Rapid Covalent Modification of Silicon Oxide Surfaces through Microwave Assisted Reactions with Alcohols

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ABSTRACT

We demonstrate the method of a rapid covalent modification of silicon oxide surfaces with alcohol containing compounds with assistance by microwave reactions. Alcohol containing compounds are prevalent reagents in the laboratory, which are also relatively easy to handle due to their stability against exposure to atmospheric moisture. The condensation of these alcohols with the surfaces of silicon oxides is often hindered by slow reaction kinetics. Microwave radiation effectively accelerates this condensation reaction by heating of the substrates and/or solvents. A variety of substrates were modified in this demonstration, such as silicon oxide films of various thicknesses, glass substrates such as microscope slides (soda-lime), and quartz. The monolayers prepared through this strategy demonstrated the successful formation of covalent surface modifications of silicon oxides with water contact angles of up to 110° and typical hysteresis values of 2° or less. An evaluation of the hydrolytic stability of these monolayers demonstrated their excellent stability in acidic conditions. The techniques introduced in this article were successfully applied to tune surface chemistry of silicon oxides to achieve hydrophobic, oleophobic, and/or charged surfaces.

INTRODUCTION

In this article, we demonstrate a rapid technique for modifying the surfaces of silicon oxides through a microwave assisted condensation of alcohol containing compounds. The formation of self-assembled monolayers (SAMs) has been widely pursued to tune the surface properties of materials as necessary for a variety of applications that include molecular electronics,[1] microelectromechanical systems (MEMS),[2] microfluidics,[3] optics,[4] catalysis,[5] drug delivery,[6] and biological interfaces.[7-9] Self-assembled monolayers have been successfully formed on silicon oxide surfaces using molecules containing reactive groups, such as silanes[10-12] and phosphonic acids.[13-16] Limitations of preparing monolayers from these reactive molecules include the procedures required to prepare these molecules,[17] robustness of their interactions with silicon oxide surfaces,[14-15] susceptibility of these molecules to side reactions and sensitivity to environmental conditions (e.g., humidity),[11, 18-20] as well as their potential to form multilayer coatings.[13] Alternative approaches to modifying the surfaces of silicon oxides are desirable.

As an alternative class of reactive molecules, alcohols have been utilized to form monolayers on silicon oxides. These monolayers (commonly referred to as self-assembled monolayers or SAMs) are covalently linked to surfaces through the formation of silyl ether (Si-O-C) bonds[21] between the alcohol functionalized molecules and the surfaces of either hydrogen terminated silicon[22-27] or silicon oxides.[28-30] Monolayers prepared from the reaction of aliphatic alcohols with SiO_x surfaces can overcome many of the challenges of using other reagents, such as organosilanes and phosphonic acids. Alcohol functionalized reagents are abundant, widely available, relatively safe to use, monoreactive and relatively insensitive to the presence of moisture. Preparation of hydrogen terminated polished silicon can pose significant safety concerns because fluoride ion containing reagents (e.g., HF, NH_4F) are required to remove any oxide film on the silicon.[25, 31] Moreover, hydrogen terminated silicon is difficult to form on glass or quartz substrates. Formation of SAMs from the reaction of aliphatic alcohols with SiO_x surfaces has been achieved using convective heating,[29] but this method requires a relatively long reaction time due to the unfavorable energetics of this condensation reaction even at elevated temperatures. These previous studies demonstrated the ability to use aliphatic alcohols as an alternative class of reactive molecules to prepare self-assembled monolayers (SAMs), but it provided limited information on the surface coverage and stability of the resulting SAMs.

In order to form uniform SAMs of alcohols on the surfaces of silicon oxides in a timely manner, a more effective and efficient strategy is needed to deliver sufficient energy to drive this condensation reaction. Microwave radiation is an attractive alternative means of providing the required thermal energy for the formation SAMs from alcohols. Microwaves can heat a reaction faster and more effectively than convective heating,[32] and microwaves have been widely utilized to initiate reactions in organic synthesis[32-36] and material science.[37-38] Recently, processes have been demonstrated that utilize microwave radiation to assist the formation of monolayers of alkanethiolates on gold,[39] alkenes on silicon carbide,[40] and alkylsilanes on glass slides,[41] cotton fabrics,[42] and silicon chips with thermally grown oxides.[43] The use of microwave radiation has been demonstrated for the reaction of alcohols on hydrogen terminated silicon[44-45] but has not been extended to the condensation reactions between alcohols and silicon oxides.

In this study, we demonstrate a microwave assisted reaction of aliphatic alcohols and surface bound silanols as an effective and efficient technique to form monolayers on various types of silicon oxide surfaces. We sought to understand the impact of microwave radiation on the reaction of alcohols with silanol groups on the surfaces of SiO_x based substrates having different compositions and structures. Hydrolytic stability of the monolayers formed with this technique was evaluated at different pH values. Finally, we demonstrate applicability of the technique towards tuning surface chemistry of silicon oxide surfaces to achieve hydrophobic, oleophobic, and/or charged surfaces.

EXPERIMENTAL SECTION

Reagents and Materials. All reagents were used as received, which included 1-octanol (Sigma-Aldrich, ACS reagent grade, CAS# 111-87-5), 1H,1H,2H,2H-perfluoro-1-octanol (Sigma-Aldrich, 97%, CAS# 647-42-7), choline chloride (Sigma-Aldrich, BioReagent, CAS# 67-48-1), glycolic acid (Sigma-Aldrich, ReagentPlus, CAS# 79-14-1), toluene (J.T. Baker, CMOS grade, CAS# 108-88-3), sulfuric acid (Anachemia Canada, Inc., ACS reagent grade, CAS# 7664-93-9), hydrogen peroxide (Fisher Scientific, CAS# 7722-84-1), hydrochloric acid (ACP Chemicals, ACS reagent grade, CAS# 7647-01-0), sodium hydroxide (BDH Chemicals, ACS grade, CAS# 1310-73-2), acetone (Fisher Scientific, reagent grade, CAS# 67-64-1), and isopropanol (Fisher Scientific, reagent grade, CAS# 67-63-0). Four inch, p-type, test grade, single-side polished, <1 0 0> silicon wafers with a resistivity between 1 to 10 Ohms·cm and either with or without a 100-nm thick dry oxide film were purchased from the Nanofabrication Facility in 4D LABS at Simon

Fraser University. Soda-lime glass microscope slides were purchased from Leica Microsystems (Surgipath precleaned Micro Slides Snowcoat X-tra) and polished quartz slides were purchased from Chemglass (Product# CGQ0640-01). The polished silicon wafers, soda-lime glass microscope slides, and polished quartz slides were diced into 1 cm by 1 cm square pieces that served as the substrates for the following experiments.

