

Surface modification of silicon and polydimethylsiloxane surfaces with vapor-phase-deposited ultrathin fluorosilane films for biomedical nanodevices

Bharat Bhushan^{a)}

Nanotribology Laboratory for Information Storage and MEMS/NEMS, The Ohio State University, 650 Ackerman Road, Suite 255, Columbus, Ohio 43202

Derek Hansford^{b)}

Biomedical Engineering Center, The Ohio State University, 270 Bevis Hall, 1080 Carmack Road, Columbus, Ohio 43210

Kang Kug Lee

Nanotribology Laboratory for Information Storage and MEMS/NEMS, The Ohio State University, 650 Ackerman Road, Suite 255, Columbus, Ohio 43202

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Ultrathin coatings of fluorosilane films for silicon and polydimethylsiloxane (PDMS) nanochannels are desirable to control the hydrophobicity of the surface and reduce or prevent undesired protein adsorption or cell interactions critical for the performance of most biomedical micro/nanodevices. Surface modifications using vapor-phase deposition become increasingly important for some biomedical nanodevices and have advantages over liquid-phase deposition since the vapor phase can permeate more efficiently into silicon nanochannels. In this study, vapor-phase deposition was used to deposit ultrathin films of four fluorosilanes on silicon and PDMS and identify deposition conditions for an optimal process. The films were characterized by means of a contact angle analyzer for hydrophobicity, an ellipsometer for film thickness, and an atomic force microscope for surface roughness of these films. Results of this study and relevant mechanisms are the subject of this article. © 2006 American Vacuum Society. [DOI: 10.1116/1.2167077]

I. INTRODUCTION

Micro/nanofluidic systems provide a powerful platform for electrophoretic and chromatographic separations for a variety of biochemical and chemical analyses.¹⁻⁶ Examples of bioassays and biological procedures include DNA sequencing, electrophoresis, DNA separation, enzymatic assays, immunoassays, cell counting, cell sorting, and cell culture. In micro/nanofluidics, small volumes of solvent, sample, and reagents are moved through micro/nanochannels. Miniaturizations of bioassays offer many advantages, including high-throughput screening for solvents, reagents, and cells, short reaction times, portability, low cost, low consumption of power, versatility in design, and potential for parallel operation and for integration with other miniaturized devices. The primary materials used in micro/nanofluidic separation systems are either silicon-based materials (e.g., silicon, SiO₂, SiN_x), thermoplastic (e.g., PMMA, polycarbonate), or polydimethylsiloxane (PDMS, silicone rubber). Surface chemistry is of great importance in micro/nanofluidic devices especially in highly miniaturized and integrated systems due to the high surface area-to-volume ratio. For gas-based separations, having hydrophobic surfaces provides several advantages, including low biofouling and higher gas transport rates.

A micrograph of an interdigitated micro/nanofluidic array based on nanochannels⁷ is shown in Fig. 1(a), showing nanochannels for separation process. Figure 1(b) shows a scanning electron microscope (SEM) exploded view of silicon nanochannels. While postproduction modification is in many cases the only method of modifying surfaces, the surface modifications of interior surfaces of nanochannels present many problems, including several limitations of transport of reactive species, self-limiting reactions, uniform distribution of reactants, and complete coverage of surfaces. The use of low-pressure vapor-phase deposition allows many of these limitations to be overcome.⁸⁻¹⁰ Vapor-phase deposition has the advantage over liquid-phase deposition since the vapor phase can permeate more efficiently into nanochannels, allowing a more uniform deposition. For gas-based separations, the desire for stable hydrophobic surfaces suggests that fluorosilanes or alkylsilanes should be deposited onto the surfaces. Proper selection of surface preparation techniques allows for the use of silane chemistry for modifying both silicon and PDMS surfaces.

