Notes

Alkyl Monolayers on Silica Surfaces Prepared Using Neat, Heated Dimethylmonochlorosilanes with Low Vapor Pressures

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Silanes with one, two, or three reactive groups, e.g., $SiCl_{1-3}$, $Si(OCH_3)_{1-3}$, or $Si(OCH_2CH_3)_{1-3}$, have long been used as agents for functionalizing silica surfaces.[1] Of these species, the monofunctional compounds, e.g., monochlorodimethylsilanes, are particularly easy to work with because, unlike di- or trifunctional silanes, they can only dimerize and not polymerize. Indeed, because surface reactions are limited to monolayer formation, these compounds have found wide technological application as stationary phases (coatings for silica gel) for liquid chromatography.[2] Linton and co-workers[3] and Watts and co-workers[4] studied monolayers of alkyldimethylchlorosilanes on silica gel that were deposited from organic solvents. Both Rabolt and co-workers,[5] who stressed the utility of monochlorosilanes, and Genzer and co-workers[6] have vapor deposited semifluorinated alkyldimethylchlorosilanes onto silicon oxide.

Monolayers of trifunctional silanes have been extensively prepared from solution and subsequently characterized. For example, Sagiv, Maoz, and co-workers[7-10] described monolayer formation from octadecyltrichlorosilane (OTS), 18-nonadecenyltrichlorosilane (CH_2dCHs $(CH_2)_{17}sSiCl_3$), and/or methyltrichlorosilane on quartz, glass, silicon (oxide), and ZnSe. Sukenik and co-workers prepared monolayers of $Cl_3SiCH_2(CH_2)_{14}CH_2X$ (X)-Br, -CN, -SCN, and-$SCOCH_3$)onoxide-coatedsilicon[11] and have recently described a facile method for the preparation of functionalized trichlorosilanes using trialkoxysilane intermediates.[12,13] Senkevich and co-workers deposited 3-mercaptopropyltrimethoxysilane and 2-(trimethoxysilylethyl) pyridine from toluene,[14] and Harris and coworkers deposited monolayers of octadecyltrimethoxysilane onto gold colloids.[15] Monolayer deposition often takes place from semidilute solutions of silanes in bulky organic solvents, e.g., bicyclohexyl,[7] under inert conditions.[16] Incubation times for the substrate in the solution range from a few minutes to several hours. If the solution is not heated, the coating may need to cure under ambient conditions for up to 24 h. It is also common to prepare silane monolayers from solutions that contain 2% silane in 95% ethanol-5% water solutions that have the pH adjusted to 4.5-5.5 with acetic acid.[17] Extensive rinsing of the surface following monolayer formation is typically required to ensure that polymerized material, which is not part of the monolayer, is removed from the surface. Surface silanization has also been reported using gasphase trifunctional silanes.[18-22]

Here we report a rapid, facile, and reproducible preparation of monolayers on silicon oxide surfaces using neat, heated dimethyl mono functional silanes. In the case of a solid silane, enough material is placed on a surface so that upon heating its melt completely covers the surface. The surface and silane are heated for 10 min in an oven at 60-120 °C.*Asasafetyprecaution,compoundswithlow boiling points were not used in this procedure.* Excess reagent is finally removed, and the surfaces are characterized with X-ray photoelectron spectroscopy, spectroscopic ellipsometry, and wetting.

Materials and Methods

Materials. Octadecyldimethylchlorosilane (95%), octenyldimethylchlorosilane (95%), and 3-glycidoxypropyldimethylethoxysilane (97%) were obtained from Aldrich Chemical Co. 3-Aminopropyldimethylethoxysilane and (tridecafluoro-1,1,2,2tetrahydrooctyl)-1-dimethylchlorosilane were obtained from United Chemical Technologies. Actone, *m*-xylene, and toluene were reagent grade, and water was obtained from a Millipore Milli-Q water system. Silicon (100) wafers (p-boron, 0-100 Ω cm, test grade) were obtained from TTI Silicon (Sunnyvale, CA).

