Synthesis of Carboxylic acid Monolayers by Ozonolysis of 10-Undecenyltrichlorosilane SAMs

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Abstract

A high-yield method has been developed for the production of hydrophilic, carboxyl-terminated alkylsiloxane monolayers on silicon using the ozonolysis and hydrolysis of 10-undecenyltrichlorosilane SAMs. Contact angles with water, a common measure of hydrophilicity, were brought to 0° on receding and approximately 16° on advancing, compared to 105° and 98° respectively before ozonation. Ellipsometry showed the presence of a full monolayer, 1 nanometer thick before ozonation, that decreases by about 0.2 nm during ozone treatment, largely due to the removal of a carbon atom in the process. This removed material coalesces as nanoparticles, observed with AFM imaging. The process has a surprisingly narrow ozone dose window, with excess ozonation resulting in complete layer removal. The carboxylate moieties allow further chemical modification of the surface in addition to the hydrophilic surface that can be produced by exposing the silicon dioxide substrate.

Keywords:

Carbyboxylated surface, alkenylsiloxane, ozonation, SAM oxidation, hydrophilic monolayer
Introduction

The synthesis of hydrophilic monolayers with a carboxyl functional group has been of recent interest due to their applications in biological research as a surface for cell culturing or for probes\textsuperscript{1-2}, and due to their utility in the three-dimensional alignment of silicon wafers\textsuperscript{3}. The carboxyl group is a particularly convenient moiety for further chemical reaction on the surface. However, the yield in producing the carboxyl termination by chemical oxidation of a deposited vinyl-terminated self-assembled monolayer (SAM) is low\textsuperscript{1,3}. Contact angles are still high. We propose a 'dry' process for the creation of these carboxyl-tipped monolayers based on the ozonolysis of the vinylic double bond, to improve the yield. We find that the process works well, with good yield and contact angles, but find that the ozone dose must be precisely controlled. Too much ozone dosing quickly removes the entire layer. The resulting surface is hydrophilic, but not carboxyl-terminated.

Effective synthesis of hydrophobic monolayers on a silicon substrate has been developed\textsuperscript{1,3,4} based on self-assembly of alkyltrichlorosilanes on the oxidized surface of the silicon, and techniques for controlled silicon dioxide layer growth have been developed using UV-ozone oxidation of such alkylsiloxane monolayers\textsuperscript{5,6}. Methods have also been developed to grow silica structures on hydrocarbon-containing media\textsuperscript{7}. However, hydrophilic organic monolayers, especially those with a carboxylic acid moiety, have been more difficult to produce since the self-assembling silane derivative in this case would have polar moieties at both ends, making it very difficult to develop a uniform monolayer with all the molecules’ carboxyl functions on the side away from the
surface. Such layers are of great interest for both hydrophilic nature and as a template for further chemical modification. Because of this, efforts at generation of monolayers with hydrophilic functional groups have focused on chemical modification of hydrophobic SAMs, in particular those formed by adsorption of a vinyl-terminated molecule such as 10-undecenyltrichlorosilane onto an SiO$_2$ surface. One method that has been used for this purpose is the oxidation of the vinyl group by basic potassium permanganate\textsuperscript{1,3}. However, yields by this method have generally been rather low, due in part to the repulsion between the carboxylate moieties and the permanganate ions (making the reaction product-inhibited), and thus the contact angles of water droplets on the monolayers were rather high.

Ozone is known to react with alkenes to form substituted 1,2,4-trioxolanes, known as secondary ozonides, which will hydrolyze to carbonyl compounds or carboxylic acids on exposure to moisture. Criegee\textsuperscript{8} proposed the accepted mechanism for this process, which proceeds through addition of ozone to the double bond to form a primary ozonide (substituted 1,2,3-trioxolane) that cleaves into a carbonyl compound and a diradical intermediate. The two compounds can either join again into a secondary ozonide, or the diradical can react with other compounds, such as water. In the end, the carbonyl compounds or carboxylic acids will be formed with the main impurities being geminal hydroxylhydroperoxides and some ether- or peroxide-bridged oligomers or polymers. In each case the products are hydrophilic, involve only the moiety that was one end of the vinyl group, and have a tendency to hydrolyze or oxidize to carboxylic acids (if they are not already carboxylic acid). These reactions will tend to occur on standing in water.
The reaction of ozone with olefinic SAMs has been investigated in studies of air pollution. Fiegland et al. exposed vinyl-terminated alkenylthiol SAMS on a gold surface to ozone and traced the reaction via infrared spectroscopy, finding evidence of the formation of carboxylic acid anhydrides that, on reaction with water, showed the absorption bands for carboxylic acid. The bands for the vinyl group were gone. Other studies set up similar reactions and actually measured the contact angle changes for water droplets on the monolayers; they tended to have a reduction by only 20%, suggesting poor yield, but their data suggests the presence of some multilayers on their surfaces and possibly the formation of polymer aggregates through reaction with ozone, each of which could have interfered with a larger contact angle drop. McIntire et al., in fact, found more direct evidence of the formation of such polymer aggregates in a similar system. We aim to minimize multilayer formation using a technique from Walker. Several studies of the products and kinetics of ozonolysis, particularly in monolayers or films, have also been done recently, and in general supported our goal of having aldehydes and carboxylic acids as our main products, at least after some hydrolysis; the reaction with ozone would also be expected to proceed fairly rapidly. Even much higher concentration ozone, used to oxidize silicon itself, has been found to be relatively undamaging to the monolayer structure.

