New Structural Model for Si/SiO_2 Interfaces Derived from Spherosiloxane Clusters: Implications for Si $2p$ Photoemission Spectroscopy

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In this Letter, we investigate the Si/SiO_2 interface structure formed by the chemisorption of $H_8Si_8O_{12}$ and other spherosiloxane clusters on Si(100). Using transition state calculations, we clearly demonstrate that the clusters do not bond to the Si(100) surface via single vertex attachment as proposed previously, but rather attach via Si-O bond cleavage. This alternative cracked cluster geometry allows us to predict the photoemission features of spherosiloxane clusters on Si(100) without invoking second nearest neighbor effects.

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Although Si $2p$ photoemission is one of the most widely used techniques for studying the Si/SiO_2 interface, there has been considerable controversy about how to interpret the spectra properly. Traditionally, Si $2p$ photoemission spectra have been interpreted based on the formal oxidation state model, which states that the binding energy shifts of the Si $2p$ core level peaks increase nearly linearly with the number of *nearest neighbor* oxygen atoms [1]. However, this model was challenged in 1993 by Banaszak Holl and McFeely, who claimed that *second nearest neighbor* oxygen atoms can cause non-negligible Si $2p$ core level shifts, up to 1.0 eV for a Si attached to the Si of a SiO_3 group [2]. Their claims were based upon a photoemission study involving the adsorption of cluster molecules such as spherosiloxane (formula $H_8Si_8O_{12}$) on Si(100) [2–5]. Arguing that the structure of the Si/SiO_2 interface formed by these clusters was "known" *a priori,* they correlated the relative peak positions and intensities in the corresponding Si $2p$ spectrum with the different Si species at the interface. Pasquarello *et al.* [6] performed a careful density functional treatment of the photoemission peak positions for this interface structure. They found that the calculated features were totally inconsistent with the experimentally observed peaks at lower binding energies, and suggested that the actual surface structure may be "more complex." Though more related work on this system has been performed [7–10], this discrepancy between theory and experiment has not been resolved.

In this paper, we use accurate first-principles calculations based on gradient-corrected density functional theory (*vide infra*) to show that the "single vertex attachment" geometry assumed by Banaszak Holl and McFeely [2] [Fig. 1(a)] is not the preferred adsorption product. Instead, we clearly demonstrate that spherosiloxanes and other related molecules break a single Si-O bond across a surface dimer to form a bridged geometry [Fig. 1(c)]. This novel "cracked cluster" configuration not only provides a much better agreement with previous infrared data [9,10] but also explains the Si $2p$ photoemission spectra within the conventional formal oxidation state formalism (i.e., without requiring second nearest neighbor effects).

Our conclusions on the chemisorption mechanisms are based on accurate theoretical studies of competing reaction pathways on related model compounds interacting with Si(100). Our starting point is a Si_9 cluster fragment which has been successfully used to model various adsorption processes on a single dimer of the (2×1) reconstructed Si(100) surface [11–18]. The severed Si-Si bonds that connect this fragment with the rest of the surface are capped with H atoms to avoid unphysical artifacts. We use the well-documented B3LYP gradient corrected density functional [19] (Becke's three-parameter exchange functional and Lee-Yang-Parr's correlation functional) with the polarized 6-31G* [20] basis set. In the cluster model, the top two layers of atoms as well as the adsorbate atoms were allowed to relax, while the lower layer atoms were held fixed along crystalline directions. The structures of the minima and the transition states (representing the saddle points connecting the minima) were then completely optimized subject to the above constraints. All the optimized structures were then rigorously characterized by evaluating the complete matrix of force constants and the associated vibrational frequencies. All calculations were performed with the GAUSSIAN98 package [20].

We illustrate the main points by considering the interaction of trimethoxysilane, $HSi(OCH_3)_3$, with the Si(100) surface. This simple molecule contains the local $HSiO_3$ group as in the case of the larger spherosiloxane clusters. We discuss the energy barriers for two different modes of dissociative attachment of this molecule across the surface dimer: (1) by breaking the Si-O bond (as in our cracked cluster model) and (2) by breaking the Si-H bond (as in single vertex attachment).