Preparation of Silicon Oxide Surfaces on Polished Silicon. Piranha cleaning of the diced silicon substrates removed surface contamination, exposing a thin (<2 nm) native silicon oxide layer. To prepare the piranha solution, roughly 4 mL of 30% (v/v) hydrogen peroxide was slowly added to 14 mL of concentrated sulfuric acid to make a 7:2 (v/v) mixture. *CAUTION: Piranha solution is a strong oxidizing agent and reacts violently with organic compounds. This solution should be handled with extreme care.* The substrates were immersed in the freshly prepared piranha solution for ~1 h followed by immersion into 18 MΩ·cm deionized water (Barnstead Nanopure DIamond water filtration system) for 5 min. These substrates were subsequently rinsed under a stream of 18 MΩ·cm deionized (DI) water for 1 min with an approximate flow rate of 25 mL per second. These cleaned wafer pieces were dried under a stream of nitrogen gas filtered with a PTFE membrane containing <200 nm pores.

Preparation of Soda-lime Glass and Polished Quartz Substrates. The diced soda-lime glass substrates were initially cleaned with hot water and glassware detergent (Sparkleen™), followed by washing sequentially with acetone and isopropanol. The diced quartz substrates were washed with acetone and isopropanol without the use of glassware detergent. Each of the cleaned substrates were immersed for 24 h in a sodium hydroxide (NaOH) solution, prepared from a mixture of 6.5 g of sodium hydroxide, 100 mL isopropanol, and 100 mL DI water. The substrates were subsequently rinsed under a stream of DI water for 1 min. These steps were necessary for ensuring minimal organic contamination prior to the standard piranha cleaning process. After drying the substrates under a stream of nitrogen (N_2) gas filtered with a PTFE membrane containing <0.2 micron pores, they were treated with a piranha solution, similar to the procedure described in the section above. The cleaned substrates were further rinsed under a stream of DI water and dried under a stream of N_2 gas.

Procedure for the Formation of Alcohol Based SAMs Using a Microwave Reactor. Each cleaned substrate was placed into a separate 10 mL test tube (Part # 908035, CEM Discover) containing a ~2 mL solution of 1-octanol. The test tube was exposed to microwave radiation using a CEM Discover microwave reactor for the desired duration (up to 30 min), and with specified limits (as noted in the following discussion) for microwave power and/or reaction temperature. Each sample was cooled for 5 min after the microwave assisted reaction before further handling. Upon completion of this microwave process, the test tube was removed from the microwave reactor. The treated substrates were removed from their cooled test tube, and washed sequentially under a stream of acetone and isopropanol. Each washed substrate was dried under a stream of filtered N_2 gas.

Formation of SAMs at 180°C Using Convective Heating. Cleaned substrates were placed into separate 10 mL glass test tubes (Part # 908035, CEM) each containing 2 mL of 1-octanol. Each test tube was held in a silicone oil bath maintained at 180°C for periods of time from 30 min to 24 h. Each sample was cooled for 5 min before handling the substrate. The substrates were removed from the cooled test tubes and washed sequentially under a stream of acetone and isopropanol. The washed substrates were dried under a stream of filtered N_2 gas.

Soxhlet Extraction Procedure. The rinsed and dried substrates were loaded into a customized glass substrate holder. This holder, loaded with the substrates, was carefully placed into a Soxhlet extractor containing CMOS grade toluene in the still pot. The still pot was heated to boil the toluene and to start the extraction procedure, while a condenser above the sample chamber was chilled with recirculating water. The extraction process was performed for up to 24 h. Once this extraction procedure was complete, the substrate holder was carefully unloaded from the Soxhlet extractor, and each substrate was dried under a stream of filtered N_2 gas.

Characterization Procedures. The solvent extracted substrates were each characterized by a series of analytical techniques to assess their surface topography, hydrophobicity, and chemical composition. Multiple measurements were obtained to determine the surface coverage of the SAMs on each substrate, as well as the consistency between substrates. The parameters for each of the analytical techniques are outlined in detail below:

(i) Water Contact Angle (WCA) measurements were performed with a contact angle goniometer (Dataphysics, Model OCA 15) in the Nanofabrication Facility of 4D LABS at Simon Fraser University. A 2 μL droplet of 18 MΩ·cm deionized water was dispensed onto the substrate for each measurement. The WCA was measured as the angle between the air-water interface of the droplet and the interface between the water and the substrate. Where applicable the error bars for the WCA measurements are reported as one standard deviation of at least five independent measurements.

(ii) Atomic Force Microscopy (AFM) images were acquired using an MFP 3D AFM (Asylum Research) operating in AC mode using silicon cantilevers from BudgetSensors (Tap 150-G, resonant frequency of 150 kHz, force constant of 5 N/m). Images were acquired from scan areas of 5 µm by 5 µm with a scan speed of 0.4 Hz and a resolution of 512 by 512. The AFM images were analyzed using Igor Pro 6.22.

(iii) X-ray Photoelectron Spectroscopy (XPS) measurements were performed to investigate chemical composition and relative surface coverage of the SAMs. These studies were conducted using a Kratos Analytical Axis ULTRA DLD system with a monochromatic aluminum source (AlKα of 1486.7 eV) operating at 150 W with a 90° take-off angle. Survey spectra (0 to 1200 eV) were acquired using a pass energy of 160 eV, a dwell time of 100 ms, and 1 sweep. High resolution spectra were obtained using a pass energy of 20 eV, a dwell time of 500 ms, and 10 sweeps. For insulating substrates such as soda-lime glass and quartz substrates, the XPS analysis had to be performed with the assistance of a charge neutralizer, due to significant charging effects of both substrates. An area of 700 µm by 300 µm was analyzed in three separate regions of each sample to check the uniformity of each surface modification. The XPS peak analysis was performed using Vision Processing.

