

# Conversion of Some Siloxane Polymers to Silicon Oxide by UV/Ozone Photochemical Processes

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A variety of linear and cross-linked polysiloxanes are transformed into silicon oxide (SiO<sub>x</sub>) through the application of a recently developed room-temperature UV/ozone conversion process. Ozone and atomic oxygen, produced by exposure of atmospheric oxygen to ultraviolet radiation, remove organic portions of the polymers as volatile products and leave a thin silicon oxide surface film. The conversion rates differ for each polysiloxane studied and are related to differences in their chemical structures. X-ray photoelectron spectroscopy (XPS) measurements of atomic ratios indicate that UV/ozone treatment removes up to 89% of the carbon from the resultant surface film, leading to an overall stoichiometry close to that of SiO<sub>2</sub>. The binding energy of Si(2p) core level photoelectrons shifts from 101.5 eV for the polymer precursors to about 103.5 eV after UV exposure, consistent with the formation of silicon that is coordinated to four oxygen atoms. Ellipsometry measurements of apparent thickness changes during conversion indicate that the SiO<sub>x</sub> film formed is limited to a thickness on the order of 20–30 nm for poly(dimethylsiloxane) substrates. The results demonstrate that a thin silicon oxide layer can be prepared at room temperature on the surface of polysiloxane films by UV/ozone-induced photochemical reactions.

## Introduction

The past few years have seen the emergence of a number of new processes for the fabrication of silicon oxide layers. SiO<sub>x</sub> films are versatile materials offering a myriad of applications due to their interesting properties. Their high resistance to oxygen and water, and high gas selectivity, for example, lead to their use as moisture barriers, protective layers, and gas separation membranes.<sup>1–18</sup> Indeed, these coatings are applicable

as barrier films to decrease gas permeability in containers for food packaging<sup>19</sup> and for extending shelf life of containers such as plastic evacuated blood collection devices.<sup>20,21</sup> Numerous studies have been published, for example, on the preparation and barrier properties of silicon oxide coatings on polymeric substrates such as poly(ethylene terephthalate).<sup>22–25</sup> Potential microelectronics applications include intermetal dielectrics in interconnections and gate oxides in amorphous silicon transistors.<sup>26–31</sup> The natural hardness of the oxide layer also makes these films suitable as scratch-resistant coatings, for instance on polycarbonate optical lenses. The high technological potential has led to a strong interest in the development of new methods for preparing silicon oxide films, particularly on organic and polymeric substrates.

Techniques used to produce SiO<sub>2</sub> thin films usually involve restrictive atmospheric conditions. Pyrolytic

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degradation of poly(dimethylsiloxane) (PDMS) for example can lead to high-quality silicon oxide films, but only at temperatures exceeding 350 °C. Poor yields are often obtained and the high temperatures required are not always suitable for all types of substrates. Finally, the cost of these processes may be prohibitive for industrial applications.

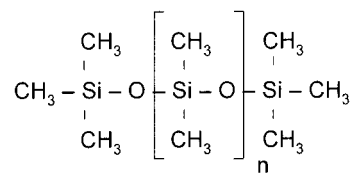
It has therefore been of recent interest to develop SiO<sub>x</sub> fabrication processes that can be applied at lower temperatures. Chemical vapor deposition (CVD) employs functional siloxane compounds, like tetraethylorthosilane (TEOS), that transform into silicon dioxide in nitrogen or oxygen plasmas.<sup>32,33</sup> Once again, these transformations require special environmental conditions and may involve toxic siloxane precursors. In 1993, Kalachev et al.<sup>4</sup> proposed one of the first low-temperature processes for conversion of a polysiloxane into silicon oxide. A poly(diethylsiloxane) Langmuir–Blodgett film was converted by oxygen plasma at 40 °C, into a quartz-like thin film.

