Silicon Epoxide: Unexpected Intermediate during Silicon Oxide Formation

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Infrared absorption spectroscopy and density functional cluster calculations are used to identify the intermediate oxide structures formed by high temperature annealing of the water-exposed Si(100)-(2 × 1) surface. We find that initially there is a strong tendency for oxygen to agglomerate on single dimer units at $T \sim 800$ K. Upon dehydrogenation, a remarkable structural transition is observed, wherein the dangling bonds recombine to form silicon epoxides (three-membered Si—O—Si rings). We demonstrate that these epoxides are the thermodynamically favored product in such constrained systems and, consequently, should be preferentially formed at silica interfaces. [S0031-9007(98)07445-6]

Understanding the formation and evolution of SiO (defect) structures at silica surfaces and Si/SiO$_2$ interfaces is of prime importance due both to the utilization of ultrathin oxide (~ 10 Å) films as the gate dielectric layer in state-of-the-art semiconductor devices [1] and to the production of ultralow loss silica-based fiber for long distance optical communications. The detailed structural understanding of such interfaces poses a formidable scientific challenge due to the lack of long-range order and critical dependence on a wide array of production parameters. Therefore, a comprehensive knowledge of the fundamental physical and chemical properties of such systems must commence with the characterization of related systems that are more reproducible and amenable to control. In accordance with this prescribed approach, a wide variety of experimental [2] and theoretical [3] studies of such model systems have been undertaken over the past decade, but have singularly failed to provide a definitive mechanistic picture. For example, previous theoretical studies have focused primarily on a few simple Si—O structures that may result from the insertion of a single oxygen into the Si(100)-(2 × 1) surface, with little exploration of the wider group of multiply oxidized structures that are subsequently formed during oxidation. Similarly, experimental studies have typically employed techniques [e.g., ultraviolet photoemission spectroscopy (UPS), x-ray photoemission spectroscopy (XPS)] and conditions that do not permit identification of the relevant discrete (sub)oxide structures formed. Recently, a combined infrared and theoretical study of the initial water-induced oxidation of Si(100)-(2 × 1) [4] has shown that oxygen is first inserted into the dimer bonds and then into the Si backbonds, although the formation of the "real" multiply oxidized Si structures (that are the constituent subunits of extended layer growth) could not be delineated, as the spectral signatures of these oxide species were below the accessible range (<1000 cm^{-1}).

In this work, we have implemented a novel spectroscopic configuration that allows access to a broad spectral range (550–4000 cm^{-1}) with submonolayer sensitivity to *all* vibrational components. We have primarily focused on the H$_2$O:Si(100)-(2 × 1) system as a model for Si oxidation, since the amount of oxygen is known exactly [0.5 monolayer (ML)] and the variation of a single parameter (temperature) provides accurate control over the oxidation process. However, we have also studied the O$_2$-induced oxidation of the same surface and find that the high temperature behavior is indistinguishable from that observed for H$_2$O, confirming the generality of our findings.

Our approach uses a dynamically aligned Fourier transform infrared spectrometer in single pass external transmission geometry (60° incidence to the surface normal), combined with precise temperature (± 0.3 °C) and purge gas flow control. This spectroscopic configuration allows *simultaneous* observation of the hitherto unobserved low frequency Si—O stretching and Si—H bending fundamentals and the (well-characterized) higher frequency Si—H and O—H stretching modes, thereby providing multiple "check points" for our theoretical treatment. This makes the *definitive* identification of novel surface structures, e.g., silicon epoxides, possible. In the following we present the first observation of such species on an oxidized silicon surface and generalize these findings to other Si and SiO$_2$ systems.