RESULTS AND DISCUSSION

Varying Duration of Microwave Radiation at a Set Reaction Temperature. A detailed investigation was performed using a microwave reactor to pursue the formation of monolayers from aliphatic alcohols with a precise control of reaction temperature and duration. This study also investigated the impact of microwave heating with composition of different SiO_x substrates. The CEM microwave reactor is used due to its ability to safely and reliably control and monitor reaction temperature and pressure while minimizing evaporation of the solvent.[34-35] All of the microwave reactions included a ramp up time of 30 s before the radiation cycle and a 5 min cool down period (in the absence of microwave radiation) to ensure repeatability and a safe experimental design.

After the completion of each reaction, the coated substrates were treated with continuous Soxhlet extraction in hot toluene for up to 24 h. The toluene extraction process was also systematically investigated by varying the duration of extraction (e.g., 1, 5, or 24 h). The results of these processes were assessed primarily by WCA measurements to determine the relative extent to which covalent bonds were formed between 1-octanol and the silanol groups as a result of microwave radiation. Surface topography was investigated with AFM for selected substrates covered with 1-octanol to assess uniformity.

The duration of exposure to microwave radiation was systematically varied to evaluate the influence of total dose of microwave radiation on quality of the monolayers. The duration of this reaction was varied from 1 to 30 min. This study was conducted using four different types of substrates containing surface bound silanols—polished silicon substrates with either a native oxide or a 100-nm thick layer of thermally grown silicon oxide, soda-lime glass (i.e. glass microscope slides), and polished quartz. The target temperature of the reaction vessel was set to 180°C to avoid over pressurizing the vessel due to significant evaporation of 1-octanol (b.p. of 1-octanol is ~195°C). The microwave power was adjusted throughout each reaction to maintain the set point temperature.

Water contact angle measurements of the modified silicon oxide surfaces were obtained after specific durations of exposure to microwave radiation. The substrates were initially hydrophilic with WCA values of ~20° for all substrates. Microwave processing in the presence of 1-octanol with a set point of 180°C resulted in a rapid increase in WCA to ~100° within 1 min of treatment (Figure 1A). This result suggests that the microwave radiation enabled a significantly more rapid reaction of aliphatic alcohols with the surfaces of silicon oxides to form hydrocarbon monolayers, compared with oil bath reaction at the same temperature (see Figure S1 in the Supporting

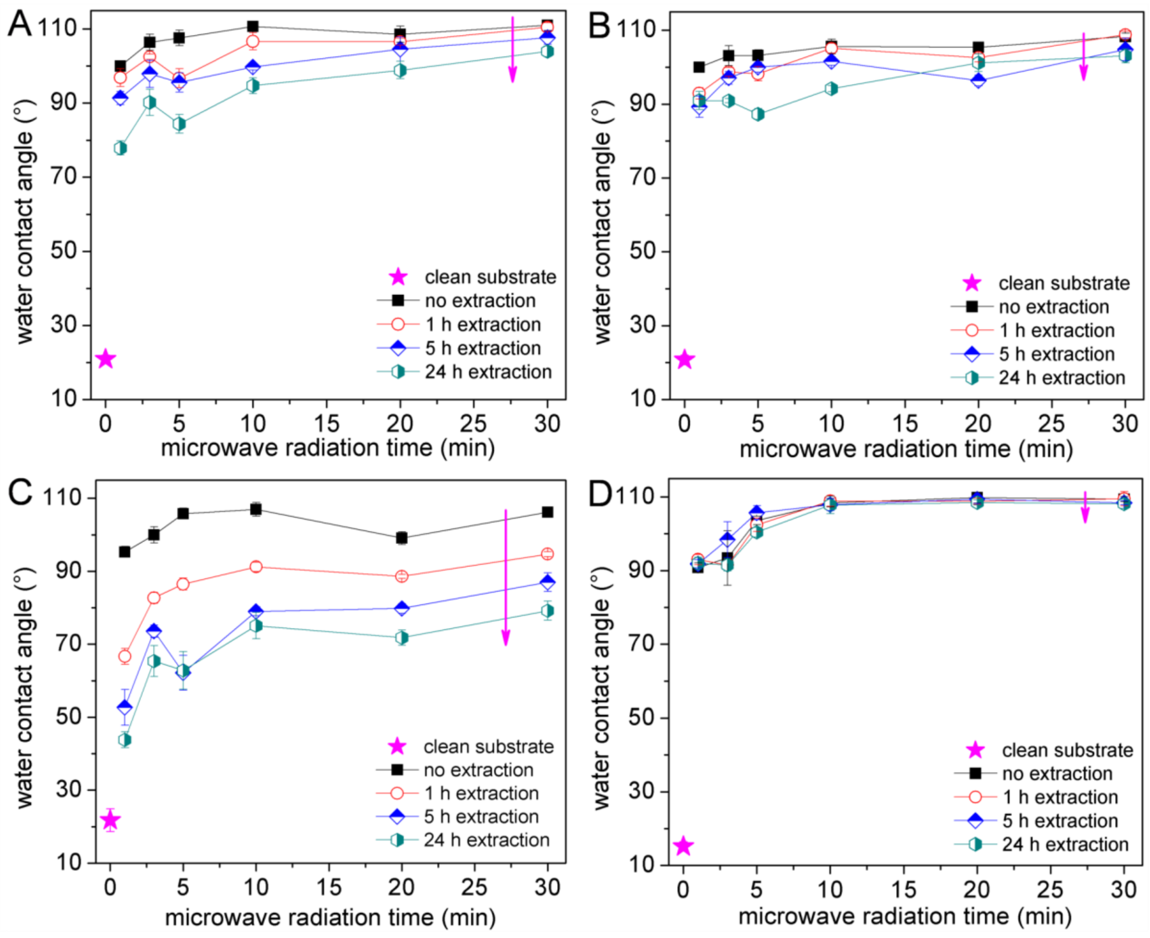


Figure 1 Water contact angle (WCA) measurements for (A,B) polished silicon substrates coated with a native oxide or 100-nm thick thermal oxide, respectively, (C) soda-lime glass, and (D) polished quartz substrates as a function of the duration of treatment with microwave radiation while immersed in 1-octanol. Corresponding WCA measurements are include for these substrates after 1, 5, and 24 h of continuous Soxhlet extraction. The pink star on each plot indicates the WCA values after piranha cleaning, but before the microwave assisted reaction with 1-octanol.