Koberstein and Mirley reported an even simpler UV/ozone room-temperature process.<sup>17,18,26,27</sup> Langmuir–Blodgett monolayers of end-functional poly(dimethylsiloxane) (PDMS), a common and inexpensive polymer, were converted to SiO<sub>x</sub> by exposure to UV light in the presence of atmospheric oxygen at ambient conditions. Ozone, an active oxidizing agent, is generated in situ from atmospheric oxygen by exposure to 185 nm UV light. The ozone produced subsequently photodissociates into molecular oxygen and atomic oxygen upon exposure to 254 nm light. The latter species reacts with the polymer to form free radicals and activated species that eventually remove organic portions of the polymer in the form of carbon dioxide, water, and a small amount of volatile organic compounds. Since silicon does not readily form volatile compounds under these conditions, a residual film of SiO<sub>x</sub> containing a small amount of carbon is formed. The simple conversion process can be accomplished with a commercial UV/ozone cleaning system.

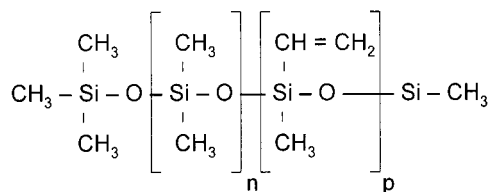
The UV/ozone method provides a facile means of generating silicon oxide films for many of the applications mentioned above, especially those applications excluded by high process temperatures that may deteriorate organic substrates. In this study, the UV/ozone method is applied to fabricate surface SiO<sub>x</sub> films on a variety of polysiloxane substrates.

## Experimental Section

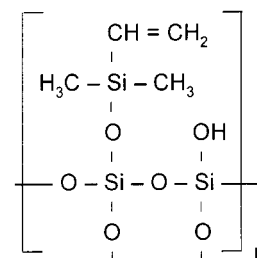
**1. Material Preparation.** All siloxane polymers and the peroxide catalyst utilized in this work were purchased from Gelest Inc., Tullytown, PA, and were used as received without further purification. Four different silicone precursors were studied as shown in Figure 1. The structure of linear poly(dimethylsiloxane) (PDMS) is shown in Figure 1a. A cross-linked silicone polymer was obtained by curing poly(dimethylvinylsiloxane-*co*-vinylmethylsiloxane) copolymers (PDMVMS) of structure presented in Figure 1b. The copolymers contain 0.2–0.3 mol % of vinyl methyl siloxane monomer and have number-average molecular weights in the range 500 000 to 900 000. The vinyl Q resin (VQR) (Figure 1c) has a molecular weight of about 4000 and was supplied as a 50 wt % solution in xylene. The poly(2-bromoethylsilsequioxane) (PBESS)



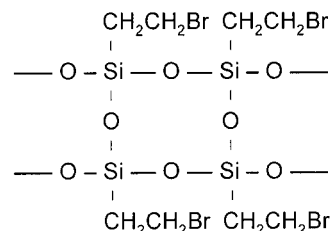
(a) Poly(dimethyl siloxane), PDMS



(b) Poly(dimethyl siloxane-*co*-vinylmethyl siloxane), PDMVMS



(c) Vinyl Q-Resin, VQR



(d) Poly(2-bromoethylsilsequioxane), PBESS

**Figure 1.** Polymer formulas: (a) PDMS, (b) cross-linked PDMVMS, (c) VQR, and (d) PBESS.

(Figure 1d) with molecular weight of 1200–2000 was received as a 20 wt % solution in methoxypropanol. The resins were spin-coated onto silicon wafers or glass slides at 2000 rpm from solutions in xylene (about 5 wt %). The speed was selected to produce films with a thickness in the range of 400–1000 nm. In the case of PDMVMS, 2 wt % of a cross-linking agent, 2,4-dichlorobenzoyl peroxide, was added to the solution before spin coating. The resultant PDMVMS films were then cured in an oven at 130 °C for 2 h to produce cross-linked PDMVMS.

**2. Equipment.** A UVOCS T10X10/OES UV/ozone cleaner was used for conversion of the polysiloxane precursor films. The apparatus contains a low-pressure mercury-quartz lamp, generating UV emissions in the 185 and 254 nm range (10 mW/cm<sup>2</sup>). Ozone is generated in situ during the UV exposure period from atmospheric oxygen. The samples were placed ~5 mm from the UV lamp.

