Si/SiO_2 Interface: New Structures and Well-Defined Model Systems

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A well-defined silicon oxide/silicon interface was synthesized by the reaction of the precursor cluster $H_8Si_8O_{12}$ with a Si(100) surface and characterized using Si 2*p* core level photoemission spectroscopy. Information gained regarding the assignments of silicon oxide group shifts and peak widths is used to evaluate assumptions and assignments of photoemission spectra of silicon oxide interfaces.

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Owing to their importance in semiconductor technology, Si/SiO_2 interfaces have been the subject of intense experimental investigation by a variety of means [1,2]. Nevertheless, issues relating to the order and disorder of the oxide phase, and to the detailed chemical structure of the interface, continue to be subjects for controversy. Complicating the task of the unraveling of the structure of this interface has been the lack of suitable model systems of known structure capable of serving as reference points for the analysis of spectroscopic results. This is a severe drawback for techniques such as photoemission spectroscopy because conclusions drawn about the interfacial structure depend upon assumptions regarding the local chemical moieties responsible for a particular spectroscopic feature (e.g., a chemical shift or the broadening of a core level by a specific amount). Lacking systems of well-defined chemical structure upon which to test the assumptions used for the assignment of local geometric structures, assignments of experimental observations to specific species making up the interfacial structure must remain, to a certain extent, in doubt. A potential solution to this problem rests in the atomic scale design and synthesis of solid-solid interfaces.

In this Letter we report that the interaction of the cluster compound $H_8Si_8O_{12}$ [3] with Si(100)-(2×1) surfaces results in the formation of a uniquely abrupt silicon/silicon oxide interface, with the oxide structure consisting of intact clusters bound homogeneously to the surface in a simple fashion. The spectroscopic results obtained for this simple structure will then be used to critically assess previous assumptions used in the assignment of core level photoemission features to local structural features in standard Si/SiO_2 interfaces.

The Si(100) substrate was prepared by flashing to 1050 °C, followed by slow cooling to room temperature. Si 2*p* core level photoemission spectra of the cleaned substrate showed the surface core level spectrum characteristic of the clean (2×1) reconstructed surface and the absence of any oxygen-induced features [4]. The substrate was then transferred in vacuum to a separate dosing chamber (base pressure 1×10^{-10} torr), and exposed for 20 min to 4.0×10^{-7} torr of $H_8Si_8O_{12}$ with the substrate at room temperature. The Si $2p_{3/2}$ spectrum obtained from the sample thus treated is presented in Fig. 1(a). A smooth background has been subtracted from the spectrum and the $2p_{1/2}$ spin-orbit component has been removed, following standard methods, in order to reduce the congestion in the spectra and to facilitate the apprehension of the individual spectral features [4]. The analogous spectrum of a "standard" thermal Si(100)/

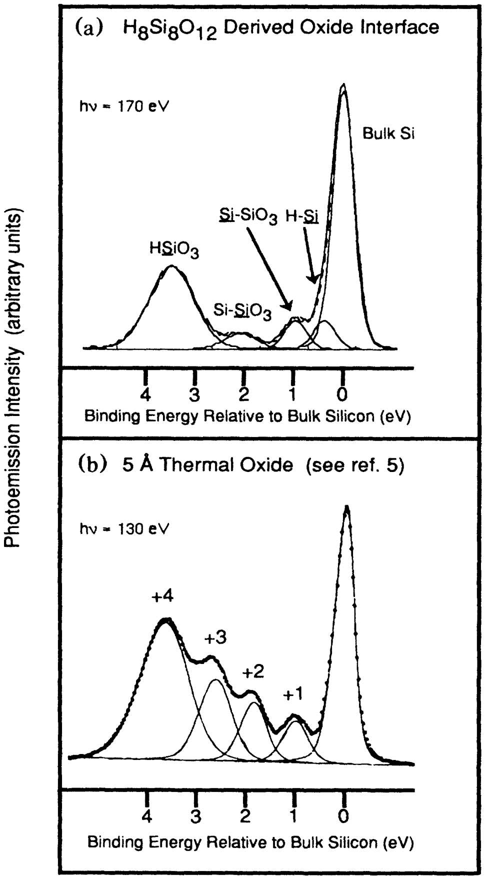

FIG. 1. Panel (a): Cluster derived silicon/silicon oxide interface. Panel (b): Thermal oxide, formal oxidation states assigned as per Ref. [5].

