Reaction of Epoxides with Silicon

Amine-Reactive Monolayers on Scribed Silicon with Controlled Levels of Functionality: Reaction of a Bare Silicon Surface with Mono- and Diepoxides**

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Herein we report a significant advance in the preparation of patterned and functionalized silicon surfaces by showing that epoxides react with scribed silicon to yield monolayers with even greater efficiency than was reported for 1-alkenes,[1–5] 1-alkynes,[2,3] 1-halo- and α,ω-dihalo- alkanes,[3,6] and alcohols.[1] But more importantly we demonstrate that amine-reactive mixed monolayers with controlled levels of functionality can be formed on scribed silicon from mixtures containing an α,ω-diepoxide. As before,[1–4,6] monolayer formation simply consisted of wetting a dry, native oxide coated silicon surface with a reactive liquid, which had not been degassed, and scribing it in the air with a diamond tipped instrument. To our knowledge this is the first report of the reaction of an epoxide and a bare silicon surface (scribed or unpassivated). We are only aware of one other independent, unpublished study of the reaction of ethylene oxide with Si(100)-(2 × 1).[7]

The epoxide ring is an important functionality for industry, as well as organic and bioconjugate[8] chemistry because of its reactivity with amines, sulfhydryls, and other nucleophiles. Other researchers have also recognized the importance of epoxide-terminated,[9,10] and otherwise amine-reactive[11–13] or amine-terminated,[14,15] monolayers. Warning: Many epoxides and diepoxides are suspected carcinogens. Appropriate care should be exercised in their use.

We have considered several mechanistic pathways on model Si(100)-2 × 1 and $(H_3Si)_3Si^\bullet$ structures that could account for the reaction between scribed silicon and monosubstituted epoxides (see Figure 1). If one assumes that the silicon surface has zwitterionic reactivity, then two modes of addition can be considered. In many respects the most logical of these paths would involve nucleophilic attack of the epoxide oxygen onto an oxyphilic silicon. Unfortunately, the polar intermediate that is formed from the first step suffers from poor orbital overlap between the silyl anion and the antibond of the weak carbon–oxygen bond. This would lead to a disfavored 5-*endo*-tet reaction according to Baldwin's rules.[16] Formation of a high energy secondary cabocation is necessary for the eventual formation of the disilaoxane shown in path A.

The alternative zwitterionic reaction has nucleophilic silicon attacking the electrophilic epoxide in an S_N2 fashion (see path B). The resulting alkoxide would rapidly close to give a disilaoxane. The position of the alkyl group, R, by path B may allow better chain packing than the products of paths A and C. Therefore, the high C1s:Si2p X-ray photoelectron spectroscopy (XPS) ratios observed for epoxides support this mechanism. However, it does not take advantage of the silicon–oxygen bond strength in the first step, the rate-determining step.

A recent theoretical study shows that alkenes bind to Si(100)-2 × 1 through a diradical mechanism.[17] The weakness of the Si=Si banana bond in Si(100)-2 × 1, which "has been estimated at values between 1 and 31 kJ mol^{-1}, with most estimates clustering between 20 and 30 kJ mol^{-1},"[18] suggests that a diradical should be a good resonance structure for it, and further suggests that scribed silicon may have significant radical character. A surface silyl radical would be expected to bond to an epoxide through its oxygen, as shown in path C. The strong silicon–oxygen bond that would be formed concomitantly with the opening of the epoxide ring would be an energetically favorable event. Our ab initio calculations on $(H_3Si)_3Si^\bullet$ are consistent with radical ring opening to give the more stable secondary radical intermediate. This species

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[**] Acknowledgment is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, to the Research Corporation, and to the David M. Kennedy Center at BYU for their support of this research.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200250846