**3. Materials Characterization.** The thickness of the polysiloxane films before and during transformation was monitored with a variable-angle spectroscopic ellipsometer (J. A. Woollam Co.). Ellipsometer data were collected over a wavelength range from 250 to 1000 nm in 10 nm steps at incidence angles of 60°, 65°, and 70°. The apparent thickness reported is the result of analysis of the data with a single layer model. Because the SiO<sub>x</sub> layer was very thin, attempts to model the film thickness by a two-layer model (i.e., PDMS plus SiO<sub>x</sub>) did not provide superior representations of the data than did a simple single layer model. An apparent total film thickness was determined from the data by fitting a single-layer Cauchy model for a single wavelength-dependent refractive index. The

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film thickness measured represents a composite sum of the thickness of the  $\text{SiO}_x$  and underlying PDMS layers. For this reason, and because different films have varying initial film thickness, we report the decrease or decrement in thickness that occurs during UV/ozone conversion.

Surface compositions of the films were measured using a Perkin-Elmer Physical Electronics PHI 5300 X-ray photoelectron spectrometer (XPS), equipped with a monochromatic Al  $K\alpha$  X-ray source (1486.6 eV) and hemispherical analyzer. The photoelectron takeoff angle was set at  $62^\circ$ . Binding energies were corrected initially using PHI supplied work functions. In cases where surface charging was observed, a flood gun was employed to shift the binding energy axis so as to obtain the carbon 1s primary signal at 284.6 eV. XPS atomic compositions and atomic ratios were calculated with the supplied PHI software. This software automatically corrects for escape depth and photoelectron yields using sensitivity factors that either were supplied by PHI or were determined experimentally by us using a variety of standard compounds. Because XPS is an integral technique, the data presented represents an integral over the composition of a thin surface layer  $\sim 7$  nm in depth. No attempts were made to derive a surface concentration depth profile or to extract the effects of underlying untreated PDMS from those of the overlying  $\text{SiO}_x$  films.

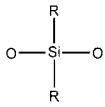
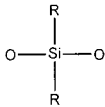
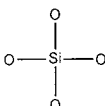
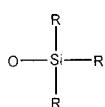
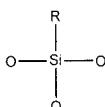
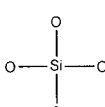
## Results and Discussion

**Surface Chemical Composition.** Four different types of polysiloxane films were prepared by spin coating onto silicon wafers. The chosen polymers were linear poly(dimethylsiloxane) (PDMS), cross-linked PDMVMS, Vinyl-Q Resin (VQR), and poly(2-bromoethylsilsesquioxane) (PBESS). Their structures (the PDMVMS before peroxide curing) are described in Figure 1. Different UV sensitivity is expected for each material because each material differs in the number of oxygen atoms coordinated to each silicon atom.

Surface composition analysis of these films, prior to and after various periods of UV/ozone treatment, was carried out by XPS. The Si(2p) binding energy data were used to determine which types of silicon-to-oxygen coordination are present at the surface. Possible tetrahedral types are reported in Table 1 along with the corresponding precursor polymers used in this study. Each tetrahedral configuration has a unique Si(2p) binding energy depending on the number of oxygen atoms in the coordination shell. The nature of changes in the silicon configuration during UV/ozone treatment can therefore be monitored through analysis of the Si(2p) binding energy. After exposure to UV/ozone, the Si(2p) binding energy (Figure 2) shifts toward that of amorphous  $\text{SiO}_2$  or to a value corresponding to tetrahedral coordination of each silicon atom to four oxygen atoms.