As trimethoxysilane is brought towards the Si(100) surface, the principal interaction is between one of the oxygens and the positive (or lower) end of the buckled dimer. In the interaction complex [Fig. 2(a)], the O-Si interaction distance is 1.94 Å (only about 0.3 Å larger than a normal Si-O bond length), with a significant binding energy of 0.6 eV. This is somewhat reminiscent of the interaction of the Si(100) surface with H_2O [12]. Analogous structures containing threefold coordinated oxygen have

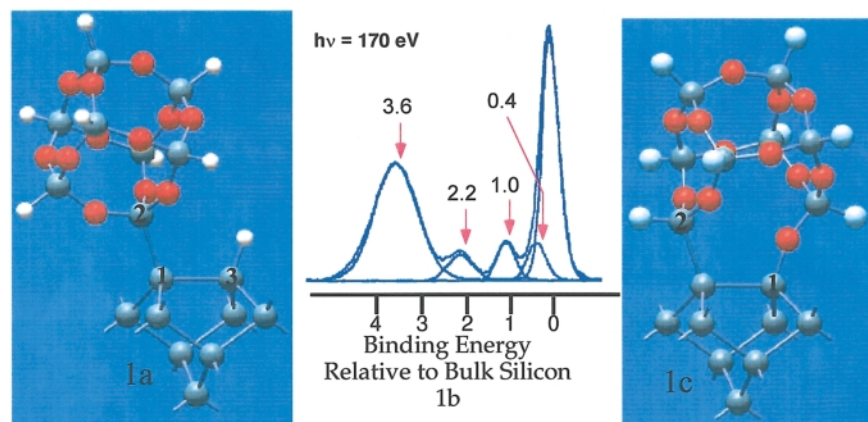

FIG. 1 (color). The structures formed from the interaction of spherosiloxane with Si(100) via Si-H bond cleavage (a) and Si-O bond cleavage (c). Si atoms are shown in gray, H atoms in white, and O atoms in red. The experimental photoemission spectrum is given in (b).

been seen in other situations also [21,22]. As the interaction proceeds, the complex Fig. 2(a) naturally leads to a four-center transition state structure [Fig. 2(b)], clearly corresponding to Si-O bond breaking across the dimer. The two Si-O distances in the transition state (one being formed and the other broken) are similar (1.84 Å) and a new Si-Si bond is beginning to form. This structure is only 0.15 eV higher in energy than the complex Fig. 2(a) and lies significantly (0.45 eV) below the separated reactants. As the reaction proceeds, it leads to the product containing a surface methoxy group [Fig. 2(c)] with no overall energy barrier.

The alternative possibility corresponds to breaking the Si-H bond in trimethoxysilane. In this case, the Si-H end of the molecule approaches the surface forming a weak complex (not shown) with a binding energy of <0.05 eV. More importantly, the transition state for this channel [Fig. 2(d)] involves a substantially higher energy barrier [by 0.8 eV relative to Fig. 2(b)]. The transition state eventually leads to the product shown in Fig. 2(e), analogous to that formed by single vertex attachment. The presence of an overall energy barrier with respect to the separated reactants is similar to that in the reaction of silane with Si(100) [11]. Interestingly, the product

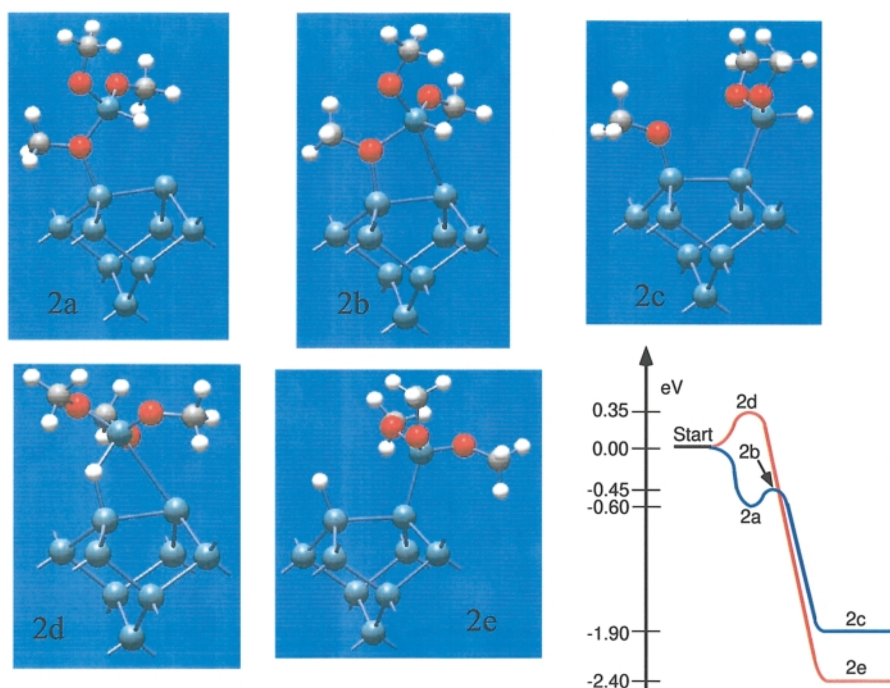

FIG. 2 (color). Calculated structures for the reaction of trimethoxysilane with the Si(100) surface. (a) is the initial interaction complex. (b) is the transition state for Si-O bond cleavage leading to the product shown in (c). Similarly, (d) is the transition state for Si-H bond cleavage leading to the product shown in (e). A schematic energy profile for the reaction is also shown.

