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# Reactive Molecular Dynamics Simulations of the Silanization of Silica Substrates by Methoxy- and Hydroxysilanes

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**Abstract:** We perform reactive molecular dynamics simulations of monolayer formation by silanes on hydroxylated silica substrates. Solutions composed of alkylmethoxysilanes or alkylhydroxysilanes in hexane are placed in contact with a hydroxylated silica surface and simulated using a reactive force field (ReaxFF). In particular, we have modeled the deposition of butyl-, octyl-, and dodecyltrimethoxysilane to observe the dependence of alkylsilyl chain length on monolayer formation. We additionally modeled silanization using dodecyltrihydroxysilane, which allows for the comparison of two grafting mechanisms of alkoxy silanes: (1) direct condensation of alkoxy silane with surface bound silanols, and (2) a two-step hydrolysis-condensation mechanism. In order to emulate an infinite reservoir of reactive solution far away from the substrate, we have developed a method in which new precursor molecules are periodically added to a region of the simulation box located away from the surface. It is determined that the contact angle of alkyl tails bound to the surface is dependent on their grafting density. During the early stages of grafting alkoxy- and hydroxysilanes to the substrate, a preference is shown for silanes to condense with silanols further from the substrate surface, and also nearby to neighboring surface-bound silanols. The kinetics of silica silanization by hydroxysilanes were observed to be much faster than methoxysilanes. However, the as-deposited hydroxysilane monolayers show similar morphological characteristics as those formed by methoxysilanes.

**Keywords:** monolayer, coating, alkoxy silane, chlorosilane, ReaxFF, OTS

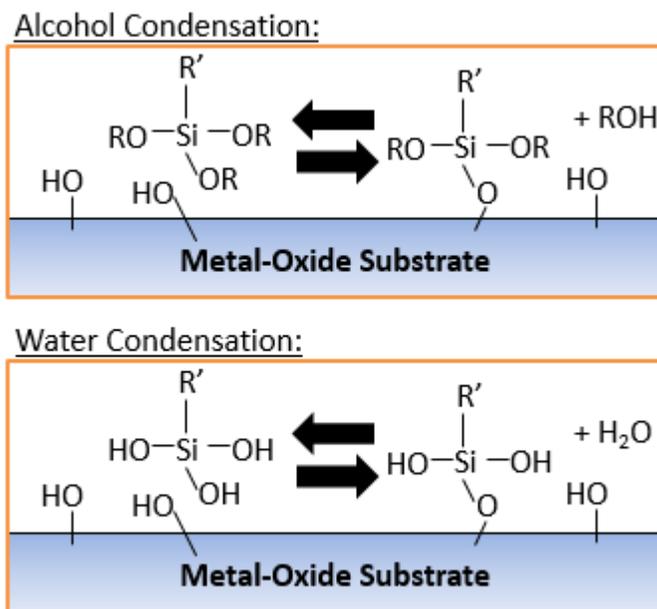
## 1. Introduction

Trialkoxysilanes are frequently used to form coatings on metal-oxide surfaces through a process known as silanization. Molecular monolayers<sup>1</sup> can form on these substrates and alter their physiochemical properties. Silane coated surfaces have a variety of applications, such as: hydrophobic<sup>2</sup> and frictionless coatings<sup>3, 4</sup>, adhesives between polymers and ceramics<sup>5, 6</sup>, or immobilizing<sup>7</sup> biological molecules on surfaces.

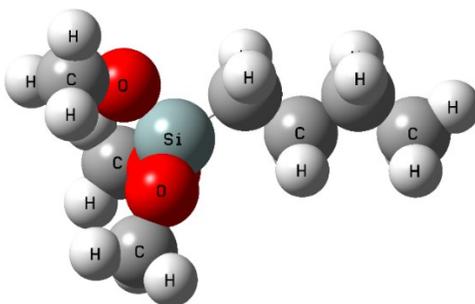
Silanes are commercially available with silyl groups of diverse chemistries. Examples include long alkyl chains<sup>2, 8, 9</sup>, amines<sup>10, 11, 12</sup>, and thiols<sup>13</sup>. Given the versatile chemistry of silyl headgroups which alter the chemical properties of surfaces, considerable research has been devoted to optimize silanization chemical conditions<sup>8, 9, 11, 12, 14, 15</sup> in order to form consistently dense and smooth monolayer coatings.

In liquid-phase silanization, alkoxy silanes diffuse from a solution and physisorb to hydroxyls bound to the metal-oxide substrate<sup>16</sup>. The silanes can then undergo a condensation reaction<sup>17</sup>

producing a siloxane which grafts the molecules to the surface (cf. Figure 1). Depending on the pH and water concentration, the alkoxy silanes may be hydrolyzed before physisorption. Under acidic/basic conditions, the hydrolysis of the silanes is much faster than at neutral pH<sup>18, 19</sup>, assuming there is water present. Under these conditions, silanization of the substrate will occur through the water condensation reaction (bottom panel, Fig. 1). Under anhydrous conditions, hydrolysis prior to condensation is impossible, and silanization will occur through the alcohol condensation reaction (top panel). Silanes with long alkane silyl groups can self-assemble<sup>1, 2</sup> on metal-oxide substrates. Schwartz et al.<sup>1</sup> showed the formation of ordered phases of hydrocarbon headgroups densely grafted to mica which followed a fractal growth mechanism. Alkoxy silanes nucleate ordered phases on metal-oxide surfaces, followed by growth through self-assembly from solution to form smooth layers<sup>8</sup> of densely grafted silanes.



**Figure 1: Illustration of alkoxy silane condensation to a metal-oxide substrate (e.g. silica in this study). Top image illustrates alcohol condensation reaction in which alkoxy silane (Si-O-R) condenses to the surface, producing alcohol. The bottom panel shows the water condensation reaction through silanol. In both reactions R' represents the silane headgroup.**



**Figure 2: Atomic representation of butyltrimethoxysilane (BTMS). The two other alkoxy silane molecules modeled in this study, octyltrimethoxysilane (OTMS) and dodecyltrimethoxysilane (DTMS), differ only in the**

**length of the alkyl chain. Dodecyltrihydroxysilane (DTHS) additionally has hydroxy rather than methoxy groups.**

Despite the widespread application of silanization processes, the underlying chemical mechanisms have not been studied in atomistic detail. Specifically, the mechanisms of chemisorption of alkoxy silanes to silica substrates remain unclear. Controllably generating monolayers with complete bonding to and coverage<sup>20</sup> of the surface remains a challenge. The chemisorption of silanes to silica substrates occurs through condensation with hydrolyzed silicons<sup>21</sup> and strained siloxane rings<sup>22</sup> on the surface. Reactive force fields for molecular dynamics simulations have recently been developed<sup>23</sup> which are capable of modeling the condensation of alkoxy silanes to a silica substrate.

We use molecular dynamics (MD) simulations to investigate the formation of silane coatings on hydroxylated silica surfaces. In order to mimic the effects of molecules diffusing to the surface from a large reservoir of solution, a region of the simulation box is maintained at constant concentration by periodically removing and inserting molecules. This allows for the surface to be densely grafted by alkoxy silanes, while maintaining the low concentration of silane in silanization processes<sup>20, 24</sup>. The influence of grafting density on the morphology of silane films chemisorbed to silica surface are investigated. Alkoxy silanes with different alkyl headgroups (butyl-, octyl-, and dodecyltrimethoxysilane) are used in order to observe the influence of alkyl headgroup chain length on the kinetics of silanization and the positioning of sorbed silanes at the surface. Figure 2 shows a butyltrimethoxysilane molecule, which bears the shortest of the alkylsilyl headgroups studied. Lastly, silanization was investigated with silanes bearing different degrees of hydrolysis prior to condensation. The rates of grafting to the substrate and the morphology of monolayers formed are compared between dodecyltrimethoxysilane and dodecyltrihydroxysilane.