The objective of this study was to use a vapor-phase deposition system¹⁰ capable of accommodating silicon wafers and PDMS or an array of silicon and PDMS chips with microfabricated nanochannels and depositing four fluorosilane films on the silicon and PDMS surfaces to obtain useful deposition parameters. Characterization of the films using atomic force microscopy (AFM), contact angle measure-

^{a)}Electronic mail: bhushan.2@osu.edu

^{b)}Author to whom correspondence should be addressed; electronic mail: hansford.4@osu.edu

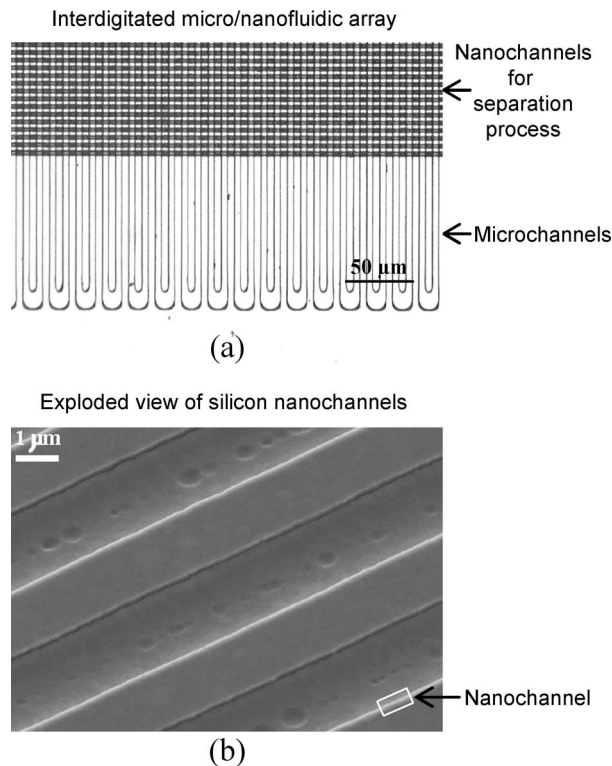


FIG. 1. Micrographs of silicon nanochannels integrated with microfluidic channels: (a) optical image of interdigitated micro/nanofluidic device, with the microfluidics connected by 5- μm long nanochannels (20-nm-wide channels) and (b) SEM exploded view of silicon nanochannels.

ment, and ellipsometry demonstrated the successful deposition of ultrathin fluorosilane films onto silicon and PDMS surfaces.

II. EXPERIMENTAL DETAILS

A. Materials and sample preparation

Test-grade silicon wafers (Wafernet) and planar PDMS (Silastic T2, Dow Corning) were prepared as substrates in this study. Four kinds of fluorosilane precursors (Fig. 2) were used for the vapor-phase deposition (ABCR GmbH & Co. KG, Karlsruhe, Germany). These chemicals were chosen because of their relatively low boiling points ($\leq 105^\circ\text{C}$), which allowed for easy evaporation, and their ability to be deposited as a monolayer which is favorable for coating inside the silicon nanochannels. In particular, the different chemical natures of the silanes were chosen to compare the relative effects on contact angle versus chemical structure. Pentafluorophenyl triethoxysilane (PFPTES) was chosen to examine the effect of an aromatic fluorosilane compared with the linear fluorosilanes. 1H,1H,2H,2H-perfluorooctyl trichlorosilane (PFOTCS) was chosen as a standard linear fluorosilane for attachment. In comparison with PFOTCS, 1H,1H,2H,2H-perfluorooctyldimethylchlorosilane (PFODCS) has only one reactive group on the silane and was used to compare the effect of reduced bonding at the surface, and therefore, theoretically, effects of monolayer orientation relative to the surface. 1H,1H,2H,2H-

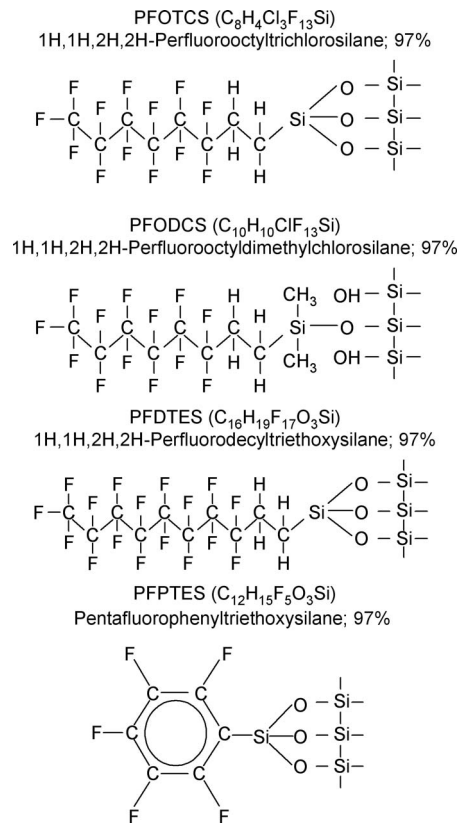


FIG. 2. Chemical structures of fluorosilane films deposited on piranha-cleaned silicon substrates.

perfluorodecyltriethoxysilane (PFDTES) contains a longer perfluoro chain and reacts with the silicon and PDMS surfaces via a different reactive group. Based on the selection of these silanes, conclusions about the effect of reactive attachment groups, aromatic chains, and chain length on monolayer performance can be derived.

