

# Perfecting Imperfect “Monolayers”: Removal of Siloxane Multilayers by CO<sub>2</sub> Snow Treatment

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Self-assembled monolayers (SAMs) of *N*-(3-triethoxysilylpropyl)-4-hydroxybutyramide were prepared on silicon oxide on silicon (Si/SiO<sub>2</sub>). Initial silane adsorption and high-temperature annealing led to a stable base monolayer with many large over-lying islands of disordered multilayers as a result of the non-self-limited growth process. The disordered multilayers were hydrolyzed and subsequently removed by CO<sub>2</sub> snow treatment. The resulting films were one monolayer thick as measured by ellipsometry. Atomic force microscopy, attenuated total reflection Fourier transform infrared spectroscopy, and contact angle analysis showed that the films were composed of monolayers with full and uniform surface coverage rather than nonuniform coverage by islands or patches of multilayers. Monolayers of octadecyltrichlorosilane were also prepared by multilayer removal via CO<sub>2</sub> treatment, showing the general applicability of the technique toward siloxane SAMs. We believe that CO<sub>2</sub> is an excellent solvent for weakly bound and hydrolyzed molecules that compose multilayers, and this ability to prepare near-perfect monolayer films from imperfect ones allows for less stringent formation conditions.

## Introduction

Uniform self-assembled monolayers (SAMs) of trialkoxy- and trichlorosilanes are of great importance for their applications in microfabrication,<sup>1</sup> surface-confined reactions,<sup>2,3</sup> and the immobilization of macromolecules in lithographically defined patterns.<sup>4–7</sup> For applications such as layer-by-layer film formation<sup>8</sup> and topographical analysis of molecularly thin films, the presence of spurious multilayer islands is undesirable. Because silanization is highly sensitive to water content, temperature, concentration, and pH,<sup>9–14</sup> much research has been devoted toward finding optimal conditions for true silane monolayer formation<sup>13–19</sup> rather than multilayer island formation.<sup>20</sup> We report a strategy toward making near perfect

monolayer films from non-self-limited growth conditions. Imperfect siloxane films containing multilayer islands formed under sub-optimal conditions can be recovered through proper “cleaning”. We find that hydrolysis followed by CO<sub>2</sub> snow treatment is an excellent method for removing loosely bound siloxane islands.

The method is based on a previous report<sup>14</sup> in which undesired multilayers were hydrolyzed and removed by soaking for 24 h in water (to our knowledge, the only other reported post-formation “cleaning” method). The authors found that multilayers were more susceptible to hydrolysis than the initial siloxane layer because of greater cross-linking in the base layer. This is consistent with the observation that multilayers are less resilient to physical abrasion than monolayers<sup>8</sup> and exhibit decreasing order with increasing numbers of layers.<sup>8,14,21</sup> The procedure is schematically shown in Figure 1 for *N*-(3-triethoxysilylpropyl)-4-hydroxybutyramide (TEOS-HBA). Adsorbed and covalently bound multilayers sit atop a highly cross-linked base monolayer (Figure 1a). After hydrolyzing the disordered multilayer islands (Figure 1b), CO<sub>2</sub> snow treatment removes the remaining adsorbed and hydrolyzed molecules more effectively than common solvents (Figure 1c).

In CO<sub>2</sub> snow cleaning, CO<sub>2</sub> gas and “snow,” small dry ice and liquid CO<sub>2</sub> particles, are directed toward a surface.<sup>22</sup> The momentum transfer from the ice particles disrupts adsorbed surface particulates. Liquid CO<sub>2</sub> particles solvate small organics such as hydrocarbons and silicones<sup>23</sup> and capture them as the liquid CO<sub>2</sub> solidifies into dry ice. The high-velocity gas stream then removes the particulates and the captured organics. However, CO<sub>2</sub> snow has been shown not to damage siloxane SAMs.<sup>24</sup>