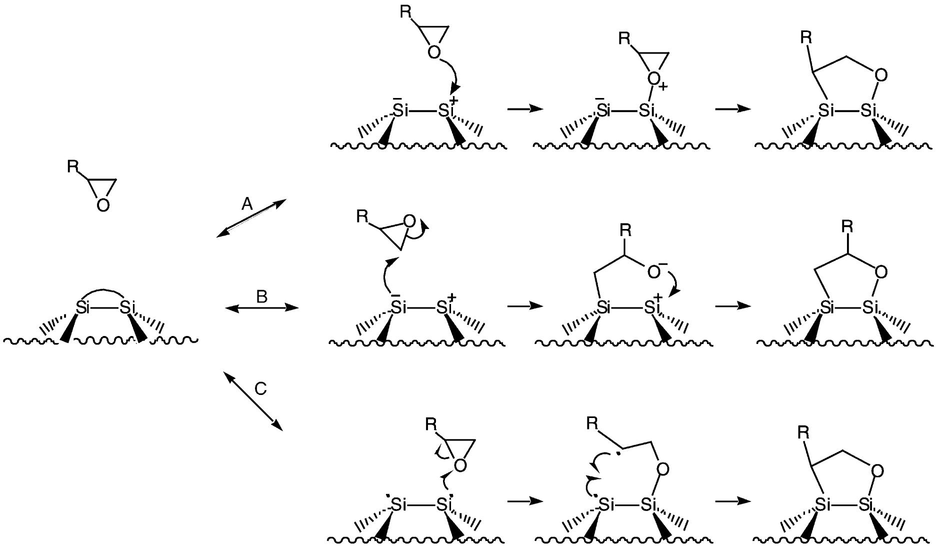


Figure 1. Possible mechanisms for the reaction of scribed silicon with epoxides. Path A: Nucleophilic attack by the epoxide oxygen. Path B: Nucleophilic attack by the silicon surface. Path C: Radical attack by the silicon surface.

would rapidly close with the silicon surface to give the ring structure shown.

The nature of the scribed silicon surface (radicaloid versus zwitterionic), the orientation(s) of the alkyl groups, the effect of the heat generated during scribing on the surface reaction, and the possibility that more than one type of mechanism accounts for bonding on scribed silicon are issues that deserve further analysis.

Figure 2 shows XPS and wetting results from surfaces prepared by scribing Si in the presence of different 1,2-epoxyalkanes and also 1,2,7,8-diepoxyoctane. The C1s:Si2p XPS ratio (Figure 2a) increases as the number of carbon atoms in the monoexpoxide increases. This result is in accord with alkyl monolayer formation by chemisorption of epoxides. A slightly larger C1s:Si2p ratio is found for 1,2,7,8-diepoxyoctane compared to 1,2-epoxyoctane. This result is consistent with a higher concentration of oxirane rings in 1,2,7,8-diepoxyoctane, compared to 1,2-epoxyoctane, thus leading to a higher surface concentration of alkyl chains. Figure 2b shows a steady increase in the ratio of chemically unshifted carbon (carbon bonded only to carbon or hydrogen) versus carbon bonded to one oxygen atom. As expected, 1) the fraction of chemically shifted carbon from the monolayers decreases as the chain length of the monoepoxide increases, and 2) there is more chemically shifted carbon on the surface prepared by scribing under 1,2,7,8-diepoxyoctane than under 1,2-epoxyoctane.

The sessile water contact angle measurements of the surfaces prepared from monoepoxides shown in Figure 2c increase as the number of methylene units in the monoepoxide increases. As before,[1] the unusually high contact angles for these surfaces is attributed to surface roughness. These results suggest increasingly thick and dense alkyl monolayers. The relatively low contact angle from the surface prepared with 1,2,7,8-diepoxyoctane is consistent with a polar head group, that is, an oxirane ring, at the monolayer surface, and attachment of diepoxides to surfaces through a single epoxide ring.

