Covalent Surface Modification of Silicon Oxides with Alcohols in Polar Aprotic Solvents

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ABSTRACT

Alcohol based monolayers were successfully formed on the surfaces of silicon oxides through reaction performed in polar aprotic solvents. Monolayers prepared from alcohol based reagents have been previously introduced as an alternative approach to covalently modify the surfaces of silicon oxides. These reagents are readily available, widely distributed, and are minimally susceptible to side reactions with ambient moisture. A limitation of using alcohol based compounds is that previous reactions required relatively high temperatures in neat solutions, which can degrade some alcohol compounds or could lead to other unwanted side reactions during the formation of the monolayers. To overcome these challenges, we investigate the condensation reaction for alcohols on silicon oxides carried out in polar aprotic solvents. In particular, propylene carbonate has been identified as a polar aprotic solvent that is relatively non-toxic, readily

accessible, and can facilitate the formation of alcohol based monolayers. We have successfully demonstrated tuning the surface chemistry of silicon oxide surfaces with a variety of alcohol containing compounds. The strategy introduced in this research can be utilized to create silicon oxide surfaces with hydrophobic, oleophobic, or charged functionalities.

INTRODUCTION

In this article, we demonstrate the formation of alcohol based monolayers on silicon oxide surfaces in polar aprotic solvents. The modification of surfaces with organic monolayers has been of great importance in the fields of electronics,[1-4] microfluidics,[4-9] separation sciences,[10-13] electrochemical sensing,[14-16] and biological interfaces.[17-23] Precursors based on silanes and phosphonic acids[17, 21, 24-26] have been widely utilized to form organic monolayers on silicon oxide surfaces. The use of these monolayers has been limited in part by the challenges of working with these precursors, such as a susceptibility to competing reactions (e.g., hydrolysis) and intermolecular polymerization, their commercial accessibility, and toxicity.

Alternative covalent surface modification strategies have been pursued to address these concerns.[19] For instance, the use of precursors such as alkenes,[27-30] alkynes,[31-33] and alkyl halides[34] have been pursued to form organic monolayers on various substrates. In addition to these alternatives, alcohols have been proposed as alternative building blocks to prepare organic monolayers on silicon oxide (SiO_x) surfaces. Alcohols are an attractive alternative for their widespread availability, low toxicity, and minimal susceptibility to side reactions with moisture.[35-38] Both hydrogen-terminated silicon and hydroxyl-terminated silicon oxide surfaces have been functionalized with alcohol reagents using reactions initiated by convective heating,[35] UV

radiation,[36] or microwave heating.[37, 39] These reports relied on reactions carried out at relatively high temperatures in mostly neat solutions. While these approaches provide a simple reaction strategy for the formation of monolayers, it can limit the choice alcohols available for the reaction due to possible thermal degradation or other side reactions at high temperatures. Moreover, neat solutions will have fundamental implications on the reaction kinetics and the formation of multicomponent monolayers.[39-42] It is desirable to identify a solvent to facilitate the formation of alcohol based monolayers for a versatile tuning of the surface chemistry of silicon oxides.

Here, we investigated the formation of alcohol based monolayers in polar aprotic solvents to modify the surface properties of silicon oxides. We selected a number of polar aprotic solvents based on their physical properties (e.g., melting and boiling points), solubility of both alcohols and water, as well as their relatively low toxicity and reactivity.[43] We screened these solvents and selected the best performing polar aprotic solvent for further investigation. This investigation included assessing changes in surface composition of silicon oxides surfaces after reacting with various solutions containing alcohol based reagents. We also sought to understand the impact of changes to the reaction temperature, as well as concentration and composition (e.g., alkyl chain lengths) of the alcohol reagents on the rate of formation and overall uniformity of the resulting monolayers. The properties of the monolayer coated silicon oxide surfaces were assessed by water contact angle (WCA) measurements, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL SECTION

Reagents and Materials. All reagents were used as received, which included dimethyl sulfoxide (DMSO, Sigma Aldrich, 99.9%, CAS no. 67-68-5), dimethylformamide (DMF, EM Science, CAS

no. 68-12-2), propylene carbonate (Sigma Aldrich, 99%, CAS no. 108-32-7), 1-octanol (Sigma Aldrich, ACS reagent grade, CAS no. 111-87-5), 1H,1H,2H,2H-perfluoro-1-octanol (Alfa Aesar, 97%, CAS no. 647-42-7), choline chloride (Sigma Aldrich, BioReagent, CAS no. 67-48-1), glycolic acid (Sigma Aldrich, 99%, CAS no. 79-14-1), thiamine hydrochloride (Sigma Aldrich, 99%, CAS no. 67-03-8), adenosine 5'-monophosphate monohydrate (Sigma Aldrich, 97%, CAS no. 18422-05-4), 5-hydroxypentanal (Sigma Aldrich, CAS no. 4221-03-8), Zonyl FSN fluorosurfactant (Sigma Aldrich, 40%, CAS no. 65545-80-4), 1-dodecanol (Sigma Aldrich, 98%, CAS no. 112-53-8), 1-tetradecanol (Sigma Aldrich, 97%, CAS no. 112-72-1), 1-hexadecanol (Sigma Aldrich, 99%, CAS no. 36653-82-4), 1-octadecanol (Sigma Aldrich, 99%, CAS no. 112-92-5), sulfuric acid (Caledon, ACS reagent grade, CAS no. 7664-93-9), hydrogen peroxide (ACP, ACS reagent grade, CAS no. 7722-84-1), acetone (Fisher Scientific, reagent grade, CAS no. 67-64-1), isopropanol (Fisher Scientific, reagent grade, CAS no. 67-63-0), and anhydrous ethyl alcohol (Commercial Alcohols, P016EAAN, CAS no. 64-17-5). Four inch, p-type, prime grade, single-side polished, <1 0 0> silicon wafers were purchased from the Nanofabrication Facility in 4D LABS at Simon Fraser University.