Silicon Cleaning. Silicon surfaces were cleaned by immersion in 50:50 (v/v) H_2O_2 (30%)/NH_4OH (concentrated) for ∼30 min at room temperature and then rinsed thoroughly with water. After the wafers were cleaned, surfaces were immersed in 5 vol % HCl (concentrated) for 60 min and then stored under water. Prior to silanization the surfaces were rinsed with water three times and dried with a jet of N_2. *Warning: The NH_4OH/ H_2O_2 cleaning solution is extremely caustic and should be used with great care.*

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Table 1. Summary of Reaction Conditions and Physical Properties of Monolayers[a]

	$ClMe_2Si\text{-}C_{18}$	$ClMe_2Si\text{-}C_2R_f$	$ClMe_2Si\text{-}C_6CHdCH_2$	$EtOMe_2Si\text{-}C_3$-glycidyl	$EtOMe_2Si\text{-}C_3NH_2$
T^b (°C)	120	60	120	100	75
thickness[c] (Å)	10.4 (1.1	6-7	7.2 (1.4	7.0 (0.36	6.9 (0.7
advancing/receding contact angles	100.1 (2.1/86 (4.2	103.2 (0.53/86.8 (2.5	90.5 (0.5/76.0 (2.2	63.3 (1.0/53.6 (0.9	66.8 (0.4/30.8 (0.4
C 1s/Si 2p	1.18 (0.08	0.62 (0.06	0.51 (0.05	0.47 (0.11	0.73 (0.04
F 1s/Si 2p		1.87 (0.19			
N 1s/Si 2p					0.083 (0.01

[a] All reaction times were 10 min. [b] Temperature at which silane and substrate were heated. [c] As measured by spectroscopic ellipsometry.

Sample Preparation. Silicon shards were placed in the recessed region (∼1 mm deep) of a machined Teflon block. The appropriate silane was then placed on the surface of the silicon, and the Teflon blocks containing the surface and reactive compound were placed in an oven (Thelco Laboratory Oven, Precision, Winchester, VA) at various temperatures (see Table 1) and times to induce a reaction. The wafers were then removed from the oven, immediately rinsed with acetone to remove unreacted silane from the surface, and placed in a Soxhlet extractor (Chemglass, Vineland, NJ) overnight with *m*-xylene as the solvent.*Warning: Thisprocedureshouldnotbeattempted above the flash point of a silane. Heated fumes from a volatile organic compound are potentially explosive.* After cleaning in the Soxhlet extractor, the samples were rinsed with water, dried in a jet of N_2, and characterized by spectroscopic ellipsometry and wetting. Samples were finally analyzed by X-ray photoelectron spectroscopy (XPS). With the exception of the surfaces prepared from octadecyldimethylchlorosilane, the ellipsometric thicknesses of silanized surfaces were the same whether they were cleaned by Soxhlet extraction or by a more simple procedure of rinsing with acetone, rinsing with water, rubbing with a soft artist's brush in the presence of aqueous 2% sodium dodecyl sulfate, and finally rinsing with water.

Instrumentation. X-ray photoelectron spectroscopy (XPS) was performed with a Surface Science spectrometer (SSX-100) with a monochromatic Al KRX-ray source and an electron takeoff angle of 35°. Variable angle spectroscopic ellipsometry (M-2000, J. A. Woollam Co.) was used to find the thicknesses of the monolayers. Optical constants in the instrument software files (SIO2.MAT and Si-jaw.mat) were used to model silicon oxide, organic monolayers, and the silicon substrate. Modeling of the surface derived from the semifluorinated silane was performed at the J. A. Woollam headquarters in Lincoln, NE. Advancing and receding water contact angles were determined using a contact angle goniometer (model 100-00, Rame-Hart, Inc., Mountain Lakes, NJ).

Results and Discussion

Native oxide coated silicon substrates were silanized with five different neat, heated silanes: octadecyl dimethyl chlorosilane ($ClMe_2SisC_{18}$), octenyldimethylchlorosilane ($ClMe_2SisC_6CHdCH_2$), 3-glycidoxypropydimethylethoxy silane ($EtOMe_2SisC_3$sglycidyl), 3-amino propyl dimethyl ethoxysilane ($EtOMe_2SisC_3NH_2$), and (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-dimethylchlorosilane ($ClMe_2SisC_2R_f$). Characterization of the native oxide prior to silanization shows that it is ∼20 Å thick by spectroscopic ellipsometry, is wet by water, and contains a small amount of adventitious carbon by X-ray photoelectron spectroscopy (XPS).