## 2. Simulation Methodology

MD simulations were performed using LAMMPS<sup>25, 26</sup> with the Velocity-Verlet algorithm at a 0.35 fs timestep. The atomic forces are computed using ReaxFF<sup>27, 28</sup>. Specifically, we use our parameters of ReaxFF<sup>29</sup> which were optimized for the polycondensation of alkoxy silanes. This force field is extensible to modeling the condensation of methoxy- and hydroxysilanes to silica substrates. The Nosé–Hoover thermostat<sup>30, 31</sup> was used in all simulations with a time constant of 50 fs. When the system pressure was fixed, the Parrinello-Rahman barostat<sup>32, 33</sup> was used with a time constant of 250 fs.

### 2.1 Preparation of Silica Surface

It is known<sup>34</sup> that the chemical conditions used to prepare silica surfaces for silanization are a major factor determining the characteristics of surface coatings formed. The ReaxFF parameter set developed by Fogarty et al.<sup>35</sup> was used to generate hydrolyzed silica surfaces as these parameters have been optimized for interfaces between silica and water.

A unit cell of  $\alpha$ -cristobalite was replicated to fill a box of 5.0 x 5.0 x 2.1 nm<sup>3</sup> with 3600 atoms. The crystal was transformed into amorphous silica using melt-quench procedure where the temperature was raised to 5000 K and cooled at a rate of 20 K/ps to 300 K. During this process the pressure is maintained at 1.0 bar to avoid the formation of cracks due to the density difference between crystalline and amorphous phases.

After the generation of an amorphous solid, two surfaces are created by cleaving the solid along the xy-plane, which are then separated by 5 nm vacuum creating a simulation box of 5.2 x 5.2 x 7.4 nm<sup>3</sup>. The cleaved surfaces are allowed to reconstruct to eliminate dangling radicals by heating to 1500 K over 400 ps. In order to hydrolyze the surfaces, 470 water molecules are inserted into the vacuum layer. Hydrolysis of the surfaces happens as the temperature is gradually cooled from 1500 K to 300 K over 1 ns. The resulting surfaces have a surface silanol (Si-O-H) concentration of 4.3 groups/nm<sup>2</sup>, comparable to the range of experimental concentrations<sup>36</sup> of 4.2 to 5.7 OH groups/nm<sup>2</sup>. The quench time (1 ns) was sufficient to ensure equilibrium in the concentration of hydroxyl groups belonging to the silica surface. It was found that the concentration of hydroxyls on silica is highly dependent on the reaction temperature. At 1400 K, a low concentration of silanol is observed (2.1 hydroxyls/nm<sup>2</sup>). As the temperature is lowered, the concentration of silanols on the surface increases. Doubling the quench rate (500 ps quench) for this procedure was tested, but the concentration of silanols was similar (4.2 hydroxyls/nm<sup>2</sup>). The silica substrates using this procedure have a ratio of singly to doubly hydroxylated silicons of 7.5. Following hydroxylation, the remaining water molecules are removed. This emulates the vacuum and nitrogen drying techniques used in experiments<sup>20, 34</sup>. Experimentally, the concentration of silanol on the surface of amorphous silica reaches a value of 4.9/nm<sup>2</sup> after vacuum drying<sup>36</sup> at 180-200 °C to remove physisorbed water. In this study, water molecules are simply removed from the simulation box instantaneously at room temperature. Hence, the concentration of silanol on our substrate may underestimate the actual value at room temperature.

The substrates of the present work assume 4.2 hydroxyl groups per nm<sup>2</sup>, with complete drying of the surface, zero percent humidity, and zero water present as impurities in the reaction solution. The hydrogens belonging to the formed surface silanols do not exhibit periodicity, and are relatively randomly distributed on the surface. The RMS roughness of the bare hydroxylated silica substrate was calculated to be 2.0 Å, which is comparable to previous studies.<sup>34, 37</sup>

## 2.2 Silanization Procedure

Following the generation of hydrolyzed silica surfaces, a solution of hexane and alkoxy silane is added to the simulation box using Packmol<sup>38</sup> to randomly place silane and hexane molecules at a 1:30 ratio between the two surfaces at a density of 1.0 g/cm<sup>3</sup>, with the constraint that all intermolecular distances must be greater than 2 Å. Four different silane molecules are used as grafting agents in this study: butyl-, octyl-, dodecyltrimethoxysilane, and dodecyltrihydroxysilane (abbreviated as BTMS, OTMS, DTMS, and DTHS). A single simulation is performed for each to study the silanization characteristics of each molecule.

Typical silanization processes<sup>1, 4, 9, 20, 39</sup> for monolayer coatings use a low concentration of silane to limit self-oligomerization prior to deposition. Monolayer coverage occurs by diffusion of the silane from the solution to the surface, where condensation occurs. MD in the NVT and NpT ensembles have a fixed number of particles and do not allow atoms to enter or leave the simulation box, which prohibits complete surface coverage by limiting the number of reactants in the system. As a solution, we define a source region of 1 nm thickness centered between the two silica surfaces which is held at constant concentration (Figure 3 right).

ReaxFF is a reactive force field, i.e. the covalent bonds between atoms break and form over the course of simulation. After a predetermined time, the bonding state of the system is used to

identify molecules. Any molecules which have a center of geometry within the 1 nm source region are removed. The number of molecules removed is used to determine the number of molecules inserted back into the source layer afterwards using Packmol.<sup>38</sup> Silane and hexane are inserted into the source layer at a ratio of 1:30. For example, if 62 molecules are removed from the source layer, 62 molecules are inserted into the source layer (60 hexane and 2 alkoxy silanes). The position and orientation of solvent and silanes being inserted into the source region are entirely random, and prior to insertion, the coordinates of the entire system are shifted by a random vector in the xy-plane, in order to avoid biasing the system along the boundaries of the simulation box during each insertion step. Afterwards, the system dynamics are again simulated until the end of the next cycle, after which this process is repeated. Different cycle lengths of 25, 50, and 150 ps are used to test the influence of this ad-hoc procedure on the thermodynamics and kinetics of silanization by OTMS. A single simulation is performed for each cycle length.

In order to accelerate reaction kinetics, the temperature used for all silanization simulations was 750 K. Higher and lower reaction temperatures were tested before selecting 750 K to perform our simulations. It was found that the rate of silanization was prohibitively slow for lower temperatures. Additionally, the rate of silanization did not increase much above 750 K. Thus, 750 K was selected as a compromise as the lowest temperature at which simulating silanization was tractable, while striving to be close to the relevant experimental conditions. In order to prevent the thermal decomposition of hexane and silane at this temperature, harmonic restraints were added to all C-H, C-C, C-O and Si-C bonds with a constant of 50 kcal/mol/Å<sup>2</sup> to ensure that these bonds stay intact. This allows the study of strictly the relevant chemical bonds (Si-O and O-H) to the reactions in Fig. 1.

A silanized substrate generated by the procedure outlined above is shown in Figure 4. This shows a visualization of dodecyltrihydroxysilane (DTHS) chemisorbed to the silica surface which was generated using VMD<sup>40</sup>. The green and black spheres represent the silane silicon and headgroup alkyl chains respectively.