Preparation of Silicon Substrates. The silicon substrates were diced into ~1 cm^2 pieces, and washed with acetone and isopropanol. These substrates were dried under a stream of nitrogen gas filtered with a PTFE membrane containing <200 nm pores. The silicon substrates were further cleaned by immersion into a piranha solution followed by rinsing with water prior to the formation of the monolayers as described in previous literature.[37] *CAUTION: Piranha solution is a strong oxidizing agent and reacts violently with organic compounds. This solution should be handled with extreme care.* The silicon substrates were immersed in the freshly prepared piranha solution for at least 1 h followed by placement for 5 min into 18 MΩ·cm deionized (DI) water (Barnstead

Nanopure DIamond water filtration system). After further washing with DI water, these cleaned substrates were dried under a stream of filtered nitrogen gas.

Formation of Monolayers. The formation of monolayers was performed in a glass round bottom flask that was placed in a silicone oil bath at the desired reaction temperatures (e.g., 50 °C or 100 °C). The flask contained 50 mL of the reaction mixture containing a reagent (e.g., 1-octanol) dissolved in a polar aprotic solvent (e.g., propylene carbonate). The silicon substrates were loaded onto a customized glass holder. This holder loaded with multiple substrates was placed into the round bottom flask containing the reaction mixture. After heating for the desired period of time, each substrate was taken out individually and immersed into separate solutions of ethanol. Each substrate was sonicated for at least 3 min in ethanol, rinsed further with ethanol, and finally rinsed with DI water. The rinsed substrates were dried under a stream of the filtered nitrogen gas.

Water Contact Angle (WCA) Measurements. Water contact angle measurements evaluated the hydrophobicity of the substrates. Each measurement was obtained from 2 µL droplets of solvent dispensed onto the substrates. The WCA was measured as the angle between the air-water interface of the droplet and the interface of the water and the substrate. Five advancing contact angle measurements were obtained for each sample by adding 2 µL for each subsequent measurement. The mean of the WCA values was determined by taking the average of the advancing contact angle measurements. One standard deviation (1σ) from the mean was evaluated for each sample and taken as the error associated with the WCA values.

Atomic Force Microscopy (AFM). The surface topography of the samples was characterized by AFM. The AFM images were acquired using an MFP 3D AFM (Asylum Research and Oxford Instruments) operating in AC mode using silicon cantilevers from BudgetSensors (Tap150-G,

resonant frequency of 150 kHz, force constant 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 image analysis and the determination of the root mean square (RMS) roughness were performed using Igor Pro 6.22.

X-ray Photoelectron Spectroscopy (XPS). Chemical composition of the surfaces of the substrates were investigated by XPS. These studies were conducted using a Kratos Analytical Axis ULTRA DLD system with a monochromatic aluminum source (Al Kα of 1486.7 eV) operating at 150 W with a 90° take-off angle. Survey scans (0 to 1200 eV) were acquired using a pass energy of 160 eV, a dwell time of 100 ms, and 1 sweep. High resolution scans were obtained using a pass energy of 20 eV, a dwell time of 500 ms, and integrating the results of 10 scans. 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 and quantification of atomic composition of the elements (e.g., carbon) was performed using Vision Processing.

RESULT AND DISCUSSIONS

Covalent Immobilization of 1-Octanol on Silicon Oxide Surfaces in Polar Aprotic Solvents. The goal of this study was to form alcohol based monolayers in polar aprotic solvents for tailoring the surface properties of silicon oxides. An appropriate solvent was sought to facilitate the formation of alcohol based monolayers. Covalent attachment of alcohols to silicon oxide surfaces is achieved through a condensation reaction between the hydroxyl groups of the alcohol reagents and surface bound silanols, forming silyl ether (Si−O−C) bonds with water as a byproduct.[35] The solvent must be able to dissolve both the alcohol containing reactants and water while avoiding side reactions or other unfavorable interactions with the reactants. It is also desirable that the

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solvent possess a low melting point and a high boiling point to carry out reactions over a wide ranges of temperatures. Non-polar solvents were eliminated for their relatively poor solubility of polar reagents, while polar protic solvents were eliminated for possible unwanted side reactions with the silanol groups. A series of polar aprotic solvents were selected for their minimal reactivity towards the silanol groups and their ability to dissolve a wide range of polar compounds. The choice of solvent was important as it would facilitate solvation and transport of alcohol molecules and water to and from the silicon oxide surfaces.

