

# Photoreactivity of Alkylsiloxane Self-Assembled Monolayers on Silicon Oxide Surfaces

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We have combined contact angle measurements, Fourier transform infrared spectroscopy (FT-IR), and atomic force microscopy (AFM) to investigate the UV photoreactivity of octadecylsiloxane (ODS) SAMs (self-assembled monolayers) in air. Contact angle measurements present evidence that ozone is not the active agent in alkylsiloxane SAM degradation under UV illumination in air. A combination of UV and oxygen is necessary for monolayer degradation to proceed. AFM measurements on submonolayer coverage SAMs provide direct evidence of the photodegradation of ODS SAMs and reveal the role of defects in the degradation process. FT-IR and AFM results suggest that the hydrocarbon chain is the reactive site of the monolayers. A microscopic mechanism of the photoreactivity involving hydrogen abstraction is suggested based on the mechanism of gas-phase oxidation of alkanes. Our results have implications in clarifying the contribution from the reactivity of alkyl chains during the photomodification of SAMs. This clarification may provide insight into optimization of the SAM photopatterning processes.

## Introduction

Pioneered by Zisman in the 1940s,<sup>1</sup> self-assembled monolayers (SAMs) have found applications in many important fields such as wettability,<sup>2</sup> corrosion protection,<sup>3</sup> chromatography,<sup>4</sup> and molecular electronics.<sup>5</sup> Alkylsiloxane SAMs<sup>6</sup> and alkanethiol SAMs<sup>7</sup> have emerged as the two types of most widely studied SAMs. Both SAMs share similarity in the close packing of hydrocarbon chains on surfaces.<sup>8,9</sup> While much attention has been paid to the preparation of the SAMs,<sup>10</sup> significantly fewer studies have been devoted to the reactivity of SAMs. Many SAMs are known to degrade under UV (ultraviolet) irradiation or even under ambient storage conditions.<sup>11</sup> Knowledge of SAM photoreactivity may help to design and prepare more stable SAMs for technological applications. An understanding of the mechanism may also help to optimize photoresist micropatterning processes involving SAMs.<sup>12–14</sup> In addition, SAM photoreactivity may provide a convenient route to attach functional groups to SAMs, enabling one to tailor wettability, adhesion, and electrical properties of the monolayers.

The photostability of alkanethiol SAMs on noble metals has been an issue of some controversy. Alkanethiol is

known to degrade under UV irradiation in air. A number of recent studies have attributed the primary degradation pathway of alkanethiol SAMs under low UV intensity ( $\mu\text{W}/\text{cm}^2$  to  $\text{mW}/\text{cm}^2$ ) to ozonolysis.<sup>15–19</sup> In this mechanism, it is suggested that photogenerated ozone and/or its decomposition products attack the thiolate headgroups to produce solvent-labile species and cleavage of the C–S bond. Scanning tunneling microscopy (STM) experiments suggest a defect-mediated pathway, the degradation occurring principally at domain boundaries.<sup>19</sup> Most UV photopatterning experiments on thiol SAMs involve masks that are in direct contact with the SAMs.<sup>12</sup> Ozone presumably cannot diffuse to the masked area to oxidize the thiol molecules therein. However, UV photopatterning of alkanethiol SAMs without the direct contact mask is reported to have submicrometer spatial resolution.<sup>14</sup> If ozone is solely responsible for the oxidation of thiol monolayers during photopatterning, it remains to be understood how the ozone reactivity can be spatially confined to micrometer size regions on the surface. A hot electron mediated mechanism was proposed to explain the spatial localization.<sup>20</sup> Hot electrons generated by UV excitation of metal surfaces can cause direct desorption of hydrocarbon or creation of  $\text{O}_2^-$ , which can oxidize thiolate group. However, this mechanism was contradicted by the experiments of Bohn et al.<sup>17</sup>

These interesting results prompted our investigation of photoinduced processes in another popular SAM, alkylsiloxane, that is important in the chemistry of  $\text{SiO}_2$  interfaces and applications thereof. The initial stage of the alkylsiloxane SAMs with ground-state atomic oxygen  $\text{O}(^3\text{P})$  has been investigated by Naaman et al. and shown to involve mainly hydrogen abstraction.<sup>21–23</sup> Moon et al. compared the ozone reactivity of alkylsiloxane in a vacuum

(1) Biglow, W.; Pickett, D.; Zisman, W. *J. Colloid Interface Sci.* **1946**, *1*, 513–538.

