

# Thermal Decomposition of Alkylsiloxane Self-Assembled Monolayers in Air

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The thermal decomposition of alkylsiloxane self-assembled monolayers in air has been studied using atomic force microscopy, X-ray photoelectron spectroscopy, and contact angle analysis. It is found that the monolayers are stable in air up to about 200 °C. Above 220 °C the monolayers primarily decompose through C–C bond cleavage, with a gradual reduction in chain length. The siloxane headgroups remain on the surface following the decomposition of hydrocarbon fragments in the monolayers.

## I. Introduction

Self-assembled monolayers (SAMs) are thin organic films which form spontaneously on solid surfaces. They have been shown to be useful as passivating layers and also for the modification of surface properties. Potential applications include wetting, adhesion, friction, chemical sensing, ultra-fine-scale lithography, and protection of metals against corrosion.<sup>1,2</sup> Several different varieties of SAMs have been investigated, including alkanethiolate monolayers on Au, Ag, and Cu, and alkylsiloxane monolayers on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, and mica.<sup>1</sup>

A class of widely used SAMs is based on alkyltrichlorosilane precursor molecules, which, through hydrolysis and polymerization, produce alkylsiloxane SAMs on many hydrophilic substrates. In the case of octadecyltrichlorosilane (OTS)-based SAMs on SiO<sub>2</sub>, adsorption takes place through the hydrolysis of the Si–Cl bonds to form Si–OH groups. All Si–Cl bonds become hydrolyzed, as no chlorine is detected following monolayer formation.<sup>3</sup> The OH groups undergo condensation reactions to form Si–O–Si cross-linking bonds between adjacent headgroups. It is believed that these also interact with OH groups on the oxidized surface, forming Si–O–Si bonds to the substrate. Water is found to play a key role in the formation step.<sup>3–5</sup> It has been proposed that a thin water film exists on the hydrophilic SiO<sub>2</sub> surface and that the OTS molecules physisorb on this water film. In this stage, the molecules are mobile while bonded to the water layer, allowing them to pack more closely before condensation reaction takes place, at which point they become pinned to the surface.<sup>6,7</sup>

The thermal behavior of SAMs has been studied not only to understand the chemical interaction between the headgroup and the substrate, but also to consider the applications. To successfully incorporate these films into the production of low surface energy structures, it is necessary for the films to withstand the temperatures used in subsequent processing and packaging steps. In a thermal desorption spectroscopy (TDS) study of octadecanethiol ( $n = 18$ ) adsorbed on Au(111), desorption of entire chains was observed at about 177 °C, indicating that desorption takes place through cleavage of the Au–S bond.<sup>8</sup> The alkylsiloxane monolayers on oxidized silicon are stable in a vacuum up to temperatures of about 470 °C. Above 470 °C the

monolayers begin to decompose through the cleavage of C–C bonds, resulting in a gradual decrease in chain length.<sup>9</sup> Through analogy with decomposition of hydrocarbons, decomposition of the monolayers was discussed in terms of a radical chain mechanism.<sup>10</sup> Cohen and Sagive have shown that the monolayers can withstand air temperatures as high as 140 °C.<sup>11</sup> Previous study using contact angle analysis has shown that water contact angles on OTS-based SAMs remain the same upon annealing for 5 min to temperatures as high as 100 °C in air.<sup>12</sup> Above this temperature the contact angle was observed to decrease, indicating degradation of the monolayers. The studies do not reveal information about the mechanism by which the monolayers degrade, however.

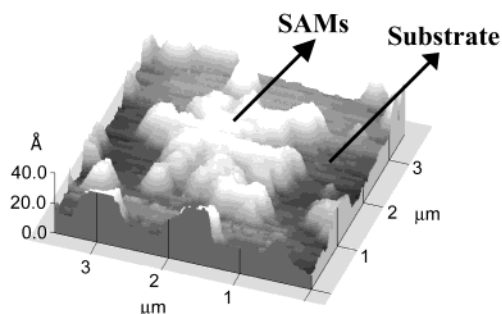
In this paper the thermal decomposition of the OTS-based SAMs in air is investigated. Using atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and contact angle analysis, it is found that the monolayers are stable in air up to about 200 °C. Above that temperature, the monolayers primarily decompose through the cleavage of C–C bonds, resulting in a gradual decrease in chain length. The decomposition temperature is about 250 °C lower than that found for the alkylsiloxane monolayers in a vacuum, supporting the idea that O<sub>2</sub> and H<sub>2</sub>O in air accelerate the cleavage of C–C bonds. The siloxane headgroups remain on the surface following the decomposition of the hydrocarbon fragments in the monolayers.