Both PDMS and cross-linked PDMVMS samples, before any treatment, present a binding energy for Si(2p) centered at 101.5 eV. This binding energy is attributed to silicon coordinated to two oxygen atoms and is in agreement with the published value for PDMS.<sup>34</sup> The binding energies for untreated VQR and PBESS films, are centered at 102.8, 101.2, and 102.0 eV, which correspond to configurations containing four, one, and three oxygen atoms, respectively (See Table 1). After exposure to UV/ozone, the Si(2p) binding

**Table 1. Binding Energies for Si(2p) Core Level Photoelectrons from Siloxane Polymers before and after Exposure to UV/Ozone**

Precursor Polymer	Structure	Binding Energies (eV)	
		Unexposed	Exposed
PDMS		101.5	102.9
Crosslinked PDMVMS		101.5	102.7
Vinyl-Q Resin		102.8	103.5
Vinyl-Q Resin		101.2	103.5
PBESS		102.0	103.6
$\text{SiO}_2$		103.6	-

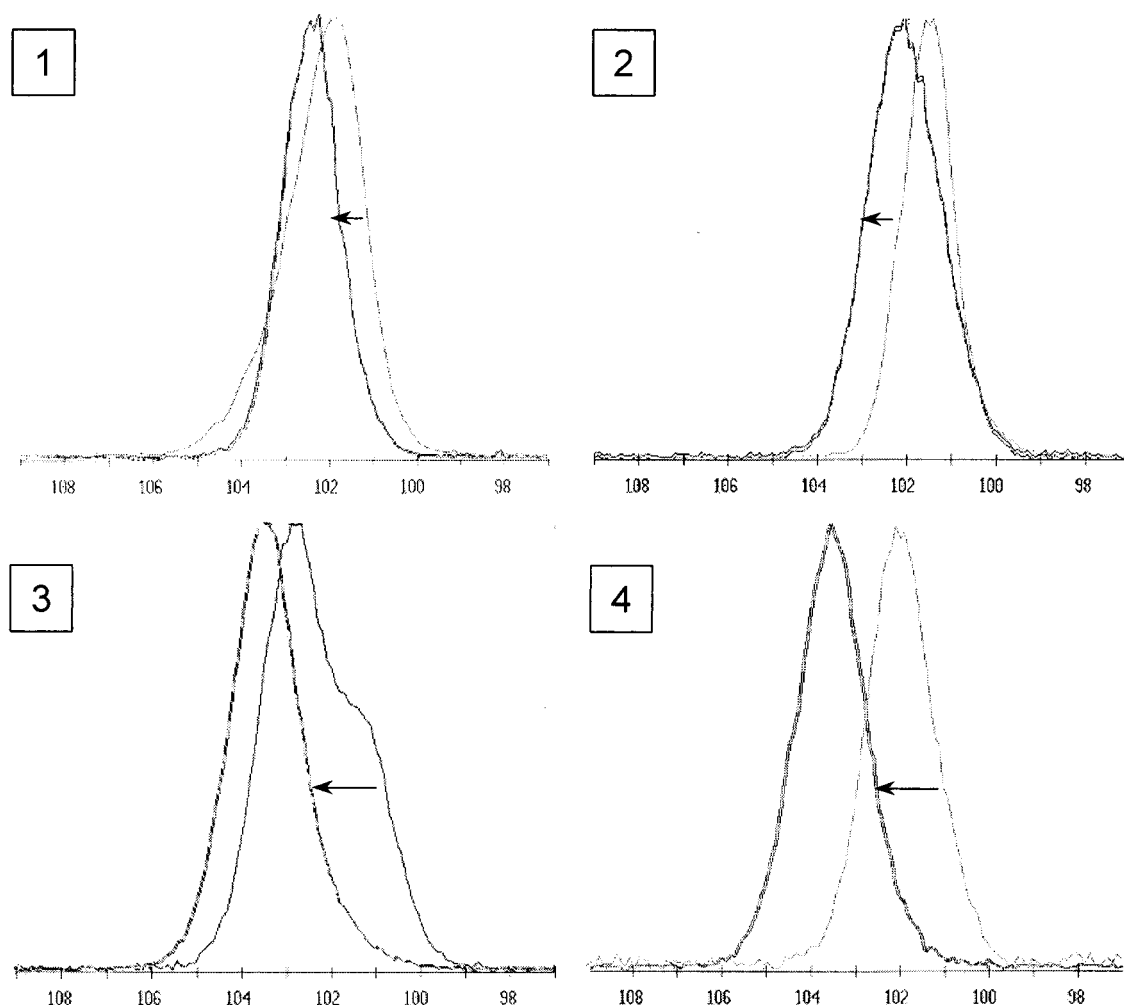
energies for all four materials shift toward that of  $\text{SiO}_2$  (103.6 eV).