The infrared spectrum of the Si(100)-(2 × 1) surface exposed to water at 220 K is presented in Figs. 1(a)–1(c). This (initial) surface has been studied extensively [2], and has been shown to consist exclusively of Si—H and Si—OH groups attached to the opposite ends of the same dimer. The characteristic infrared signatures are ν(Si—OH): 824 cm^{-1}; δ(SiO—H): 895 cm^{-1}; ν(Si—H): 2085 cm^{-1}; ν(SiO—H): 3657 cm^{-1}. Our extended spectral range makes it possible to also observe the low frequency Si—H bending mode at 619 cm^{-1} for the first time, yielding unambiguous support to this assignment. The broader importance of this capability is underscored by the observation of an additional bending mode at 604 cm^{-1} that can be correlated with the 785 cm^{-1} and 3674 cm^{-1} features, and assigned to the effects of hydroxyl-mediated interdimer coupling [5].
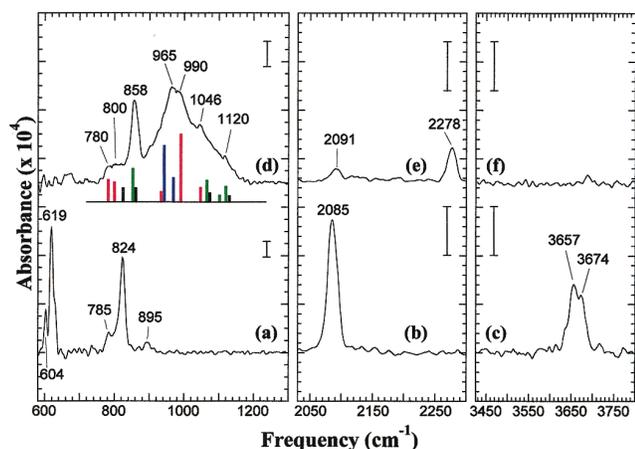
FIG. 1(color). Infrared spectra of the Si(100)-(2 × 1) surface exposed to H_2O under ultrahigh vacuum conditions: (a)–(c) following initial exposure at 220 K and (d)–(f) after annealing at 870 K. The vertical scale indicators denote unit (1×10^{-4}) absorbance for each spectrum. The colored bars denote the theoretically predicted frequencies and intensities as follows: red—$(O_2)SiØSi(O_2)$; blue—$SiØSi(O_2)$; green—$^{*}(O_2)SiOSi(O_2)H$; black—$H(O_2)SiOSi(O_2)H$. Note: The predicted intensities are only *qualitatively* comparable for modes of similar type (e.g., Si—H modes are not comparable with Si—O modes). The mode at 2091 cm^{-1} is attributed to a small amount of residual (unoxidized) Si—H, formed by background adsorption.

Profound changes are apparent on annealing this HSiSiOH terminated surface to temperatures above 750 K [Figs. 1(d)–1(f)]. All the features associated with the surface hydroxyl moieties and "pure" Si—H species are clearly absent so that the spectrum is now dominated by a strong, broad absorption band with peaks at 965 and 990 cm^{-1} and a pronounced shoulder at 1046 cm^{-1}. In addition, a relatively sharp absorption band is observed at 858 cm^{-1}, together with a very weak feature at 1120 cm^{-1} that constitutes part of a broad high frequency tail to the main absorption band. Importantly, the overall attenuation of features from 2100–2200 cm^{-1} indicates that the vast majority of the hydrogen has desorbed after annealing to 875 K [Fig. 1(e)]. The remaining peak at 2278 cm^{-1} is definitively assigned to an Si—H species with the Si bound to three oxygen atoms, and correlated with the 858 and 1120 cm^{-1} low frequency modes; all three modes (858, 1120, and 2278 cm^{-1}) show identical thermal behavior and disappear upon annealing to 925 K, at which temperature all hydrogen has desorbed (data not shown). In contrast, the 965/990 and 1046 cm^{-1} modes are essentially unchanged even after annealing to 950 K, as is the weak broad absorption at 780–800 cm^{-1}, strongly suggesting that these features are due to *de*hydrogenated, oxygen-containing surface structures. These observations are consistent with our earlier demonstration [4] that the Si—O stretching modes of multiply oxygenated hydrogenated dimers such as HSiOSi(O)H occur *exclusively* above 1000 cm^{-1} and *increase* continuously with oxygen content.

Two important observations point to the novel origin of the 965/990 and 1046 cm^{-1} features. First, upon isotopic substitution (i.e., $H_2{}^{18}O$ exposure at 220 K and anneal to 875 K), the 965/990 cm^{-1} features shift by only 30 cm^{-1} and the modes comprising the weak band at 780–800 cm^{-1} exhibit an even smaller, ~20 cm^{-1} shift. These ^{18}O induced shifts are substantially smaller than the 45 cm^{-1} redshift observed for the 1120 cm^{-1} mode, which is in good agreement with the 50–55 cm^{-1} shifts reported for hydrogenated oxide structures in porous Si [6]. Second, the 780–800, 965, and 990 cm^{-1} modes are well below the stretching frequency range of commonly observed extended oxide structures [6,7]. Therefore, while these low frequency features are clearly associated with Si—O stretching vibrations, both the frequency and the isotopic shift are unprecedented so that a detailed theoretical treatment of this system is clearly required in order that specific assignments can be made.