The thin film produced by silanizing with neat, heated $ClMe_2SisC_{18}$ for 10 min is approximately 10 Å thick, its advancing water contact angle is ∼100°, and XPS of this surface shows a substantial carbon peak. The values reported for the thickness, water contact angles, and C 1s/Si 2p XPS ratio for $ClMe_2SisC_{18}$ in Table 1 are the averages of measurements taken from 40 separate surfaces that were prepared using this compound. The standard deviations of these data (the errors in Table 1) show the excellent reproducibility of this method, as do the data from surfaces silanized using $ClMe_2SisC_6CHd\ CH_2$, $EtOMe_2SisC_3$sglycidyl, $EtOMe_2SisC_3NH_2$, and $ClMe_2SisC_2R_f$, which were prepared 11, 7, 11, and 11 times, respectively. As expected, the surface made from $ClMe_2SisC_{18}$ has a higher C 1s/Si 2p XPS ratio than those prepared from shorter silanes(see Table1).Together these results suggest the formation of a hydrocarbon monolayer that has substantial methylene character[23] and that has alkyl chains that are significantly tilted, as was previously observed in Genzer and co-worker's NEXAFS study of a semifluorinated monochlorosilane.[6] This tilt is attributed to the inability of monofunctional silanes to polymerize and to the presence of two methyl groups on the silane silicon atom that should sterically limit chain packing. Identical physical properties for the monolayers were obtained if the reaction time between $ClMe_2SisC_{18}$ and the surface was increased to 15 min, suggesting that the reaction is complete in 10 min.

Table 1 shows that the ellipsometric thicknesses from surfaces silanized with $ClMe_2SisC_2R_f$, $ClMe_2SisC_6CHd\ CH_2$, $EtOMe_2SisC_3$sglycidyl, and $EtOMe_2SisC_3NH_2$ are all 6-7 Å, where these molecules contain 10, 10, 8, and 5carbonatoms,respectively.Towithinexperimentalerror, surfaces silanized by immersion in refluxing 3.3 vol % $ClMe_2SisC_2R_f$ in toluene for 45 min had identical (slightly lower) water contact angles and thicknesses. Monolayers prepared from an analogous compound ($(CH_3O)_3SiCH_2CH_2(CF_2)_5CF_3$) in the gas phase were reported to have essentially the same thickness.[18] The unexpectedly high thickness for the $EtOMe_2SisC_3NH_2$ surface is attributed to the presence of adventitious material. This hypothesis is supported by an analysis of the XPS data for this surfacesthe corrected C 1s/N 1s ratio is ∼15:1 instead of the expected 5:1 value. That this surface contaminates is not unexpected because of the anticipated high free energy of a surface of amino groups.

As expected, the advancing and receding water contact angles for our silanized surfaces decrease with increasing polarity of the silane. That is, the advancing water contact angles vary from 100° to 103° to 91° to 63° to 67° for $ClMe_2SisC_{18}$,

$ClMe_2SisC_2R_f$, $ClMe_2SisC_6CHdCH_2$, $EtOMe_2SisC_3$sglycidyl, and $EtOMe_2SisC_3NH_2$, respectively. In comparison, water contact angles of monolayers on silicon oxide made from the trifunctional silanes $Cl_3Si(CH_2)_{17}CH_3$,[8] $Cl_3Si(CH_2)_{17}CHdCH_2$,[8] $(CH_3O)_3Si(CH_2)_{17}CH_3$,[20] and $(CH_3O)_3SiCH_2CH_2(CF_2)_5CF_3$,[24] where the latter two surfaces were prepared by gas-phase deposition, were 115°, 103°, 105°, and 106°, respectively. Monolayers of $HS(CH_2)_{21}CH_3$ and $HS(CH_2)_2(CF_2)_5CF_3$ on gold have advancing water contact angles of 112° and 118°, respectively.[25] We again attribute the lower water contact angles of our monolayers derived from $ClMe_2SisC_{18}$ and $ClMe_2$-$SisC_2R_f$ to tilt in the alkyl chains and steric hindrance imposed by the methyl groups.[6]