Fig. 2(e) is about 0.5 eV more stable than that formed by breaking the Si-O bond [Fig. 2(c)]. However, since the energy barrier to the formation of Fig. 2(e) is substantially higher, the reaction is unlikely to proceed by this channel. A schematic of the energy profile illustrates these points in Fig. 2.

We have performed preliminary calculations on the analogous reactions of spherosiloxane ($H_8Si_8O_{12}$) and find similar results. When there is a competition between the breaking of a Si-O bond or a Si-H bond, the former occurs due to the energy barrier being lower. Again, this is influenced strongly by the initial interaction between one of the oxygens in the cluster and the buckled dimer. We conclude that $H_8Si_8O_{12}$ reacts to form the cracked cluster geometry shown in Fig. 1(c).

Confirmation of our analysis is provided by a careful comparison of the calculated and experimental vibrational frequencies of $H_8Si_8O_{12}$ clusters on Si(100). In these calculations, optimized geometries and normal mode frequencies were obtained for both structures 1(a) and 1(c) using the B3LYP density functional [19]. The first layer (dimer) silicons from the cluster and all the adsorbate atoms were allowed to relax while the deeper layer atoms were constrained to be in ideal crystalline positions. The polarized 6-31G** basis set [20] was used for the surface and adsorbate atoms while a 6-31G basis was used for the interior frozen atoms.

Table I compares the normal mode frequencies calculated for both structures 1(a) and 1(c) with infrared data of $H_8Si_8O_{12}$ on Si(100). Note that the experiments [9,10] were performed with a buried cobalt silicide metallic layer which makes the measurements sensitive only to the modes polarized perpendicular to the surface. Comparison between theory and experiment reveals two major discrepancies for the single vertex attachment geometry. First,

TABLE I. Calculated and experimental infrared vibrational frequencies (600–1600 cm^{-1}).

Theory [a]		
Single vertex attachment geometry [Fig. 1(a)]	Cracked cluster geometry [Fig. 1(c)]	Experiment [b]
	806 (m)	815
840 (w)	867 (s)	859
894,900 (s)	885 (m)	889
917 (w)	896,902 (s)	911
	1061 (w)	1058
1101 (s)	1108 (s)	1101
1128 (s)	1130 (m)	broad peak
1140 (m)	1146,1151 (s)	broad peak
1148,1152 (s)	1164 (s)	1178

[a]The infrared intensities, denoted as weak (w), medium (m), and strong (s), have the following calculated ranges: w = 50-200, m = 200–500, and s = >500 km/mol (1 km/mol = 0.02367 $D^2/Å^2$ amu).
[b]Experimental values from Ref. [10]. The values from Ref. [9] are very similar.

although the normal mode calculations predict a surface Si-H stretching mode around 2100 cm^{-1} (polarized mostly perpendicular to the surface) no such mode has been observed [9,10]. Second, the calculations show poor agreement with infrared spectra in the region between 800–870 cm^{-1}, by predicting only a very weak mode at 840 cm^{-1}. Experimentally, two relatively strong modes at 815 and 859 cm^{-1} have been observed [10]. Thus, we see that the normal mode calculations which start with the single vertex attachment model cannot predict the modes between 800–870 cm^{-1}. In contrast, the normal mode calculations for the cracked cluster geometry show much better overall agreement. For example, no vibrational features are predicted at 2100 cm^{-1}, because no perpendicular surface Si-H is generated by the cracked cluster geometry. More importantly, the degree of symmetry breaking for a cracked cluster is sufficient to produce relatively strong new modes at 806 and 867 cm^{-1}, which correlate well with the features at 815 and 859 cm^{-1}. The 806 cm^{-1} mode is specific to the δ(Si-H) bending vibrations of the $HSiO_2$ group bonded to the surface and provides strong evidence for the correctness of our model. The 867 cm^{-1} feature is related to a δ(Si-H) mode of the surface-bound $HSiO_3$ and appears as a result of stronger symmetry breaking of the octahedral siloxane in the cracked cluster geometry. It also has smaller contributions from the $HSiO_2$ group. Finally, modes calculated between 1061 and 1166 cm^{-1} for the cracked cluster are in good agreement with the experimental features between 1058 and 1178 cm^{-1} [the ν_a(Si-O-Si) region], whereas the single vertex geometry gives features only in the region between 1101 and 1153 cm^{-1}.