Polar aprotic solvents with boiling points >150 °C were initially selected for the reaction. In particular, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and propylene carbonate were initially chosen. Piranha cleaned silicon substrates were immersed into each solvent containing 600 mM 1-octanol and heated at 100 °C for 24 h. The substrates reacted with 1-octanol dissolved in DMSO or DMF yielded water contact angle (WCA) values of 17°±5° and 4°±3°, respectively. The hydrophilicity of these substrates suggested a negligible amount of 1-octanol reacted with these substrates. These results deviate from previous literature that successfully demonstrated the formation of silyl ether (Si−O−C) bonds in DMF during the synthesis of organic compounds.[44-45] This deviation could be attributed to differences in the steric hindrance of the silanol groups, which were immobilized on the silicon oxide surfaces. Adsorption of DMF molecules could form ammonium complexes with the silicon oxide surfaces, hindering the reaction with 1-octanol. It is possible that DMSO hinders the reaction in a similar manner to DMF. On the other hand, the substrates reacted with 1-octanol in propylene carbonate yielded a WCA of 108°±3°, indicating a significant change in hydrophobicity. This result suggested that the monolayers could be successfully formed on silicon oxide surfaces from alcohol based reagents dissolved in propylene carbonate. In addition to its relatively high boiling point, propylene

carbonate possess a number of other desirable properties, such as its relatively low price, high solubility of polar reactants and byproducts, and relatively low toxicity.[43] Although monolayers derived from 1-octanol were not achieved using DMF or DMSO as a solvent, propylene carbonate was demonstrated to be a suitable solvent. Propylene carbonate was selected for a detailed investigation into the formation of monolayers on SiO_x surfaces that are derived from a variety of alcohol containing reagents.
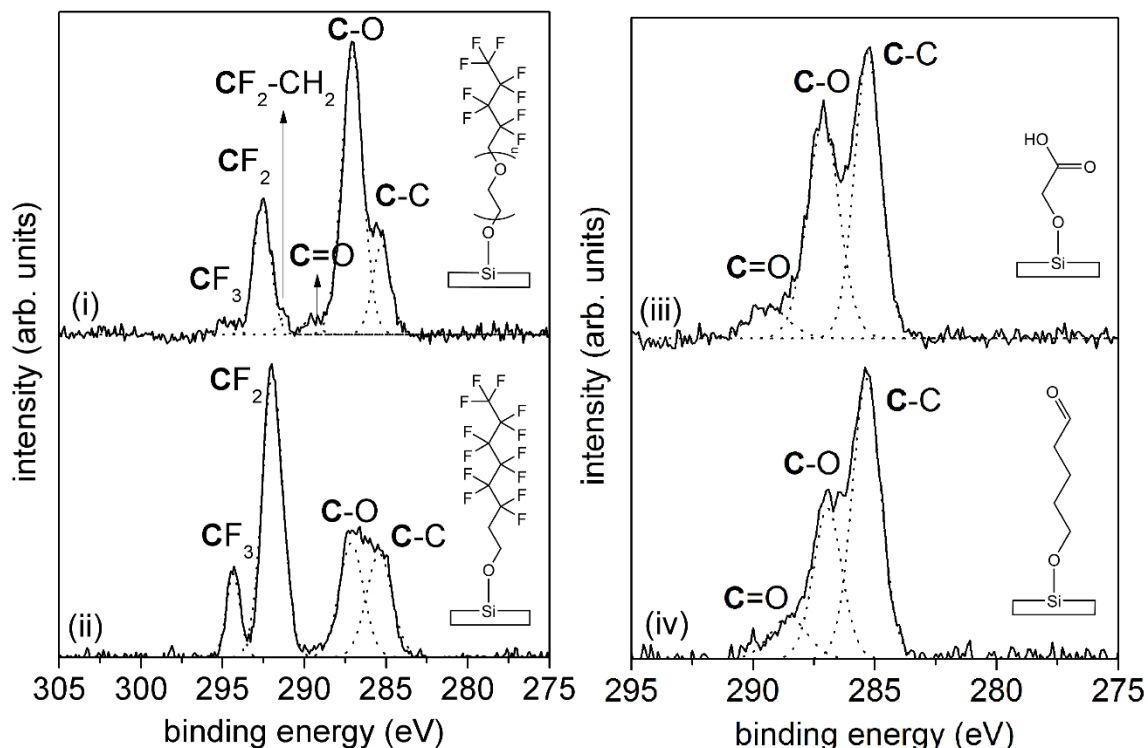

Figure 1. High resolution C1s XPS of piranha cleaned silicon substrates after reacting with (i) Zonyl (ii) 1H,1H,2H,2H-perfluoro-1-octanol, (iii) glycolic acid, and (iv) 5-hydroxypentanal.

Covalent Surface Modification of Silicon Oxides with Various Alcohol Compounds. A series of reactions were carried out to tune the surface chemistry of silicon oxides. These reactions analyzed various types of alcohol containing reagents that were dissolved in propylene carbonate. High resolution C_{1s} XPS results displayed distinguishable surface compositions for the substrates