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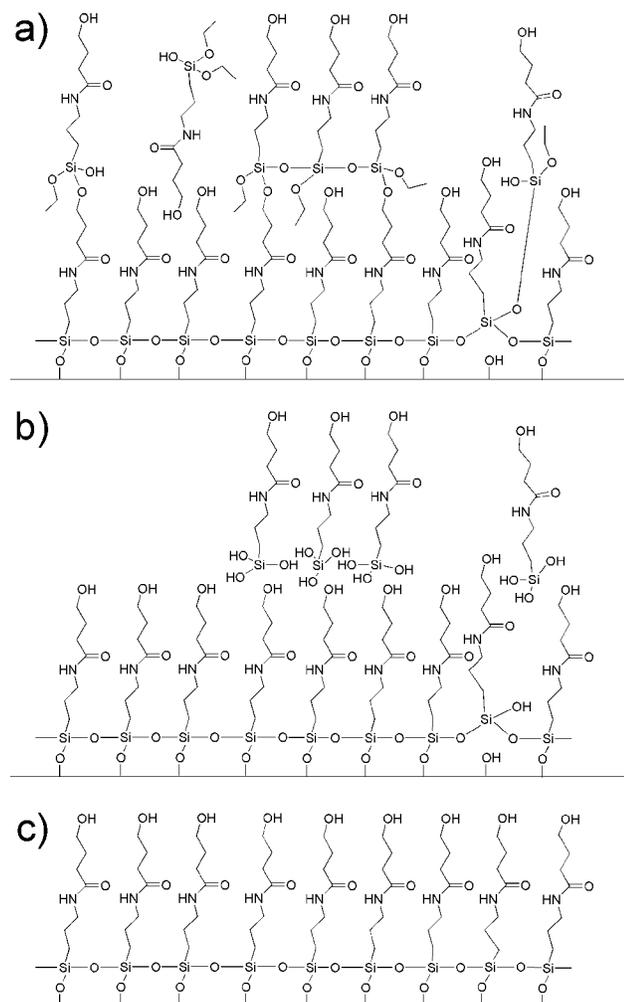
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**Figure 1.** Scheme of TEOS-HBA siloxane multilayer removal by CO<sub>2</sub> treatment. The underlying base layer is highly cross-linked after annealing. (a) Multilayers form by adsorption, alkyl chain intercalation, and covalent bonds (Si–O–Si or Si–O–C) with various degrees of cross-linking. (b) Adsorbed, intercalated, and poorly cross-linked siloxanes/silanes are hydrolyzed and partially removed by soaking in distilled water. (c) CO<sub>2</sub> efficiently removes all remaining hydrolyzed silane molecules.

Given that it would not destroy highly cross-linked monolayers despite its effectiveness in removing adsorbed siloxanes, we presumed that CO<sub>2</sub> would be an excellent solvent for multilayers composed of loosely bound and hydrolyzed silane molecules.

CO<sub>2</sub> snow cleaning was utilized for the preparation of two different siloxane SAMs. Hydroxyl-terminated siloxane monolayers were prepared for their utility in oligonucleotide chips.<sup>25</sup> Preparing true monolayers of hydroxyl-terminated molecules is particularly difficult because they are thermodynamically more likely to form multilayers by bond formation between the hydroxyl terminus and another silanol ( $\Delta H_{\text{Si-OH}} \approx 0$  kcal/mol) than amine- ( $\Delta H_{\text{Si-N}} = 9.4$  kcal/mol) and thiol-terminated ( $\Delta H_{\text{Si-S}} = 18.5$  kcal/mol) silane molecules, where  $\Delta H$  is the enthalpy of formation with respect to the silanol intermediate, Si–OH. Hydroxyl-terminated “monolayers” reported in the literature likely contain multilayers but are conceptualized as monolayers for simplicity.<sup>25</sup> In our attempts to synthesize oligonucleotide arrays on silicon using standard

literature silanization procedures,<sup>26,27</sup> poor siloxane films containing multilayers were typically obtained. To show the general applicability of CO<sub>2</sub> snow cleaning of siloxane SAMs, octadecyltrichlorosilane (OTS) monolayers were also prepared. Although they do not contain reactive terminal groups, self-limited OTS monolayers are still difficult to prepare due to varying amounts of water in the preparation environment.<sup>15</sup>

