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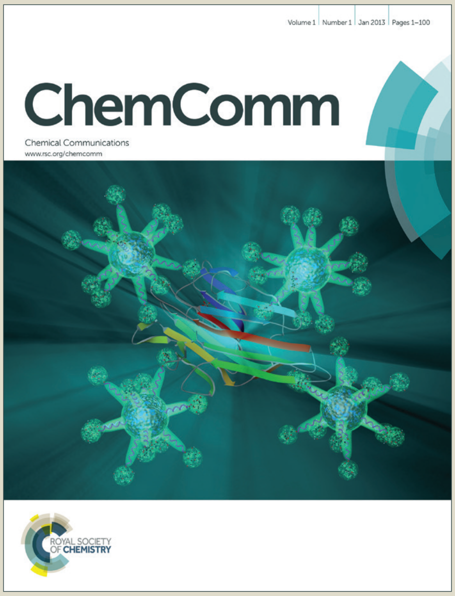

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Microwave Assisted Formation of Monoreactive Perfluoroalkylsilane-based Self-Assembled Monolayers

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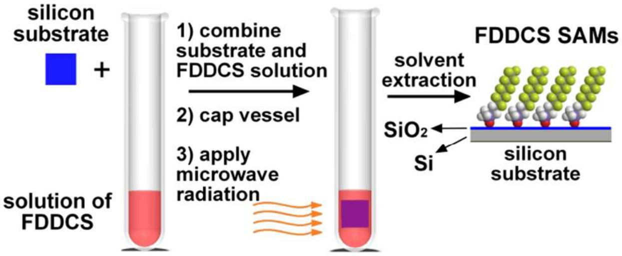
We demonstrate the use of microwave radiation as a tool to accelerate the formation of perfluoroalkylsilane based self-assembled monolayers (SAMs) on silicon oxide surfaces. Surface coverage of these SAMs of monoreactive perfluoroalkylsilanes increased in proportion to the duration over which the solutions were heated by microwave radiation.

Reactive alkylsilane molecules have been widely used for the formation of self-assembled monolayers (SAMs) since their introduction by Sajiv.[1] These SAMs can be formed on the surfaces of silicon[1-4], glass[5], aluminum[6] and copper[7] substrates. The most commonly used alkylsilane molecules in the literature include n-octadecyltrichlorosilane (OTS)[2, 3, 8-13] and 1H,1H,2H,2H-perfluorodecyltrichlorosilane (FDTS).[13-15] The SAMs formed with these molecules have been used to modify the properties of surfaces[4, 12, 16] and to create patterns of varying surface chemistry used in micro- and nano-fabrication processes[3, 17]. Many applications require SAMs of a high-quality, since defects in these single-molecule thick films lead to degradation of the surface properties or corrosion of underlying materials.[18, 19] Although trichlorosilane molecules such as OTS or FDTS are effective at modifying the surface properties of a variety of substrates, they can easily cross-link to form an intermolecular polymer.[20] This process often leads to the formation of non-uniform SAMs.[9, 17] In order to minimize unwanted intermolecular polymerization, trichlorosilane molecules are typically handled in an anhydrous environment. Creating the conditions that regulate hydrolysis and control the rate of condensation of these molecules can be difficult.

To minimize the impact of intermolecular polymerization during the formation of SAMs, monoreactive alkylsilane molecules are used in place of their trireactive counterparts. Monoreactive alkylsilane molecules can either react with the oxide surfaces or with one other molecule in solution. On the other hand, condensation of the monoreactive silane molecules is slow.[16] This can lead to incomplete formation of SAMs, leaving defects in the monolayers. In an effort to minimize defects and to prepare densely packed, uniform SAMs, a number of studies have varied the processing conditions. The simplest way to obtain uniform SAMs is to immerse the substrate into a solvent containing the silane molecules for a sufficiently long duration. However, such a process can take over 10 days to grow densely packed, uniform SAMs.[9] In order to accelerate the formation of these SAMs, heat can be applied to the solution during their formation, [2, 10, 16] but can still require a relatively long processing time. Silane molecules can also form SAMs on oxide surfaces through multiple iterations of the deposition process to improve their quality,[19, 21] but this approach can be cumbersome and induce unwanted intermolecular polymerization. Physical adsorption of silane molecules and surface contamination acquired from each deposition process can also decrease the uniformity of the SAMs. An alternative method was sought to more effectively and efficiently form uniform SAMs of monoreactive alkylsilane molecules.