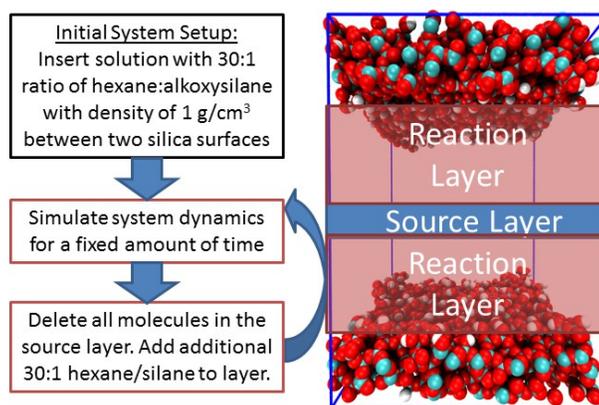
### 2.3 Measurement of Chemical Groups and Coating Properties from Simulations

ReaxFF is a force field which calculates the bond order (i.e. the number of covalent bonds) between two atoms. The bond order is treated as a continuous function rather than discrete integers such as 1 or 2 for single or double bonds. The bond order topology from the simulation was used to determine the concentration of chemical groups. The oxygen atoms were used to distinguish between the alkoxy silane (Si-O-C), silanol (Si-O-H), water (H-O-H), alcohol (C-O-H), and siloxane (Si-O-C) states by detecting the two atoms sharing the highest bond order with the O. By detecting the formation of siloxanes in which one silicon atom belongs to the surface, and one to the silanes, chemisorbed silanes were detected. If a silicon atom from a silane was detected to be within 4 Å of a silicon atom from the substrate, the silane molecule was labeled to be “sorbed” (either chemi- or physisorbed). The carbon atoms belonging to this silane were noted and used to compute various chain-related properties (radius of gyration, tilt angle, etc.)

The in-plane molecular area was determined using a subtractive method. First, the fraction of exposed surface area was determined. A two-dimensional grid was extended over the xy-plane of the simulation box, in which the grid points were spaced at a distance of 0.2 Å. This resulted in over 66,000 grid points in the xy-plane, which was placed at the same axial position of the silica surface. If the x- and y-distance of a grid point was within 1.925 (C) or 1.625 Å (Si) of an atom,

the grid point was labeled as occupied. These cutoff distances are determined from half the van der Waals radii of the OPLS<sup>41</sup> “united atom” (for alkyl carbons accounting for bound hydrogens) and “all atom” (for silicon) force field parameters. The fraction of unoccupied grid spaces is used to calculate the fraction of exposed substrate. The number of sorbed silanes is divided by the occupied area to calculate the in-plane molecular area of each grafted silane. Surface roughness of the hydroxylated silica surface was calculated considering the root mean square z-coordinate of oxygens of surface bound silanols (Si-O-H). For silanized substrates, the roughness is calculated based on the positions of silanol oxygens, and all grafted silane atoms.

To determine the dependence of the measured properties on temperature, a sample OTMS surface (after 4 ns of simulation time, and 1.28 sorbed silicons per nm<sup>2</sup>) was quenched to 300 K at a rate of 20 K/ps. It was found that at 300 K the concentration of sorbed silanes increases by 11%, corresponding to additional physisorption on the substrate surface at lower temperature. Other coating properties, such as the in-plane molecular area, surface roughness, and radius of gyration, did not change appreciably after quenching.



**Figure 3: Simulation workflow used in this study. After a predetermined simulation time (25 ps, 50 ps, or 150 ps), all molecules in the source layer are removed and replaced with a mixture of hexane and silane at a molar ratio of 30:1.**

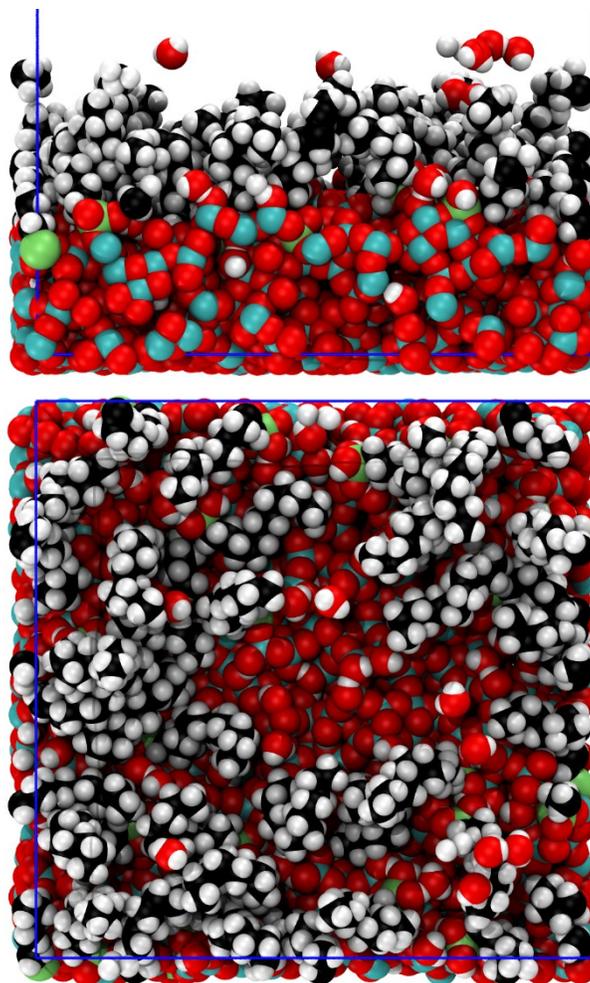


Figure 4: Visualization of silanization of a silica surface by DTHS from the side (top image) and from above (bottom image). The substrate hydrogen (white), oxygen (red), and silicon (blue) atoms are represented using spheres. The silane headgroups silicon, carbon, and hydrogen atoms are represented using green, black, and white respectively. In both images the substrate has 1.5 bonded silanes per  $\text{nm}^2$ .

### 3. Results

#### 3.1 Effects of Exchange Interval on Silanization Kinetics

A study of the effects of the length of the exchange interval was motivated by the need to understand the influence of the exchange rate (effectively the flow rate of reactant replenishment) of the source layer on silanization kinetics. It is anticipated that if the interval between exchanges is too small, the molecules contained within may not have enough time to diffuse out of the layer. If the interval is too large, the source layer will be depleted of alkoxy silane molecules, and fail to mimic a bulk solution at constant concentration.

We find that OTMS has a diffusion coefficient of  $0.028 \text{ nm}^2/\text{ps}$  in hexane. For a 1 nm thick source layer, a molecule must diffuse an average distance of 0.87 nm (the distance from the center of the source layer to its edge based on  $45^\circ$  angles to the axes from the surface plane). This yields an approximate diffusion time of 26.8 ps for a molecule to leave the source layer.

This rough estimate implies that the interval durations (25-150 ps) are on the same order as the diffusion time.

Figure 5 compares the evolution of sorbed silanes for the three different replenishment cycles. The criterion for sorption is that a silicon atom of the alkoxy silane is within four angstroms of a substrate silicon, this includes both physisorbed and chemisorbed molecules. The majority of silicon atoms are chemisorbed. As Figure 5A demonstrates, the number of molecules sorbed to the silica surface increases with time. Sorption occurs fastest when the exchange rate of the source layer is  $(25 \text{ ps})^{-1}$ . This is not surprising as a faster exchange rate ensures that alkoxy silane enters the system at a greater rate. The differences between the 25 and 50 ps exchange times are not as great as between 50 and 150 ps. At the slow exchange rate of  $(150 \text{ ps})^{-1}$ , the silanes of the system react with the surface fast compared to the rate they are entering the source region, leading to a lower concentration of silane in the solution phase and a slower condensation kinetics for 150 ps.