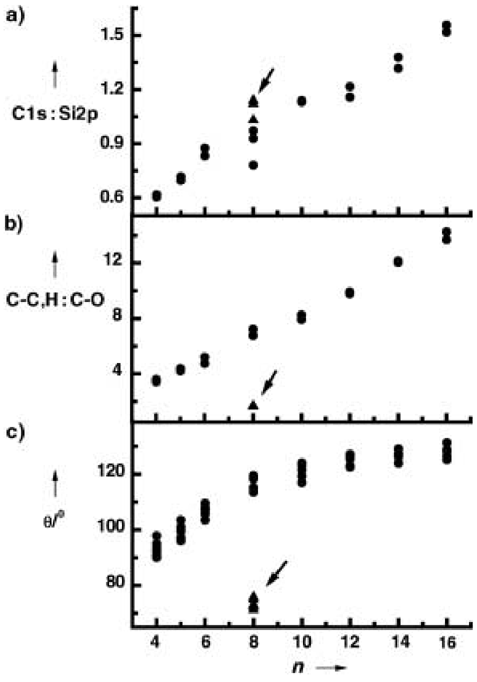
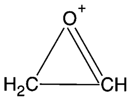
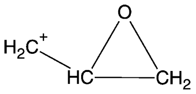
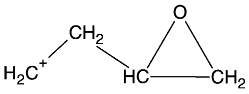


Figure 2. Physical properties of silicon scribed under 1,2-epoxyalkanes (circles) and 1,2,7,8-diepoxyoctane (triangles, note arrows) as a function of the number of carbon atoms, n, in the reactive liquid: a) C1s:Si2p XPS uncorrected area ratio, b) XPS ratio of carbon (bonded to carbon or hydrogen) to carbon bonded to one oxygen atom, and c) sessile water contact angles, θ, (in degrees).

Monolayers prepared from 1,2-epoxyoctane and 1,2,7,8-diepoxyoctane were also characterized by time-of-flight secondary ion mass spectrometry (ToF-SIMS). Table 1 shows peak areas of selected masses from the resulting spectra. As expected, 1) more $(CH_2)_nC_2H_3O^+$ ($n = 0, 1, 2$), CHO^+, and CH_2O^+ appear in the mass spectra of surfaces

Table 1: Intensities of cationic fragments in ToF-SIMS of Si scribed under 1,2-epoxyoctane and 1,2,7,8-diepoxyoctane.

Fragment (with proposed structure)	1,2-epoxyoctane[a]	1,2,7,8-diepoxyoctane[a]
	0.023 ± 0.003	0.066 ± 0.002
	0.014 ± 0.003	0.023 ± 0.006
	0.0043 ± 0.0016	0.0070 ± 0.0014
$C_5H_9O^+$	0	0
CHO^+	0.0104 ± 0.0012	0.0527 ± 0.0147
CH_2O^+	$0.0002 \pm$ [b]	0.0031 ± 0.0004
CH_3^+	0.0569 ± 0.0092	0.0648 ± 0.0128
$CH_2CH_3^+$	0.1866 ± 0.0281	0.0976 ± 0.0122
$(CH_2)_2CH_3^+$	0.1234 ± 0.0247	0.0659 ± 0.0068
H^+	0.0178 ± 0.0048	0.0374 ± 0.0067

[a] Values are the ratio of the area of the fragment in question to the area of the $^{28}Si^+$ peak in the same spectrum. [b] In three of four measurements no signal was observed. Errors are $\frac{ts}{\sqrt{N}}$, where $t = 3.18$ for 95 % confidence with three degrees of freedom, s is the standard deviation of four measurements, and $N = 4$.