reacted with 1*H*,1*H*,2*H*,2*H*-perfluoro-1-octanol, Zonyl fluorosurfactant, glycolic acid, or 5-hydroxypentanal (Figure 1). The substrate coated with Zonyl fluorosurfactant exhibited a difluorocarbon (CF$_2$) peak at 292.6 eV and a trifluorocarbon (CF$_3$) peak at 294.7 eV.[46-50] This XPS analysis also indicated the presence of C−O species at 287.1 eV and C−C species at 285.3 eV. A shift in these binding energies relative to literature values was attributed to charging effects during the XPS analysis of the insulating layers of SiO$_x$ and fluorocarbon based monolayers.[51-52] A higher intensity of the C−O peak in comparison to that of the C−C peak was attributed to the poly(ethylene glycol) (PEG) content of the Zonyl based monolayers.[53-54] An XPS analysis of the substrate coated with 1*H*,1*H*,2*H*,2*H*-perfluoro-1-octanol yielded a CF$_2$ peak at 291.9 eV, a CF$_3$ peak at 294.4 eV, a C−O peak at 287.1 eV, and a C−C peak at 285.4 eV. These peaks agree with the previously reported peak positions for these respective species based on the high resolution C$_{1s}$ XPS of fluorinated monolayers.[37, 39, 46-48] Monolayers derived from either glycolic acid or 5-hydroxypentanal contained three distinct peaks in their high resolution C$_{1s}$ XPS analyses. For the substrate reacted with glycolic acid, the peaks attributed to C−C, C−O, and C=O were located at binding energies of 285.3 eV, 287.1 eV, and 289.4 eV, respectively. The binding energies of these peaks correlate with carboxyl-terminated SAMs previously reported on both stainless steel[55] and Si(111).[56] For the substrate reacted with 5-hydroxypentanal, the peaks attributed to C−C, C−O, and C=O were located at binding energies of 285.3 eV, 286.9 eV, and 288.5 eV, respectively. The binding energies of these peaks are in agreement with aldehyde-terminated, silane based SAMs on silicon oxide surfaces.[57] The observed differences in binding energies of the C=O peaks for monolayers derived from glycolic acid and 5-hydroxypentanal (289.4 and 288.5 eV, respectively) was attributed to their differences in the groups adjacent to the terminal carbon species. In monolayers derived from 5-hydroxypentanal, the outer most carbon was the aldehyde moiety

(H−C=O), whereas for monolayers derived from glycolic acids the outer most carbon was a carboxylic acid moiety (HO−C=O).
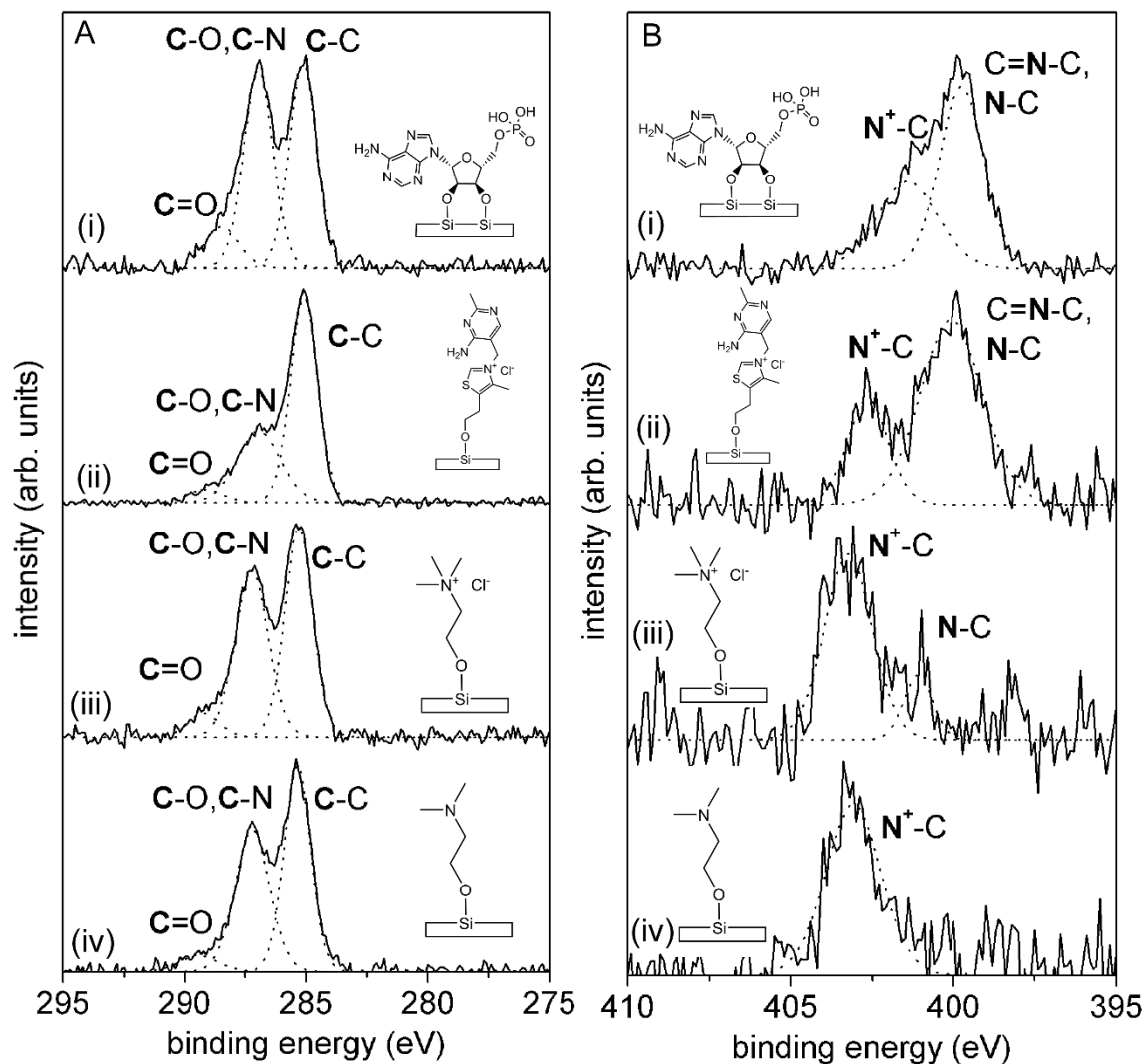

Figure 2. High resolution (A) C_{1s} and (B) N_{1s} XPS of polished piranha cleaned silicon substrates after reacting with (i) adenosine monophosphate (AMP), (ii) thiamine, (iii) choline chloride, and (iv) 2-dimethylaminoethanol.