Typical silanization times for alkoxy silanes in experiments are on the order of hours<sup>21, 34, 42</sup>. The elevated temperature in our simulations allows for accelerating silanization, potentially at the loss of some self-assembly<sup>1</sup> which is influenced by weak van der Waals forces, which are lost at high temperature.

Available surface silanol sites disappear with time, which slows condensation. For this reason, the slopes of the profiles in Fig. 5A are reduced at longer time. Following the condensation of alkoxy silane molecules to the silica substrate, alcohol is produced (top panel Fig. 1). These alcohol groups can chemisorb to silanol on the surface, generating surface bound alkoxy silanes. The concentration of alkoxy groups on the silica surface is shown in Figure 5B. Clearly, the number of alkoxy groups chemisorbed to the surface is correlated with the number of sorbed silanes.

The reaction of alcohols with silica surfaces has been studied by spectroscopy<sup>43, 44</sup>. Silica surfaces in the absence of water can be alkoxyated at room temperature, either reacting with surface bound silanols<sup>43</sup> or strained siloxane rings on the surface.<sup>22, 45</sup> Zipoli et al.<sup>22</sup> indicated that the condensation of alkoxy silanes strained siloxanes on the substrate surface results in the production of a grafted silane and an alkoxyated surface group. This reaction was highly exothermic with low activation barrier (-50.7 and 4.6 kcal/mol). Wet silica surfaces have been shown to be susceptible to alkoxylation at elevated temperatures of 400-600 K. In these conditions<sup>46</sup> the alkoxylation reaction was endothermic with an activation energy of 21.9 kcal/mol, with the concentration of alkoxy groups on the surface increasing with temperature. As the temperature is lowered from the alkoxyated state, water can hydroxylate the alkoxy ligands. Based on our anhydrous conditions, high reaction temperature, and potential presence of strained siloxanes near the substrate surface, the existence of surface bound alkoxy groups is supported experimentally. However, it is not clear if alkoxy groups will form on silica substrates at lower temperature, or with wet surfaces.

The chemisorption of alcohol reduces the concentration of silanol available to condense with alkoxy silane, which slows the kinetics of silanization. Therefore, the generation of surface bound alkoxy groups is undesirable. Acidic conditions<sup>21, 42, 47</sup> are frequently used in silanization. Low pH accelerates hydrolysis<sup>47</sup> of alkoxy silanes in the sol-gel process, and may additionally limit alkoxy

sorption during silanization. Therefore, these groups will only limit grafting of silanes under anhydrous, neutral conditions.

The concentration profile (perpendicular to the substrate surface) of alkoxy silane is presented in Figure S1 in supporting information at different simulation times. The number of silane molecules sorbed to the surface increases with time. The concentration of silanes in the solution ( $2 \text{ nm} < z < 5.5 \text{ nm}$ ) is nearly constant. The profiles are from the 150 ps cycle. It can be clearly seen that a monolayer is beginning to form on the surface.

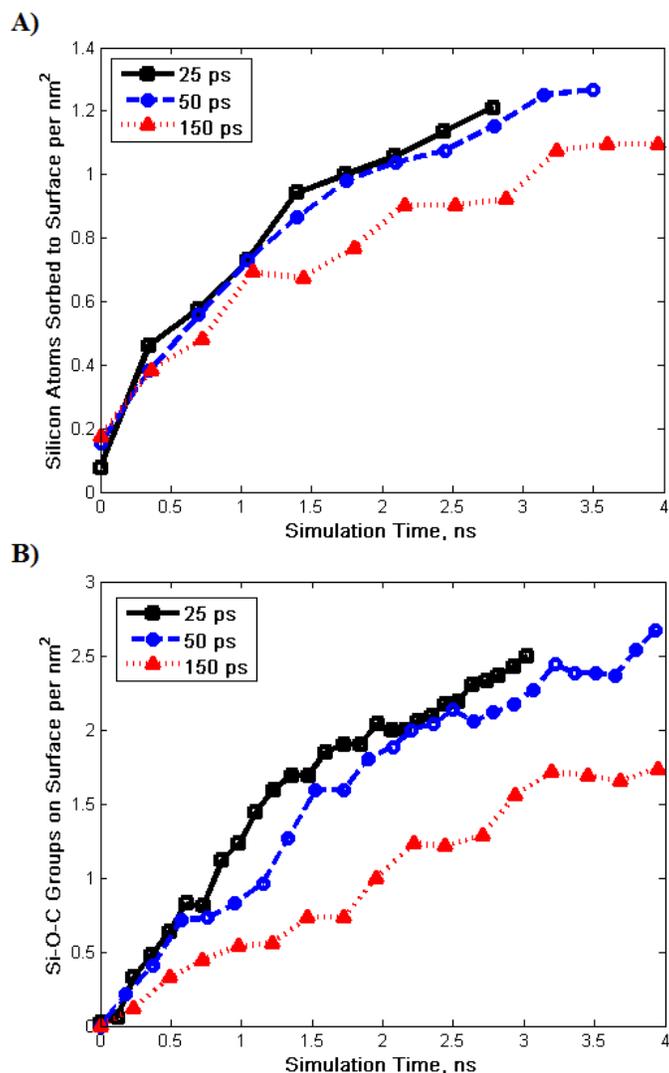


Figure 5: Surface concentration of (A) sorbed silane molecules, and (B) alkoxy groups (Si-O-C) bonded to the silica substrate.

### 3.2 Effects of Alkylsilyl Headgroup Size and Grafting Density on Coating Morphology

To determine the influence of the alkylsilane headgroup size on silanization of the silica surface, three different alkoxy silane molecules were considered: BTMS, OTMS, and DTMS. A 50 ps exchange of the source region in Fig. 3 was used for each simulation. The condensation of BTMS, OTMS, and DTMS to the silica surface occurs at very similar rates. Figure 6 shows the evolution of the concentration of silanes chemisorbed to the surface. Despite the difference in the headgroup size of the silanes, the diffusion coefficients in hexane are similar, which may explain the similarity in the kinetics. Due to the scarcity of statistical sampling, caution is advised in comparing the data as only one simulation was performed for each silane. The ratio of chemisorbed to physisorbed silanes changes throughout the simulation. At the start of each run (for all silane molecules), close to 40% of silanes on the substrate are chemisorbed. When the silane grafting densities reach  $0.5/\text{nm}^2$ , 80% of the silanes are chemisorbed. When the grafting density reaches  $1.0/\text{nm}^2$ , almost all of the silanes are chemically grafted to the substrate.

Figure 7 shows the dependence of tilt angle and radius of gyration on grafting density for the three different monomers. For all cases there is a clear increase in tilt angle (Fig. 7A) with grafting density likely due to crowding. At low grafting density the average tilt angle has a value between 35 and 45 degrees. As grafting density increases, the average tilt angle increases. The headgroups of the alkoxy silanes approach an average tilt angle of 55 degrees. Black et al.<sup>37</sup> investigated the dependence of grafting density on tilt angle. There was no clear correlation of the tilt angle with respect to chain length of the alkyl headgroups in agreement with our data (Figure 7A). In all cases, the standard deviation of the tilt angle of all silane headgroups is quite large, which implies the existence of a disordered monolayer at these low grafting densities.

With increasing length of the silane alkyl headgroup (BTMS, to OTMS, and DTMS) the radius of gyration increases (Fig. 7B). The radius of gyration slightly increases with grafting density of silanes on the silica surface, representing the reduced degree of freedom of the headgroups, and a more extended conformation of the chemisorbed alkylsilyl chains. The bars in Fig. 7B represent the standard deviations of the radius of gyration for the chains. DTMS headgroups clearly show a greater variation in the radius of gyration than BTMS, owing to its more flexible, longer alkyl chain.