## II. Experimental Section

**Sample Preparation.** The Si substrates were cut from n-type (100) wafers with resistivity in the range 1–5 Ω cm. The Si substrates were initially treated by a chemical cleaning process, which involves degreasing, HNO<sub>3</sub> boiling, NH<sub>4</sub>OH boiling (alkali treatment), HCl boiling (acid treatment), rinsing in deionized water, and blow-drying with nitrogen, proposed by Ishizaka and Shiraki<sup>13</sup> to remove contaminants and grow a thin protective oxide layer on the surface.

Alkylsiloxane SAMs were formed by placing the Si samples in a 2.5 mmol solution of OTS precursor dissolved in 4:1 hexadecane/chloroform for 1 h. The samples were then washed in carbon tetrachloride to remove excess reactants and dried with nitrogen. The quality of the monolayers was checked by XPS and water contact angle measurements. The water contact angle is about 110°, and the C(1s):Si(2p) peak area ratio measured by XPS is about 1.7. A partial OTS monolayer was

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**Figure 1.** AFM image of a partial OTS-based monolayer grown on SiO<sub>2</sub> for 8 s.

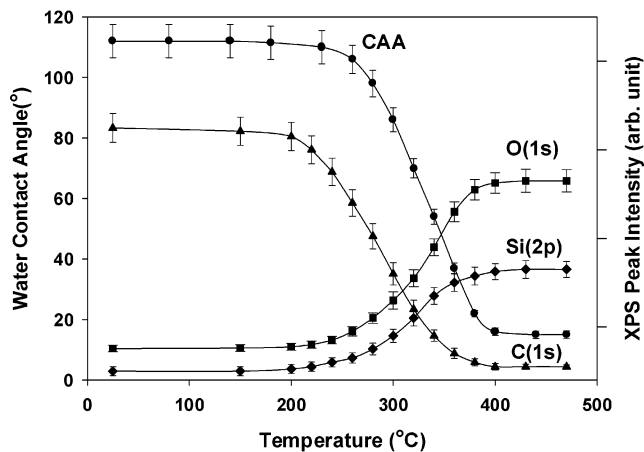
made by removing the Si substrates from the OTS solution after 8 s and rinsing them in carbon tetrachloride.<sup>7</sup> At this point, the partial monolayer consists of islands (~25 Å high) of close-packed, fully extended chains, as shown by the AFM image in Figure 1.

A patterned monolayer of OTS on the Si substrate was made by using microcontact printing. A poly(dimethylsiloxane) (PDMS) stamp having 2.5 μm parallel lines and 3.5 μm spaces was fabricated according to a previously reported procedure.<sup>14–16</sup> The PDMS stamp was inked with a 10 mM hexane solution of OTS and dried with nitrogen. The stamp was placed in contact with the Si substrate for 30 s. The stamp was carefully peeled off, and the substrate was blown dry with nitrogen.