Microwave induced heating has been widely used in molecular synthesis,[22-24] and the rapid assembly of nanomaterials[22,25] for its advantages in fast and effective heating.[26] Recently, microwave heating has been utilized in assisting the formation of alkene[27] and thiol[28] based SAMs on silicon carbide and gold surfaces, respectively. Silane based SAMs have been formed with microwave heating of glass slides[26] and cotton fabrics.[29] Although these studies demonstrated the utilization of microwave to the formation of SAMs, they did not provide insight into the impact of microwaves on the quality of SAMs.



(FDDCS = 1H,1H,2H,2H-perfluorodecyldimethylchlorosilane)

Scheme 1. Microwave-assisted formation of silane-based self-assembled monolayers (SAMs) on silicon oxide surfaces.

The use of microwaves to selectively heat molecules and solids is pursued for accelerating the formation of silane-based SAMs (Scheme 1) on silicon substrates with 100 nm dry oxide in order to observe the impact of microwave radiation on the quality of silane based SAMs. Microwave reactor (CEM Discover) was used for this study for the advantages of using a closed vessel and for consistency between the experiments.[24] Microwave induced heating is sought to shorten the period of time required to form these monolayers. Microwave heating offers a number of other competitive advantages. Dielectric heating induced by microwave radiation causes a rapid increase in temperature within solids with a high dielectric loss value, such as doped silicon wafers. When the solid is immersed in a liquid, this process releases heat into solution from the surfaces of this solid. Heat can be released at the interface where silane-based SAMs are forming to provide the energy necessary to drive the condensation reaction. The dielectric heating of the polar silane molecules assists with this process, and will also contribute to an increased mass transfer of molecules to and from these interfaces.

The molecule of choice to demonstrate the microwave assisted formation of SAMs was 1H,1H,2H,2H-perfluorodecyldimethylcholorosilane (FDDCS). A perfluorinated backbone was chosen in part because it is more easily characterized by XPS than a hydrocarbon backbone.[16] To observe the impact of microwave radiation on the formation of FDDCS SAMs, samples were treated with microwave radiation for up to 10 min at a constant power of 300 W. Time increments of 1 min were investigated to evaluate the progressive change in surface coverage of SAMs with an increased duration of exposure to microwave radiation. The substrates were each left in a solvent containing the silane molecules for a total immersion time of 18 min. A consistent immersion time was used to evaluate the influence of microwave radiation on the formation of SAMs without being significantly influenced by variations in contact with the solution. After the microwave treatment and reaching 18 min of immersion in the solvent, Soxhlet extraction was performed to remove adsorbed molecules and contaminants from the surfaces as per previously described procedures.[16] Extraction was performed for 1 h to effectively rinse the surfaces and remove physisorbed molecules. The impact of microwave radiation on quality of these SAMs was explored by observing the relative change in hydrophobicity and hysteresis for water contact angle (WCA) measurements, as well as through atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) analysis of the surface topography and composition, respectively, of the monolayer modified surfaces.

The hydrophobicity of the perfluoroalkylsilane coated silicon oxide surfaces was probed using water contact angle (WCA) measurements. The hydroxyl terminated silicon oxide surfaces obtained following piranha cleaning of these substrates were hydrophilic. The WCA of these substrates was ~20 degrees. The formation of perfluoroalkylsilane-based SAMs would create surfaces coated with the fluorinated chain of FDDCS, and these surfaces would become hydrophobic. The higher the surface coverage of FDDCS, the more hydrophobic should be these surfaces. In other words, a higher WCA could suggest the formation of higher quality, more densely packed monolayers. As shown in Figure 1A, a significant increase in hydrophobicity was correlated with an increase in the length of time of exposure to microwave radiation. These results suggest the surface coverage of the SAMs increased in proportion to the length of time for dielectric heating. For example, the monolayers formed using a 30 mM solution of FDDCS in toluene with 6 min of exposure to microwave radiation reached a WCA of ~90 degrees, which is comparable to previous literature values for Soxhlet extracted surfaces of FDDCS SAMs.[16] The WCA values for this sample remained relatively constant at longer durations (i.e. 10 min) of microwave radiation, which could be attributed to a deminished number of surface reactive sites. The formation of SAMs at lower concentrations of the perfluoroalkylsilane resulted in significantly lower WCA values in comparison to those observed for the 30 mM solutions (Figure 1A). The trend associated with the progressive treatment by microwave radiation for each concentration of FDDCS in toluene further demonstrated that the WCA values increased in proportion to the duration of this treatment. These results suggest that microwave radiation can assist in the formation of monolayers with a high surface coverage of perfluoroalkylsilanes on silicon oxide surfaces.