The XPS Si(2p) spectra for all of the polysiloxane precursors after UV/ozone treatment indicate essentially complete conversion to  $\text{SiO}_x$ . The sampling depth of XPS, however, is only of the order of 7 nm and thus indicates near complete conversion to form a  $\text{SiO}_x$  surface layer that is at least 7 nm thick. Thickness measurements from ellipsometry that follow indicate that transformation is limited and that only a thin surface oxide layer is produced.

XPS estimates of surface atomic composition ratios document the chemical changes that occur during UV/ozone conversion. Theoretical atomic ratios for the four precursor polymers prior to conversion, calculated from the stoichiometry represented in Figure 1, are in excellent agreement with experimental atomic ratios determined by XPS (see Table 2). The bromine content of PBESS is somewhat lower than expected, but this result is not surprising considering the labile nature of bromine.

Figures 2 and 3 present silicon:carbon (Si/C) and oxygen:carbon (O/C) ratios as a function of UV/ozone exposure time. The Si/C and O/C ratios initially increase almost linearly with UV exposure time. One can assume that the amount of silicon at the surface remains unchanged during the photochemical reaction process induced by UV/ozone because silicon does not form species that are volatile at room temperature. The increase in the Si/C and O/C ratios can therefore be attributed to a reduction in the amount of carbon and

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**Figure 2.** Si(2p) XPS spectra for the siloxane polymer films before and after exposure to UV/ozone for 120 min: (1) PDMS, (2) cross-linked PDMVMS, (3) VQR, and (4) PBESS. The arrows indicate the Si(2p) peak shift observed between the unexposed (thinner line) and exposed (thicker line) samples.

**Table 2. Comparison of Theoretical and Experimental (Determined by XPS) Surface Chemical Compositions of Polymer Precursor Films Prior to UV/Ozone Exposure**

precursor polymer	XPS experimental and stoichiometric atomic ratios							
	Si/C		O/C		O/Si		Br/C	
	exptl	stoich	exptl	stoich	exptl	stoich	exptl	stoich
PDMS	0.50	0.5	0.5	0.5	0.98	1.0	0	0
cross-linked PDMVMS <sup>a</sup>	0.52	0.51	0.49	0.51	0.94	1.0	0	0
Vinyl-Q Resin <sup>b</sup>	0.78	0.8	1.11	1.11	1.43	1.38	0	0
PBESS	0.55	0.5	0.69	0.75	1.26	1.5	0.33	0.5

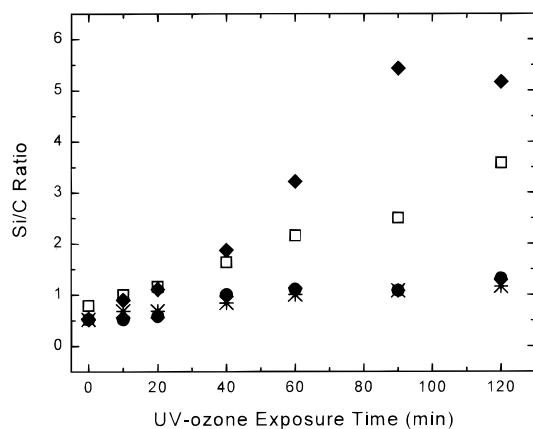
<sup>a</sup> Assumes 0.2–0.3% vinyl siloxane monomer. <sup>b</sup> Assumes 45% vinyl siloxane monomer and 55% of the tetraoxysilane structure.

an increase in the amount of oxygen within the converted surface film. This result agrees with the postulate made previously, that a photooxidative reaction involving in situ generated atomic oxygen removes the organic content of the polysiloxane precursors. Organic portions are transformed into low molecular weight species, including carbon dioxide, water, and small amounts of volatile carbonaceous compounds,<sup>31</sup> leaving a surface film consisting primarily of SiO<sub>x</sub>.