Information). The findings of our study also present a significant improvement in reaction time in comparison to the results previously reported for the modification of either hydrogen terminated silicon or silanol terminated SiO_x using other methods that include UV illumination (2.5 h),[25] assistance from metal catalysis (1 h to 72 h),[28] or convective heating (2.5 h).[29] The WCA values continued to increase with an increasing duration of exposure to microwave radiation until reaching a value of 110°. This high WCA was obtained after only 10 min of exposure to microwave radiation for the native oxide coated substrates. The WCA plateaued at 110°, in agreement with values reported in the literature on hydrocarbon terminated surfaces.[46] These results suggested that the surfaces were covered with aliphatic alcohols after only 10 min of treatment with microwave radiation. This rapid reaction rate could be attributed in part to the effective removal of surface adsorbed water layer by means of dielectric heating.[34] It was previously reported that an efficient removal of water adsorbed on the surfaces of silica could lead to the preparation of monolayers with a high surface coverage.[30] Water molecules effectively absorb microwave radiation due to their dielectric properties, which could result in a thermally induced removal of these molecules from the surfaces of the substrate. This simple, effective mechanism for microwave assisted water removal from the reactive interfaces of the SiO_x substrates could facilitate the condensation reaction.

Soxhlet extraction of the monolayer modified SiO_x surfaces was performed to evaluate the extent to which these surfaces were covalently modified with the aliphatic alcohols. The extraction process should remove 1-octanol that is only weakly interacting with the substrates.[43, 47] The relative change in WCA following extraction continued to decrease with an increasing duration of microwave radiation (Figure 1). In other words, hydrophobicity of the monolayer covered surfaces remained consistent after prolonged extraction with hot toluene when the monolayers are prepared with a longer (e.g., 30 min) duration of microwave treatment. The measured hysteresis for these WCA measurements also improved after a prolonged Soxhlet extraction, decreasing from an average value of ~4° to ~1° (see Table S1 to S8 in the Supporting Information). These results indicated that the uniformity of the measured hydrophobicity of the native SiO_x surfaces after reaction with 1-octanol was proportional to the length of exposure to microwave radiation for periods of up to 30 min. Monolayers formed on either the native oxide and 100-nm thick SiO_x surfaces exhibited a similar results to those observed for the native oxide substrates. (Figures 1A, 1B). The microwave assisted reaction of 1-octanol with silanol groups to form hydrophobic monolayers was effective for both types of substrates.

One of the most significant advantages of forming monolayers on surface bound silanols through condensation with alcohols is its applicability in the wide variety of substrates that can be modified using the technique. To demonstrate this versatility, monolayers of aliphatic alcohols were also prepared by treatment with microwave radiation in the presence of soda-lime glass and polished quartz substrates. This study provided further insight into the impact of composition of the SiO_x substrates on the quality of the resulting monolayers. The WCA measurements for soda-lime glass and quartz substrates after microwave reaction with 1-octanol are plotted in Figures 1C and 1D. The WCA increased from ~20° to 110° for both substrates as a function of increased duration of exposure to microwave radiation. The rates of reaction and degree of change in WCA for these systems were comparable to the results obtained for the thin films of SiO_x on polished silicon (Figures 1A and 1B). As mentioned for the study using a silicon substrate, the formation of monolayers on SiO_x substrates is likely influenced by the dielectric heating of the adsorbed water layer. The relatively rapid formation of SAMs on both soda-lime glass and polished quartz substrates could also be attributed to the removal of this surface water layer. Significant differences were, however, observed following the hot toluene extraction. The WCA values decreased significantly with extraction of the soda-lime substrates (Figure 1C). This result suggested that a significant amount of 1-octanol was physically adsorbed onto these surfaces, which was subsequently removed during the toluene extraction process. In contrast, the WCA values remained consistent throughout the extraction process for the quartz substrates with an average WCA value of 108° and a hysteresis of 0° after 24 h of Soxhlet extraction (see Table S9 to S16 in the Supporting Information). The larger decrease in WCA values for the treated soda-lime substrates could be attributed to the significant amount of impurities (e.g., Na, Mg, Ca) present in these substrates (see Figure S5 in the Supporting Information). Unlike multireactive silanes (e.g., alkyltrichlorosilanes) that can form multilayers via intermolecular polymerization,[48] the aliphatic alcohols do not crosslink to form an extended polymer because each aliphatic alcohol will only react with one surface bound silanol group. Molecules adsorbed onto the soda-lime surfaces without covalent bonding are easily removed during the Soxhlet extraction procedure. The monolayers could also be compromised due to the breakage of covalent bonds induced by the diffusion of impurities within these surfaces during the Soxhlet extraction process. Quality of the monolayers on soda-lime glass substrates can be improved by the deposition of an additional layer of silica, such as by sol-gel processing, prior to the formation of monolayers (see Figures S9 and S10 in the Supporting Information). In contrast, the quartz substrates had significantly fewer surface impurities (see Figure S6 in the Supporting Information). Monolayers prepared from 1-octanol on the polished quartz substrates exhibited the highest surface coverage and the highest quality following Soxhlet extraction.

Surface topography of the monolayer modified SiO_x substrates was analyzed by AFM. Specifically, piranha cleaned silicon substrates treated with microwave radiation while immersed in 1-octanol for either 1 or 30 min were analyzed after 24 h Soxhlet extraction to correlate observations made by WCA analyses to surface features. The surfaces depicted a relatively smooth topography with an RMS roughness of 0.23 and 0.10 nm after 1 and 30 min of treatment with microwave radiation, respectively (Figures 2A, 2B). The higher roughness factor for samples