### Experimental Section

**Substrate Preparation.** The hydroxyl-terminated SAMs were prepared as follows. Silicon wafers ((100), n-type, WaferNet) were piranha-cleaned and oven-dried at 200 °C. All reagents were used as received but handled in Teflon containers (Savillex) and dispensed with new polystyrene syringes so that the silanization was not affected by the history of the surface, because glassware can be modified by silanes.<sup>14</sup> Substrates were soaked for 1 h in 0.5% (v/v) TEOS-HBA (Oakwood Chemicals) with 0.05% (v/v) triethylamine catalyst<sup>28</sup> (Aldrich) in anhydrous toluene (Aldrich) under N<sub>2</sub>. The substrates were then briefly soaked in denatured alcohol (S.D.A. 3-A, Ricca Chemical), dried under N<sub>2</sub> (40 psi), and annealed for 18 h in air at 200 °C. After slowly cooling to room temperature, multilayers were hydrolyzed by soaking for 18 h in deionized water (dH<sub>2</sub>O; Millipore, 18.2 MΩ·cm) and dried under N<sub>2</sub>. The substrates were then treated with CO<sub>2</sub> snow (Applied Surface Technologies) for 5 s at ≈75° and 7.5–10 cm distance. This treatment further aided in the removal of the destabilized siloxane multilayers. Residual ice (CO<sub>2</sub> and H<sub>2</sub>O) was removed by washing with 2-propanol and drying under N<sub>2</sub>.

**Substrate Analysis.** Samples were analyzed by ellipsometry, water contact angle measurements, attenuated internal reflection Fourier transform infrared (ATR-FTIR) spectroscopy, and atomic force microscopy (AFM). Specific details can be found in Supporting Information.

### Results and Discussion

Ellipsometry measurements showed that TEOS-HBA films were  $0.9 \pm 0.1$  nm thick, which is approximately the expected value for a fully extended chain with an assumed 30° tilt based on experimental<sup>29</sup> and simulation<sup>30</sup> data on similar silane compounds. Consistent ellipsometry values prior to CO<sub>2</sub> treatment were not attainable due to varying degrees of multilayer formation. Because ellipsometry measurements are average measurements over large areas, the post-CO<sub>2</sub> measured film thickness could have resulted from a monolayer with complete surface coverage or patches of multilayers with nonuniform surface coverage. As can be seen by the AFM image in Figure 2b, these films were indeed composed of monolayers with complete and uniform surface coverage (root-mean-square (RMS) roughness = 0.179 nm,  $1 \times 1 \mu\text{m}$ ), rather than large multilayer islands. Considering their sparse coverage, small size, and thickness, multilayers negligibly contribute to the ellipsometric film thickness. The effectiveness of the CO<sub>2</sub> treatment can be seen in the pre- and post-treatment AFM images in Figure 2. Prior to CO<sub>2</sub> treatment, the islands are more numerous and thicker (evident by the white haze indicative of high multilayer density) than after hydrolysis and CO<sub>2</sub> treatment. The largest feature observed in the pretreated scan (Figure 2a) was roughly 10 additional layers thick, and most islands had