The silane coupling chemistry is proposed to be identical for any hydroxylated silicon or oxygenated PDMS surface. In the case of silicon substrate, the silanes react with the siloxyl groups of the native oxide formed on the silicon substrate to form covalent bonds. The trifunctional silanization reaction occurs for silanes, a head group of the vapor silane, with three active groups attached to the silicon atoms in the case of the PFOTCS, PFDTES, and PFPTES films. After the silanes react with hydroxyl groups on the surface, strong covalent bonds are formed on the silicon surface. The monofunctional silanization reaction occurs for silanes with one active group in the case of the PFODCS film. The PDMS surface can be oxygenated using an oxygen plasma, which removes surface methyl groups and leaves siloxyl groups on the surface with similar chemistry to the hydroxyl groups of the native oxide surface.

In addition to comparing the attachment of silanes to silicon and PDMS, two different surface treatments were performed on silicon to compare their effects on silane attachment. All surface treatments were designed to provide siloxyl surface groups for reaction with the chloro- and ethoxy-silane groups. One surface treatment for silicon wafers was

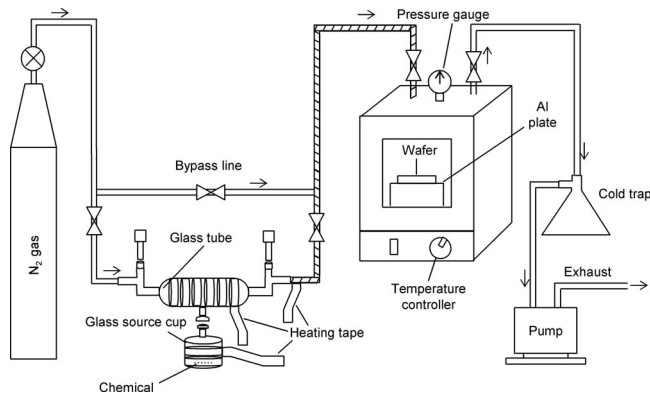


FIG. 3. Schematic of the apparatus for vapor-phase deposition of self-assembled monolayers.

cleaning in piranha solution (a mixture of 3:1 v/v 98% sulfuric acid: 30% hydrogen peroxide) at 90 °C for 30 min followed by a triple rinse in de-ionized water. The other surface treatment for silicon as well as for PDMS was an oxygen plasma treatment [40 W, 30 SCCM (specific cubic centimeter per minute) oxygen, 10 s]. The piranha-cleaned wafers and PDMS were placed in a vapor-phase deposition system¹⁰ for the film deposition.

B. Vapor-phase deposition system

A diagram of the apparatus for vapor-phase deposition is shown in Fig. 3. The system consists mainly of three parts: a vacuum chamber, a glass source cup and glass tube, and a nitrogen gas flow system. The vapor phase deposition process was carried out in a vacuum oven (VWR model 1400E, 110 V, 50/60 Hz, 550 W). The valves and fittings from Swagelok (Nos. SS-42S4, SS-400-3, and SS-400-9) were used as connectors between sections of Teflon tubing. All Teflon tubing for the system were from Fisher Scientific (No. 14-176-179, 890FEP). The glass tube and the glass source cup were designed for this system with input and output port valve plugs and O-rings for sealing. The glass tube and the glass source cup were connected using a clip and O-ring for sealing. These features provide a convenient way to fill chemicals by separating the glass tube from the glass source cup. A heating tape used for heating the glass source cup, glass tube, and Teflon line was a FluidX model (No. BHB-SAT101002, Salt Lake City). The chemicals were put into the glass source cup, which was maintained at a constant temperature during processing by a heating tape. The final major component in this system is the nitrogen carrier gas system. Ultra-high-purity nitrogen gas was dispensed from the gas cylinder using a pressure regulator before it was delivered to the glass tube and source cup. The nitrogen gas could either be introduced into the bypass line or the direct-flow line over the glass source cup. The bypass line was used before and after the deposition process to purge the chamber, and the direct-flow line was used during the deposition processes. After the samples were loaded, nitrogen gas was used to purge the chamber of moisture for about 5 min. Following this purge step, for the fluorosilane deposition a steady-state