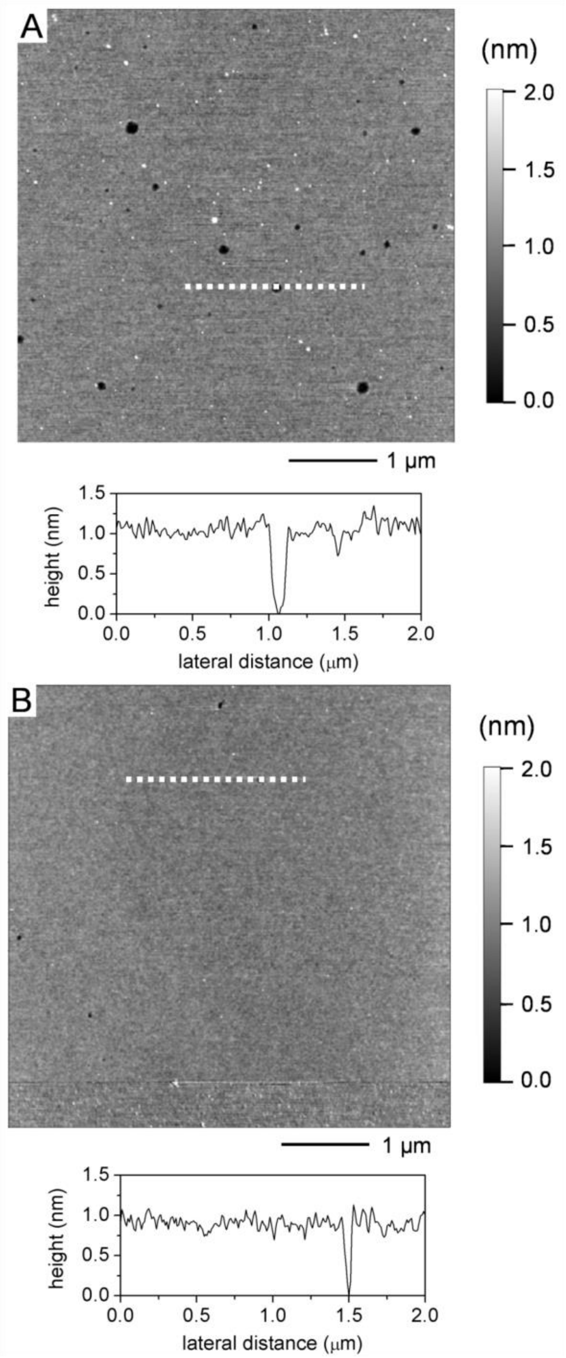
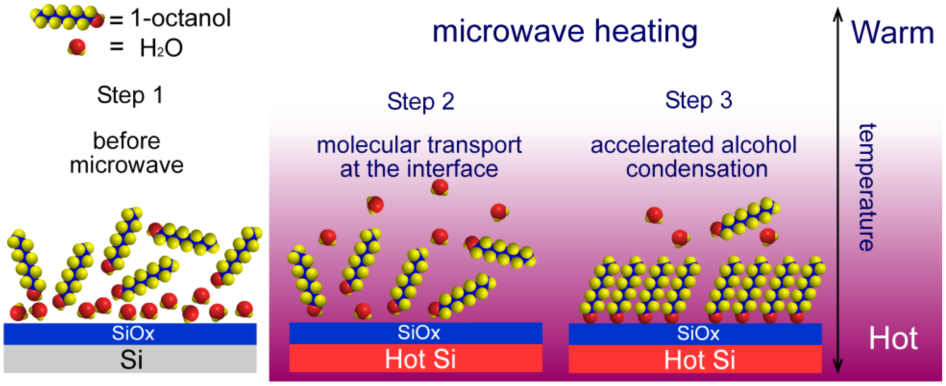


Figure 2. Atomic force microscope (AFM) images and cross-sectional profiles (corresponding to the white dashed lines) for piranha cleaned polished silicon substrates after microwave induced reaction with 1-octanol for (A) 1 min and (B) 30 min. Substrates were treated with 24 h continuous Soxhlet extraction in hot toluene before analysis by AFM.

treated for 1 min was attributed to the defects observed in the monolayers. The samples treated for 30 min with microwave radiation had a similar roughness to that of the piranha cleaned silicon substrate (i.e. 0.11 nm, see Figure S7 in the Supporting Information). These AFM analyses suggested that the SAMs on the native oxide are relatively uniform with a few distinguishable defects after 1 min of microwave radiation. These defects were ~1 nm in height, corresponding to the approximate molecular length of 1-octanol. Significantly fewer defects were observed in the SAMs after 30 min of microwave treatment. These results further supported the assessment that a higher surface coverage of 1-octanol is achieved with a longer exposure to microwave radiation.

In summary, a systematic study into the microwave assisted reaction of 1-octanol with various silicon oxide substrates was performed using the CEM microwave reactor. Increases in the duration of exposure to microwave radiation up to 30 min increased the hydrophobicity of these substrates, quickly achieving WCA values of 110°. These values were in agreement with the accepted literature value for uniform SAMs prepared from linear, methyl terminated species.[46] Furthermore, consistent WCA values with an average hysteresis <2° after an extensive Soxhlet extraction further demonstrated the uniformity of these monolayers. The quality of monolayers were largely dependent on the composition of the underlying silicon oxide surfaces.

Influence of Microwave Induced Substrate Heating on the Monolayer Formation. A kinetic study into the microwave assisted formation of SAMs on SiO_x substrates was pursued for both polished silicon and quartz substrates to investigate the impact of microwave induced substrate heating. Microwave radiation can induce heating of materials by ionic or electronic conduction losses.[49-50] This process can induce selective heating of conductive materials, such as metals[50-51] and other conductive thin films.[52] Microwave heating of the p-type doped silicon



step 1 - Before microwave reaction, a layer of water molecules are adsorbed on the surfaces of the substrate, separating these surfaces from a neat solution of aliphatic alcohols.
step 2 - Microwave radiation accelerates heating of the substrate. Molecular transport at the interface is accelerated.
stpe 3 - The alcohols form SAMs by a condensation reaction. Transport of water molecules, a by-product of the reaction, is accelerated.

Scheme 1. Depiction of the formation of self-assembled monolayers (SAMs) microwave assisted reaction of aliphatic alcohols with silicon oxide surfaces.

substrates could influence the kinetics of the reactions of 1-octanol with the SiO_x surfaces. Microwave heating of the doped silicon substrates could yield high temperatures at the SiO_x surfaces, where the condensation of 1-octanol takes place (Scheme 1). In order for the reaction to occur, the alcohol molecules need to interact with surface bound silanol groups. Molecular transport of the adsorbed water layer away from the surfaces and of the aliphatic alcohol towards these surfaces are accelerated by the dielectric heating of water molecules and conduction loss of the substrate.[34, 50] Aliphatic alcohols form covalent silyl ether (Si-O-C) bonds through a condensation reaction, analogous to a Williamson ether synthesis.[29] This condensation reaction is activated through the thermal energy provided by the microwave heating. Microwave radiation will further assist the reaction by also enhancing mass transport of water molecules produced as a byproduct of this reaction. In summary, microwave radiation can effectively induce the rapid covalent surface modification of SiO_x surfaces.