Nitrogen containing alcohol based compounds were also grafted onto the silicon oxide surfaces using the same strategy of dissolving these reagents in propylene carbonate and heating the mixture

to 50 °C for 24 h. The selected reagents included adenosine 5'-monophosphate (AMP), thiamine, choline chloride, and 2-dimethylaminoethanol. The reacted substrates were characterized by high resolution C_{1s} and N_{1s} XPS (Figure 2). The primary peaks in the C_{1s} spectra at binding energies 285.3 eV and 287.0 eV, respectively, are attributed to C−C and overlapping contributions from C−O and C−N. The peak intensity for the C−O and C−N species is relatively high due to a significant contribution from covalently attached carbon and nitrogen. The high resolution N_{1s} XPS analyses exhibited distinct binding energy profiles for each of these substrates. The XPS analysis of the substrates coated with AMP had N_{1s} peaks at 401.4 eV and 399.7 eV, which were attributed to the charged and uncharged nitrogen of the primary amine and the aromatic nitrogen of adenine.[58-59] The XPS analysis of the substrates coated with thiamine also exhibited two distinct nitrogen peaks, but with binding energies of 402.7 eV and 400.1 eV.[60-61] A strong N_{1s} peak was observed for the substrates coated with either choline chloride or 2-dimethylaminoethanol at a binding energy of 403.2 eV. No significant shift in the N_{1s} binding energies between these two substrates suggested a positive charge associated within the terminal tertiary amine of the 2-dimethylaminoethanol based monolayers. A weak N_{1s} peak was observed at a binding energy of 401.1 eV for the substrates coated with choline chloride. This species was attributed to terminal quaternary ammonium groups in close proximity to the silicon oxide surfaces due to electrostatic interactions.[37]
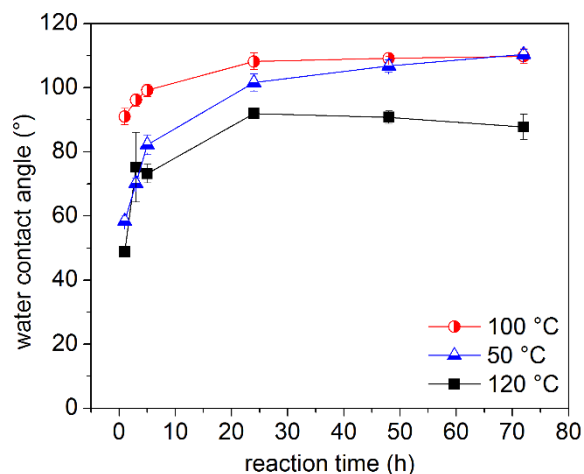
Figure 3. Water contact angle (WCA) measurements for piranha cleaned silicon substrates reacted with 600 mM 1-octanol in propylene carbonate at different temperatures as indicated in the legend.

Formation of Monolayers Derived from Aliphatic Alcohols in Propylene Carbonate at Different Temperatures. The formation of alcohol based monolayers was performed at different temperatures (i.e. 50 °C, 100 °C, and 120 °C) to investigate the influences of varying reaction conditions on the uniformity of the monolayers and the rate of their formation. The WCA values for piranha cleaned silicon substrates were measured after their reaction with 1-octanol for different durations, such as 1, 3, 5, 24, 48, and 72 h (Figure 3). These WCA values increased with a longer reaction time until the WCA values plateaued at ~110° for the substrates reacted at 50 °C and 100 °C. It took up to 24 h for the WCA value to reach 110° for the reaction performed at 100 °C, while up to 72 h were required to achieve similar results for the reaction held at 50 °C. The WCA values of ~110° indicate a relatively high surface coverage of the SAMs as the values are comparable to those reported in literature for methyl-terminated monolayers.[37, 62] This result demonstrated a comparable quality to the monolayers prepared using a reaction of neat 1-octanol with polished silicon oxide surfaces using either convective heating at 196 °C for 2.5 h[35] or a microwave assisted reaction at 180 °C for 30 min.[37] The ability to achieve relatively high quality