(2) Zisman, W.; Adam, N. K.; Good, R. J. *Contact Angle, Wettability and Adhesion*; American Chemical Society: Washington, DC, 1964.

(3) Laibinis, P. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 9022–9028.

(4) Wirth, M. J.; Fairbank, R. W. P.; Fatunmbi, H. O. *Science* **1997**, *275*, 44–47.

(5) Collet, J.; Bonnier, M.; Bouloussa, O.; Rondelez, F.; Vuillaume, D. *Microelectron. Eng.* **1997**, *36*, 119–122.

(6) Sagiv, J. *J. Am. Chem. Soc.* **1980**, *102*, 92–98.

(7) Nuzzo, R.; Allara, D. *J. Am. Chem. Soc.* **1983**, *105*, 4481–4483.

(8) Allara, D. L.; Parikh, A. N.; Rondelez, F. *Langmuir* **1995**, *11*, 2357–2360.

(9) Parikh, A. N.; Allara, D. L. *J. Chem. Phys.* **1992**, *96*, 927–945.

(10) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533–1554.

(11) Schoenfish, M. H.; Pemberton, J. E. *J. Am. Chem. Soc.* **1998**, *120*, 4502–4513.

(12) Tarlov, M. J.; Burgess, D. R. F.; Gillen, G. *J. Am. Chem. Soc.* **1993**, *115*, 5305–5306.

(13) Huang, J. Y.; Dahlgren, D. A.; Hemminger, J. C. *Langmuir* **1994**, *10*, 626–628.

(14) Behm, J. M.; Lykke, K. R.; Pellin, M. J.; Hemminger, J. C. *Langmuir* **1996**, *12*, 2121–2124.

(15) Ferris, M. M.; Rowlen, K. L. *Appl. Spectrosc.* **2000**, *54*, 664–668.

(16) Lewis, M.; Tarlov, M.; Carron, K. *J. Am. Chem. Soc.* **1995**, *117*, 9574–9575.

(17) Zhang, Y. M.; Terrill, R. H.; Tanzer, T. A.; Bohn, P. W. *J. Am. Chem. Soc.* **1998**, *120*, 2654–2655.

(18) Norrod, K. L.; Rowlen, K. L. *J. Am. Chem. Soc.* **1998**, *120*, 2656–2657.

(19) Poirier, G. E.; Herne, T. M.; Miller, C. C.; Tarlov, M. J. *J. Am. Chem. Soc.* **1999**, *121*, 9703–9711.

(20) Huang, J. Y.; Hemminger, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 3342–3343.

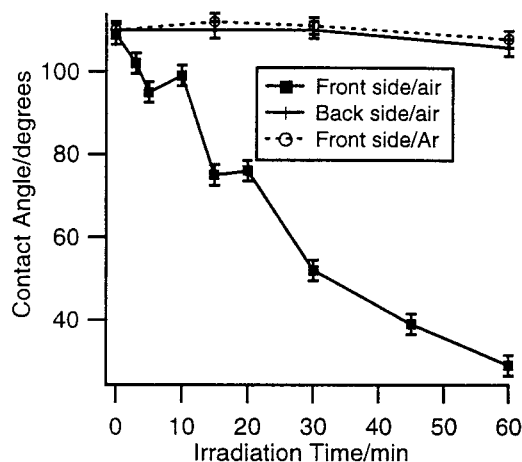
with and without UV irradiation using X-ray photoelectron spectroscopy.<sup>24</sup> It was suggested that the UV dissociates ozone into atomic oxygen, which is responsible for the degradation. However the reactive sites, the resulting nanoscale morphology, and the reaction mechanism of the photodegradation process remained unclear. Our investigations have combined contact angle measurement, Fourier transform infrared spectroscopy (FT-IR), and atomic force microscopy (AFM) to study the UV degradation of alkylsiloxane SAMs in air. Contact angle measurements present evidence that ozone is not the active agent in alkylsiloxane SAM degradation under UV illumination in air. A combination of UV and oxygen is necessary for monolayer degradation to proceed. AFM measurements on submonolayer coverage SAMs provide direct evidence of the degradation of ODS SAMs and reveal the role of defects in the degradation process. FT-IR and AFM results suggest that the hydrocarbon chain is the reactive site of the monolayers. A microscopic mechanism of the degradation involving hydrogen abstraction is suggested based on the mechanism of gas-phase oxidation of alkanes. Our results have implications in clarifying the contribution from the reactivity of alkyl chains during the photomodification of SAMs that may well be more general than the case of alkylsiloxane investigated here. This clarification may provide insight into optimization of the SAM photopatterning processes.