To further investigate the impact of microwave induced substrate heating, the native oxide coated silicon and the quartz substrates were separately treated with microwave radiation at predetermined levels of microwave power for a constant duration (i.e. 5 min) without temperature constraints. After microwave processing, Soxhlet extraction was performed for 24 h before obtaining WCA measurements (Figure 3A). This analysis indicated a clear discrepancy in reaction rates between these two types of substrates. As microwave power increased, a significant increase in WCA was observed for both substrates. The WCA values for the monolayers on the polished silicon quickly reached a plateau at ~100°, while the WCA values for the monolayers on polished quartz more steadily approached 80°. This result indicated that the rate of formation of the monolayers was significantly faster on the polished silicon than on the polished quartz substrates. The discrepancy between these reaction rates is attributed to the differences in the rate of substrate heating induced by the microwave radiation. To better assess the microwave induced heating of the substrates, the silicon and quartz substrates were treated with microwave radiation in the absence of aliphatic alcohols for 15 s while supported on an acrylic plate (Figures 3B). The thermal image in Figure 3C portrays a significant difference in temperature between the substrates after exposure to microwave radiation. Differences in substrate heating could be attributed to dielectric and electronic loss of these materials.[50] These differences in substrate heating were also observed when monitoring changes in solution temperature induced by microwave radiation at 300 W over 5 min (Figure 3D). Although the amount of microwave energy delivered to the reaction vessels was kept consistent between these experiments, the temperature of the solution was higher for the reaction vessel containing the polished silicon substrates than that for the polished quartz substrates. The increased reaction rate observed for the polished silicon could be attributed to differences in temperature of the reaction, likely induced by substrate heating. In summary, the

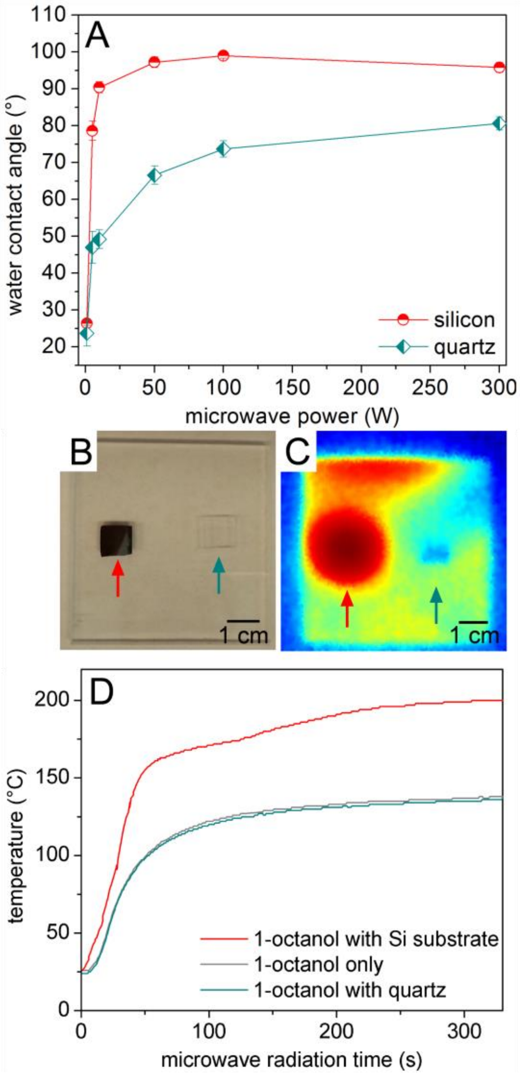


Figure 3. (A) Water contact angle trends for polished silicon and polished quartz substrates as characterized after a 5 min exposure to various levels of microwave power. (B) Visible light and (C) infrared images of the silicon and quartz substrates supported on an acrylic plate obtained after direct exposure to microwave radiation for 15 s. (D) Temperature profiles recorded in a 1-octanol solution during exposure to microwave radiation at 300 W for up to 5 min in the presence of either a silicon or quartz substrate, as well as in the absence of either substrate.

properties of the substrate materials could alter the rate of the microwave assisted reaction. In particular, the doped silicon substrates coated with a native oxide film were more efficient at absorbing the microwave energy than the quartz substrates. While high quality monolayers can be achieved for both types of substrates (Figures 1A, 1D) at a prolonged duration of exposure to microwave radiation, the rates of reaction can be substantially different. In conclusion, differences in electronic and dielectric characteristics of the substrates can play a significant role in the efficiency of microwave induced heating, influencing the overall rates of reaction for the condensation of 1-octanol on surface bound silanols.

Hydrolytic Stability of Monolayers Derived from Microwave Assisted Reactions with Alcohols. The stability of covalently attached monolayers are of a great interest.[53] Monolayers derived through the condensation reaction of alcohols with surface bound silanols would contain silyl ether (Si-O-C) bonds, which could hydrolyze upon immersion in either acidic or basic aqueous solutions.[54] Hydrolytic stability of monolayers of 1-octanol on SiO_x substrates prepared by microwave assisted reactions were evaluated by published procedures.[53] In particular, hydrolytic stability of the monolayers were evaluated at room temperature while immersed in aqueous solutions at different pH values for different periods of time (e.g., 1 day and 7 days).

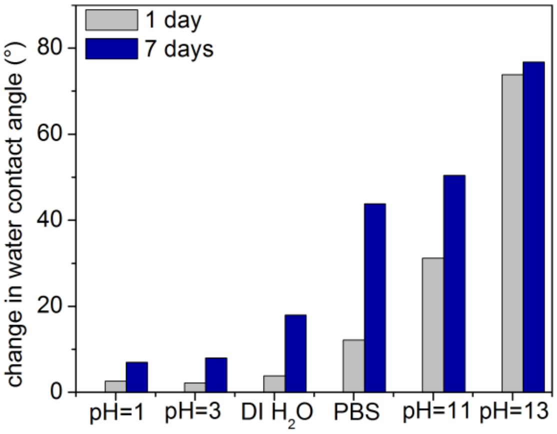


Figure 4. Hydrolytic stability of monolayers formed on piranha cleaned silicon substrates through a microwave induced reaction with 1-octanol evaluated by WCA measurements.