monolayers at lower reaction temperatures is attributed to the increased reaction time and to the increased solubility of both the reactants and byproducts in the polar aprotic medium. Propylene carbonate can enhance the molecular transport of water from and 1-octanol molecules to the silicon oxide interfaces, which facilitates the formation of the alcohol based monolayers. The WCA values plateaued at ~90° for the substrates held at 120 °C during the reaction, which was significantly lower than the WCA values achieved at 50 °C and 100 °C. This result suggested the formation of lower quality, less uniform monolayers at 120 °C. It is likely that the mixture of propylene carbonate and 1-octanol underwent unwanted side reactions at reaction temperatures of 120 °C.[63] This conclusion was supported in part from the change in color of the mixture from a clear transparent solution to a light yellow solution. Further analyses were required to understand the results of the WCA measurements. Insight was sought through an analysis of the changes in the surface topography of the substrates after reacting at the specified temperatures.
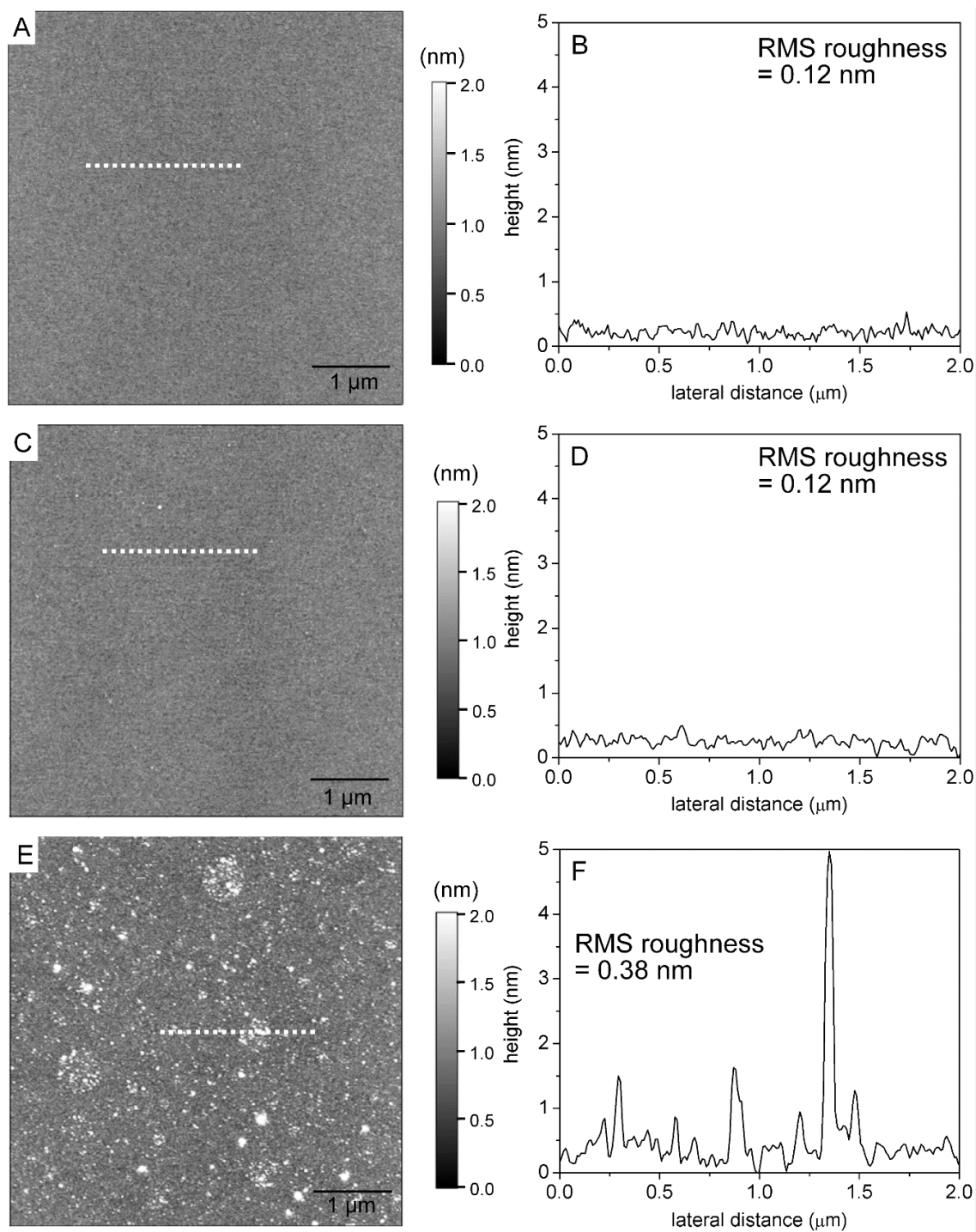
Figure 4. Atomic force microscopy (AFM) images and representative cross-sectional profiles (corresponding to the white dashed lines) for silicon substrates after reacting with 600 mM 1-octanol in propylene carbonate at: (A,B) 50 °C; (C,D) 100 °C; (E,F) 120 °C for 72 h.