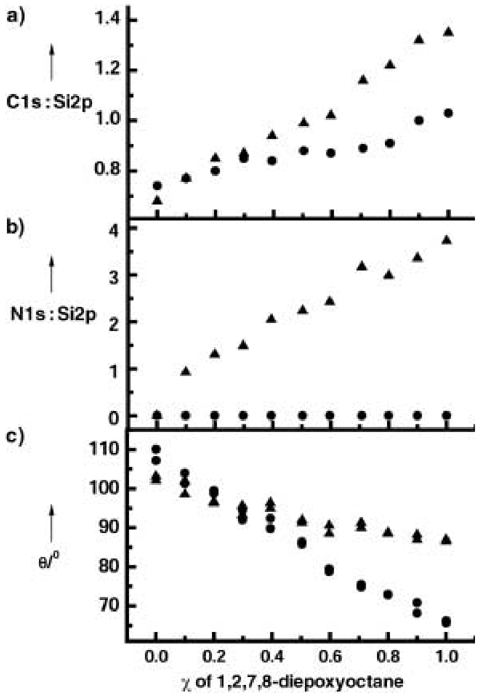


Figure 3. Physical properties of mixed monolayers prepared by scribing silicon under binary solutions of 1,2-epoxyoctane and 1,2,7,8-diepoxyoctane before (circles) and after (triangles) reaction with 1-aminooctane: a) C1s:Si2p XPS uncorrected area ratio, b) N1s:Si2p XPS uncorrected area ratio, and c) sessile water contact angles. χ = molar fraction.

prepared by scribing under 1,2,7,8-diepoxyoctane than under 1,2-epoxyoctane, and 2) the yield of $CH_3CH_2^+$ and $CH_3CH_2CH_2^+$ is greater in surfaces derived from the monoepoxide than from the diepoxide.

An important method of tailoring surface reactivity and properties is to create mixed monolayers through chemisorption of more than one reactive species.[19,20] Figure 3 shows the physical properties of mixed monolayers that were prepared by scribing silicon in the presence of mixtures of 1,2,7,8-diepoxyoctane and 1,2-epoxyoctane. As expected from the results in Figure 2, the C1s:Si2p XPS ratio increases (see Figure 3 a) and the sessile water contact angles decrease (see Figure 3 c) as the mole fraction of 1,2,7,8-diepoxyoctane increases. As before,[1] these results suggest kinetic, and not thermodynamic control in monolayer formation.

The amine reactivity of epoxides is used to couple proteins in bioconjugate chemistry[8] as well as in many industrial processes. Figure 3 shows the reaction of mixed monolayers prepared from 1,2,7,8-diepoxyoctane and 1,2-epoxyoctane with 1-aminooctane. After this reaction, the C1s:Si2p (Figure 3 a) and N1s:Si2p (Figure 3 b) XPS ratios, as well as the water contact angles (Figure 3 c) increase above initial levels with increasing 1,2,7,8-diepoxyoctane concentration in the scribing liquid. Thus, amine-reactive surfaces with controlled degrees of available functionality are prepared on scribed silicon by using a mixture of a mono- and a bifunctional epoxide.

Epoxides react with gaseous HCl, and this reaction has been used to label them for XPS studies.[21,22] Functionalized patches[1] prepared from neat 1,2,7,8-diepoxyoctane and from neat 1,2-epoxyoctane were exposed to fumes of concentrated HCl for 1 hr at room temperature. Following this exposure the surfaces derived from 1,2-epoxyoctane had no Cl by XPS but those derived from 1,2,7,8-diepoxyoctane showed significant amounts of Cl (~27 C atoms per Cl atom, or ~3.5 alkyl chains per Cl atom). After HCl exposure, ToF-SIMS of the diepoxide surface showed pairs of fragments with the same ratio and spacing as naturally occurring ^{35}Cl and ^{37}Cl; these masses were attributable to CH_2Cl^+, $CHOHCH_2Cl^+$, and CH_2Cl^-. Corresponding pairs of peaks were neither obtained from the monoepoxide surface after HCl exposure, nor in the mass spectra of the surfaces prior to reaction.

Thus, a combination of instrumental characterization and chemical studies indicate that scribed silicon reacts with mono- and di-epoxides to produce alkyl monolayers. Materials and methods for the amine reaction, the surface characterization, and semiempirical calculations are given in the Supporting Information.

Received: December 27, 2002
Revised: June 17, 2003 [Z50846]

Keywords: chemisorption · monolayers · nucleophilic addition · radical reactions · silicon

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[1] T. L. Niederhauser, Y.-Y. Lua, G. Jiang, S. D. Davis, R. Matheson, D. A. Hess, I. A. Mowat, M. R. Linford, *Angew. Chem.* **2002**, *114*, 2459–2462; *Angew. Chem. Int. Ed.* **2002**, *41*, 2353–2356.