Stability of the monolayers was assessed by monitoring changes in surface hydrophobicity. As depicted in Figure 4, the monolayers exhibited significant differences in change in their hydrophobicity when immersed in aqueous solutions of different pH values. The hydrolytic stability of the monolayers demonstrated a comparable result to monolayers derived from 1-octadecene on silicon oxide surfaces when immersed in acidic solutions, but the hydrolytic stability of the 1-octanol monolayers were worse in both DI water or PBS buffer.[53] This discrepancy could be attributed to the difference in length of the alkyl chains used in these studies. Monolayers derived from 1-octanol contain a backbone of eight carbons, whereas the monolayers derived from 1-octadecene possess a backbone of eighteen carbons. The longer carbon chain would improve the passivation of the surfaces to hydrolysis of the silyl ether bond, providing further stability to the SAMs. The substrates coated with 1-octanol undergone catastrophic failure when immersed in an aqueous solution at pH 13. These substrates also had white, opaque spots, suggesting that the underlying silicon oxide film had been etched. This result could be attributed to the fact that the hydrolysis of the silyl ether bond (Si-O-C) under basic conditions, which would compromise the integrity of the monolayers. A high concentration of hydroxide ions can also promote degradation of the silicon oxide films, which would accelerate degradation of the monolayers. This instability of the monolayers is attributed to water and hydroxide ion penetration into the monolayers at high pHs, which can hydrolyze the Si-O-C bonds that anchor the 1-octanol to the SiOx substrates.[55] The monolayers of 1-octanol were more stable under acidic conditions in comparison to deionized water or more basic solutions. Quality of monolayers were retained possibly due to significantly less hydroxide ions available in solution to drive cleavage of the silyl ether bonds. In conclusion, monolayers formed by the microwave assisted condensation of aliphatic alcohols are more stable under acidic conditions, and less stable under basic conditions.

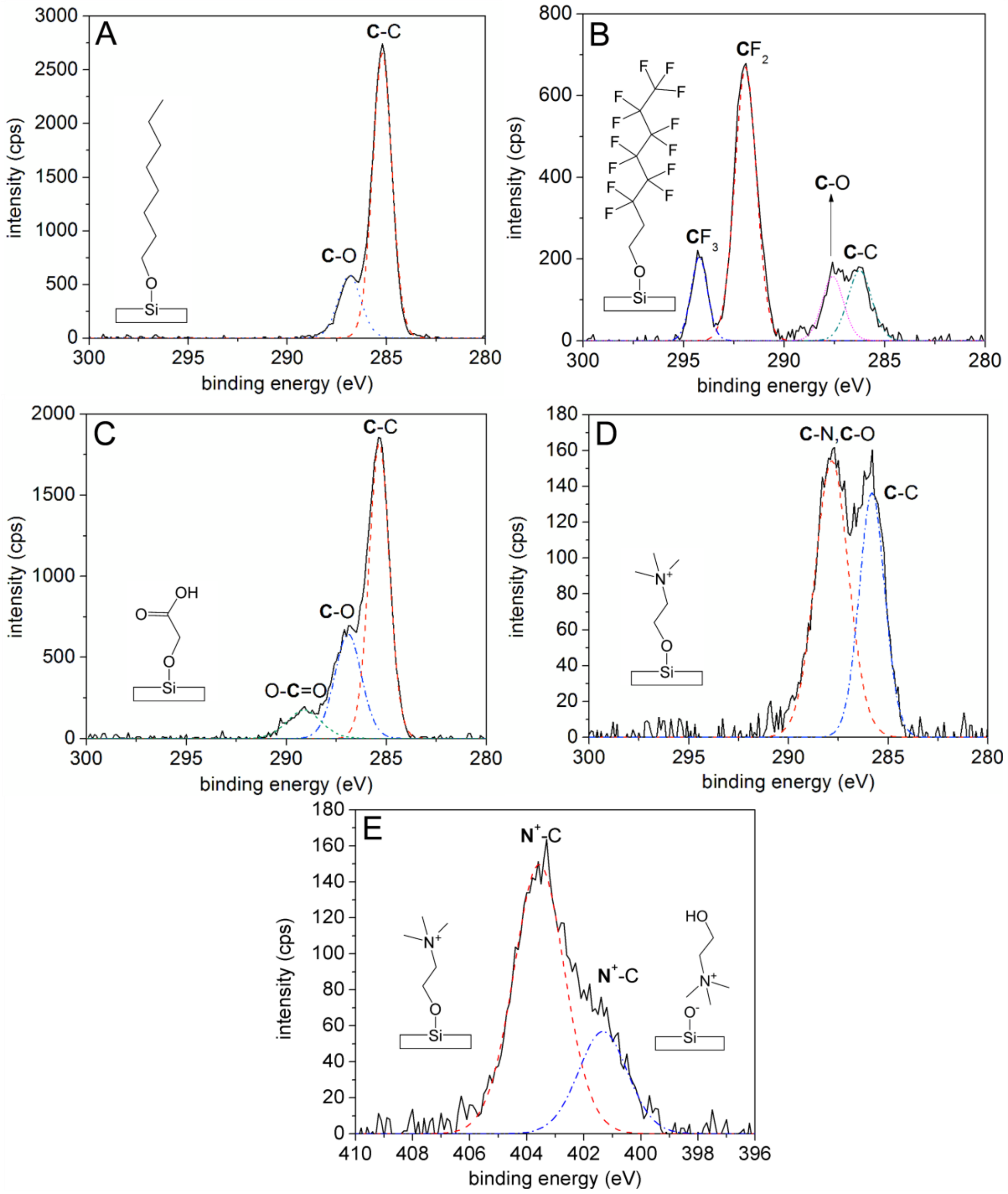


Figure 5. High resolution XPS spectra of silicon substrates after microwave assisted reactions with different functional alcohols. Carbon spectra (C_{1s}) after microwave reactions of (A) 1-octanol, (B) 1H,1H,2H,2H-perfluoro-1-octanol, (C) 1 M glycolic acid, and (D) 1 M choline chloride. (E) Nitrogen (N_{1s}) spectrum for the substrate reacted with 1 M choline chloride.