In conclusion, we describe a rapid method of silanizing silicon oxide surfaces, which simply consists of heating the surface in the presence of a neat silane under ambient conditions. This method can be used with a number of different nonvolatile compounds. An advantage of the present method is the speed with which surfaces can be functionalized and that no deposition solution of the silane needs to be prepared. Disadvantages are that thick, densely packed monolayers analogous to those made from trichlorosilanes are not obtained and that this procedure uses more compound than other methods that employ dilute solutions of silanes. However, we expect that neat, heated di- and trifunctional silanes will also yield monolayers in an analogous fashion. To preserve compound (many silanes are expensive),we intend to silanize surfaces by wetting them with a solution of a silane in a nonvolatile solvent and then immediately heating the surface and solution under ambient conditions to rapidly drive a reaction. To be safe, the temperature during this process should not exceed the flash point of the solution.

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(1) Plueddemann, E. P. *Silane Coupling Agents*; Plenum Press: New York, 1991.
(2) Young, C. S.; Weigand, R. J.*LCGCNorth America* **2002**, *20*, 464-473.
(3) Simko, S. J.; Miller, M. L.; Linton, R. W. *Anal. Chem.* **1985**, *57*, 2448-2451.
(4) Brown, V. A.; Barrett, D. A.; Shaw, P. N.; Davies, M. C.; Ritchie, H. J.; Ross, P.; Paul, A. J.; Watts, J. F. *Surf. Interface Anal.* **1994**, *21*, 263-273.
(5) Hoffmann, P. W.; Stelzle, M.; Rabolt, J. F. *Langmuir* **1997**, *13*, 1877-1880.
(6) Genzer, J.; Efimenko, K.; Fischer, D. A. *Langmuir* **2002**, *18*, 9307-9311.
(7) Maoz, R.; Sagiv, J. *J. Colloid Interface Sci.* **1984**, *100*, 465-496.
(8) Frydman, E.; Cohen, H.; Maoz, R.; Sagiv, J. *Langmuir* **1997**, *13*, 5089-5106.
(9) Maoz, R.; Sagiv, J. *Langmuir* **1987**, *3*, 1045-1051.
(10) Maoz, R.; Sagiv, J. *Langmuir* **1987**, *3*, 4-1044.
(11) Collins, R. J.; Sukenik, C. N. *Langmuir* **1995**, *11*, 2322-2324.
(12) Barness, Y.; Gershevitz, O.; Sekar, M.; Sukenik, C. N. *Langmuir* **2000**, *16*, 247-251.
(13) Balachander, N.; Sukenik, C. N. *Langmuir* **1990**, *6*, 1621-1627. (14) Senkevich, J. J.; Mitchell, C. J.; Yang, G.-R.; Lu, T.-M. *Langmuir* **2002**, *18*, 1587-1594.
(15) Olson, L. G.; Lo, Y.-S.; Beebe, T. P., Jr.; Harris, J. M. *Anal. Chem.* **2001**, *73*, 4268-4276.
(16) Offord, D. A.; Griffin, J. H. *Langmuir* **1993**, *9*, 3015-3025.
(17) *Silanes, Silicones and Metal-Organics*, 2nd ed.; Gelest, Inc.: Tulleytown, PA, 1998.
(18) Terris, B.; Manim, H.; Best, M.; Logan, J.; Rugar, D. *Appl. Phys. Lett.* **1996**, *69*, 4262-4264.
(19) Jo¨nsson, U.; Olofsson, G.; Malmqvist, M.;Ro¨nnberg, I. *Thin Solid Films* **1985**, *124*, 117-123.
(20) Sugimura, H.; Hozumi, A.; Kameyama, T.; Takai, O. *Surf. Interface Anal.* **2002**, *34*, 550-554.
(21) Tada, H.; Nagayama, H. *Langmuir* **1995**, *11*, 136-142.
(22) Tada, H.; Shimoda, K.; Goto, K. *J. Electrochem. Soc.* **1995**, *142*, L230-L232.
(23) Ulman, A. *An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to Self-Assembly*; Academic Press: Boston, 1991.
(24) Hozumi, A.; Ushiyama, K.; Sugimura, H.; Takai, O. *Langmuir* **1999**, *15*, 7600-7604.
(25) Bain, C. D.; Evall, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 5-7164.