[2] T. L. Niederhauser, G. Jiang, Y.-Y. Lua, M. J. Dorff, A. T. Woolley, M. C. Asplund, D. A. Berges, M. R. Linford, *Langmuir* **2001**, *17*, 5889 – 5900.

[3] Y.-Y. Lua, T. L. Niederhauser, R. Matheson, C. Bristol, I. A. Mowat, M. C. Asplund, M. R. Linford, *Langmuir* **2002**, *18*, 4840 – 4846.

[4] Y.-Y. Lua, T. L. Niederhauser, B. A. Wacaser, I. A. Mowat, A. T. Woolley, R. C. Davis, H. A. Fishman, M. R. Linford, *Langmuir* **2003**, *19*, 985 – 988.

[5] B. A. Wacaser, M. J. Maughan, I. A. Mowat, T. L. Niederhauser, M. R. Linford, R. C. Davis, *Appl. Phys. Lett.* **2003**, *82*, 808 – 810.

[6] T. L. Niederhauser, Y.-Y. Lua, Y. Sun, G. Jiang, G. S. Strossman, P. Pianetta, M. R. Linford, *Chem. Mater.* **2002**, *14*, 27 – 29.

[7] R. A. Wolkow, **2002**, personal communication.

[8] G. T. Hermanson, *Bioconjugate Techniques*, Academic Press, SanDiego, **1996**.

[9] J. M. Abad, M. Vélez, C. Santamaría, J. M. Guisán, P. R. Matheus, L. Vázquez, I. Gazaryan, L. Gorton, T. Gibson, V. M. Fernández, *J. Am. Chem. Soc.* **2002**, *124*, 12845 – 12853.

[10] D. G. Kurth, G. K. Broeker, C. P. Kubiak, T. Bein, *Chem. Mater.* **1994**, *6*, 2143 – 2150.

[11] R. G. Chapman, E. Ostuni, L. Yan, G. M. Whitesides, *Langmuir* **2000**, *16*, 6927 – 6936.

[12] R. L. Cicero, P. Wagner, M. R. Linford, C. J. Hawker, R. M. Waymouth, C. E. D. Chidsey, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **1997**, *38*, 904 – 905.

[13] P. Wagner, S. Nock, J. A. Spudich, W. D. Volkmuth, S. Chu, R. L. Cicero, C. P. Wade, M. R. Linford, C. E. D. Chidsey, *J. Struct. Biol.* **1997**, *119*, 189 – 201.

[14] N. Balachander, C. N. Sukenik, *Langmuir* **1990**, *6*, 1621 – 1627.

[15] A. B. Sieval, R. Linke, G. Heij, G. Meijer, H. Zuilhof, E. J. R. Sudhölter, *Langmuir* **2001**, *17*, 7554 – 7559.

[16] J. E. Baldwin, R. C. Thomas, L. T. Kruse, L. Silberman, *J. Org. Chem.* **1977**, *42*, 3846 – 3852.

[17] X. Lu, *J. Am. Chem. Soc.* **2003**, *125*, 6384 – 6385.

[18] R. J. Hamers, Y. Wang, *Chem. Rev.* **1996**, *96*, 1261 – 1290.

[19] J. P. Folkers, P. E. Laibinis, G. M. Whitesides, *Langmuir* **1992**, *8*, 1330 – 1341.

[20] D. A. Offord, C. M. John, M. R. Linford, J. H. Griffin, *Langmuir* **1994**, *10*, 883 – 889.

[21] L. J. Gerenser, J. F. Elman, M. G. Mason, J. M. Pochan, *Polymer* **1985**, *26*, 1162 – 1166.

[22] J. M. Pochan, L. J. Gerenser, J. F. Elman, *Polymer* **1986**, *27*, 1058 – 1062.