chamber pressure of 200 Torr was achieved by flow control of the carrier nitrogen gas and the vacuum line. The carrier gas was used to remove excess, unreacted chemicals. The deposition process was followed by an annealing step for 20 min. Once the deposition process was completed, the inlet/outlet valves were closed to isolate the glass tube and pump down the chamber. After the deposition was completed, typically 50 min, the bypass carrier gas line was opened, introducing pure nitrogen gas into the vacuum chamber to complete the removal of by-products and unreacted chemicals. Finally, the samples were removed from the vacuum chamber and transferred into a vacuum desiccator until characterization.

The optimal deposition parameters were selected based on measured static contact angle (SCA) or film thickness as a function of the temperature of deposition, the chamber pressure during deposition, and the time of deposition. An optimal film was considered the one with the highest SCA and lowest film thickness (a monolayer film).

C. Instrumentation

Static contact angles were measured in air with high-purity de-ionized water by a sessile-drop method using a contact angle goniometer (model 100, Rame-Hart Inc., Mountain Lakes, NJ, USA) to determine the hydrophobicity of the modified surfaces. Values of the contact angle on at least three samples were measured for statistics. The thickness of the films on at least three samples was measured on a Gaertner L116SF ellipsometer, which was equipped with a He-Ne laser (632.8 nm) set at an incident angle of 70° to maximize the sensitivity in the range close to the Brewster angle of the films. The rms roughness values and adhesion measurements of the films on at least three sample locations were characterized by a commercial AFM system (Dimension 3000, Digital Instrument, Santa Barbara, CA, USA).⁸ Square pyramidal Si₃N₄ tips with a nominal 30-50 nm radius mounted on gold-coated triangular Si₃N₄ cantilevers with spring constants of 0.58 N/m were used. The roughness images were obtained under ambient conditions and all scans were 1 × 1 μm² in size. To obtain the adhesive force between the AFM tip and the film surface, the force-distance curve was recorded and the pull-off force was calculated, which is the adhesive force.⁸

III. RESULTS AND DISCUSSION

A. Films on silicon substrate

Figure 4 summarizes the results of characterization of the deposition process for the four different fluorosilanes on piranha-cleaned silicon substrates. The effects of chamber temperature, chamber pressure, and deposition time on the film thickness and SCA are shown from top to bottom, respectively. The left column in the figure shows the effect of treatment on the SCA, and the right column shows the effect of treatment on the measured film thickness. The top graphs show the effect of deposition temperature on the SCA and thickness. Error bars show the variation between at least