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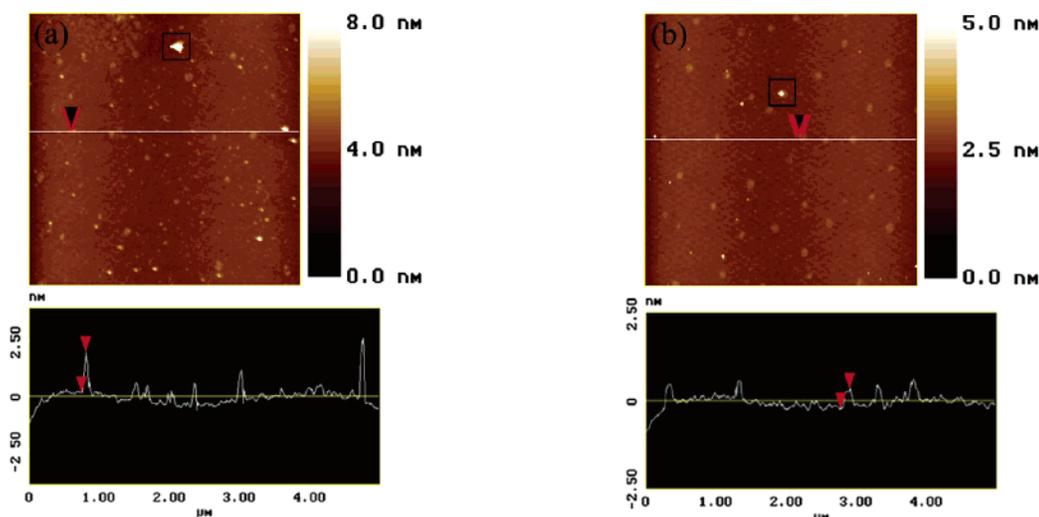
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**Figure 2.** Tapping-mode AFM images of TEOS-HBA. (a) Film before CO<sub>2</sub> treatment. The island featured in the box measured roughly 10 additional layers thick. The majority of the multilayers are one or more additional layers thick. (b) Film after CO<sub>2</sub> treatment. The ellipsometric film thickness was  $0.9 \pm 0.1$  nm, and the RMS roughness was 0.179 nm. The multilayer featured in the line-section analysis measured 0.557 nm in height. Nearly all islands were less than one additional layer thick. The largest island, featured in the box, measured four additional layers thick.

one or more additional layers, whereas the additional multilayers post-CO<sub>2</sub> treatment (Figure 2b) were of submonolayer thickness (0.5–0.6 nm). The largest remaining post-CO<sub>2</sub> multilayer island had four additional layers (featured in the box in Figure 2b). Interestingly, the surviving multilayer islands were often semi-regular, suggesting that they may have formed by a diffusion-limited aggregation mechanism.<sup>31</sup> Because partially polymerized multilayers are easily hydrolyzed,<sup>14</sup> the resistance to hydrolysis likely indicates that the remaining multilayers were highly polymerized.

In Figure 2a, the pretreated image is “average” in its “dirtiness”, showing ~85% perfect monolayer coverage (areas with less/more multilayers were observable on the substrate). However, the post-treatment image (Figure 2b) showing ~97% perfect monolayer coverage is a typical image seen across the entire substrate area (~4 cm<sup>2</sup>). Because of the varying levels of multilayer coverage in pretreated samples, reporting a percentage improvement is not particularly informative. However, the quality of the post-clean sample is repeatable so long as the sample has a uniform base layer. Given the uniformity over the entire substrate area, this technique should be scalable to very large sizes suitable for wafer level processing.

The TEOS-HBA films yielded advancing water contact angle measurements of  $\theta_a = 34 \pm 1^\circ$  after CO<sub>2</sub> treatment and, thus, presented a more ordered and less contaminated hydroxyl surface than the multilayer films obtained prior to CO<sub>2</sub> treatment ( $\theta_a \approx 50^\circ$ ). The ATR-FTIR spectrum (Supporting Information) showed that the amide I peak in the monolayer is red-shifted from the peak in chloroform (1648 from 1656 cm<sup>-1</sup>), indicating a small degree of hydrogen-bonding within the monolayer. Although the hydrogen bonding effects within the monolayer were not as large as those observed in similar amide-containing thiols on gold substrates,<sup>32</sup> siloxane monolayers do not exhibit the same degree of long-range molecular order as alkylthiol monolayers on gold substrates.<sup>10</sup>