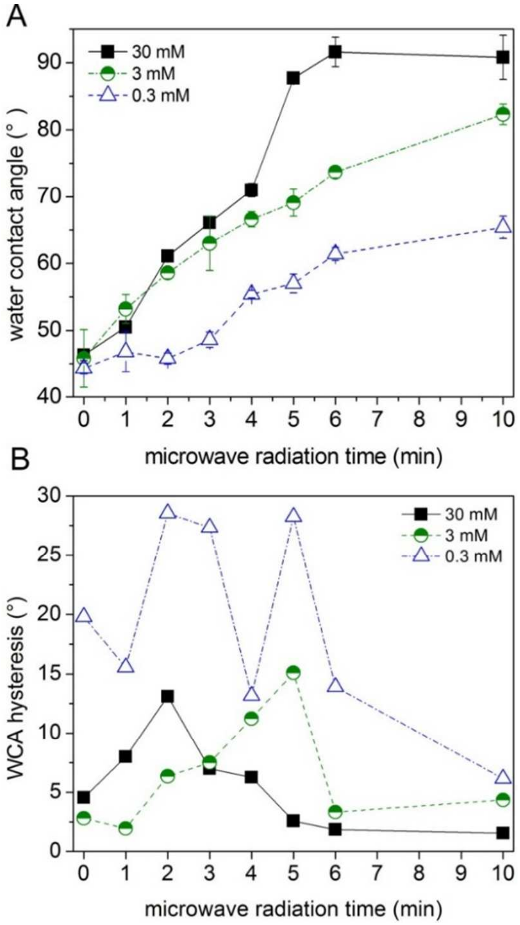


Figure 1. (A) Water contact angle (WCA) measurements of silicon oxide coated silicon substrates after immersion in a toluene solution of monoreactive perfluorinated silanes and treatment with microwave to form self-assembled monolayers (SAMs). Average advancing WCA measurements are plotted with an error bar of one standard deviation from three independent measurements. (B) Hysteresis in the WCA measurements, as determined by taking the difference between the average advancing WCA and the average receding WCA measurements.

Hysteresis of the WCA measurements was evaluated to gain further insight into the uniformity of the SAMs formed with the assistance of microwave radiation. A large hysteresis in the WCA measurements is indicative of a large variation in uniformity of the monolayers.[30] Hysteresis increased proportionally with an increased duration of microwave radiation between 0 and 2 min for samples immersed in a 30 mM solution of perfluoroalkylsilane (Figure 1B). Uniformity of the WCA initially decreases with longer microwave treatments, but a decrease in hysteresis and corresponding increase in quality of the SAMs was observed with an increase of microwave radiation from 2 to 6 min. The formation of these silane-based monolayers could be iniated by the assembly of FDDCS molecules into islands on the silicon oxide surfaces creating an initially non-uniform surface coverage. As more FDDCS molecules react with the surfaces, these molecules start to form a more uniform coating as indicated by the subsequent decrease in hysteresis with increasing length of exposure to microwave radiation. The sample treated with 10 min microwave radiation had a similar hysteresis to that treated with 6 min microwave radiation, indicating that both samples had SAMs of a comparable uniformity. For a 3 mM solution of FDDCS, the hysteresis progressively increased up to 5 min before decreasing at 6 min of microwave radiation. A longer duration of microwave radiation was required for this solution to form more uniform SAMs. The hysteresis of monolayers prepared from immersion in a 0.3 mM solution of FDDCS was significantly higher than that observed for the other samples. Monolayers were not uniformly formed at this low concentration of perfluoroalkylsilane. The WCA hysteresis measurements suggest there are non-uniformities in the surface density of covalently attached molecules, but this variation could also be attributed to adsorbed species present in each sample. Further analysis was required to discern the potential contributing factors to this variance in the uniformity of the FDDCS SAMs.