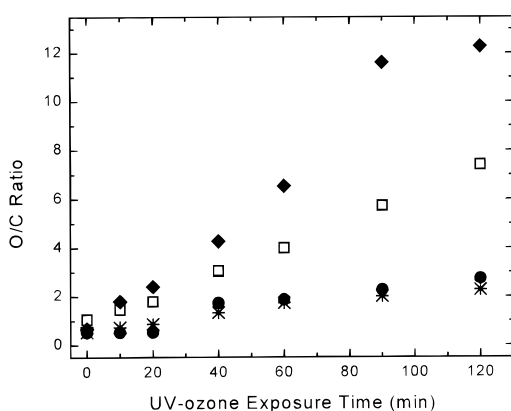
Siloxane polymers with different chemical structures present different rates for the photoinduced elimination of carbon, illustrated by the curves presented in Figures 3 and 4. The values of Si/C ratios for PDMS, cross-linked PDMVMS, VQR, and PBESS are 1.1, 1.3, 3.5, and 5.0 respectively, after 120 min of UV/ozone exposure. Since the amount of silicon at the surface should remain

unchanged, this result indicates that more than 55% of the carbon atoms can be eliminated from the surface of the PDMS film, 60% from the cross-linked PDMVMS film, 78% from the VQR film, and 89% from the PBESS film, after 2 h of UV/ozone exposure.

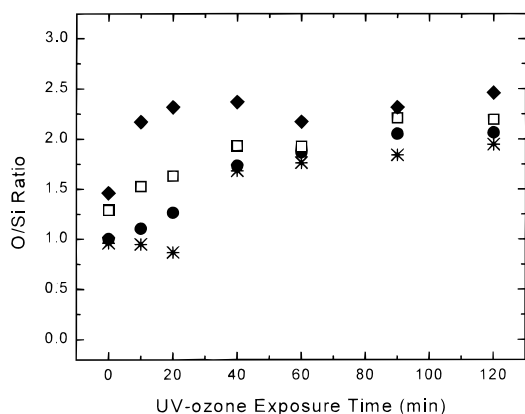
The reactivity to UV/ozone exposure follows the order PBESS > VQR > PDMS ≈ cross-linked PDMVMS. The rate of carbon removal from PDMS and cross-linked PDMVMS is about the same. PBESS and VQR present the highest rates of carbon removal. Their structural differences make these latter polymers readily convertible by UV/ozone as they present a high initial content of silicon that is coordinated to four oxygen atoms, as is found in the desired product, SiO<sub>2</sub>. Furthermore, PBESS and VQR are UV-sensitive polymers: vinyl side groups present in both PBESS and VQR are sensitive



**Figure 3.** XPS Si/C ratios as a function of UV/ozone exposure time: (\*) PDMS, (●) cross-linked PDMVMS, (□) VQR, and (◆) PBESS.



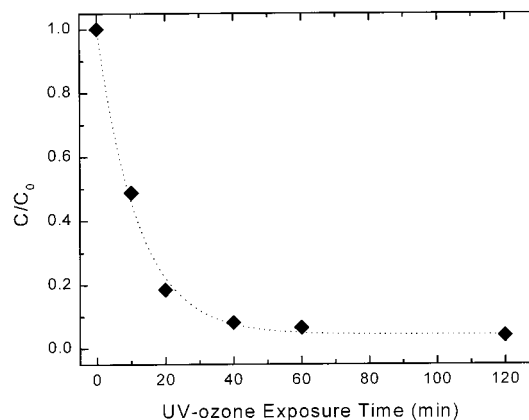
**Figure 4.** XPS O/C ratios as a function of UV/ozone exposure time: (\*) PDMS, (●) cross-linked PDMVMS, (□) VQR, and (◆) PBESS.



**Figure 5.** XPS O/Si ratios as a function of UV/ozone exposure time: (\*) PDMS, (●) cross-linked PDMVMS, (□) VQR, and (◆) PBESS.

to UV/ozone, and bromine atoms in PBESS are known to be directly eliminated from the polymer by exposure to UV light alone. Thus, even before the formation of ozone from atmospheric oxygen, these polymers are subject to UV-induced reactions. These reactions are accelerated upon formation of oxidizing agents such as atomic oxygen and free radicals.