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SiO_2 interface, obtained from the oxidation of a similarly prepared Si(100) substrate with 2×10^{-5} torr O_2 at 750 °C for 20 s, is shown in Fig. 1(b) [5]. Spectra of the $H_8Si_8O_{12}$ derived interface were acquired using a 170 eV photon energy because this maximized surface sensitivity while avoiding the dramatic differences in photoionization cross section observed at lower photon energies for the various chemical moieties [5].

The spectrum obtained from the reaction of $H_8Si_8O_{12}$ with Si(100) is substantially different from the spectrum obtained from a thermally oxidized surface, the most obvious difference being the greatly diminished intensity in the region generally assigned to contain Si in the formal oxidation states 1+, 2+, and 3+. The undecomposed clusters are strongly attached, i.e., chemisorbed to the silicon surface. If the reactive dimer sites on the clean Si(100) surface are blocked, for instance, by the preadsorption of water, chemisorption of the clusters is completely suppressed. Furthermore, the cluster based surfaces are chemically quite robust. A freshly prepared and characterized sample was removed from the system of ultrahigh vacuum chambers and exposed to the ambient atmosphere for 20 min. Subsequent reinsertion and reanalysis of the Si 2*p* core level revealed no significant spectral changes.

The curves in Fig. 1 give the least-squares decompositions of the spectra into their constituent peaks. The spectrum of the cluster-exposed surface, panel (a), consists of five individual component peaks. Four of them, the bulk Si peak and the features shifted by 1.04, 2.19, and 3.64 eV, are immediately apparent from peaks or pronounced shoulders in the spectrum. The fifth, at a shift of 0.4 eV, has no analog in the spectrum of the thermal oxide in Fig. 1(b), and is manifested only by an asymmetric tailing to the high binding energy side of the bulk peak. The peak is included on the basis of both numerical and *a priori* chemical considerations. Numerically, it was found to be impossible to fit this region accurately without it. If the bulk peak full width at half maximum (FWHM) was such as to fit the leading edge of the spectrum accurately, the best fits lacking the 0.4 eV feature necessitated an unphysical FWHM of the 1.04 eV feature to values in excess of 1 eV, substantially larger than the analogous feature in the amorphous thermal oxide, and even then the fits were clearly poor. From a chemical standpoint, it is quite difficult to imagine any means of strong attachment of the clusters to the surface (excluding gross decomposition which we rule out below) other than the addition of a Si-H bond across a surface dimer site, leaving an attached cluster and a chemisorbed hydrogen atom. The chemisorption mechanism is analogous to that exhibited by SiH_4 with Si(100) [6]. The binding energy for this spectral feature was not allowed to vary initially, but was set to the value of 0.3 eV given by Himpsel *et al.* for the shift induced by hydrogen atoms following water chemisorption on Si(100) [4]. Fitted spectra essentially identical to that shown in Fig. 1(a) were obtained. The total variance of the fits is not very sensitive to the position of the peak and removal of the constraint on the $\underline{\mathrm{Si}}$-H derived spectral feature resulted in a shifting of the peak to 0.40 eV. With this mechanism of attachment, one $H_7Si_8O_{12}$ cluster would attach to the surface for each hydrogen, as shown schematically in Fig. 2.

The 1.04 eV shifted feature arises from the surface Si atom to which the cluster is attached ($\underline{\mathrm{Si}}$-SiO_3). Its small shift, relative to the cluster Si atoms, is the consequence of its having no direct bonds to oxygen. Given the mode of binding shown in Fig. 2, this feature should possess the same intensity as the surface $\underline{\mathrm{Si}}$-H derived feature. Accordingly, identical intensities were imposed on the fit as a subsidiary condition. When the spectrum was fitted in this fashion, the peak widths for the surface atoms were within 0.05 eV of the bulk Si peak, consistent with the widths observed for such states in analogous systems, such as H_2O chemisorption [4]. The remaining two peaks, at 2.19 and 3.64 eV, are assigned to the Si-$\underline{\mathrm{Si}}O_3$ (the cluster Si at the binding vertex) and to the H$\underline{\mathrm{Si}}O_3$ silicons at the other vertices, respectively. Although both of these features could be considered as formally Si^{+3}, both initial state effects, the differing electronegativity of Si and H, and final state effects, the greater ability of the Si lattice to donate charge to stabilize the core hole state, serve to lower the binding energy of the Si-$\underline{\mathrm{Si}}O_3$ peak.