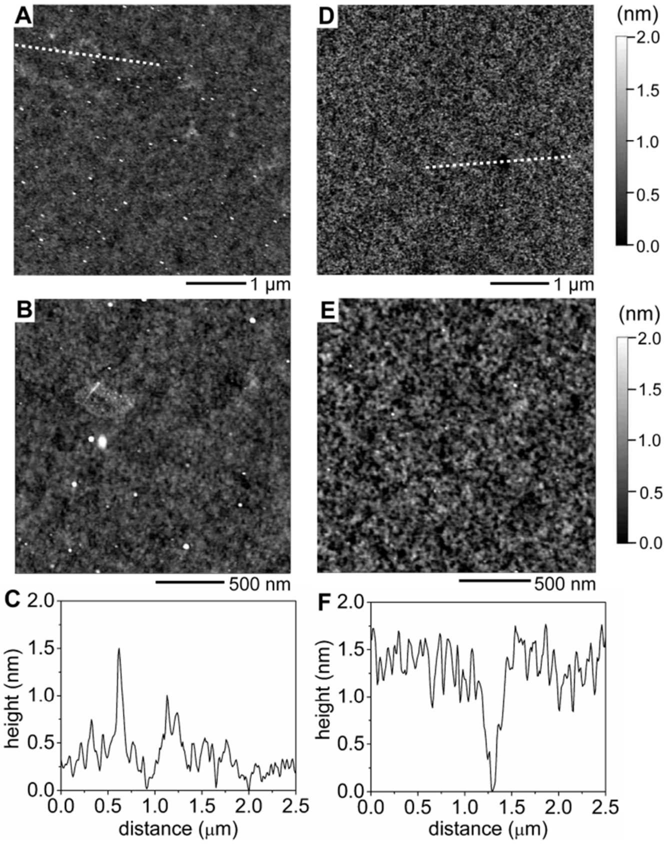


Figure 2. Atomic force microscopy (AFM) analysis of silicon oxide surfaces coated with SAMs formed by immersion in a toluene solution of 30 mM monoreactive perfluoroalkylsilanes and treated with microwave radiation for either 2 min (A–C) or 6 min (D–F). Cross-sectional profiles (C,F) correspond to the regions indicated by white dotted lines in the images (A,D). Tapping mode AFM imaging was performed with a scan speed of 0.5 Hz for scans of 5 µm by 5 µm (A,D) or 2 µm by 2 µm (B, E) with 512 by 512 resolution.

Atomic force microscopy measurements were used to analyze changes in the topography of silicon oxide surfaces when modified with SAMs prepared by microwave assisted processing. Although the WCA results indicated an increase in hydrophobicity of the silicon oxide surfaces when coated with the perfluoroalkylsilane molecules, further investigation was needed to determine the surface coverage of these molecules. The WCA measurements indicated that surface modifications with the highest uniformity and surface coverage of SAMs were achieved with 30 mM FDDCS in toluene and 6 min of treatment by microwave radiation. The solvent extracted samples were imaged by AFM. A comparison was made between monolayers prepared by either 2 or 6 min of microwave radiation while immersed in a 30 mM solution of perfluoroalkylsilane (Figure 2). These samples were chosen based on the significant differences in their WCA and hysteresis. It was anticipated that at 2 min of microwave radiation the sample would have a large variation in surface topography from the formation of islands of FDDCS molecules. Those samples treated with 6 min of microwave radiation should have a higher coverage of SAMs with fewer defects based on its significantly higher WCA and lower hysteresis. The AFM data showed a clear difference between these two types of samples. For the surfaces treated with 2 min of microwave radiation in the presence of 30 mM FDDCS in toluene, islands with heights of 1.1 ±0.1 nm were attributed to regions of densely packed monolayers. Those samples treated with 6 min of microwave radiation had a higher surface coverage of the FDDCS monolayers. An average height of 1.3 ± 0.2 nm was observed between the tallest features and the lowest recesses within these monolayers. Contributions to the errors in these measurements included tip-sample interactions and surface roughness (see ESI). Small defects observed in these SAMs could be attributed to blocked reactive sites or the existence of non-reactive surface sites. Height of the FDDCS monolayers at 6 min of microwave processing was proportional to the length of these perfluoroalkylsilane molecules (~1.34 nm).