Figure 8 shows radial distribution functions (RDF) between various groups sorbed to the silica substrate at  $1.0$  silanes per  $\text{nm}^2$ . The radial distribution of hydrogen of the surface bound silanol (Si-O-H) was measured to quantify the positions of silanols with respect to each other. The RDF shows two peaks at approximately 2 and 4 Å. The silanol hydrogens which are separated by a short distance of 2 Å are not bonded to the same oxygen atom, but represent different silanols. This distance is surprisingly short, and might represent two silanols hydrogen bonded to the same alkoxy silane, or residual water molecules which have not fully dissociated on the surface. In the case of BTMS and DTMS, a third peak in the H-H RDF can be resolved at 6-6.5 Å. This, and the peak at 4 Å, imply that there is some degree of order of the silanols on the substrate. Fig. 8B shows the RDF between sorbed silicon atoms. The existence of several peaks in the Si-Si RDF indicates there is a preferential sorption of silanes nearby others on the substrate, owing to the positioning of the silanol groups. Markedly, the first peak in the Si-Si RDF (3.25 Å) is shifted to larger distances compared to H-H (2 Å). This implies that the molecular radius of the silanes is greater than the separation distance between the silanol groups. Thus, at full silanization of the substrate, not all silanols will have reacted. The RDF in Fig. 8C corresponds to the carbons belonging to the silane headgroups. The low value of the RDF at any

distance further supports the conclusion that a disordered monolayer is formed at these reaction temperatures with little self-assembled characteristics.

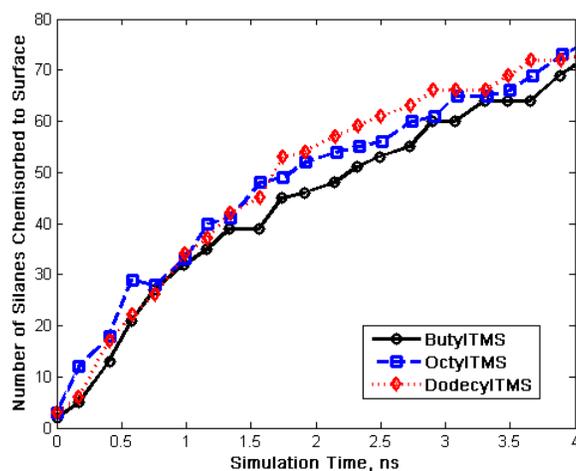
Figure S2 shows a normalized distribution of the separation distances between silanol hydrogens. For each hydrogen atom bound to the surface, only the nearest silanol hydrogen is included. Fig. S2A shows a bimodal distribution of inter-hydrogen distances for a fresh silica substrate which has not been exposed to the silane solution. At a distance of 2 Å, there is a peak corresponding to the H-H RDF in Fig. 8A. The probability of a hydrogen having a neighbor at this distance is nearly 0.40. Beyond this, the average distance between hydrogens is near 4 Å. Fig. S2B shows the distribution of inter-hydrogen distances on a substrate grafted by silanes at a density of 1.0/nm<sup>2</sup>. The prevalence of the peak at 2 Å is significantly reduced, corresponding to reactions of silanes with the surface silanols. The average inter-hydrogen distance increases from 2.7 to 3.7 Å, owing to the increased scarcity of silanols on the substrate. The occurrence of inter-hydrogen distances above 7 Å is markedly increased after silanization of the surface, and implies that some silanol groups on the substrate are isolated.

Table 1 contains additional data on the properties of BTMS, OTMS, DTMS coatings of the substrate at two grafting densities (0.5 and 1.0/nm<sup>2</sup>). The in-plane molecular area for DTMS is much greater than that of BTMS, owing to larger headgroup adopting a tilted angle with respect to the interface. As the grafting density increases, each silane adopts to a smaller in-plane area, representing the increased packing of headgroups on the surface and the alkyl chains adopting a more perpendicular conformation with respect to the interface. Linearly extrapolating the in-plane area to full coverage (zero exposed surface area), the in-plane area of BTMS, OTMS, and DTMS grafts are 18.5, 21.1, and 31.4 Å<sup>2</sup> respectively, corresponding to maximum densities of 5.4, 4.7, and 3.2 grafted silanes/nm<sup>2</sup>. In the case of BTMS and OTMS, these values exceed the concentration of silanol groups on the surface. The projected grafting density at full coverage decreases with the size of the headgroup. As larger headgroups have a larger lateral profile on the surface, there will be less room for additional silanes to bond. These projected values are only predictions based on linear interpolation, and should be taken with caution. Silanization of silica substrates by partially fluorinated undecyltrichlorosilane (C<sub>11</sub>-Si) was shown<sup>48</sup> to result grafting densities of 3.1/nm<sup>2</sup>, which is reasonably close to our extrapolated densities at full coverage for DTMS (C<sub>12</sub>-Si). In a different study<sup>42</sup>, the grafting density of BTMS on fumed silica was estimated between 1-3.1/nm<sup>2</sup> and 1.8-2.1/nm<sup>2</sup> for OTMS, well below our interpolation, but in agreement with the trend that increasing the alkyl chain length will lead to decreasing grafting density.

Another interesting effect shown in Table 1 is that the surface roughness (predicted using the axial positions of the silanols and the silane headgroups) decreases as the grafting density increases. This is also seen in atomic force microscopy experiments for silanization of silica surfaces<sup>49, 50</sup>. As the coverage of the silica surface increases, the surface roughness decreases. However, it should also be noted that the roughness of the bare silica surface (2.0 Å) is lower than all roughness values in Table 1. Therefore, we postulate that the initial grafting of silanes to the interface increases surface roughness, but this subsequently decreases with additional grafting. The distance between the average z-coordinate of silanols and sorbed silicons is initially positive for grafting densities of 0.5/nm<sup>2</sup>. This demonstrates that the silanols extended away from the silica surface are more susceptible to condensation. However, at grafting densities of 1.0/nm<sup>2</sup>, the average z-position of the sorbed silicons decreases, perhaps representing additional

condensation reactions of the surface to the silanes (there are an average of 1.8 Si-O-Si per silane at this grafting density). On the contrary, the difference between the average z-coordinate of sorbed silicons and the carbon atoms belonging to the silane headgroups is always positive, which demonstrates that the headgroups are extended away from the interface. The extension of the headgroups increasing with grafting density, which corresponds to the increase in the silane tilt angle. Additionally, the extension of the headgroups increases in the order of BTMS, OTMS, and DTMS. The mean extension of carbon atoms in DTMS away from the surface is 5.2 Å. Yang et al.<sup>34</sup> used ellipsometry to measure a thickness of 1 nm for a decyltriethoxysilane coating at full coverage. This implies that our simulated DTMS coatings are far from the thickness achieved at greater coverage.

The densities of grafted silanes obtained here (from 0 – 1.3/nm<sup>2</sup>) according to Schwartz<sup>49</sup> correspond to the “vapor-like” and “liquid-like” phases on the substrate. The beginning of the deposition process corresponds to a “vapor-like” phase in which the silanes are randomly deposited on the surface. At a grafting density of ~1/nm<sup>2</sup>, the arrangement of silanes on the surface corresponds to a “liquid-like” phase in which the silane tails are disordered and lying relatively flat to the interface. At higher grafting densities, a densely packed “solid-like” phase should emerge in which silane headgroups are arranged in an ordered fashion, more perpendicular to the surface.