Controlling Surface Chemistry using Microwave Assisted Reactions with Alcohol Compounds. Tuning the functionality of SiO_x surfaces is often desired for their use in fields of study that include microelectronics[2] and biological interfaces.[7-9, 41] The techniques introduced in this article can be expanded to further modify the surface chemistry of SiO_x surfaces. For instance, these surfaces can be functionalized with fluorocarbons, a quaternary ammonium, or carboxylic acids. Piranha cleaned silicon substrates was treated with microwave radiation while immersed in a neat solution of 1H,1H,2H,2H-perfluoro-1-octanol, 1 M choline chloride, or 1 M glycolic acid at 120°C for 30 min. We have chosen a lower reaction temperature for these processes to prevent potential thermal degradation of these reagents. The modified substrates were thoroughly washed and sonicated with a series of solvents including acetone, isopropanol, ethanol and water upon completion of the microwave reaction. The substrates were characterized with X-ray photoelectron spectroscopy (XPS). High resolution carbon spectra (C_{1s}) of these substrates after the microwave induced reaction exhibited a clear difference in the chemical composition of their surfaces (Figure 5). Two carbon peaks were observed for surfaces reacted with 1-octanol, which were attributed to C-C and C-O peaks at binding energies of 285.2 eV and 286.9 eV, respectively. The substrates reacted with 1H,1H,2H,2H-perfluoro-1-octanol exhibited four carbon peaks with a significant contribution of fluorocarbons (CF_3 and CF_2) at binding energies of 294.2 eV and 291.9 eV. The ratio between the peak areas of CF_3 and CF_2 was 0.22. This fluorocarbon reactant contains five CF_2 and one CF_3 per a molecule, respectively. The peak area ratio matches the ratio of CF_3 to CF_2 anticipated from the molecular structure, suggesting composition of these monolayers agrees with the chemical structure of the reactant. Additional peaks associated with C-O and C-C were identified at binding energies of 287.5 eV and 286.3 eV, respectively. The higher binding energies observed for the C-O and C-C peak positions relative to those observed for 1-octanol could be attributed to the more electronegative backbone of the fluorocarbon.

The SiO_x substrates can also be coated with monolayers that exhibit a polar functional group. For instance, glycolic acid can be grafted onto the silicon oxide to exhibit a carboxylic acid functionalized surface. The glycolic acid was dissolved in deionized water prior to the microwave assisted reaction. Three peaks were observed in the high resolution C_{1s} XPS spectrum of these modified substrates, corresponding to C-C, C-O, and O-C=O peaks at binding energies of 285.4 eV, 286.9 eV, and 289.1 eV, respectively (Figure 5C). Choline chloride can also be covalently attached if it is desired to derive SiO_x substrates with surfaces exhibiting quaternary ammonium functional groups. Similar to glycolic acid, choline chloride was dissolved in deionized water prior to the microwave assisted reaction. The presence of choline chloride was confirmed by high resolution XPS C_{1s} and N_{1s} spectra (Figure 5D, 5E). Doublets of the carbon peaks were assigned as overlapping C-O and C-N peaks (287.8 eV) and a C-C peak (285.8 eV).[56] The high resolution N_{1s} spectrum had a significant intensity in comparison to the intensities in the C_{1s} spectrum. The N_{1s} spectrum exhibited with two peaks (403.4 eV and 401.3 eV) assigned to charged nitrogen at two different states.

SUMMARY AND CONCLUSIONS

In summary, we have successfully demonstrated a microwave assisted reaction of silicon oxide surfaces with alcohol containing compounds. These prevalent laboratory reagents can be utilized for covalent surface modification of silicon oxide surfaces without any specific considerations needed to control exposure to ambient moisture in the laboratory. Systematic studies demonstrated the formation of monolayers with 1-octanol on various SiO_x surfaces using a microwave reactor.

For these studies with 1-octanol, a reaction time of as little as 1 min could render each of the surfaces sufficiently hydrophobic to achieve WCA values up to 100°. The WCA values for these substrates plateaued at ~110° after further treatment with microwave radiation. The quality of the 1-octanol monolayers, as measured by the extent to which these monolayers covalently modify the SiO_x surfaces, were evaluated using a Soxhlet extraction process with hot toluene. The WCA and hysteresis values remained relatively consistent, demonstrating the formation of high quality monolayers. The rates of reaction were also studied for polished silicon and quartz substrates at a constant microwave power and durations of exposure to microwave radiation to investigate the impact of substrate heating when exposed to microwave radiation. It was determined that the rate of the reaction was significantly faster for polished silicon substrates than for polished quartz substrates as observed from trends in their resulting WCA values. Hydrolytic stability was also assessed for monolayers of 1-octanol. It was determined that these monolayers were relatively stable under acidic conditions, but exhibited only a moderate stability in deionized water or PBS buffer. The monolayers significantly degraded under basic conditions. The microwave assisted reactions introduced in this article can be utilized to control surface chemistry of a variety of silicon oxide surfaces. The techniques demonstrated in this study can be utilized to covalently modify silicon oxide surfaces using a variety of molecules containing alcohols.

ASSOCIATED CONTENT

Supporting Information. Additional data available includes: i) WCA analysis of silicon substrates after convective heating; ii) advancing and receding WCA measurements and associated hysteresis for each type of silicon oxide substrate modified with 1-octanol; iii) XPS survey scans for each type of substrate modified with 1-octanol; iv) AFM images of clean silicon substrates; v) AFM images of silicon substrates with a 100-nm thermal oxide film modified with 1-octanol; vi) WCA analysis of octyltriethoxysilane monolayers prepared using a previously published procedure; and vii) WCA and XPS analyses of 1-octanol modified soda-lime glass with a sol-gel processed silica film. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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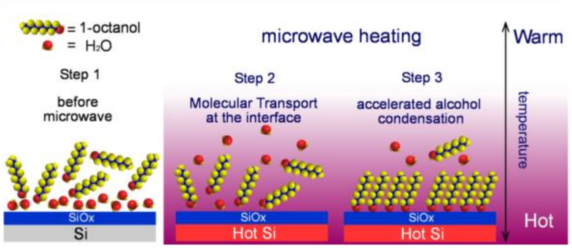

Table of Contents Graphic

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