We have performed first-principles gradient-corrected density functional calculations on model clusters to investigate the oxidation of the Si(100)-(2 × 1) surface. The cluster used (Fig. 2) employs boundary conditions that provide an accurate representation of a multiply oxidized dimer unit. In all clusters evaluated, the unsaturated valences that result from truncation of bulk Si—Si bonds are terminated with H atoms to remove unphysical effects caused by the excess dangling bonds that would otherwise be present. The constraints imposed on each nine-silicon atom fragment in the extended surface case are simulated by fixing terminating H atoms, as well as 3rd and 4th layer Si atoms, in tetrahedral latticelike positions for the course of the geometry optimization. In this way, the first two layers that comprise the oxide "cap" are free to expand as necessary, while the underlying Si effectively retains near bulk dimensions, so a strained 2–3 interlayer naturally results. Importantly, under the experimental
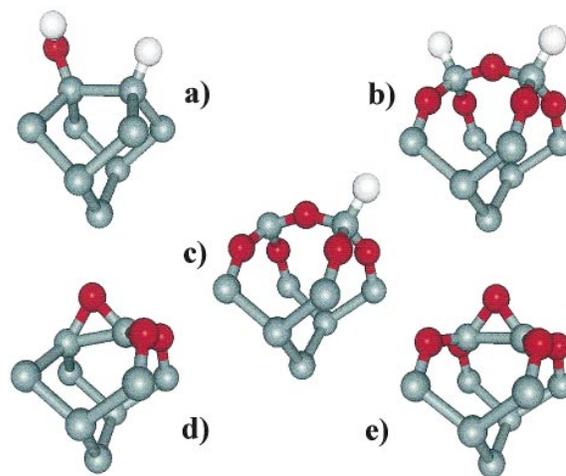
FIG. 2(color). Observed surface silicon epoxide structures and their precursors: (a) HSiSiOH; (b) $H(O_2)SiOSi(O_2)H$; (c) $^{*}(O_2)SiOSi(O_2)H$; (d) $SiØSi(O_2)$; (e) $(O_2)SiØSi(O_2)$. Silicon atoms are colored in gray, oxygens are red, and hydrogens are white.

conditions investigated herein (where the extent of oxidation is limited by the initial 0.5 ML surface coverage), this single dimer model should provide accurate information on the relevant energetics and spectroscopic signatures of the different species.

For each oxidized structure, we have determined the optimized geometry and the harmonic vibrational frequencies with the B3LYP functional and a polarized double-zeta basis set [8]. The calculated frequencies were corrected for anharmonicity and some systematic errors of the computational method, by means of a single, experimentally derived correction that is mode specific (e.g., Si—H stretch, X—Si—H bend, etc.) [9], but transferable between modes of a given type. The applicability of this methodology is confirmed by reference to previous studies of the one- and two-oxygen inserted [HSiOSiH and HSiOSi(O)H] surface structures, both of which are exceptionally well described using this approach [4,10].

The theoretical results demonstrate that the Si—H bond energy increases with the degree of oxidation. In fact, this increase is found to be nonlinear in the number of O atoms, with relative Si—H bond strengths for HSi, HSi(O), HSi(O)$_2$, and HSi(O)$_3$ given by 0.8:0.83:0.88:1.0. Indeed, the predominance of a 2278 cm^{-1} Si—H feature in the 875 K spectrum confirms that only three, four, or five oxygen-containing dimers [which possess the necessary HSi(O)$_3$ structural unit] are present at this temperature. Moreover, the calculations show [10] that the three- and five-oxygen-containing structures, HSiOSi(O$_2$)H and H(O$_2$)SiOSi(O$_2$)H, are thermodynamically favored relative to *all* other (one, two, and four O-containing) possible structures. In addition, upon annealing, the possible existence of *partially* dehydrogenated structures, such as *SiOSi(O$_2$)H and *(O$_2$)SiOSi(O$_2$)H (where * denotes a dangling bond) must also be considered, since they also possess the (O$_3$)SiH structural unit, and are likely intermediates in the dehydrogenation process.