Figure 5 presents O/Si ratios as a function of UV/ozone exposure time for the siloxane polymers. The O/Si ratios increase rapidly up to an exposure time of about 60 min. At longer times, the rate of oxygen incorporation

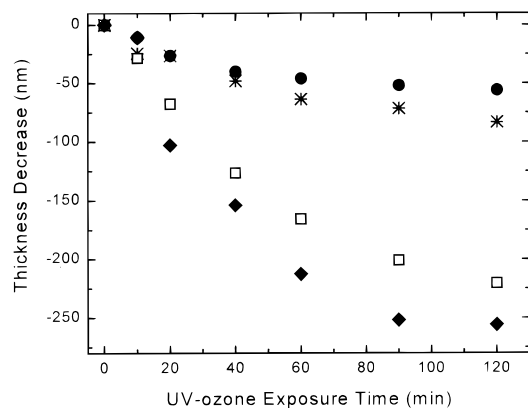


**Figure 6.** Variation of bromine content in PBESS as a function of UV/ozone exposure time (normalized by initial bromine concentration).

slows considerably. There exist several possible explanations for the slow in oxidation rate. First, these data may suggest a change to a diffusion-controlled mechanism, consistent with models of oxide growth developed to explain silicon oxide formation from polysiloxanes exposed to O<sub>2</sub> plasma.<sup>17,34</sup> These models proposed two regions of growth rate behavior. The first region involved the removal of carbonaceous species before a contiguous barrier layer of SiO<sub>x</sub> is formed. The second region occurred after an effective SiO<sub>x</sub> barrier had been formed and the diffusion of oxidative species became rate limiting.

Alternatively, the apparent plateau in rate behavior may be related to the limited sampling depth probed by the XPS technique. That is, the O/Si ratio should reach a constant value of 2.0 when the entire depth probed by XPS (~7 nm) is converted to SiO<sub>2</sub>. The Si/O data for all four materials do tend to level off at a value of about 2.0, suggesting that the apparent decrease in oxidation rate after 60 min of exposure is simply related to the finite sampling depth of XPS. The converted layer, however, still contains carbonaceous material at this time, as illustrated in Figures 3 and 4, and the removal of carbon continues almost linearly with time up to the longest times (i.e., 2 h) studied. After 2 h of treatment, the overall stoichiometry of the SiO<sub>x</sub> surface layers on PDMS, cross-linked PDMVMS, VQR, and PBESS films is respectively Si<sub>1.00</sub>O<sub>1.90</sub>C<sub>0.87</sub>, Si<sub>1.00</sub>O<sub>2.01</sub>C<sub>0.78</sub>, Si<sub>1.00</sub>O<sub>2.15</sub>C<sub>0.29</sub>, and Si<sub>1.00</sub>O<sub>2.41</sub>C<sub>0.20</sub>Br<sub>0.01</sub>. The deviation from pure SiO<sub>2</sub> may be caused by imperfect domains in the converted layers, the limitations of the UV/ozone process and possibly by the effects of underlying unconverted polysiloxane if the overall thickness of the converted oxide layer is smaller than the effective sampling depth of XPS. Our results are similar to those reported by Mirley and Koberstein<sup>17,18</sup> in previously published works on the UV/ozone treatment of Langmuir–Blodgett films of end-functionalized PDMS. One important difference is that they were able to completely convert their monolayer films, whereas we have produced thin silicon oxide surface layers on top of various underlying polysiloxane substrates.

Figure 6 shows the decrease of bromine content in PBESS with UV/ozone exposure time. Bromine is almost completely eliminated from the surface of the PBESS film after only 20 min. This observation is consistent



**Figure 7.** Thickness decrement as a function of UV/ozone exposure time: (\*) PDMS, (●) cross-linked PDMVMS, (□) VQR, and (◆) PBESS.

with the kinetics of oxygen incorporation in PBESS films, shown in Figure 5, and indicates that the rapid photoinduced elimination of bromine is responsible for the higher rate of  $\text{SiO}_x$  formation observed for PBESS.