Experimental Methods

To prepare the vinyl-terminated SAMs for oxidation, silicon wafers (either 4-inch-diameter N-type double-polished wafers from Wafer World, Inc., or 10-centimeter-
diameter P-type single-polished wafers from Montco Silicon Technologies, Inc.) were cleaned for 20 seconds in an SPI Supplies Plasma Prep II plasma cleaner, flushed with oxygen from Machine and Welding Supply Company, and with dummy wafers at both ends of the wafer holder to distribute the plasma flow. Then initial ellipsometric measurements were taken, and the wafers were placed under isopropanol from Fisher Scientific for transfer into a drybox (vented with boil-off from liquid nitrogen from National Welders’ Supply Company). There they were washed with isopropanol again and then with dichloromethane, chloroform, and anhydrous hexadecane in that order; the dichloromethane and chloroform were also obtained from Fischer Scientific, while the hexadecane was obtained from Sigma Aldrich. Finally they were left overnight in a 2% solution of 10-undecenyltrichlorosilane in hexane (this solution was reused for multiple wafers). They were then washed with the hexadecane, chloroform, dichloromethane, and isopropanol twice, in that order, to remove additional alkyltrichlorosilane molecules on top of the monolayer; they were then transferred out of the drybox under isopropanol, broken into pieces with a diamond cutter, and cleaned on a spin coater with isopropanol before beginning measurements.

Ellipsometric measurements were all taken using the thin-oxide-layer-on-silicon program (211) on a Rudolph Research AutoEL ellipsometer.

Contact angles were measured by placing a drop of water on the surface, tilting it so one side would be advancing and the other receding, and then placing it on a stage, taking a picture of it with a Nikon Coolpix 5700 digital camera equipped with a macro lens (as in Fig. 1), and finding the angle on the computer using GIMP.
Unless they were just plasma or ozone cleaned, all samples were spin-cleaned with isopropanol before ellipsometry or contact angle measurements, using a Chemat Technology Spin-Coater KW4A.

The oxidation process was performed in a Novascan PSD-UV ozone cleaner; the wafers were placed in the cleaner face up and exposed to ozone for the appropriate amount of time; the lamps were turned off and the cover removed upon completion of the time interval. The oxygen flow rate into the cleaner was 145 mL/s, which should provide an ozone concentration less than 100 ppm. Oxygen was obtained from National Welders Supply Co.

Hydrolysis was performed by placing the wafers in deionized water in a petri dish and leaving them there overnight, or for the appropriate number of days for longer soaking trials.

Results and Discussion

Several parameters were varied to find the procedure with the optimal result; the wafers were placed for varying amounts of time in the ozone cleaner, and hydrolysis times were varied as well. Hydrolysis in dilute aqueous ammonia or acetic acid, as well as in aqueous hydrochloric acid, were also attempted, but the ammonia and HCl completely destroyed the layer, as shown by ellipsometry, while the acetic acid did not produce nearly as strong a decrease in contact angle (it is possible that the acetic acid bound to the membrane). Therefore, experiments were performed to find the optimal ozonation and hydrolysis times.
The effects of ozonation times on ellipsometric measurements are shown in Figure 2. We plot the change in layer thickness from that measured before ozonation, averaged over several places on the sample. In general, increased ozonation times removed first approximately 0.2 nm of layer, and then the rest of the layer. This can be understood as the ozone first attacks the double bond, so the carbon atom above the double bond is removed, reducing the layer thickness by 0.2 nm. What is somewhat more surprising is the sharp onset of almost complete layer removal once the double bonds are all gone, at about 200 s exposure.

Contact angles with water, shown in Fig. 3A, fell as the first 2 angstroms were eroded, and usually reached 0° on receding when the layer had been removed. After a 30 minute hydrolysis, Fig. 3B, the contact angles were further reduced, particularly at the higher ozone doses. Of interest is the data at 150 s ozonation time. Here, the double bond has been ozonolyzed but the layer is not destroyed (as shown by ellipsometry), and the contact angle dramatically drops, to 0° receding. A 0° advancing contact angle was not obtained except on the pure silicon oxide surface left by complete removal of the layer (275 s). To obtain an optimal hydrophilic, carboxyl-tipped monolayer that is still intact, with 0 receding contact angle, the ozonation time must be in the window that permits hydrolysis to a small contact angle, but not removal of the layer. This time was around 150 s on the day the above data was taken, but due to variability in the ozone flow rate on the ozone cleaner, other days produced different results and thus some calibration is necessary to reproduce this technique. The results indicate a much more hydrophilic surface was obtained with our ozonation process than could be obtained with chemical oxidation.
Water soaking times also affected the contact angle significantly, as shown in Fig. 4. However, times longer than approximately 30 minutes did not have a noticeable effect, and many wafers seemed to become contaminated when soaked for longer periods, such as overnight or more, as evidenced by large rises in contact angle. A half an hour is an appropriate hydrolysis time. For comparison, contact angles with water of the original 10-undecenyltrichlorosilane monolayers averaged 105° on advancing and 98° on receding.