### Experimental Section

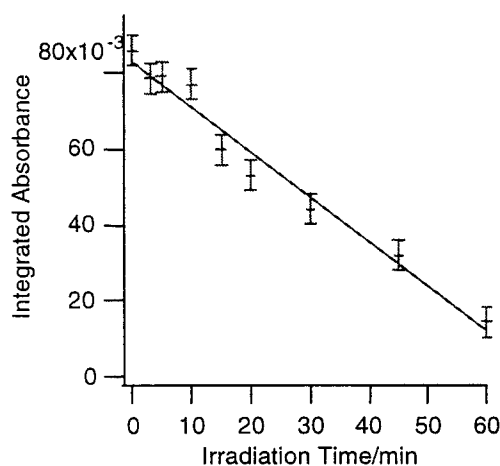
ODS monolayers were prepared on microscope glass slides (Fisher Scientific) and oxidized Si(100) wafers (n-doped, 50  $\mu\text{m}$  epitaxial layer, 13–16  $\Omega/\text{cm}$ , Wacker) by immersion in millimoles per liter octadecyltrichlorosilane solutions prepared in mixtures of hexadecane,  $\text{HCCl}_3$ , and  $\text{CCl}_4$ .<sup>6,25,26</sup> The silane molecules are believed to undergo hydrolysis to form siloxane and cross-link on the hydrophilic oxide surfaces. Subsequently siloxane head-groups covalently bond to the substrate Si–O groups. The structure and degree of completeness of the monolayers were controlled via the temperature and immersion times. For example, islands of ordered high-density SAMs were made using short reaction times <1 min at 10  $^\circ\text{C}$ .<sup>26</sup> The samples were irradiated in a homemade UV chamber with a low-pressure Hg/Ar lamp (Oriental Instruments) with total intensity of 2  $\text{mW}/\text{cm}^2$  at a working distance of 3 cm. The primary wavelength of the lamp is 254 nm. It is believed that the UV light at 185 nm, albeit constituting 1% of total intensity, is responsible for the ozone generation.<sup>18</sup> AFM images were acquired with a Digital Instrument Dimension 3100 AFM system in tapping mode. The system includes an integrated optical microscope and translation stage, allowing accurate repositioning of the sample.

### Results and Discussion

The water contact angle as a function of irradiation time, shown in Figure 1, decreased with increasing UV irradiation in air, indicating that the initially hydrophobic monolayer became increasingly hydrophilic under UV irradiation. The increasing hydrophilicity suggests conversion of the alkyl chain to hydrophilic groups, e.g., OH or aldehyde, or increasing coverage of the hydrophilic substrate due to the etching of the monolayer during the



**Figure 1.** Water contact angle vs time of UV irradiation of ODS SAM on glass.



**Figure 2.** Integrated FT-IR  $\text{CH}_2$  asymmetric mode absorbance ( $2920 \text{ cm}^{-1}$ ) as a function of UV irradiation time of ODS SAM on glass.