The topography of the silicon substrates was assessed by AFM after reacting with 1-octanol in propylene carbonate. Each of these studies was performed on substrates that had been reacted for 72 h, and results were compared for reactions held at different temperatures. The substrates held at 50 °C and 100 °C exhibited relatively uniform surface topographies (Figures 4A and 4C). The measured root mean square (RMS) roughness for each of these substrates was 0.12 nm (Figures 4B and D), which is comparable to the RMS roughness of the native SiO_x surfaces. This result further suggested that these monolayers were uniform, as indicated by the WCA measurements. In contrast, the substrates reacted at 120 °C exhibited non-uniform surface topographies containing randomly distributed features with heights up to ~5 nm and an overall RMS roughness of 0.38 nm (Figures 4E and 4F). The increased surface roughness after performing the reaction at 120 °C was likely due to the deposition of byproducts produced from unwanted side reactions between the propylene carbonate and aliphatic alcohol.[63] Further analyses were required to better understand the impact of not only changing the reaction temperature, but also the chemical composition of the reaction mixtures on the quality of the resulting monolayers.
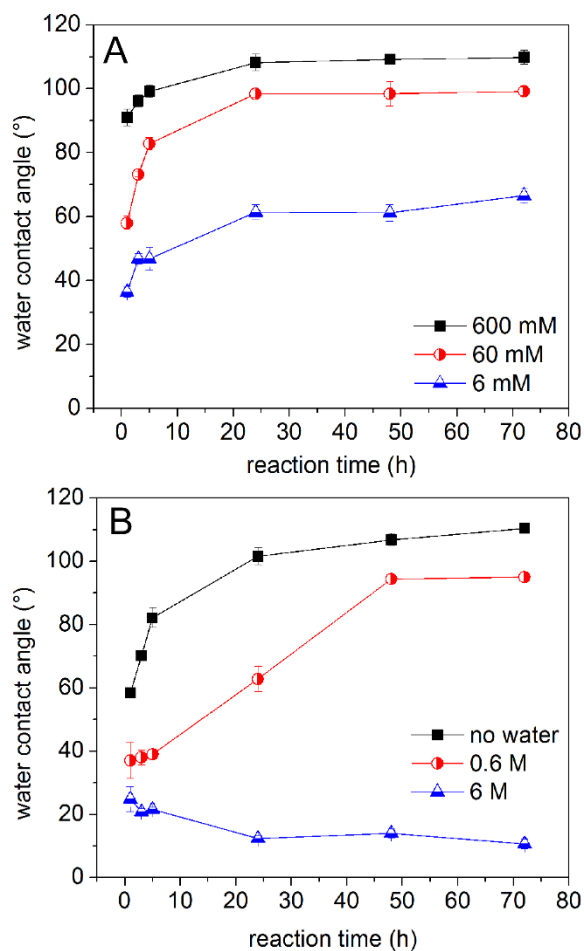
Figure 5. Water contact angle (WCA) measurements for polished silicon substrates after reacting with a series of 1-octanol solutions in propylene carbonate. (A) In one series of reactions, the concentration of 1-octanol was varied from 6 to 600 mM while maintaining a reaction temperature of 100 °C. (B) In another series of reactions, increasing amounts of water (see legend) were added to solutions of 600 mM 1-octanol in propylene carbonate and subsequently reacted at 50 °C.

Formation of Monolayers Derived from Aliphatic Alcohols in Propylene Carbonate – Impact of the Concentration of Alcohols and Water. A series of reactions were performed to study the impact of changes in the concentration of an aliphatic alcohol on the formation of alcohol based monolayers on silicon oxides. In the case of thiolate based monolayers on gold surfaces, the

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concentration of precursors is inversely proportional to the reaction time uniform monolayers.[4] It was anticipated that a similar relationship exists for the formation of aliphatic alcohol based monolayers on silicon oxides. The hydrophobicity of substrates reacted at 100 °C in 600, 60, and 6 mM solutions of 1-octanol in propylene carbonate were analyzed as a function of reaction time through a series of WCA measurements (Figure 5A). The WCA values plateaued at ~110° for the substrates reacted in the 600 mM solution of 1-octanol, while the values plateaued at ~90° and ~65° for the 60 mM and 6 mM 1-octanol, respectively. The rate of formation of the monolayers was anticipated to decrease with a decrease in the concentration of the reactants.[4] The rate of formation of these SAMs was significantly hindered at the lower concentrations of 1-octanol in the propylene carbonate. This trend deviates from observations of the formation of monoreactive silane or thiol based monolayers. Uniform monolayers of these silanes or thiols could be achieved for a wide range of concentrations of reactants (e.g., 0.1 mM to 100 mM) after a sufficient period of time.[4, 19] The incomplete formation of monolayers derived from 1-octanol at the lower concentrations could be attributed in part to the mechanism of the condensation reaction between these alcohols and the silanols at the silicon oxide interface. The condensation reaction is a reversible reaction with water molecules created as a byproduct.[35, 64-65] If the concentration of aliphatic alcohols and water molecules in the solution is comparable, hydrolysis of the silyl ether bond to form silanol groups at the interface could compete with the condensation reaction of alcohols.

Further investigation was conducted to understand the impact of water in the reaction mixture. Different amounts of water were added to a 600 mM 1-octanol solution and subsequently heated at 50 °C (Figure 5B). The lower reaction temperature was selected to minimize evaporation of water during the reaction. The addition of water molecules significantly impacted the formation of

the alcohol based monolayers. When the reaction was performed with 6 M of water, the substrates remained hydrophilic and the WCA values approached a plateau below 15°. Hydrophobicity of the substrates exhibited a more gradual increase when 600 mM water was added to the reaction mixture. This mixture yielded modified substrates that approached a plateau in its WCA of ~90° after 72 h. The rate of change in hydrophobicity as a function of reaction time suggested a slower formation of the monolayers due to the increases in water content of solution. This result further suggested that monolayers formed on silicon oxides could be partially removed through hydrolysis of the silyl ether bond in the presence of water at elevated temperatures. In summary, decreasing the concentration of 1-octanol leads to a decrease in the rate of formation of monolayers on silicon oxide surfaces. Furthermore, water content of the reaction mixture could further decrease the reaction rate and compromise the uniformity of these monolayers.
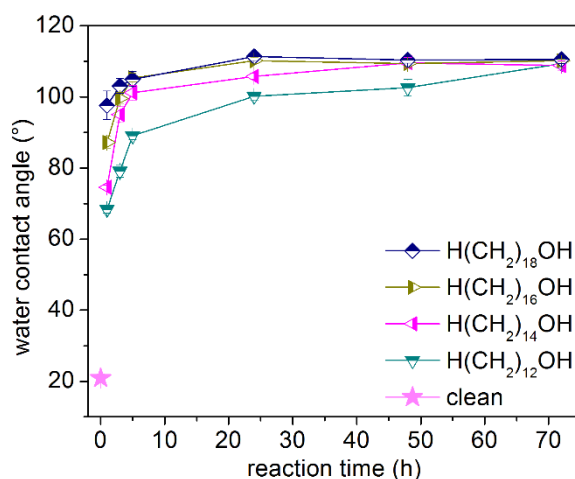