AFM images were taken of the layers after several different amounts of treatment. Figure 5 shows images from the qualitatively different ozonation stages. The stages that leave the layer intact (excepting the 0.2 nm loss discussed above) are shown in Fig. 5A,B. Both exhibit surface roughness of about 0.6 nm. Much of this is presumably due to the roughness of the oxide layer under the SAM, since the ellipsometric data suggests a fairly uniform monolayer. This is in fact in agreement with previous results regarding the stability of the layer under silicon-oxidizing ozonation\textsuperscript{18}. Both samples have nanodots in the 2-7 nm size range. The density of these dots is slightly higher in the Fig. 5B image, and a few dots larger than 10 nm are observed, as expected with the longer ozonation time. We have verified that the nanodots result from the layer treatment, since they do not occur on samples that do not have SAM layers. It is likely that the nanodots are formed from formaldehyde polymers or other reaction products. To test this hypothesis, we calculated the volume of material in the nanodots, and calculated the thickness it would account for if spread evenly across the surface. In particular, a threshold placed in the histogram, chosen at the sharp drop in the histogram (also ~10% of the points above it), separated the nanodots from normal surface roughness. The histogram was used to sum the nanodot volume, and the height corresponding to the histogram peak value was used
as the background. The thickness increase if the nanodots were spread evenly was found to be 0.21 nm and 0.18 nm for Fig. 5 A and B, respectively. This is very close to the ellipsometric 0.2 nm thickness decrease, and gives credence to the reaction product source of the nanodots. The sample with the destroyed SAM layer, Fig. 5C, has a higher roughness (~1 nm) and significantly more nanodots at the few nm level, and several at the ~40 nm size range. The thickness increase if these nanodots were evenly spread on the surface is 0.32 nm, significantly less than the ~1 nm layer thickness, indicating that much of the layer has been volatized.

The chemistry of these transformations appears to be a standard ozonolysis-hydrolysis reaction, as described by Criegee\textsuperscript{8}, with aldehyde functions on the monolayers being oxidized to carboxylate functions over the course of the soaking time, as might be expected, and interchain peroxide or other linkages commonly found after ozonolysis being hydrolyzed. The aldehyde branch of the reaction seems to be favored, since hydrolysis is required to produce the very small contact angles obtained. Previous studies with ozone exposure of similar species would suggest the production primarily of aldehyde and carboxylic acid functions in similar amounts\textsuperscript{11}. The one-carbon species released into the water, if released as formaldehyde, would likely be expected to polymerize in water, and that is a plausible explanation for the objects found on the layer in the AFM images. Formate or other one-carbon compounds are almost certainly produced as well in some concentration. Several reactions are available to ozone that could result in destruction of the carbon chain at higher ozone doses, such as attack at carbons adjacent to a double bond or to a heteroatom, or simply at carbon-hydrogen or carbon-carbon bonds in the alkyl chain.
Conclusions

In conclusion, an effective method has been developed that significantly improves the production of monolayers on silicon with carboxylate moieties, achieving contact angles of 0° on receding and around 16° on advancing, and with ellipsometry showing a uniform monolayer. The reaction shows the characteristics of a fairly standard Criegee mechanism. This method is likely to be useful for a variety of applications either requiring a hydrophilic substrate, or a carboxylate moiety for further reaction, such as biological applications, nano-orifice coating, or capillary-force driven processes. The ozone exposure, however, requires tight process control, and some reaction products are left as nanodots on the surface.

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References


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Figure Legends

**Figure 1.** Images used to determine contact angles, from the most hydrophilic (A) to least (C) ozonated layers.

**Figure 2.** Change in Layer Thickness versus Ozonation Time

**Figure 3.** Contact Angles versus Ozonation Time, (A) just after the ozonation, and (B) after a 30 minute hydrolysis in water

**Figure 4.** Averaged Advancing and Receding Contact Angle versus Soaking Time in Several Differently Ozonated Wafers

**Figure 5.** AFM images of 1 micron square regions of wafers after several different ozonation times: (A) 100 seconds, insufficient to obtain 0° receding contact angle; (B) 150 seconds, the optimal treatment, sufficient to obtain 0° receding contact angle while leaving the monolayer intact; and (C) 185 seconds, sufficient to remove the entire monolayer.
Figure 1
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Figure 2
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Figure 3
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Figure 4

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Figure 5
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