As a free molecule, $H_8Si_8O_{12}$ has the form of a distorted cube, with each silicon vertex being hydrogen terminated. The chemisorbed structure shown in Fig. 2 shows the cluster attached via a single vertex. A close examination of the structure of the cluster and of the surface reveals that it is geometrically possible for more than one vertex of the cluster to react with surface Si dimers to produce a cluster which is multiply rather than singly attached to the surface. In fact, this does not appear to occur to any significant extent, and the local structure indicated in Fig. 2 is, within experimental uncertainty, characteristic of all of the chemisorbed clusters. This conclusion is based upon the observed core level intensity level ratios. For the singly attached structure shown in Fig. 2, the intensities of the $\underline{\mathrm{Si}}$-H, $\underline{\mathrm{Si}}$-SiO_3, Si-$\underline{\mathrm{Si}}O_3$, and $O_3\underline{\mathrm{Si}}$H features should be in the relation 1:1:1:7. If the

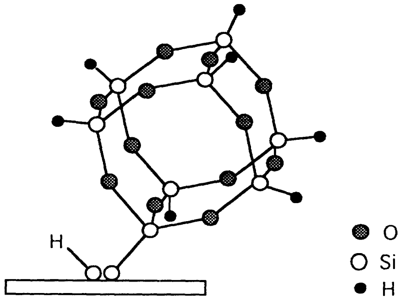

FIG. 2. Schematic of cluster attached to Si(100).

cluster was attached via two vertices along a cluster edge, the ratio would be 1:1:1:3, while if the cluster was bound across an entire face, via the reaction of four vertices, all of the features should be of equal intensity. Any other binding mechanism, including all reasonable modes of partial cluster decomposition, necessarily involve the oxidation of the surface and the reduction of the cluster silicon atoms. This would introduce additional features in the spectrum of Fig. 1(a) in the region between the bulk Si peak and that of the $O_3\underline{Si}H$ feature. In particular, the interface contains no Si 2*p* core level feature corresponding to the formal 2+ oxidation state, as would be expected upon the partial reduction of the Si^{+3} cluster silicons. Such partial decomposition scenarios can thus be safely dismissed.

The intensities of the peaks in Fig. 1(a) are in the ratio of 1.2:1.2:1:7.4. The crucial ratio of the attached-vertex silicon intensity versus that of the unreacted vertices is in excellent agreement with the 1:7 ratio expected for a surface composed entirely of singly attached clusters. The somewhat higher than expected values for the intensity of the peaks shifted by 0.4 and 1.04 eV may be attributed to the coadsorption of a small amount of water, which probably is the inevitable consequence of a small degree of hydration of the source material. Chemisorption of water produces Si-H and Si-OH on the surface, the latter giving rise to a 1.0 eV chemical shift which overlaps the Si-$\underline{Si}O_3$ signal. Water is very effective in suppressing the chemisorption of the clusters, and we have found that the lowest intensity values obtained for the 0.4 and 1.04 eV shifted features and the highest values for the other peaks are obtained only after pumping directly on the source material for over 1 h immediately prior to exposure, so as to rigorously degas any water of hydration.

Additional confirmation of the assigned structure was obtained in the course of investigating the thermal stability of the cluster-Si(100) structure. The interface was found to be completely stable to 400 °C, but significant decomposition was achieved by heating to 600 °C for 2 min. The resulting spectrum is shown in Fig. 3. Clearly a considerable redistribution of formal oxidation states of silicon has occurred. Most striking are the appearances of peaks at 2.57 and 1.73 eV, reminiscent of peak shifts generally seen in thermal oxides and conventionally assigned to Si^{+3} and Si^{+2}, respectively. Accompanying the growth of these peaks is a dramatic decrease in the intensity of the $O_3\underline{Si}H$ derived peak. These are exactly the types of changes expected for the decomposition of the proposed interface structure.