Comparison of the predicted Si—H bending and Si—O stretching frequencies with the experimentally observed ones provides strong evidence for the existence of a hydrogenated five-oxygen structure (Table I). In particular, the broadband observed above 1100 cm^{-1} can be assigned only to H(O$_2$)SiOSi(O$_2$)H (dominant mode at 1131 cm^{-1}) or *(O$_2$)SiOSi(O$_2$)H (dominant mode at 1120 cm^{-1}) surface structures [Figs. 2(b) and 2(c)], as all other less oxidized local surface structures give rise to Si—O stretching modes exclusively between 1000 and 1100 cm^{-1}. We deduce that the fully hydrogenated species is a minority structure based on the absence of a feature at 819 cm^{-1} (predicted to be as intense as the 858 cm^{-1} experimental mode), leaving the partially dehydrogenated *(O$_2$)SiOSi(O$_2$)H as the predominant (O$_3$)SiH species. In order to understand the origin of the remaining spectral features (below 1000 cm^{-1}), we must consider the effect of dehydrogenation on the energetics of the oxidation process.

TABLE I. Summary of calculated and observed frequencies for assigned surface structures. Note: Only modes that possess significant dipole moments are listed. "BB" stands for "broadband" and indicates that although no discrete feature could be resolved at a given frequency, there is substantial spectral intensity over the frequency range in question.

Species	Mode	Freq. (cm^{-1}) (^{18}O shift)	
		Theoretical[9]	Experimental
H(O$_2$)SiOSi(O$_2$)H	(O$_3$)Si—H	819 (2)	···
	(O$_3$)Si—H	856 (2)	858 (5)
	Si—O(a)	1075 (47)	1070 (45)[11]
	Si—O(a)	1131 (51)	BB
	Si—H(s)	2251 (0)	2278 (2)
*(O$_2$)SiOSi(O$_2$)H	(O$_3$)Si—H	847 (3)	858 (5)
	Si—O(a)	1023 (43)	BB
	Si—O(a)	1034 (45)	BB
	Si—O(a)	1063 (46)	1070 (45)[11]
	Si—O(a)	1102 (52)	···
	Si—O(a)	1120 (51)	1120 (45)
	Si—H	2250 (0)	2278 (2)
SiØSi(O$_2$)	Si—O(s)	747 (26)	···
	Si—O(a)	941 (37)	BB
	Si—O(a)	969 (37)	965 (30)
(O$_2$)SiØSi(O$_2$)	Si—O(s)	774 (18)	~780 (~20)
	Si—O(s)	798 (22)	~800 (~20)
	Si—O(a)	936 (42)	BB
	Si—O(a)	991 (36)	990 (30)
	Si—O(a)	1048 (35)	1046 (40)

We find that there are two principal structural possibilities for the oxidized dimer units upon removal of both H atoms [12]: (a) The (trivial) formation of a pair of Si "dangling" bonds (denoted *SiOSi*) or (b) structural rearrangement to form a Si—Si bond as one side of a threefold ring comprised of two silicons and an oxygen (denoted by SiØSi), which we term a Si "epoxide" linkage, by reference to the analogous structure in carbon chemistry. Remarkably, a comparison of the relative energetics of the corresponding isomers reveals that the formation of the exotic epoxide structure is strongly favored in *highly oxidized dimer units,* while dangling bond formation is expected to predominate for the one- and two-oxygen containing dimers. Specifically, the dangling bond isomers *SiOSi* and *SiOSi(O)* are more stable than their alternative isomers by more than 10 kcal/mol. However, the situation changes for O ≥ 3; the SiØSi(O$_2$) and (O$_2$)SiØSi(O$_2$) epoxides [Figs. 2(d) and 2(e)] are stabilized by 2 and 18 kcal/mol, respectively, over their dangling bond isomers.

It is thus clear that epoxide formation should be observed as the local concentration of oxygen increases (i.e., agglomeration occurs). Importantly, the existence of *(O$_2$)SiOSi(O$_2$)H and H(O$_2$)SiOSi(O$_2$)H (Fig. 2) provides clear experimental evidence for such agglomeration, despite the low initial O coverage (0.5 monolayer). From a theoretical standpoint, this observation can be rationalized by consideration of "aggregation" energies, which reveals that there is a clear propensity of oxygens towards

aggregation, as high as 2.6 kcal/mol and 5.4 kcal/mol for the three-oxygen and five-oxygen epoxides, $SiØSi(O_2)$ and $(O_2)SiØSi(O_2)$, respectively.