To prove the general applicability of perfecting imperfect monolayers by CO<sub>2</sub> treatment, OTS films were also

treated. The monolayers were prepared similarly to TEOS-HBA but soaked without the catalyst, annealed at room temperature to prevent high temperature induced disorder,<sup>33</sup> and washed with anhydrous toluene (Supporting Information). The resulting post-CO<sub>2</sub> treatment ellipsometric thickness, advancing contact angle, and contact angle hysteresis ( $\Delta\theta = \theta_a - \theta_r$ , where  $\theta_r$  = receding contact angle) were  $2.5 \pm 0.1$  nm,  $110 \pm 2^\circ$ , and  $6 \pm 3^\circ$ , respectively, which were consistent with the expected values for good OTS monolayers.<sup>15</sup> While the thickness and advancing contact angle differ only slightly from the pretreatment values ( $2.4 \pm 0.3$  nm,  $\theta_a = 109 \pm 3^\circ$ ), the contact angle hysteresis improved from  $\Delta\theta_{N_2(40PSI)} = 11 \pm 4^\circ$  to  $\Delta\theta_{CO_2} = 6 \pm 3^\circ$ . Contact angle hysteresis is a telling measure of roughness and inhomogeneities, where small values are indicative of homogeneous surfaces with low contamination levels.<sup>20</sup> The small but measurable hysteresis change with CO<sub>2</sub> cleaning would indicate a decrease in surface inhomogeneities and contamination. The AFM images in Figure 3 more clearly show that CO<sub>2</sub> treatment yielded near-perfect films (RMS roughness = 0.157 nm,  $1 \times 1 \mu\text{m}$ ) from initially imperfect ones. Interestingly, the multilayers in Figure 3b also appeared to have formed by diffusion-limited aggregation. As stated previously, varying levels of multilayer coverage in pretreated samples (~94% in Figure 3a) make it difficult to report percent improvements, but the near 100% uniformity post-treatment is repeatable.

The increased cleanliness of the OTS monolayer over the TEOS-HBA monolayer sample reflects the differences in multilayer formation. TEOS-HBA and OTS can form multilayers by random adsorption of individual silane molecules and polymers formed in solution, alkyl chain intercalation,<sup>34,35</sup> or covalent Si–O–Si bonds, but only TEOS-HBA can form covalent Si–O–C bonds. While multilayers typically show decreasing order with an increasing numbers of layers,<sup>8,14,21</sup> very stable multilayers that exhibit high siloxane cross-linking have also been

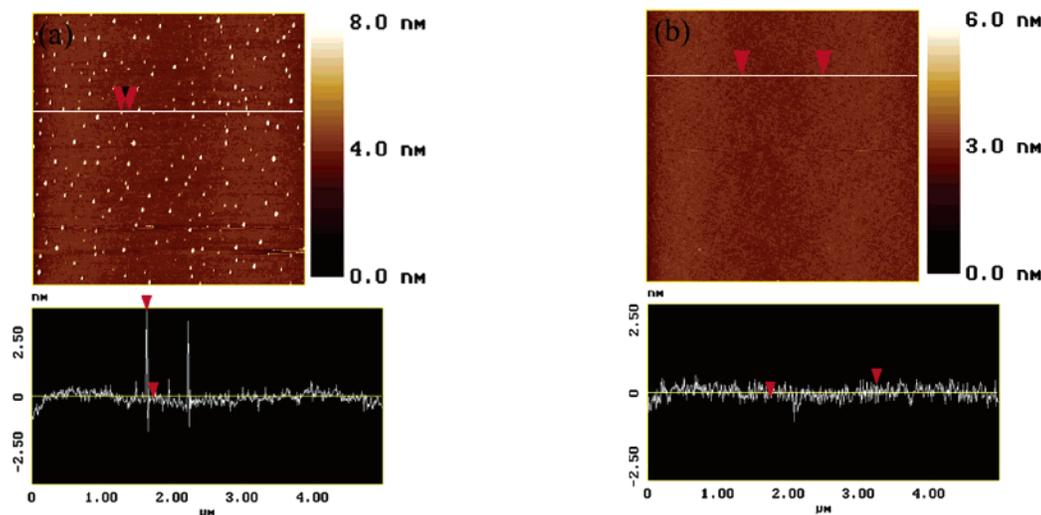
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**Figure 3.** Tapping-mode AFM images of OTS. (a) Film before CO<sub>2</sub> treatment. Multilayer islands appear to have formed by diffusion-limited aggregation. The largest island in the scan area measured five to six additional layers thick. The majority of the multilayers are one or more additional layers thick. (b) Film after CO<sub>2</sub> treatment. The ellipsometric film thickness was  $2.5 \pm 0.1$  nm, and the RMS roughness was 0.157 nm.