UV irradiation. When the UV irradiation chamber was flushed with argon, there was little change in contact angle after irradiation. Remarkably, the side of the slides facing away from the irradiation source showed very low reactivity. As the glass slides are opaque to UV wavelengths below 300 nm, this result suggests that UV and  $\text{O}_2$  are both necessary for the reaction to proceed. In agreement with Moon et al.,<sup>24</sup> we found ozone was not the active reagent in our system. The lifetime of ozone is sufficient to maintain a roughly uniform concentration across the UV chamber.<sup>27</sup> If ozone is the active reagent, the different kinetics displayed by the two sides of the slide cannot be explained. Our results suggest that UV-generated short-lifetime oxygen-containing radicals, unable to reach the backside of the sample, are responsible for the monolayer degradation.

The FT-IR spectra of the monolayer on glass were similar to those at full monolayer coverage in the literature.<sup>28,29</sup> Integrated absorbance FT-IR as a function of time in Figure 2 shows a nearly complete reduction of the absorbance of the asymmetric  $\text{CH}_2$  stretch mode at  $2920 \text{ cm}^{-1}$  after 1 h of UV irradiation in air. The reduction

(21) Paz, Y.; Trakhtenberg, S.; Naaman, R. *J. Phys. Chem.* **1992**, *96*, 10964–10967.

(22) Paz, Y.; Trakhtenberg, S.; Naaman, R. *J. Am. Chem. Soc.* **1994**, *116*, 10344–10345.

(23) Paz, Y.; Trakhtenberg, S.; Naaman, R. *J. Phys. Chem.* **1994**, *98*, 13517–13523.

(24) Moon, D. W.; Kurokawa, A.; Ichimura, S.; Lee, H. W.; Jeon, I. C. *J. Vac. Sci. Technol., A* **1999**, *17*, 150–154.

(25) Brzoska, J. B.; Shahidzadeh, N.; Rondelez, F. *Nature* **1992**, *360*, 719–721.

(26) Carraro, C.; Yauw, O. W.; Sung, M. M.; Maboudian, R. *J. Phys. Chem. B* **1998**, *102*, 4441–4445.

(27) Zhukov, V.; Popova, I.; Yates, J. T., Jr. *J. Vac. Sci. Technol., A* **2000**, *18*, 992–994.

(28) Parikh, A. N.; Allara, D. L.; Azouz, I. B.; Rondelez, F. *J. Phys. Chem.* **1994**, *98*, 7577–7590.

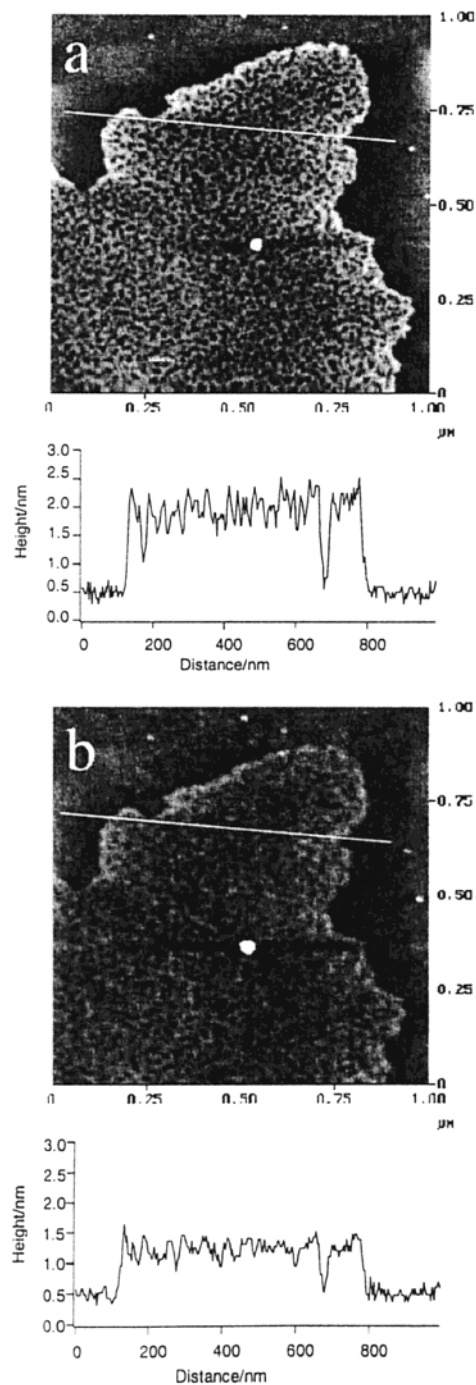
(29) Flinn, D. H.; Guzonas, D. A.; Yoon, R. H. *Colloid Surf., A* **1994**, *87*, 163–176.