**Figure 6: Surface concentration of chemisorbed butyl-, octyl-, and dodecyl-trimethoxysilane molecules.**

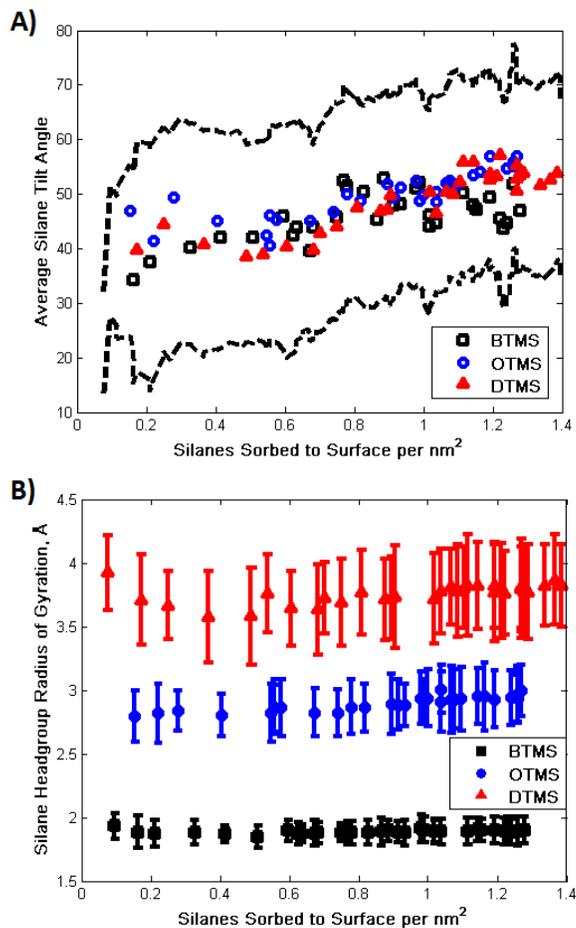
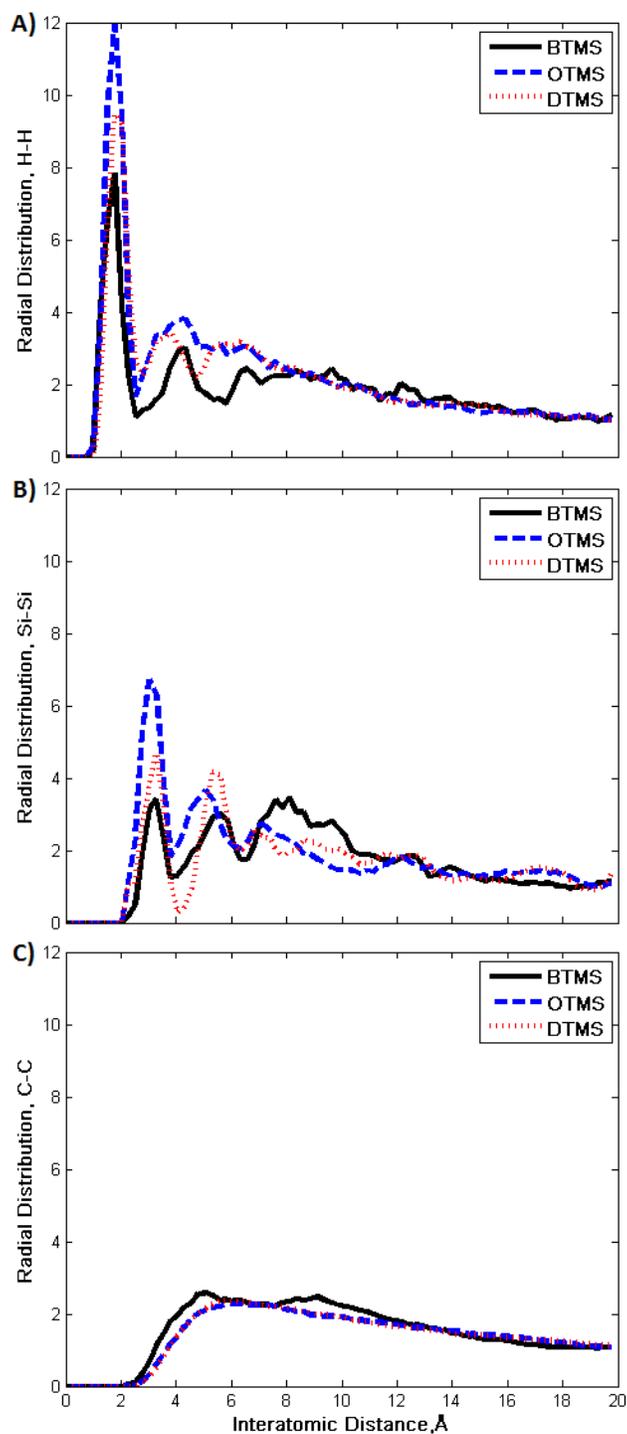


Figure 7: (A) Tilt angle of the alkane chains (angle formed between substrate, silicon of the silane, and carbon atoms of the silanes), and (B) radius of gyration of hydrocarbon headgroup attached to BTMS, OTMS, and DTMS as function of grafting density on the silica surface. In the top figure, the maximal standard deviation of the BTMS, OTMS, and DTMS silane headgroup tilt angles is represented using dashed lines. For the bottom figure, the standard deviation is represented using error bars.



**Figure 8: Radial distribution functions (RDF) between the following groups: A) silanol (Si-O-H) hydrogens attached to the substrate, B) chemi- and physisorbed silicon, and C) carbon atoms not sharing the same headgroup chain (i.e. only inter-chain C-C pairs). The radial distribution is computed at distances in intervals of 0.25 Å and at simulation times when silane density on the substrate has reached 1.0/nm<sup>2</sup>.**

**Table 1: Additional properties of BTMS, OTMS, DTMS, and DTHS silane coatings on silica substrates**

Species	Silane Grafting Density	Molecular In-Plane Area, Å <sup>2</sup>	Fraction of Surface Exposed	Surface Roughness, Å	$\Delta_z$ (Sorbed Si, Surface SiOH), Å†	$\Delta_z$ (Headgroups, Sorbed Si), Å†	Distance Between Closest Silanol Hydrogens, Å‡
BTMS	0.5/nm <sup>2</sup>	26.7±0.7	0.86±0.01	3.4±0.1	1.1±0.2	1.9±0.3	2.8±1.4
	1.0/nm <sup>2</sup>	24.8±0.6	0.76±0.01	2.6±0.1	-1.7±0.2	2.3±0.5	4.4±2.2
OTMS	0.5/nm <sup>2</sup>	40.4±1.0	0.78±0.01	3.4±0.1	0.4±0.4	3.1±0.8	2.7±1.4
	1.0/nm <sup>2</sup>	35.1±1.0	0.65±0.01	3.2±0.1	-1.6±0.4	4.0±0.8	3.5±1.8
DTMS	0.5/nm <sup>2</sup>	55.6±1.0	0.72±0.02	3.7±0.1	0.9±0.2	3.4±0.4	2.7±1.4
	1.0/nm <sup>2</sup>	47.0±1.6	0.51±0.01	3.8±0.1	0.4±0.2	4.8±0.5	3.3±1.6
DTHS	0.5/nm <sup>2</sup>	53.8±2.7	0.73±0.03	4.0±0.1	1.5±0.2	3.9±0.5	2.6±1.4
	1.0/nm <sup>2</sup>	48.9±1.3	0.50±0.06	3.5±0.2	0.9±0.1	4.3±0.4	2.9±1.2

†: Relative Difference in the averaged z-coordinates belonging to the two groups in parenthesis

‡: Average distance between a silanol hydrogen and the next closest silanol hydrogen

### 3.3 Effects of Hydrolyzation of Silane Molecule

In the previous sections, silanization of silica substrates by alkoxysilanes under neutral conditions was investigated. In anhydrous solution, with a substrate that has been thoroughly dried under vacuum conditions, water is absent and the hydrolysis of alkoxysilane groups (Si-O-C) to silanol (Si-O-H) is unlikely. However, typical silanization processes do not use neutral conditions, but add an acid or base as catalyst to improve reaction kinetics. Additionally, some trace water may be physisorbed to the substrate or present in the solution. Under these conditions the water condensation reaction (bottom panel of Figure 1) takes place as silanol will be present in the reaction solution. Chlorosilanes also react rapidly with water to form silanol. In order to compare the silanization of silica by hydroxyl- and alkoxysilanes, exposure to the substrate by dodecyl-trihydroxysilane DTHS was additionally investigated.