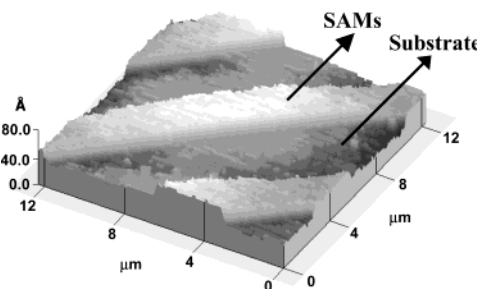
The OTS-based monolayers were also formed on TiO<sub>2</sub> thin films, prepared by atomic layer deposition (ALD). The Si substrates were introduced into the ALD system Cyclic 4000 (Genitech). The TiO<sub>2</sub> thin films were deposited onto Si(100) substrates using Ti(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub> (Strem Chemicals) and water as ALD precursors. Ar served both as a carrier and as a purging gas. The Ti(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub> and water were evaporated at 80 and 20 °C, respectively. The number of ALD cycles in a run was kept at 400. The cycle consisted of a 2 s exposure to Ti(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub>, 5 s Ar purge, 2 s exposure to water, and 5 s Ar purge. The total flow rate of the Ar was 20 sccm. The TiO<sub>2</sub> thin films were grown at temperatures of 200 °C under 2 Torr of pressure. The thickness of the TiO<sub>2</sub> films, measured by transmission electron microscopy (TEM; JEOL), is about 200 Å. The OTS-based SAMs were formed by placing the TiO<sub>2</sub> samples in a 2.5 mmol OTS solution for 1 h. The water contact angle of the monolayers on the TiO<sub>2</sub> is about 110°, in good agreement with the value for them on the SiO<sub>2</sub> sample. The monolayers are formed by Si–O–Ti bonds to the TiO<sub>2</sub> substrate through condensation reactions. It is believed that Si–O–Si bonds are also formed between adjacent headgroups, creating a cross-linked network at the surface.

Immediately after the samples were prepared, the SAM-coated samples were introduced into a controlled environmental chamber with an oven. The samples were annealed at temperatures between 25 and 480 °C for 10 min. The relative humidity was kept in all experiments at 40%.

**Analysis Techniques.** The samples were introduced into the XPS chamber by means of a load lock system. Both the XPS chamber and the load lock system have been described previously.<sup>17</sup> The base pressure is  $1 \times 10^{-10}$  Torr. All XP spectra were recorded on a VG Scientific ESCALAB MK II spectrometer using a Mg Kα source run at 15 kV and 10 mA. The binding energy scale was calibrated to 284.6 eV for the main C(1s) peak. Each sample was analyzed at a 90° angle relative to the electron analyzer. Peak areas were calculated using Shirley background subtraction and were corrected by the elemental sensitivity factors.<sup>18</sup>



**Figure 2.** Water contact angle and XP peak intensities as a function of annealing temperature for the OTS-based SAMs on SiO<sub>2</sub>.



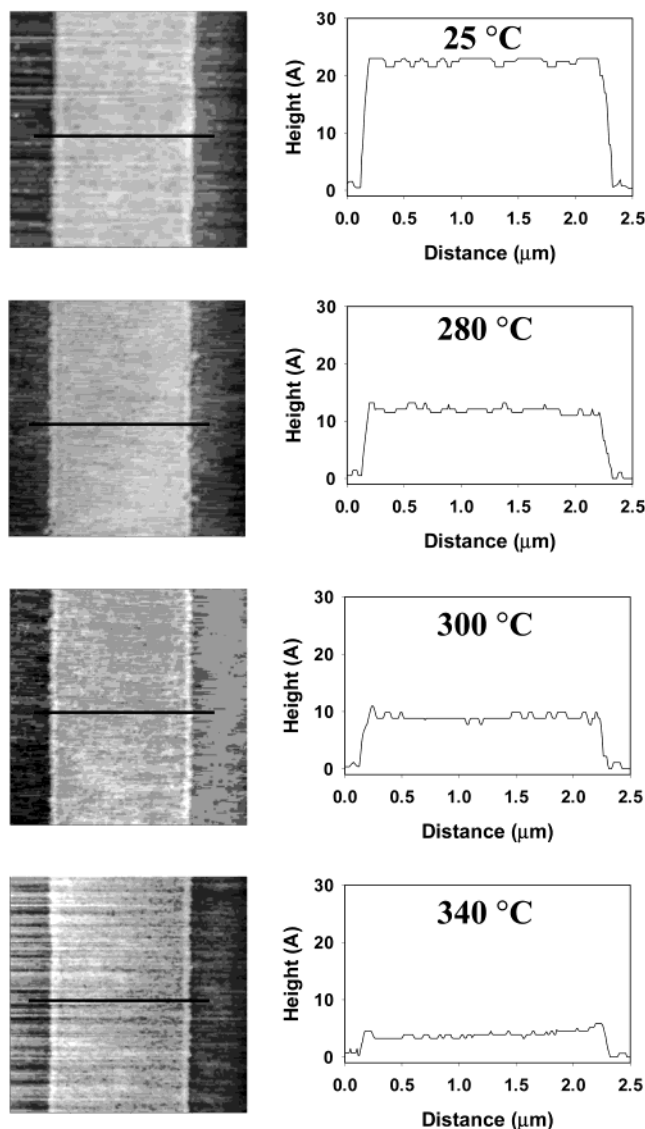
**Figure 3.** AFM images for the patterned OTS-based monolayer on SiO<sub>2</sub>.