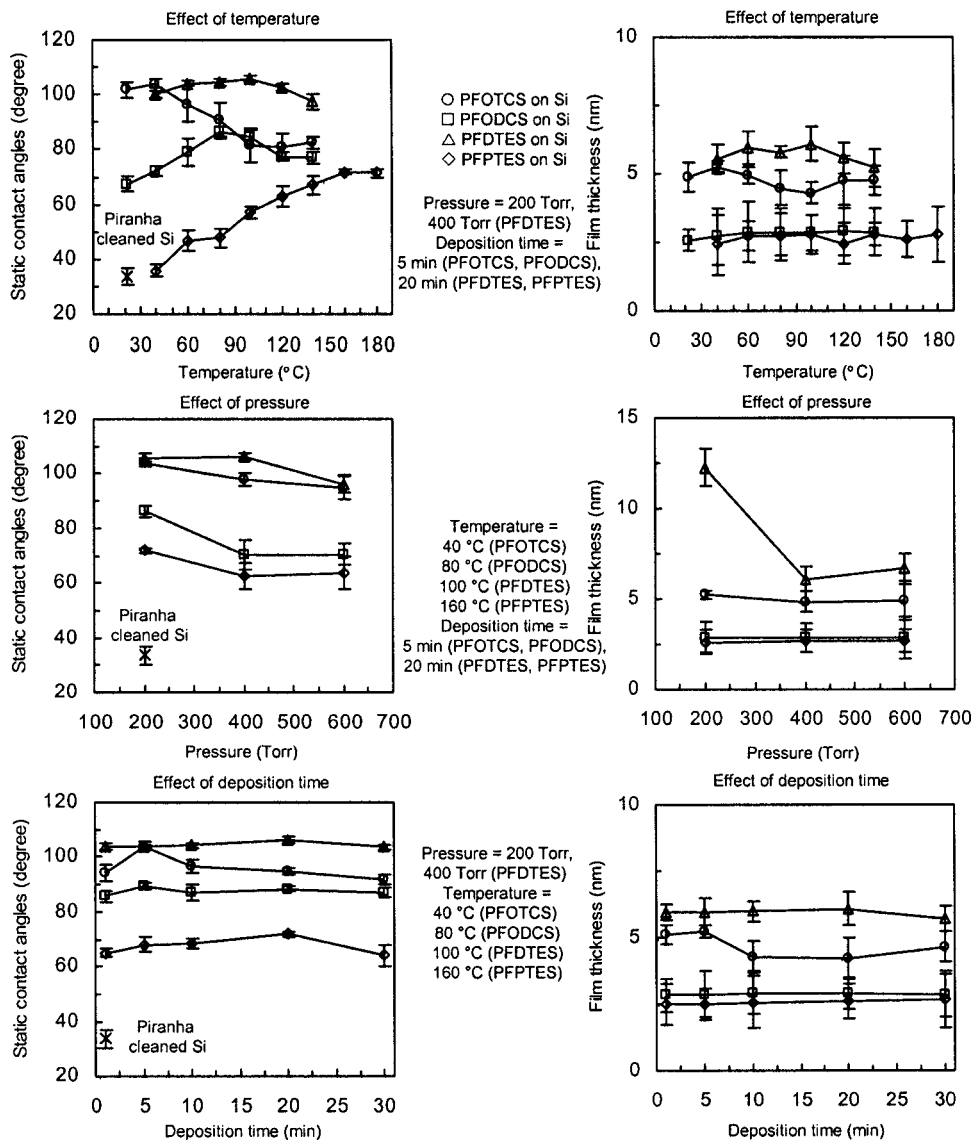


FIG. 4. Static contact angle and film thickness measurements for optimizing the process condition as functions of temperature, pressure, and deposition time. Contact angle for piranha-cleaned Si is also shown.

three samples for each treatment. For ethoxysilanes, the deposition process was 20 min and the annealing process was 20 min to find the optimum temperature, determined to be 100 and 160 °C for PFDTES and PFPTES, respectively, based on the SCA values. For the chlorosilanes, 5 min of deposition time was selected as it gave the highest SCA. It was used to find the optimum temperature, determined to be 40 and 80 °C for PFOTCS and PFODCS, respectively, based on the SCA values.

The middle graphs of Fig. 4 show the effects of the chamber pressure on SCA and film thickness. The optimum pressure of 200 Torr was determined for three of the fluorosilanes based on the SCA values. However, the optimum pressure of the PFDTES film was 400 Torr based on the film thickness (with insignificant difference in SCA for the three pressures). The bottom graphs in Fig. 4 show the effects of deposition time on the SCA and thickness of the films. There were no observed effects on measured film thickness, as expected for

the deposition of stable monolayers. No significant differences in SCA were measured based on deposition time.

The thickness of the four films on silicon was not affected by chamber temperature, chamber pressure, and deposition time as expected for the deposition of a monolayer. The one exception was a large decrease of film thickness between the chamber pressures of 200 and 400 Torr for the PFDTES film. This may be because of cross-linking between silanes which might be produced in the lower pressure (as a function of reduced carrier nitrogen concentration). The chamber temperature demonstrated an observable effect on the static contact angle for all of the fluorosilanes other than PFDTES, likely due to annealing of the monolayers. Little effect on contact angle was observed for chamber pressure or deposition time for any of the fluorosilane films.

The optimized PFDTES film on silicon surface showed the largest increase in SCA value (106°) of the four perfluorosilanes, as compared with the piranha-cleaned silicon sur-

face (34°). PFOTCS showed a similar increase in SCA (104°), followed by PFODCS (85°) and PFPTES (72°). From the above observations, it can be concluded that the surface wettability could be considerably modified from hydrophilic to hydrophobic by the vapor-phase deposition.

Measurements of surface roughness were obtained from at least three samples for each treatment. The rms roughness value of the piranha-cleaned silicon was measured as 0.16 nm. The rms roughness values of the PFOTCS, PFODCS, PFDTES, and PFPTES films were measured as 0.16, 0.19, 0.18, and 0.19 nm, respectively. This shows that the presence of fluorosilane films does not appear to affect the roughness of the substrata, presumably because the films were coated as a uniform monolayer.