reported in the literature.<sup>8,36,37</sup> Therefore, it is likely that only highly polymerized patches with very few extra layers could withstand the aggressive hydrolysis step followed by the semi-abrasive CO<sub>2</sub> treatment. The effectiveness of CO<sub>2</sub> treatment on loosely bound and hydrolyzable Si–O–Si bonds in OTS multilayers reinforces the notion that the post-treatment multilayers in TEOS-HBA resisted hydrolysis because of a high degree of polymerization.

To summarize the formation and cleaning process, silane adsorption and annealing first leave a uniform underlying base layer that is highly cross-linked. Multilayers form either by adsorption or covalent bonding by diffusion-limited aggregation. Some of the multilayer molecules are partially volatilized by the high-temperature annealing process. Soaking in dH<sub>2</sub>O removes most of the remaining adsorbed and intercalated molecules and also hydrolyzes the poorly cross-linked, covalently bound multilayer islands. The CO<sub>2</sub> treatment removes nearly all the remaining molecules more effectively than common solvents. The few remaining multilayers are highly cross-linked, as evident by their resistance to hydrolysis. It should be noted that even though this letter reports the ability to clean imperfect monolayers, efforts were still made to prevent multilayer growth. For example, the aggressive hydrolysis by soaking in dH<sub>2</sub>O for 18 h is not an absolute requirement but rather is performed to show improvements from literature-reported cleaning by hydrolysis.<sup>14</sup> Similar results can be obtained with CO<sub>2</sub> snow cleaning after shorter soaking times, and in some cases, hydrolysis by exposure to air during sample preparation is sufficient.

At this time, it is unknown whether the interaction between ambient water molecules and CO<sub>2</sub> leads to any acid-catalyzed siloxane bond breakage, but previous reports on silanization of silica surfaces using supercritical CO<sub>2</sub> (scCO<sub>2</sub>) as the solvent<sup>38</sup> would indicate that the acid catalysis is negligible. However, the solid/liquid CO<sub>2</sub> snow plays an active role in removing the already hydrolyzed multilayers. Washing and drying OTS samples with N<sub>2</sub> (160 psi) at nearly twice the pressure of the CO<sub>2</sub> treatment

was not as effective as CO<sub>2</sub> treatment, as determined by AFM analysis and contact angle measurements ( $\Delta\theta_{N_2(160PSI)} = 10 \pm 3^\circ$ ,  $\Delta\theta_{CO_2} = 6 \pm 3^\circ$ ). This indicates that the cleaning action of the CO<sub>2</sub> treatment was not the result of high-pressure gas flow alone.

An interesting possibility for future research is the use of supercritical fluids (SCFs) in place of the CO<sub>2</sub> snow. Even though delivering a SCF is more difficult than creating a CO<sub>2</sub> snow, SCFs could potentially be more effective than the snow treatment, as scCO<sub>2</sub> is known to be capable of solvating ions and heavy organics such as photoresist<sup>39,40</sup> and has been reported as yielding higher silanization densities on silica than films deposited in traditional solvents such as toluene.<sup>38,40,41</sup>

### Summary

Given the difficulty in preparing perfect self-limited siloxane monolayers, we have demonstrated an alternative strategy toward monolayer preparation by removing multilayer defects via CO<sub>2</sub> treatment. The technique proved more effective than traditional solvents in removing weakly bound molecules, perhaps because of the high momentum transfer and unique capture/solvation mechanism of the treatment. The ability to clean monolayers of OTS shows the general applicability of the process, making CO<sub>2</sub> treatment a promising route toward preparing perfect monolayers from imperfect films.

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**Supporting Information Available:** Substrate analysis details, ATR-FTIR and FTIR spectra, and the preparation of OTS monolayers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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