Atomic force microscopy images of the samples were obtained on a PSI CPII operating in tapping mode. Contact angle analysis was performed using a model A-100 Ramé-Hart NRL goniometer to measure water contact angles in room air using the Sessile drop method.<sup>19</sup>

### III. Results and Discussion

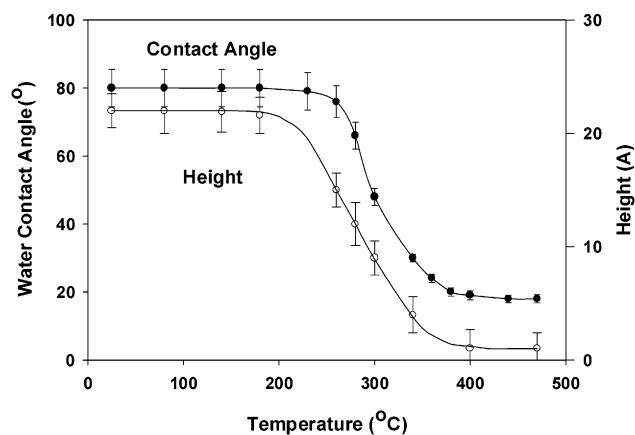
**OTS Full Monolayers on Si Substrate.** The water contact angle and XP peak intensities for OTS-based SAMs on the oxidized Si were measured as a function of annealing temperature in air. Figure 2 shows that the contact angle remains almost constant at about 110° up to 220 °C and then declines above 220 °C. The intensity of the C(1s) peak remains intact up to temperatures of about 200 °C, consistent with the notion that the monolayers are stable up to this temperature. Upon annealing to 220 °C, however, the intensity of the C(1s) peak decreases while the intensities of the O(1s) and Si(2p) peaks increase. These changes all indicate that the OTS-based SAM is stable up to about 200 °C and begins to decompose at about 220 °C. Upon annealing to 260 °C, the intensity of the C(1s) peak decreases to 74% while the contact angle remains high at 106° (95%). The XPS data suggest that the monolayers have significantly decomposed, yet the contact angle data show that the monolayers are still reasonably well ordered. Upon annealing to 300 °C, the water contact angle and the intensity C(1s) peak further decrease. After annealing to 400 °C, the monolayers have almost completely decomposed as indicated by the water contact angle of 15°, which is the same as that of the clean SiO<sub>2</sub> surface.

**Patterned OTS Monolayers on Si Substrate.** Figure 3 shows AFM image of a patterned OTS monolayer on the oxidized Si. The master used to fabricate this patterned stamp was based on a mask with 2.5 μm parallel lines and 3.5 μm

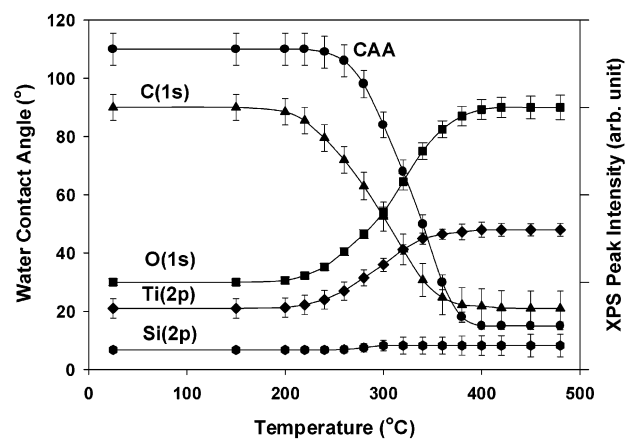


**Figure 4.** AFM images and cross-sections as a function of annealing temperature for the patterned OTS-based monolayer on SiO<sub>2</sub>.