Figure 9 shows a side view of the simulation box. Similar to alkoxysilanes, the silanes graft to the silica surface and form a layer adjacent to the substrate. The water condensation reaction shown in the bottom panel of Figure 1 releases water after the silanes replace silanols with siloxane grafts. Some water molecules can be seen in the bulk solution represented by ball and stick models in Fig. 9. Typically a low concentration of silane is used for silanization to prevent self-condensation (aggregation) which form clusters in solution and lead to disordered coatings on the substrate (and potentially thicker super-monolayer coatings). In this sense, the solutions used in this study are overly concentrated in silanes. Corresponding to these conditions, for DTHS we observe an aggregate in solution (shown in Figure 9). This aggregate consists of silanes which have siloxane bridges (Si-O-Si) and hydrogen bonds in the hexane solution. These clusters are not observed for any simulations containing methoxysilanes, as these silanes are not capable of condensing or hydrogen bonding with each other in anhydrous solution.

Figure 10 shows the kinetics of silica silanization by DTHS versus DTMS. Condensation is much faster when DTHS is used as the grafting agent. It is possible that the smaller size of the silanol group compared to the methoxy group on the grafting agent (Si-O-H vs. Si-O-Me) is responsible for this difference. The smaller size of the silanol group allows easier access to the silicon atom<sup>17</sup> in the grafting agent by the surface bound hydroxyl oxygens, which enhances the rate of condensation. The methoxy groups are bulkier and may hinder condensation. Past studies<sup>18, 23</sup> have indicated that bulky alkoxysilane groups hinder hydrolysis and condensation. Another possible explanation for the enhanced kinetics of silanization is the lack of surface

bound methoxysilane groups. In the case of DTMS, condensation with surface-bound silanols produces water. The addition of water catalyzes silanol condensation reactions.<sup>17</sup> For both DTMS and DTMS grafting agents, there is evidence of multiple Si-O-Si grafts to the interface per silane molecule. After 1 ns of simulation time, there are on average 1.8 grafts per sorbed silane molecule.

Figure 10C demonstrates an increase in the DTMS headgroup contact angle with grafting density. The average silane tilt angle increases from 41 to 52 degrees with large standard deviation. This resembles a disordered monolayer at the interface. Previous studies have indicated the formation of rough island structures<sup>1, 49</sup>, which transition into smooth layers once full coverage is achieved. Such island domains are not observed here.

Similar to silanization by alkoxy silanes, Table 1 shows a decrease in the in-plane molecular area of DTMS molecules relative to grafting density. Due to increases in the packing density of the silanes at the interface, the headgroups must adopt a smaller in-plane area. The fraction of surface remaining exposed after grafting to 1.0 groups per nm<sup>2</sup> remains at 0.50. Thus, maximal silanization of the surface will likely have more than two silanes grafted per nm<sup>2</sup>. The surface roughness decreases as more silanes are grafted to the interface. This agrees with the results of atomic force microscopy measurements<sup>49, 50</sup>. As was shown with the alkoxy silanes in the previous section, the silanes initially graft to locations above the average axial position of silanols on the surface. This implies that the more exposed silanols are more susceptible to reaction. However, with increase in simulation time, these sites become further grafted to the interface and are closer to the substrate. The average extension of DTMS headgroups away from the sorbed silicon atoms is similar to that of DTMS, with the average z-coordinate of the headgroups being around 4 Å above that of the sorbed silicons.

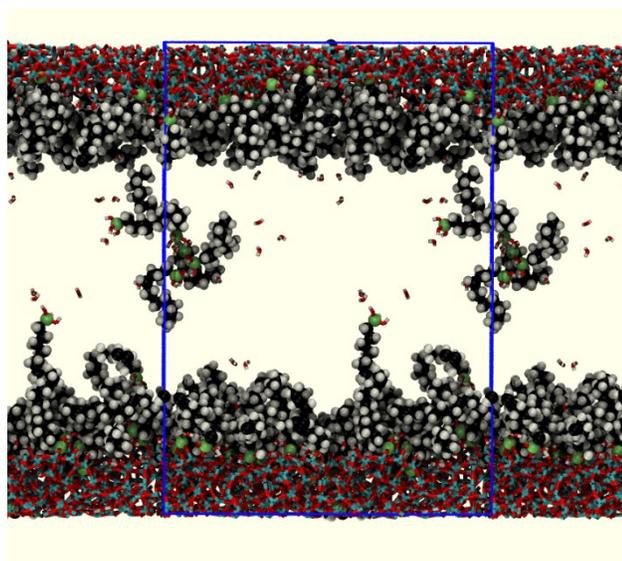


Figure 9: Simulation snapshot visualizing silica silanization from the side. The substrate oxygen (red), and silicon (blue) atoms are shown as tubes. DTMS silicon, carbon, and hydrogen atoms are represented using green, black, and white spheres respectively. In the image the substrate has 1.5 grafted DTMS per nm<sup>2</sup>.

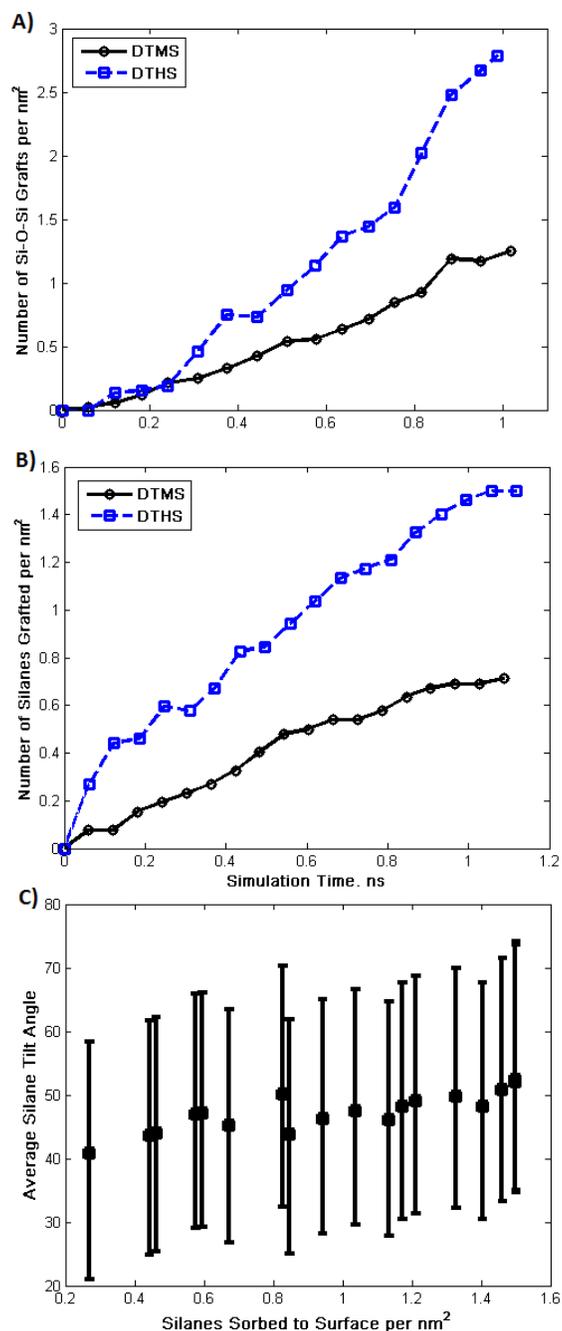


Figure 10: (A) Number of Si-O-Si grafts between the DTMS or DTMS silanes and the substrate vs. simulation time, (B) number of silanes grafted to the substrate, and (C) average tilt angle of DTMS headgroups bonded with the substrate vs. grafting density.