**Changes in Film Thickness.** The conversion of polysiloxanes to  $\text{SiO}_x$  generally causes a loss in mass due to the removal of organic portions of the molecule. The loss in mass is also accompanied by a decrease in thickness. The pyrolysis of PDMS, for example, results in a mass loss of 25.5 wt % to 60.3 wt %, depending on the conditions of pyrolysis.<sup>11</sup> Pyrolysis of poly(2-chloroethylsilsequioxane), a polymer analogous to PBESS but only heat sensitive, yields a silicon oxide film with a thickness loss of 50%.<sup>3</sup> The aforementioned UV/ozone conversion of a Langmuir–Blodgett film of low molecular weight PDMS led to a 50% thickness loss.<sup>17</sup> If one assumes that the silicon content does not change during UV conversion, the hypothetical loss in thickness for PDMS transforming into  $\text{SiO}_x$  is ~55%.<sup>35</sup>

Figure 7 shows the apparent thickness decrement of the siloxane polymer films with initial thickness of 400–1000 nm as a function of UV/ozone exposure time. Rather different behaviors in thickness loss are observed for each polymer precursor and can be explained as follows. The procedure used to deposit the polymers onto substrates produces thicker layers of PBESS and VQR than PDMS. In addition, we have shown previously that the transformation rate was more rapid for PBESS and VQR. Greater initial thickness and faster conversion explains the difference in thickness decrement between PBESS, VQR, and PDMS.

The plateau observed in all the thickness decrement curves indicates that the UV/ozone conversion of polysiloxane into silicon oxide is a self-limiting process. Analysis of the data for PDMS, showing an apparent

thickness decrement of about 50 nm, suggests that the thickness of the surface  $\text{SiO}_x$  film that can be formed by UV/ozone treatment is of the order of 20–30 nm. A more quantitative interpretation of the data is not possible, since only a single-layer model was employed to obtain a composite thickness that includes the surface oxide layer and any remaining underlying substrate. The formation of a thin continuous layer of silicon oxide over the underlying polysiloxane substrate causes the oxidation reaction to become controlled by the rate of ozone diffusion. Ozone is not the primary reactant, however, as we find that ozone alone does not lead to significant  $\text{SiO}_x$  formation.<sup>35</sup> The reactant responsible for conversion of the polysiloxanes to  $\text{SiO}_x$  is actually atomic oxygen produced by the photodissociation of ozone. The atomic oxygen is too short-lived to diffuse appreciable distances, and thus must be generated in situ within a region of unconverted polysiloxane in order to continue the conversion process. After a certain thickness of  $\text{SiO}_x$  has been formed, all of the ozone will photodissociate before it reaches unconverted polysiloxane, whereupon further transformation to  $\text{SiO}_x$  will cease. We have developed a model for ozone diffusion through an  $\text{SiO}_x$  layer with simultaneous photodissociation, and the results conform well to the transformation kinetics and self-limiting behavior observed for UV/ozone conversion of PDMS. These results will be reported separately.

## Conclusions

A thin silicon oxide layer can be created on the surfaces of a variety of siloxane polymers by a UV/ozone-induced photochemical conversion process that involves exposure to UV radiation at room temperature in the presence of atmospheric oxygen. Different siloxane polymers exhibit rates of photoinduced conversion that can be related to details of their chemical structures. Polymers with a larger number of oxygen atoms coordinated to each silicon atom convert more rapidly, but all films present a great loss in carbon content after treatment. X-ray photoelectron spectroscopy demonstrates the effectiveness of the transformation, showing in particular that after conversion, the binding energies of the  $\text{Si}(2p)$  photoelectrons shift to a value that is very close to that of pure silicon dioxide and the silicon-to-carbon ratio is ~2 as expected for  $\text{SiO}_2$ . The reaction is self-limiting and produces a surface oxide layer that has an estimated thickness of ~20–30 nm on poly(dimethylsiloxane) substrates.

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