spaces. This image clearly shows that the patterned monolayer retains the dimensions of the master pattern without noticeable line spreading. Additionally, the height of the patterned monolayer is about 23 Å, which is close to that for a densely packed OTS monolayer. To study the thermal decomposition mechanism of the OTS-based SAMs, the patterned monolayer was annealed at temperatures between 25 and 480 °C for 10 min. Atomic force microscopy images of the patterned monolayer were obtained as a function of annealing temperature. AFM images and cross-sections are displayed in Figure 4. After the patterned monolayer is annealed to 280 °C, the height of the monolayer is uniformly reduced to 13 Å. The width and shape of the monolayer remain intact, suggesting that the line edge of the monolayer does not display enhanced reactivity. There is no evidence for growth of the pinholes found within the monolayers. After annealing to 300 °C, the height has been reduced to approximately 10 Å. Upon further heating to 340 °C, the height of the monolayer is down to 5 Å with no change of the width and shape. The water contact angle and the average height of the patterned monolayer were measured as a function of annealing temperature in air. Figure 5 shows that the average height of the monolayer decreases rapidly upon annealing to 260 °C, while the contact angle remains high.



**Figure 5.** Water contact angle and height as a function of annealing temperature for the patterned OTS-based SAMs on SiO<sub>2</sub>.



**Figure 6.** Water contact angle and XP peak intensities as a function of annealing temperature for the OTS-based SAMs on TiO<sub>2</sub>.

These changes all indicate that the OTS-based SAM in air decomposes through C–C bond cleavage, with a gradual reduction in chain length. Safarik and Strausz proposed that the decomposition of *n*-alkanes occurs through a radical chain mechanism.<sup>20</sup> The initiation step is homolytic cleavage of a C–C bond, creating two alkyl radicals. The propagation steps consist of hydrogen abstraction from another chain and radical decomposition. Radical decomposition involves cleavage of the C–C bond at the  $\beta$  position from the radical, resulting in an alkene and a shorter alkyl radical. A similar process is possible for decomposition of the alkylsiloxane monolayers. Following the initiation step, two radicals are created, one of which is no longer bound to the surface. The unbound radical may encounter another chain, resulting in a hydrogen abstraction reaction and the propagation of the radical. The alkyl radical on the surface decomposes, with the C–C bond at the  $\beta$  position breaking, thus creating another radical and an alkene. The decomposition reaction can be repeated, and the alkene desorbs, resulting in a reduction in chain length.<sup>10</sup>

The decomposition temperature of the alkylsiloxane monolayers in air is about 250 °C lower than that in a vacuum, indicating that O<sub>2</sub> and H<sub>2</sub>O in air may accelerate the propagation steps described above.

**OTS Full Monolayers on TiO<sub>2</sub>.** To investigate the thermal behavior of the alkylsiloxane headgroups, the water contact angle and XP peak intensities for an OTS-based SAM on TiO<sub>2</sub> were measured as a function of annealing temperature in air. Figure 6 shows that the monolayer begins to decompose at about 220 °C and has almost completely decomposed by 400 °C. This

behavior of the monolayer on  $\text{TiO}_2$  is in good agreement with that on  $\text{SiO}_2$ . The intensity of the  $\text{Si}(2p)$  peak, which purely comes from the OTS molecules, almost remains intact even after annealing to 480 °C. These observations suggest that the siloxane headgroup remains on the surface following the decomposition of the alkyl chain in the OTS-based monolayer.

In summary, the thermal decomposition mechanism of alkylsiloxane SAMs has been studied using AFM, XPS, and contact angle analysis. The monolayers are stable in air up to temperatures of about 200 °C. Above 220 °C the monolayers primarily decompose through C–C bond cleavage, with a gradual reduction in chain length. The siloxane headgroups remain on the surface following the decomposition of hydrocarbon fragments in the monolayers until about 480 °C.

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