of the surface. Indeed, we observed that reinforced nylon parts dissolve slowly in concentrated, aqueous hydrochloric acid.

Discussion

Based on the results in this paper, 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 crosslinking/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:

\[(1) \text{R-NCO} + \text{H}_2\text{O} \rightarrow \text{R-NH}_2 + \text{CO}_2\]

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 surface 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 \(-\text{NH}_3^+ -\text{OOC}^-\)) may form strong amide linkages (-\(\text{NH-C(O)}\)-) with evolution of water.\(^{23}\) These interactions should help stabilize films of these materials. In the final step of our chemistry, the \(\text{R}_f-\text{Cl}\) 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 isocyanto silane layer and the substrate appear to act as a water reservoir to facilitate this condensation (see Figure 5).

**Conclusion**

We have shown a two-silane, chemical vapor deposition (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 X-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectrometry, 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 ca. 1 hr using industrial equipment (the YES-1224P), and the polymer surfaces modified using the 1224P are superhydrophobic. Fourth, the thickness of the \(\text{R}_f-\text{Cl}\) 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 \(\text{R}_f-\text{Cl}\) silane.

**Acknowledgement**

While this particular project was not funded by Yield Engineering Systems (YES), YES is currently supporting Dr. Linford’s research.

**Supporting Information**

XPS of surfaces after plasma oxidation, and after deposition of the isocyanato silane.

**References**

18) The 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.
19) While 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.
Figure Caption

**Figure 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.

**Figure 2.** XPS survey and C1s narrow scans of spin coated nylon (left) and bulk reinforced nylon (right) before plasma treatment (top) and after plasma treatment (below).

**Figure 3.** XPS after deposition of the Rf-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.

**Figure 4.** Results from abrasion tests (advancing water contact angles vs. number of cycles in the abrasion tester) of surfaces silanized with the Rf-Cl silane, with and without the adhesion promoter (isocyanato silane).

**Figure 5.** Thickness of the Rf-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 table yielded Rf-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 minutes, hydrolysis temperature: 100 - 106°C, temperature for the Rf-Cl silane reaction: 105-106°C, time for the reaction: 45 minutes.)

**Figure 6.** XPS survey spectrum of isocyanato silane treated silicon dioxide.

**Figure 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 Rf-Cl silane, all in the YES-1224P tool.

**Figure 8.** Representative SEM micrographs of a reinforced nylon coupon left) before silane deposition, and right) after the two-silane deposition in the YES-1224P.
Figure 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.
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Figure 8. Representative SEM micrographs of a reinforced nylon coupon left) before silane deposition, and right) after the two-silane deposition in the YES-1224P.
Table 1. Advancing water contact angles ($\theta_a$(H$_2$O)) of substrates before and after plasma cleaning, and after treatment with the isocyanato silane

<table>
<thead>
<tr>
<th>Substrates</th>
<th>Before Plasma Cleaning</th>
<th>After Plasma Cleaning</th>
<th>After NCO Silane Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare Si/SiO$_2$</td>
<td>40°</td>
<td>&lt; 15°</td>
<td>82 ± 6°$^a$</td>
</tr>
<tr>
<td>Spin coated nylon</td>
<td>60 ± 3° (5)</td>
<td>34 ± 3° (6)</td>
<td>82 ± 7°$^b$</td>
</tr>
<tr>
<td>Reinforced nylon</td>
<td>69 ± 2° (3)</td>
<td>32 ± 2° (5)</td>
<td>87 ± 3° (5)</td>
</tr>
</tbody>
</table>

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 2 – 3 surfaces, each of which was characterized.

These values are the average and standard deviation of measurements made on seven$^a$ and six$^b$ different surfaces prepared in three separate experiments.
**Table 2.** Spectroscopic ellipsometric thicknesses of coatings on bare silicon and spin coated nylon surfaces at different stages of the deposition.

<table>
<thead>
<tr>
<th>Substrates</th>
<th>After NCO silane treatment and hydrolysis</th>
<th>After R$_f$–Cl Silane Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare Si*</td>
<td>29.1 ± 0.6 Å</td>
<td>78 ± 7 Å</td>
</tr>
<tr>
<td>Spin Coated Nylon</td>
<td>125.9, 138.8, 124.3, 136.4 Å</td>
<td>272.3, 192.1, 196.2, 202.7 Å</td>
</tr>
</tbody>
</table>

*The thicknesses of the films reported here include the thickness of the native oxide, which was 18.0 ± 0.5 Å.
Table 3. 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.

<table>
<thead>
<tr>
<th>Substrates</th>
<th>$\theta_a$(H$_2$O)</th>
<th>$\theta_a$(artificial sweat)</th>
<th>$\theta_a$(hexadecane)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare Si</td>
<td>126º</td>
<td>118º</td>
<td>75º</td>
</tr>
<tr>
<td>Spin coated nylon</td>
<td>127º</td>
<td>120º</td>
<td>72º</td>
</tr>
<tr>
<td>Reinforced nylon</td>
<td>132º</td>
<td>130º</td>
<td>71º</td>
</tr>
<tr>
<td>Average</td>
<td>128º ± 3º</td>
<td>123º ± 6º</td>
<td>73º ± 2º</td>
</tr>
</tbody>
</table>

Each of the experiments reported in these columns was performed once.
Table 4. Advancing water contact angles for glass fiber reinforced nylon after oxygen plasma treatment.

<table>
<thead>
<tr>
<th>Substrates</th>
<th>With adhesion promoter</th>
<th>Without adhesion promoter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare Si</td>
<td>48 ± 8 Å</td>
<td>117 ± 13 Å</td>
</tr>
<tr>
<td>Spin coated nylon</td>
<td>67 ± 11 Å</td>
<td>233 ± 37 Å</td>
</tr>
</tbody>
</table>

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

b. The thickness of the native silicon oxide layer on silicon was subtracted from the total ellipsometric thicknesses to give the results in this table.
Table 5. Advancing water contact angles for glass fiber reinforced nylon after oxygen plasma treatment.

<table>
<thead>
<tr>
<th>Plasma treatment time (minutes)</th>
<th>$\theta_a$(H2O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>47 ± 0 (3)</td>
</tr>
<tr>
<td>2.5</td>
<td>45 ± 0 (3)</td>
</tr>
<tr>
<td>5</td>
<td>37 ± 0 (3)</td>
</tr>
<tr>
<td>7.5</td>
<td>34 ± 0 (3)</td>
</tr>
</tbody>
</table>

a. The number in parenthesis indicates the number of surfaces used for the contact angle measurements.
Scheme 1. Structures of 3-isocyanatopropyltriethoxysilane (the “isocyanato silane”) and (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane (the “Rf–Cl silane”).
Scheme 2. Reaction of plasma treated nylon with the isocyanato and Rf-Cl silanes.

Supporting Information for:
A Two-Silane Chemical Vapor Deposition Treatment of Polymer (Nylon) and Oxide Surfaces that Yields Hydrophobic, Abrasion-Resistant Thin Films

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Supporting Information, Figure 1. XPS of the spin coated nylon surface (top), native oxide coated silicon surface (middle), and glass reinforced nylon surface (bottom) after oxidation (left panels), and after deposition of the isocyanato silane (right panels).