Having established the simple local structure of this interface, we are in a position to evaluate some of the assumptions which have been made in the assignment of photoemission features from spectra of thermally grown amorphous oxide/Si(100) interfaces. Grunthaner *et al.* have proposed, on the basis of resolution enhancement analyses, that the large width (~1.2 eV) of the SiO_2 derived peak in amorphous thin films is a consequence of a number of different Si-O ring sizes being present [7]. The $H_8Si_8O_{12}$ cluster-derived interface is completely homogeneous in this regard, containing only eight-membered Si-O rings, yet the peak width for the $O_3\underline{Si}H$ fragment is 1.1 eV, virtually identical to that observed for the amorphous overlayer. This strongly suggests that oxide ring size variations are not the cause of this large peak width, but rather that it is a consequence of the dynamics of the photoemission process. While structural inhomogeneities are no doubt present in the amorphous films, the width of this photoemission feature provides no evidence for their nature. Furthermore, preliminary results utilizing the related cluster D_{2d}-$H_{12}Si_{12}O_{18}$, which contains both eight- and ten-membered rings, show no resolvable features in the $O_3\underline{Si}H$ peak. This argues further against any observable effect in the photoemission spectra of Si/SiO_2 interfaces due to ring size variations.

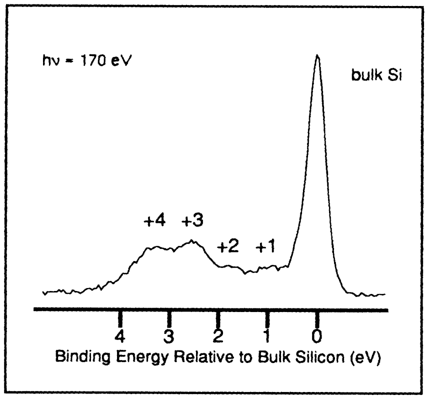

FIG. 3. Interface after heating to 600 °C. Conventional formal oxidation state assignments are indicated for convenience.

Simple interpretations of the structural origin of the Si^{+1} feature in Si/SiO_2 interfaces are also called into question by this work. Himpsel *et al.* and others have assigned this feature, shifted by 1 eV from bulk Si, to Si atoms bound to one oxygen and three other silicons [5]. This work shows that silicon bound to three other bulk Si atoms and to a $-SiO_3$ moiety gives rise to an almost identical chemical shift. In retrospect, this is not too surprising, considering that the geometric mean of the electronegativities [8] of the SiO_3 group is 2.9, comparable to that of a hydroxyl group (2.8). However, this observation highlights a more general problem, the application of the so-called "group shift model" [9] to the assignment of interface structures. The group shift model has been utilized extensively in the assignment of the structure of the Si/SiO_2 interface, but in a manner which only takes account of the first nearest neighbors. This work clearly shows that such an approach is overly simplistic [10]. The cluster-interface spectra demonstrate that chemical shifts resulting from second nearest neighbor effects can be essentially coincident with those arising from first nearest neighbor effects. Group shift models must be applied in a more sophisticated manner incorporating true *group* effects. Similar complications might also be expected in spectra of silicon/halogen systems.

Finally, the assignment of Si-H moieties in photoemission spectra of Si/SiO_2 interfaces has been addressed by several groups [11-13]. The O_3SiH group has generally been assigned to come at a shift of ~2.6 eV. The direct observation of O_3SiH groups at a relative binding energy of 3.64 eV in this work casts significant doubt on these assignments and the idea that peaks at ~2.6 eV constitute evidence for O_3SiH species extending up into the film [11]. However, one can speculate that an O_3SiH moiety bound directly to bulk silicon via the oxygen atoms would have a lower binding energy shift, and 2.6 eV is not unreasonable based upon the electronegativity trends with binding energy observed in this work.

In summary, the reaction of $H_8Si_8O_{12}$ with Si(100) produces a structurally simple silicon/silicon oxide interface with geometry and composition controlled on the atomic scale. Information gained by synthesizing and characterizing such an interface can be applied to further our understanding of the general class of silicon/silicon oxide interfaces. Studies of the structures formed by the related cluster compounds D_{5h}-$H_{10}Si_{10}O_{15}$, D_{2d}-$H_{12}Si_{12}O_{18}$, and D_{3h}-$H_{14}Si_{14}O_{21}$ with Si(100) are currently in progress.

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