These thermodynamic considerations are supported by analysis of the remaining vibrational modes in the spectrum of the annealed surface [Figs. 1(d)–1(f)]. The experimental spectrum observed after annealing to 875 K can be assigned only to a combination of *two* such species: the three- and five-oxygen-containing epoxide structures (Table I). Specifically, the 990 and 1046 cm^{-1} features are in excellent agreement with the theoretically predicted modes at 991 and 1048 cm^{-1} for the $(O_2)SiØSi(O_2)$ structure. Furthermore the 30 cm^{-1} shift observed for these features upon ^{18}O isotopic substitution is in good agreement with the predicted 35–36 cm^{-1} and is considerably smaller than that for the 1120 cm^{-1} mode of $H(O_2)SiOSi(O_2)H$ (predicted at 51 cm^{-1} and observed at 45 cm^{-1}). The $(O_2)SiØSi(O_2)$ structure is also predicted to possess a pair of symmetric Si—O stretches at 774 and 798 cm^{-1} that show characteristic isotopic shifts of 18 and 22 cm^{-1}, respectively, in excellent agreement with the $\sim$20 cm^{-1} experimentally observed shift of the 780–800 cm^{-1} band. Lastly, the frequency and isotopic shift of the 965 cm^{-1} mode, together with the significant intensity around $\sim$940 cm^{-1}, similarly supports assignment to a $SiØSi(O_2)$ structure (Table I).

The origin of the unique epoxide vibrational signatures is revealed by inspection of the geometric parameters associated with these structures. The bonding in $(O_2)SiØSi(O_2)$ is characterized both by an ultrashort 2.16 Å Si—Si bond and long 1.71 Å Si—O bonds (cf. 1.64–1.68 Å in hydrogenated, oxidized structures); the formation of a genuine Si—Si bond is apparent from an analysis of the topology of the electron density, which shows a buildup of electron density (with extent characteristic of a "single" bond) between the two Si centers. This bond also possesses unusual curvature, greater than that usually seen in three-membered ring structures. The longer Si—O bonds give rise to the unusually low vibrational frequencies observed for these epoxides, whereas the small isotopic shift observed for the epoxide modes can be attributed to the substantial component of Si—Si motion involved. The geometry in $SiØSi(O_2)$ is similar, although it possesses a longer (strained), 1.78 Å Si—O bond on the side without O in the backbonds. This strain is largely relieved by the flexibility introduced by additional backbond Si—O—Si linkages (hence the increased stability of the multiply oxidized epoxide structures). This analysis now readily explains the results of previous theoretical treatments [3] that found that the so-called "on-dimer" position for oxygen was at best *meta*stable in the one-oxygen limit.

The formation of a three-membered Si—O—Si epoxide ring is also thermodynamically favorable in small molecules such as $H_2SiØSiH_2$, suggesting that such bonding is likely to occur in a variety of situations. Indeed,

West *et al.* have previously synthesized and isolated a number of such molecular analogs [13]. By analysis of several such molecules, we find that the epoxide arrangement is favored by over 30 kcal/mol over the (triplet) isomer with two dangling bonds. Comparison with the corresponding value for the five-oxygen surface epoxide indicates that there is 12 kcal/mol worth of residual strain in the surface structure relative to the molecular analogs.

The identification of silicon epoxides as the stable product resulting from the recombination of adjacent dangling bonds strongly suggests that the epoxide bonding may also be common in silicate materials. Indeed, we find that such structures are particularly likely to be present on silicate surfaces and in oxygen-deficient or inhomogeneous silicates (and even germanates). Alternatively, although the interfacial epoxide structure is unlikely to survive further oxidation, we suggest that it will be the dominant surface intermediate and, as such, its formation will dictate the kinetics in the (kinetic) growth of ultrathin oxide films. Consequently, this work should provide strong motivation for future experimental and theoretical studies of the role that these intermediates play in determining the ultimate oxide quality in such technologically important materials.

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[11] Under certain experimental conditions a distinct feature at 1070 cm^{-1} was also observed in concert with the 858 and 1120 cm^{-1} features, but is not apparent in the averaged spectrum presented in Fig. 1.

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