Figure 6. Water contact angle measurements for a series of silicon substrates reacted with different aliphatic alcohols. Each reaction was carried out at 100 °C in 0.05 M alcohol reagent dissolved in propylene carbonate.

Formation of Monolayers Derived from Aliphatic Alcohols in Propylene Carbonate – Effect of Alkyl Chain Length. Chain length of the aliphatic alcohols could play a key role in the rate of formation of the monolayers, and influence their uniformity. Differences in the intermolecular interactions, molecular transport, steric hindrance and interactions with the solvent could each influence the efficiency of the condensation reaction.[41] It is important to understand the impact of changes in the alkyl chain length on the rate of formation of these monolayers in propylene carbonate. A series of reactions were performed at 100 °C in solutions of 0.05 M aliphatic alcohol in propylene carbonate. The reactants included 1-dodecanol $[H(CH_2)_{12}OH]$, 1-tetradecanol $([H(CH_2)_{14}OH]$, 1-hexadecanol $[H(CH_2)_{16}OH]$, and 1-octadecanol $[H(CH_2)_{18}OH]$. The differences observed in the rate of increase in the WCA values with reaction time indicated that the monolayers formed faster with an increase in the length of the alkyl chain. This result is in agreement with previous studies that reported a preferential adsorption of longer chain alkyl thiols on gold surfaces.[41] The trend suggests that the aliphatic alcohols, similar to their thiol analogues, are influenced by intermolecular interactions between the hydrocarbon chains during formation of the monolayers. These interactions could facilitate the formation of the monolayers. These results could also be attributed to the preferential adsorption of the longer chain alcohols due to a relative decrease in their solubility in the polar medium. Other factors, such as diffusion or steric constraints, were relatively insignificant as these factors should facilitate the formation of monolayers from shorter alkyl chains.[41] In conclusion, chain length of the aliphatic alcohols has a similar impact to their thiolate analogues, with the rate of formation of the monolayers increasing in proportion to their chain lengths.

CONCLUSIONS

In summary, we have demonstrated the formation of monolayers on silicon oxides using a variety of alcohol containing compounds dissolved in propylene carbonate. The reactions performed in this polar aprotic medium enable a diverse array of surface modifications to the silicon oxides. The reagents included a series of readily available alcohols. The silicon oxides were successfully modified with monolayers containing fluorocarbons, aldehydes, carboxylic acids, quaternary ammonium cations, vitamins, or nucleic acids. The formation of monolayers from aliphatic alcohols was studied in further detail to investigate the influences of reaction temperature, concentrations of both reactants and moisture, and chain length of the reactants. It was determined that increases in the reaction temperature up to 100 °C aided the formation of the alcohol based monolayers. A further increase in reaction temperature to 120 °C results in an incomplete formation of monolayers due to possible side reactions in the reaction mixture. Increasing the concentration of the reacting molecules increases the rate of monolayer formation, but the presence of relatively large amounts of water added to the propylene carbonate slow down or inhibit the formation of the monolayers. Chain length of the aliphatic alcohols can also have a large impact on the rate of formation of the monolayers. While uniform monolayers were formed using alcohols of varying alkyl chain length, their rate of formation increased in proportion to the lengths of the alkyl chains. This result implies that, similar to thiol based self-assembled monolayers (SAMs), cohesive interactions between the hydrocarbon chains and solubility of the aliphatic alcohols in propylene carbonate had a significant impact on the formation of monolayers on silicon oxides. The use of propylene carbonate as a solvent for alcohol based reagents increases the diversity of surface chemistries that can be prepared on silicon oxides. Although these condensation reactions draw a number of analogies to the reactions of alkanethiols on gold, there are a number of unique attributes and limitations that are specific to the formation of alcohol based monolayers.

Understanding these features enables the design of further reactions aimed at tuning the surface chemistry of silicon oxides through the use of alcohol containing reactants.

ASSOCIATED CONTENT

Supporting Information. Data available includes details on additional polar aprotic solvents evaluated for their potential use in the sought after route to prepare alcohol based monolayers, as well as the data associated with the water contact angle measurements corresponding to the plots in the manuscript.

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Author Contributions

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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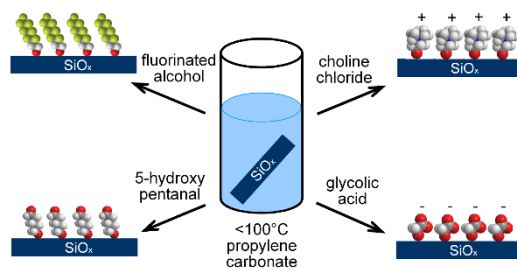
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