#### 4. Conclusions

The silanization of silica surfaces with alkoxy silane monolayers has been explored with reactive molecular dynamics simulations. Our recently developed force field<sup>29</sup> has been applied to observe the early stages of monolayer formation. A hydroxylated silica substrate was exposed to a solution containing hexane and silane (butyl-, octyl-, dodecyl-trimethoxysilane, or dodecyl-

trihydroxysilane). For the first time, the condensation of alkoxysilanes to a metal oxide surface has been studied using MD.

The typical concentration of silanes for monolayer formation is small ( $10^{-4}$  to  $10^{-2}$  M)<sup>1, 20, 24</sup>. In order to mimic the silica substrate being exposed to bulk solution, we created a methodology where silane molecules can be inserted into a “source region” of the simulation box, located away from the surface. All molecules inside of the region are periodically deleted. A 30:1 molar mixture of hexane and silane is then inserted in the source layer. This ad-hoc method allows new silane reactant to enter the system and reach reasonable surface coverage while maintaining low concentration of free silane. Both the density ( $1.0 \text{ g/cm}^3$ ) and the concentration of silane (about 0.24 M) of the mixture inserted into the source layer are far from experimental conditions. By estimation, assuming an ideal mixture, the density of the solution should be near  $0.71 \text{ g/cm}^3$ . The high concentration of silane was used here in order to make simulations tractable and achieve reasonably high grafting densities. In this work the source region was located only a short distance from the surface. A future study could probe the influence of the distance of the source layer from the substrate surface.

The substrates used in this study were produced by cleaving amorphous silica in the xy-plane and relaxing the surface at high temperature to eliminate dangling oxygens. The surface was reacted with water in a 1 ns simulation by cooling from 1500-300 K. This resulted in a substrate containing  $4.3 \text{ silanols/nm}^2$ . The density and positions of silanol on the substrate will have a significant impact on the morphological characteristics of the silane coating. It has also been indicated that strained siloxanes<sup>22, 45</sup> on the surface of substrates pretreated at high temperature can bond to silanes. Hence, different pre-processing conditions the substrate (pressure, temperature, quench time, pH) may lead to silane coatings with different characteristics. For example, hydroxylation of the silica surface by hydrogen peroxide<sup>37</sup> has been used in simulation to achieve a silanol density of  $5.8/\text{nm}^2$  on amorphous silica. The influence of pretreatment conditions on the silane coatings are not the primary focus of this study, but is an interesting topic for future work.

It has been shown elsewhere that the silanol density has a significant effect on the grafting density.<sup>51</sup> Increases in the silanol density will not necessarily lead to an increased silane density in the coating, due to steric repulsion existing from the silane headgroups. It has been shown that increases in the concentration of isolated silanols provides a greater number of sites for reaction.<sup>51</sup> Some sorbed silanes in our simulations lie flat on the substrate surface, which may block access to reaction sites. Nevertheless, our work is limited to the initial stages of silane sorption, and it is unclear how these factors will impact the equilibrium grafting density of silanes to the substrate.

In order to identify the effects of the exchange frequency of the source layer on the kinetics of silanization, three systems are modeled with different exchange times (25 ps, 50ps, and 150ps). The average time required for a silane molecule to diffuse out of the source layer is 27 ps. An exchange at 150 ps leads to a depletion of silane in the source layer slowing the silylation of the surface. For faster exchange times only small differences were noticed. The dynamics of the real system might be diffusion limited, where the “source layer”, which is really the bulk solution, is located far away from the surface (much further than the 2 nm here). This may force the concentration of unreacted silanes near the surface to be greater than reality. Our method is

thus not suited for diffusion-limited silanization, and only applicable to the reaction-limited regime.

The conformation of the silane alkyl tails is dependent on the grafting density on the substrate. The radius of gyration and tilt angle of the alkyl tails increase with grafting density in agreement with experiments<sup>1</sup>. An increase in the tilt angle implies that the alkylsilane chains are becoming more perpendicular to the silica surface. The radius of gyration slightly increases due to a more stretched conformation of the chains at higher packing densities. The extension of the headgroup chains above the substrate surface increases with grafting density of the silanes. At higher densities, the chains adopt a more perpendicular orientation with respect to the surface. Both, radius of gyration and monolayer thickness increase with headgroup size.<sup>49</sup>

Alkoxy groups are formed on the substrate which we believe hinder the kinetics of silanization of methoxysilanes under neutral conditions, by reacting with silanol groups. The reaction with silanols is likely a consequence of using anhydrous, neutral pH, and high temperature conditions for our simulations, as silica has been shown elsewhere to be alkoxyated under these conditions.<sup>44, 45, 46</sup> The acidic conditions<sup>17</sup> typically used in experiments can accelerate the hydrolysis of these groups, but our model<sup>29</sup> is not currently capable of modeling hydrolysis and condensation in the presence of acids.

To further investigate this issue, a comparison was made to the methoxysilanes by simulating silanization using DTHS as a grafting agent. DTHS is fully hydrolyzed compared to the methoxysilanes, and thus cannot alkoxyate the substrate. The silanol groups of DTHS react with the silica surface at a much faster rate compared to DTMS, perhaps corresponding to the reduced shielding the silane silicon. The smaller size of the hydroxyl groups in comparison with bulkier methoxy groups, as ligands on the silanes, enables easier accessibility for condensation with the surface.<sup>23</sup> Despite the accelerated kinetics of DTHS in comparison to DTMS, the formed monolayers show similar morphological characteristics, such as surface roughness, in-plane molecular area, tilt angle, and radius of gyration. This indicates that the alkoxylation of the substrate had little effect on the properties of the formed monolayer.

In the early stages of silanization by both hydroxyl- and methoxysilanes, a preference was observed for condensing to hydroxyl groups located above the silica surface, and also those with neighboring (within 3 Å) silanol groups. This suggests that steric influences come into play during silanization, and that catalytic effects of neighboring silanols may enhance condensation.

Future simulations could provide additional insight to the silanization process by considering silica surfaces with different features or chemistries. We have only modeled the silanization of hydroxylated silica surfaces. Substrates which are not hydroxylated, or surfaces with physisorbed water could provide interesting and useful insight into the silanization process. The modeling techniques used here could be expanded by modeling silanization with solvents other than hexane. In addition to alkanes<sup>20, 24</sup>, other solvents such as alcohols<sup>21</sup>, toluene<sup>42</sup> and cycloalkanes<sup>39</sup> are applied in silanization. Additionally, our study is limited to the early stages of silanization. The high reaction temperature (750 K) prevents the observation of self-assembly behavior during silanization, as these mainly depend on weak intermolecular van der Waals forces. However, such temperatures were necessary here to overcome the high activation energy of silanization processes, and to observe the reactions on molecular dynamics timescales (nanoseconds). To capture self-assembly and solvent effects more accurately in future

simulations, enhanced sampling techniques, such as the developed bond boost<sup>52, 53</sup> or replica exchange methods<sup>54, 55</sup>, will be useful in the future to probe silanization under more realistic conditions.

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