We now proceed to reinterpret the photoemission data based on the new proposed structure. Figure 1(b) shows a Si $2p$ photoemission spectrum recorded after exposing a clean Si(100) surface to the $H_8Si_8O_{12}$ clusters. The original assignments by Banaszak Holl and McFeely were based on structure 1(a). In this structure, there are eight SiO_3 groups: seven $HSiO_3$ groups in the cage and one SiO_3 bonded directly to the surface. Since the $HSiO_3$ groups should have the largest chemical shifts, they were assigned to the 3.6 eV feature in Fig. 1(b). Controversially, Banaszak Holl and McFeely assigned the SiO_3 group bonded directly to the surface (labeled as 2) to the 2.2 eV feature, and the surface Si(1) attached to the SiO_3 group to the 1.0 eV feature, even though it has a formal oxidation state of zero [2]. Finally, a feature at 0.4 eV, which arises from curve fitting of the asymmetric bulk Si peak, was assigned to the surface Si(3) attached to H. The relative intensity of the features at 3.6, 2.2, 1.0, and 0.4 eV is 7:1:1:1, consistent with the relative abundance of the respective Si atoms in Fig. 1(a). The implication of this assignment is that three second nearest neighbor oxygen atoms can cause a chemical shift of 1.0 eV, and that their effects are not negligible in Si $2p$ photoemission studies [2].

It is immediately obvious that our proposed "cracked cluster model" has silicons in $+1$, $+2$, and $+3$ formal oxidation states. To predict the magnitude of these shifts relative to the bulk peak, we make use of the following: (1) the presence of one, two, or three nearest neighbor oxygens contributes a 1.0, 1.8, or 2.5 eV shift to the Si $2p$ core levels, respectively, (2) the presence of a nearest neighbor H contributes a shift of 0.3 eV, and (3) for Si^{+3} species not directly bonded to the interface, there is an additional 0.7 eV shift due to final state effects. This last assertion is based upon density functional calculations which showed that core hole relaxation effects cause an additional ~0.7 eV shift in the Si $2p$ core levels of $HSiO_3$ groups not directly attached to the surface (for example, in a $H_7Si_8O_{12}$ cluster), relative to the Si $2p$ core levels of Si^{+3} groups bonded directly to the Si substrate [6]. Using these three rules, we assign silicon (1) in Fig. 1(c) to the 1.0 eV feature, since it is bonded to one oxygen and three silicons. The 2.2 eV feature is assigned to silicon (2), which the formal oxidation state model would predict at 2.1 eV, with contributions from the presence of two oxygen atoms (1.8 eV) plus a hydrogen atom (0.3 eV) in the nearest neighbor coordination sphere. Additionally, the $HSiO_3$ groups in the remainder of the cluster should give rise to a feature at 3.5 eV which has contributions from three oxygen atoms (2.5 eV), one hydrogen atom (0.3 eV), and final state effects (0.7 eV). On this basis, we assign the 3.6 eV feature in Fig. 1(b) to the $H\underline{Si}O_3$ groups in the remainder of the cluster. Finally, note that the ratio of relative intensities for the three photoemission features is 7:1:1, corresponding to seven $HSiO_3$ groups, one $HSiO_2$ group, and one oxidized Si dimer atom. These relative intensities are in good agreement with the *resolved* photoemission features in Fig. 1(b). We do not assign any feature at 0.4 eV since it arises purely from *curve fitting* of the slightly asymmetric bulk Si peak. In summary, by applying the formal oxidation state model to the cracked cluster geometry shown in Fig. 1(c) (and taking into account final state effects), we have been able to predict both the peak positions and relative peak intensities of the resolved features in the photoemission spectrum. Using exactly analogous arguments, the photoemission features of all other related spherosiloxane clusters can be quantitatively assigned without invoking any second neighbor effects [2–5].

Our overall conclusions have profound implications to the analysis of Si $2p$ photoemissions of the Si/SiO_2 interface and resolve a long-standing controversy. In particular, the 1.0 and 2.2 eV photoemission features seen by Banaszak Holl, McFeely, and co-workers are due to the presence of Si^{+1} and Si^{+2} species resulting from the dissociative attachment of a Si-O bond across the surface dimer. We conclude that the conventional analysis in terms of first nearest neighbor coordination and group additivity effects is valid as a good starting point for the interpretation of photoemission experiments of the Si/SiO_2 interface.

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