in absorbance suggests removal of hydrocarbon from the surface. The decay of the  $\text{CH}_2$  asymmetric mode absorbance displays roughly zero-order kinetics, indicating that the rate of degradation does not depend on the concentration of  $\text{CH}_2$  group. This result stands in contrast with previous studies of alkanethiol monolayers, which display a decrease of  $\text{CH}_2$  decay rate as the oxidation proceeds.<sup>18</sup> The FT-IR result suggests that the cross section for the reaction remains the same during the degradation.

To further investigate the mechanism of photoreactivity and the possible role of defect sites in alkylsiloxane photooxidation, the evolution of the SAM morphology was tracked by tapping mode AFM. Submonolayer coverage octadecylsiloxane (ODS) SAMs were prepared on Si wafers covered with native oxide. It was convenient to study substrates partially covered with high-density SAM islands. This made morphological changes easier to follow as well as facilitating accurate repositioning of samples after ex situ irradiation. In fact no morphological changes could be detected on substrates covered by full monolayers. Interestingly, our AFM results in Figure 3 indicate that defect sites do not appear to nucleate the degradation of ODS SAMs. Thus, defects do not play an important role in this surface process. On the contrary, we see a uniform reduction in the height of monolayer ODS islands from 1.7 to 0.8 nm after 15 min of UV/ozone exposure. The shape of the islands remains remarkably uniform, suggesting that the island perimeter does not display enhanced reactivity. There is little evidence for growth of the pinholes found within these islands. The cross sectional AFM segment shows, as an example, that a defect observed in the cross section in Figure 3a did not widen during irradiation within the limit of AFM resolution (10–20 nm). The defects do not appear to be sites of enhanced reactivity.

Our results stand in contrast to the degradation mode of alkanethiol SAMs, revealed by STM experiments, which suggest the nucleation role of defects.<sup>19</sup> The contrasting roles of defects in alkanethiol/Au and alkylsiloxane/ $\text{SiO}_2$  provide insight into the reactive site of the SAM degradation. The thiolate headgroups of alkanethiol are known to be reactive.<sup>20</sup> It is difficult for the reactive species to penetrate the densely packed alkyl chains of a full monolayer to reach the thiolate groups. The impinging reactive species can easily access the thiolate group from defect sites in the monolayer. By contrast, the siloxane headgroups in the ODS SAM do not appear to be the reactive site judging from the lack of growth of defect sites in the monolayer. Both AFM and FT-IR results point to a microscopic reaction pathway that involves the reactivity of hydrocarbon chains instead of headgroups. The hydrocarbon chains are gradually shortened during photooxidation. This also explains why morphological changes in full monolayers could not be observed. UV irradiation reduces the SAM thickness, but AFM can only detect this change if there are regions of bare substrate from which SAM height can be determined. Because of the lack of reactivity of the headgroups, the coverage of SAM domain remains unchanged throughout the reaction, resulting in the constant decay rate of  $\text{CH}_2$  groups deduced from FT-IR (Figure 2).