B. Films on PDMS substrate

Figure 5(a) shows the static contact angle for substrates with and without surface treatments. The SCA value of the untreated PDMS is 105° which is hydrophobic, due to the $-\text{CH}_3$ termination groups on the PDMS surface. The SCA values of oxygen-plasma-treated PDMS (36°), piranha-cleaned silicon (34°), and oxygen-plasma-treated silicon (33°) were low compared with those of untreated PDMS and HF-cleaned silicon. The similar contact angles show that they have nearly identical surface energies, demonstrating a similar surface chemistry of siloxyls after their respective surface treatments. The SCA value of HF-cleaned silicon is 68° because the surface has a $-\text{H}$ termination group, which is an unstable surface that reverts to siloxyl termination in water or air. After the films were deposited on the surfaces, the SCA values of the films dramatically increased as shown in Fig. 5(b), indicating that the fluorosilanes were successfully attached to the substrata. The data also show the dependency of the SCA values for the various films on the underlying substrate surface. For all four silanes, the PDMS surface has a higher contact angle (10° – 15°) compared with the two silicon surfaces. Conversely, the two types of treated silicon surfaces have the same contact angle for the same fluorosilane films, indicating the same amount of surface coverage of the silanes for the two surface treatments.

Figure 5(c) shows the adhesion force for the deposited fluorosilanes on the three substrates, obtained by AFM. The adhesive forces of the films, obtained using force calibration method, show the expected trend that films with lower surface energy exhibit lower adhesion forces. These data deviate slightly from the trend in that the PFOTCS film has the lowest adhesive force, while the PFDTES film has the highest contact angle.

C. Discussion

From the measured values of this study, it can be observed that the trifunctional silanes with linear perfluoro chains (PFOTCS and PFDTES) exhibit a higher degree of hydrophobicity than the monofunctional linear fluorosilane (PFODCS) and the aromatic fluorosilane (PFPTES). The difference with monofunctional fluorosilanes is likely due to the angle of molecular attachment that results from a single co-

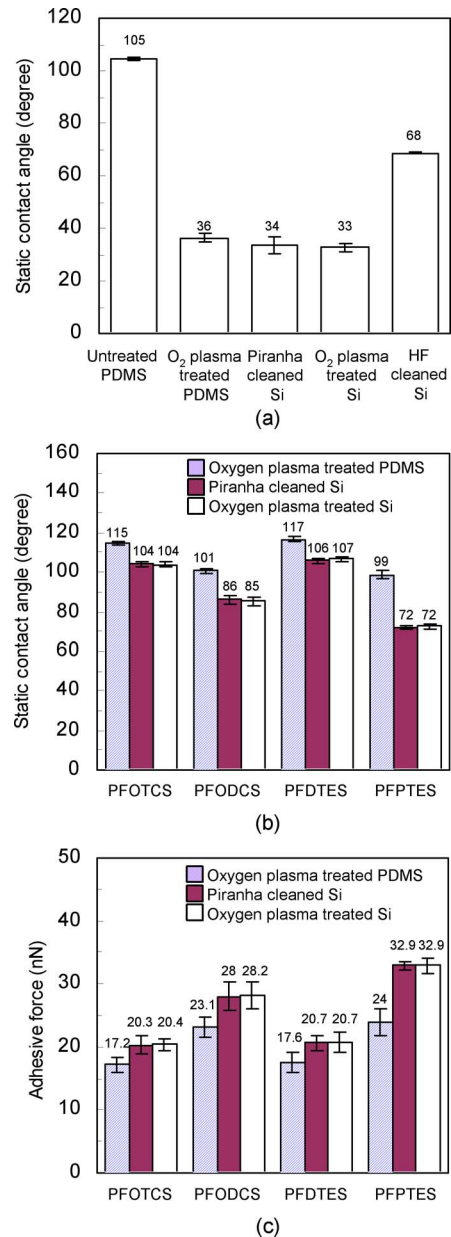


Fig. 5. Summary of static contact angle variation of (a) different surface-treated substrates, (b) four different kinds of fluorosilanes, and (c) adhesive forces of four different kinds of fluorosilanes.