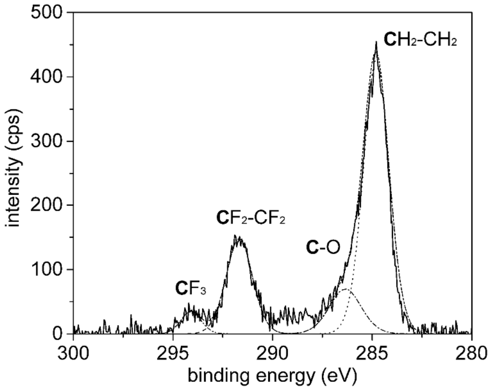


Figure 3. High resolution C_{1s} XPS spectrum for silicon oxide surfaces coated with monoreactive perfluoroalkylsilane SAMs. These monolayers were formed on substrates immersed in a toluene solution of 30 mM perfluoroaklylsilane and treated by microwave radiation for 6 min, followed by 1 h extraction with refluxing toluene.

An XPS study was performed on the sample treated with 6 min microwave in a 30 mM FDDCS solution in order to verify the elemental composition and the quality of the FDDCS. The XPS analysis detected the presence of F, Si, C, and O in this sample (see ESI). There were no detectable impurities from other elements. Surface coverage of FDDCS was further assessed by comparing the relative amount of F and Si detected in the sample. A ratio of 0.41 was obtained by integrating the areas for the F_{1s} to Si_{2p} peaks.[16] This value is comparable to previous literature on FDDCS based SAMs prepared from immersion in 1 mM FDDCS in toluene for 1 h at 80°C followed by Soxhlet extraction.[16] To gain further insight into the density of the SAMs formed by microwave processing, high resolution XPS analysis was performed on the C_{1s} region to assess the relative signals for $\mathbf{C}F_2$-CF_2 and $\mathbf{C}F_3$ (Figure 3).[16] A comparison of the ratio of the integrated areas for $\mathbf{C}F_2$-CF_2 and $\mathbf{C}F_3$, as determined by high resolution XPS analysis, was used to assess the packing density of the perfluoroalkylsilane molecules.[16, 31] Increased density of perfluoroalkylsilane molecules results in an increased CF_3 to CF_2 signal.[32] Samples treated with microwave radiation for 6 min had a ratio of 0.18 between the CF_3 peak area at 295.1 eV (integrated area = 45.1) and the CF_2-CF_2 peak area at 292.7 eV (integrated area = 249.2). This ratio is comparable to previous literature that reported values of 0.2 for high-quality SAMs of FDDCS.[16] Contributions to the errors in these measurements included surface roughness, peak fitting analysis, and measurement error. The XPS results suggested that FDDCS SAMs of a relatively high density can be formed with the assistance of microwave radiation within approximately one-tenth of the processing time reported in previous literature.[16]

In summary, microwave radiation was introduced as a technique to facilitate the formation of monoreactive perfluoroalkylsilane based SAMs on a thin film of silicon oxide coated onto a doped and polished silicon wafer. Microwave heating is an effective method to provide thermal energy to both the surfaces of this substrate and to a solution containing the monoreactive silane molecules. To study the effect of microwave radiation on the quality of the resulting SAMs, the duration of treatment by microwave radiation was varied by up to 10 min during formation of the monolayers. The WCA for surfaces coated with these SAMs demonstrated an increased hydrophobicity with an increase in the duration of microwave treatment. Furthermore, WCA hysteresis measurements revealed non-uniform coatings formed at relatively short durations of treatment with microwave radiation, while more uniform and dense coatings were formed upon treatment with longer durations of microwave radiation. The surface topography of the samples was studied by atomic force microscopy. Single molecule thick islands were observed in the samples treated by a relatively short duration of microwave radiation (2 min). A more uniform surface topography was observed for samples treated with a longer duration of microwave radiation (6 min). The XPS analysis validated the composition of these SAMs and further verified a relatively high density of molecules within the monolayers prepared by treatment with 6 min of microwave radiation. The use of microwave radiation to assist the formation of silane-based SAMs significantly improved the efficiency of this process in contrast to convective heating methods. The results presented in this study also demonstrate the use of microwave radiation as a simple and quick method to enhance the quality of silane-based SAMs on silicon oxide surfaces.

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Notes and references

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