In summary, our studies reveal a stark contrast between the photooxidation mechanism of alkylsiloxane SAMs and that reported for alkanethiol SAMs. Our results suggest that the hydrocarbon chains are the reactive sites of alkylsiloxane SAMs, whereas the thiolate headgroups are reported to be the vulnerable groups in alkanethiol SAMs under UV irradiation. Unlike UV degradation of alkanethiol SAMs, ozone is not the reactive species in



**Figure 3.** (a) AFM image (1000 nm  $\times$  1000 nm) and cross section of ODS SAM on  $\text{SiO}_2/\text{Si}$  surface with no UV irradiation SAM island height =  $1.7 \pm 0.2$  nm. (b) AFM image (1000 nm  $\times$  1000 nm) and cross section of ODS SAM on  $\text{SiO}_2/\text{Si}$  surface with 15 min of UV irradiation SAM island height =  $0.8 \pm 0.2$  nm.

alkylsiloxane degradation. The difference stems from the difference in chemical reactivities in the two different systems. The terminal thiolate group, with its lone pairs, can be oxidized without cleavage of other bonds. In fact, gas-phase oxidation of thiols with atomic oxygen showed nearly zero reaction activation barrier.<sup>30</sup> By contrast, to oxidize the valence saturated siloxane group, cleavage of the Si–C bond (bond energy  $\approx 300$  kJ/mol<sup>31</sup>) is required.

(30) Tevault, D. E.; Mowery, R. L.; Smardzewski, R. R. *J. Chem. Phys.* **1981**, *74*, 4480–4487.

(31) Colvin, E. W. *Silicon in Organic Synthesis*; Robert E Krieger Publishing Co.: Malabar, FL, 1985.



This renders the oxidation process kinetically unfavorable. Ozone is not known to react with linear alkanes in gas phase.<sup>32</sup> Nor do we attribute the reactivity of hydrocarbon chains in ODS SAMs to ozone. Instead, we attribute the reactivity of ODS SAMs to OH radical and/or atomic oxygen. OH radical and atomic oxygen are mainly the products of UV dissociation of ozone.<sup>33</sup> Atomic oxygen has been reported to degrade the alkylsiloxane SAMs.<sup>21–23</sup> We assume that the mechanism of UV degradation of ODS SAMs to be similar to that of photooxidation of gas-phase alkanes.<sup>34</sup> First, it involves hydrogen abstraction to form alkyl radicals. The alkyl radicals further react to form alkoxy radicals, which can be oxidized to form carbonyls that dissociate via direct photolysis or attack from radicals, finally resulting in loss of carbon.

Our study raises the interesting question of reactivity of hydrocarbon chains on alkanethiol SAMs under low UV intensity ( $\mu\text{W}/\text{cm}^2$  to  $\text{mW}/\text{cm}^2$ ). Though ozone is reported to be responsible for the oxidation of thiolate groups under low UV intensity, it remains unclear to what degree the reactivity of hydrocarbon chain participates in the oxidation. Our investigation of ODS SAMs, which have little reactivity on the headgroups, allows one to isolate

the contribution from the reactivity of hydrocarbon chain during photooxidation. In our ambient photooxidation experiments with a low-pressure mercury lamp with intensity of  $2 \text{ mW}/\text{cm}^2$ , the ODS monolayer is degraded by about 40% in 20 min, judging from IR (Figure 2). This result suggests that the reported ambient photooxidation degradation of alkanethiol SAMs with UV intensity exceeding  $1 \text{ mW}/\text{cm}^2$  proceeds via the oxidation of the hydrocarbon chains as well as the established reaction of thiolate headgroups. The contribution from hydrocarbon chain oxidation in alkanethiol SAM degradation can explain the spatial resolution of UV patterning, since more spatially confined radicals or even UV photons are required for the etching of hydrocarbon chains. More systematic studies on the alkylsiloxane SAM photooxidation, including its wavelength dependence, intensity dependence, and reaction intermediates, may provide a deeper understanding of the reactivity of SAMs, thereby enabling the design of more robust monolayers and providing insight into monolayer modification strategies.

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(32) Atkinson, R. *J. Phys. Chem. Ref. Data* **1994**, *Monograph 1*, 1–216.

(33) Finlayson-Pitts, B.; Pitts, J. *Atmospheric Chemistry: Fundamentals and Experimental Techniques*; John Wiley & Sons: New York, 1986.

(34) Cox, R.; Patrick, K.; Chant, S. *Environ. Sci. Technol.* **1981**, *15*, 587–592.