valent bond between the silane and the surface, compared with the trivalent formation of a molecular pyramid on the surface. This will theoretically lead to a thinner film for the same molecular size, as demonstrated in the film thickness data (Fig. 4, right column), with higher levels of bleedthrough from the underlying surface energy. The angled film may also result in a lower density of silanes, which would also be exhibited in a lower net film thickness. The aromatic fluorosilane consistently had lower values of SCA and film thickness, indicating that it would not make an ideal choice for producing a stable hydrophobic surface on silicon or PDMS. This may be due to a lack of ordering of the film (potentially indicated by the increasing SCA values for deposition temperature) or from the bleedthrough of the underly-

ing surface energy through the thinner film. The ability to produce films of the fluorocarbons with ten carbons (PFDTES) and eight carbons (PFOTCS) with similar SCA values for different film thickness values (Figs. 4 and 5) demonstrates that an eight-carbon fluorocarbon chain may provide close to a maximal increase in SCA. Therefore, PFOTCS may be more suitable for applications such as nanochannels where a space confinement affects the choice of surface modification.

The SCA value of the modified oxygen-plasma-treated PDMS is consistently higher than those of piranha-cleaned silicon and oxygen-plasma-treated silicon, presumably due to bleedthrough of the silicon surface properties compared with the PDMS. Another potential explanation is that the silane films deposited were a nonfully packed monolayer, so methyl groups from the native PDMS may influence the SCA compared with the silicon surfaces. The SCA values of the films on piranha-cleaned silicon is nearly identical to those of the films on oxygen-plasma-treated silicon indicating that they have the same surface termination group. This is further confirmed by the SCA values of the as-treated surface values in Fig. 5(a). Values of SCA for the PFODCS (101°) and PFPTES (99°) on oxygen-plasma-treated PDMS compared with the native PDMS surface (105°) indicate that the less-dense films of fluorosilanes are more polar than the native methyl-terminated surface, yielding a net higher SCA. The PFOTCS and PFDTES films provide stable monolayers that increase the hydrophobicity of both the PDMS and silicon surfaces. Characterization of the static contact angles and adhesion forces of the films demonstrates the usefulness of the vapor-phase deposition process.

IV. CONCLUSION

A vapor-phase deposition system was designed to coat uniform, conformal fluorosilane self assembled monolayer films on the silicon and PDMS surfaces. Four different perfluorosilane films were deposited onto three different sub-

strates: piranha-cleaned silicon, oxygen-plasma-treated silicon, and oxygen-plasma-treated PDMS. Optimal deposition parameters were found by examining the effects of deposition temperature, chamber pressure, and deposition time on the static contact angle and film thickness of deposited films on piranha-cleaned silicon. All the films were deposited as monolayers with the silane reaction controlling the processing conditions. The SCA value of all the films on piranha-cleaned silicon is almost the same as that of the films on oxygen-plasma-treated silicon since they have the same surface chemistry. The use of oxygen plasma to modify surfaces may be important for modification of nanochannels. The surfaces modified by the fluorosilane films consistently have dramatically higher water contact angles and lower adhesive forces than the unmodified silicon surfaces.

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¹P. Gravesen, J. Branebjerg, and O. Jensen, *J. Micromech. Microeng.* **3**, 168 (1993).

²L. J. Kricka, in *Biochip Technology*, edited by J. Cheng and L. J. Kricka (Harwood Academic, New York, 2001), pp. 1–16.

³P. A. Auroux, D. Iossifidis, D. R. Reyes, and A. Manz, *Anal. Chem.* **74**, 2637 (2002).

⁴S. K. Sia and G. M. Whitesides, *Electrophoresis* **24**, 3563 (2003).

⁵A. van der Berg, *Lab-on-a-Chip: Chemistry in Miniaturized Synthesis and Analysis Systems* (Elsevier, Amsterdam, 2003).

⁶*Springer Handbook of Nanotechnology*, edited by B. Bhushan (Springer, Heidelberg, Germany, 2004).

⁷D. J. Hansford, T. A. Desai, and M. Ferrari, in *Biochip Technology*, edited by J. Cheng and L. J. Kricka (Harwood Academic, New York, 2001), pp. 341–362.

⁸B. Bhushan, *Nanotribology and Nanomechanics An Introduction* (Springer-Verlag, Heidelberg, Germany, 2005).

⁹T. Kasai, B. Bhushan, G. Kulik, L. Barbieri, and P. Hoffman, *J. Vac. Sci. Technol. B* **23**, 995 (2005).

¹⁰K. Lee, B. Bhushan, and D. Hansford, *J. Vac. Sci. Technol. A* **23**, 804 (2005).