*J. Am. Chem. Soc.* **1994,** *116,* 11819–11826

# Synthetic Control of Solid/Solid Interfaces: Analysis of Three New Silicon/Silicon Oxide Interfaces by Soft X-ray Photoemission

**Sunghee Lee,[†] Sanjeev Makan,[†] Mark M. Banaszak Holl,*,[†] and F. R. McFeely[‡]**

*Contribution from the Department of Chemistry, Brown University,*
*Providence, Rhode Island 02912, and IBM Thomas J. Watson Research Center,*
*P.O. Box 218, Yorktown Heights, New York 10598*

*Received April 11, 1994*[⊗]

**Abstract:** Three new silicon/silicon oxide interfaces have been synthesized using the spherosiloxane clusters $H_8Si_8O_{12}$, $H_{12}Si_{12}O_{18}$, $H_{14}Si_{14}O_{21}$, and Si(100)-(2×1). The structure of the interfaces have been characterized by Si 2p core level photoemission spectroscopy. Reactions of $H_8Si_8O_{12}$ with Si(111)-(7×7) and Ge(100)-(2×1) were also explored. The use of the cluster derived interfaces as spectroscopic models for thermal $Si/SiO_2$ interfaces is discussed in terms of current methods for assigning photoemission spectra at solid/solid interfaces and the structural models proposed for the $Si/SiO_2$ interface.

## Introduction

Synthesis of atomically well-defined solid/solid interfaces combines the problems of morphological manipulation of solid state phases with the additional difficulty of controlling structure where two phases meet. Designing the structure of solid/solid interfaces at the level of atomic composition, connectivity, bond angles, and ring sizes has remained a challenge for the physical and synthetic communities. The problem has been 2-fold: 1) development of appropriate synthetic methods and (2) development of spectroscopic methods capable of making atomic scale structural assignments of buried, perhaps amorphous, interfaces.

Atomic scale control of the $Si/SiO_2$ interface, an important example of this genre, is of particular interest as the dimensions for microelectronic devices shrink to a scale of tens of angstroms.[1] The standard synthetic method, direct oxidation of crystalline silicon, while generating a very useful interface, does not lend itself to *a priori* control of structure or the subsequent identification of the chemical moieties formed. Further progress in this area requires the application of more sophisticated synthetic methods. Size-selected silicon clusters[2] and gas-evaporated silicon particles[3] have been used to generate $Si/SiO_x$ interfaces. However, the molecular structures of these small particles and clusters were not known and specific structural and spectroscopic assignments of the interface species not possible.

We have begun to address some of the morphological and characterization problems by synthesizing interfaces of unique geometry which can also serve as spectroscopic models for the more general problem of characterizing the $Si/SiO_2$ interface. An initial study of the structure and core-level spectroscopy of the interface derived from the spherosiloxane cluster $H_8Si_8O_{12}$ (**1**) and Si(100)-(2×1) has recently been published.[4] We now report our efforts exploring the types of structures which can be generated, as well as further developing the uses and limitations of photoemission spectroscopy in making structural assignments for the interfaces formed. Core-level and valence band VUV synchrotron photoemission spectroscopy results are presented for interfaces formed using the spherosiloxane clusters $H_8Si_8O_{12}$ (**1**), $H_{12}Si_{12}O_{18}$ (**2**), and $H_{14}Si_{14}O_{21}$ (**3**). Utilizing these clusters we have been able to directly study the effect of Si–O ring size and film thickness on the core-level and valence band spectra for three different silicon/silicon oxide interfaces on Si(100). In addition, we have examined the reactions of **1** with Si(111) and Ge(100). Thermal decomposition of the interfaces has also been studied by photoemission and volatile products analyzed by mass spectroscopy.

The general approach of using chemically robust cluster complexes has been used previously to study the effects of boron and carbon doping of silicon. Evidence for the orientation of carborane clusters on Si(111) has been presented based upon angle-resolved photoemission and MNDO calculations.[5] Additional studies using STM characterization have been carried out.[6] Calzaferri and co-workers have previously published the reaction of $Cl_8Si_8O_{12}$ clusters with a variety of hydroxylated semiconductor surfaces.[7]

## Experimental Section

$H_8Si_8O_{12}$ was prepared by the method of Agaskar and sublimed.[8] All spherosiloxane clusters were loaded into stainless steel vessels fitted with bellows sealed valves and attached directly to an ultrahigh vacuum (UHV) dosing chamber. Prolonged pumping (>24 h) into a UHV system with base pressure 2 × $10^{-10}$ Torr resulted in a significant reduction in water and hydrocarbon contamination. Hydrocarbon

---

[†] Brown University.

[‡] IBM Thomas J. Watson Research Center.

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1994.

[1] (a) *The Physics and Technology of Amorphous $SiO_2$*; Devine, R. A. B., Ed.; Plenum Press: New York, 1988. (b) Pantelides, S. T., Lucovsky, G., Eds. $SiO_2$ and Its Interfaces Eds, In *Mat. Res. Soc. Symp. Proc.* **1990**. (c) *The Physics and Technology of Amorphous Silicon Dioxide*; Helms, C. R., Deal, B. E., Eds.; Plenum: New York, 1988. (d) *The Physics and Chemistry of $SiO_2$ and the Si–$SiO_2$ Interface 2*; Helms, C. R., Deal, B. E., Ed.; Plenum: New York, 1993.

[2] Bower, J. E.; Jarrold, M. F. *J. Chem. Phys.* **1992**, *97*, 8312–8321.

[3] Hayashi, S.; Tanimoto, S.; Yamamoto, K. *J. Appl. Phys.* **1990**, *68*, 5300–5308.

[4] Banaszak Holl, M. M.; McFeely, F. R. *Phys. Rev. Lett.* **1993**, *71*, 2441–2444.

[5] Lee, S.; Li, D.; Dowben, P. A.; Perkins, F. K.; Onellion, M.; Spencer, J. *J. Am. Chem. Soc.* **1993**, *115*, 8444–8447.

[6] Avouris, P. *J. Phys. Chem.* **1990**, *94*, 2246–2256.

[7] (a) Beer, R.; Bürgy, H.; Calzaferri, G.; Kamber, I. *J. Electron Spectrosc. Relat. Phenom.* **1987**, *44*, 121–130. (b) Bürgy, H.; Calzaferri, G.; Kamber, I. *Mikrochim. Acta* **1988**, *1*, 401–403.

[8] Agaskar, P. A. *Inorg. Chem.* **1991**, *30*, 2707–2708.

0002-7863/94/1516-11819$04.50/0

problems could be directly monitored using the C 1s core level. Water contamination was more problematic since the clusters also contained oxygen derived core levels and valance bands; however there is a 0.5 eV difference between the water derived O 1s core level (532.5 eV) and the cluster derived core level (533.0 eV). Heating the samples to 60 °C while pumping (an *in situ* sublimation step at $10^{-7}$ Torr) speeded the purification process considerably. Purification methods were repeated until reproducible results were obtained.

Conventional X-ray photoelectron spectroscopy (XPS) experiments were performed at Brown using a Perkin Elmer model 10-360 spherical capacitor analyzer fitted with a multichannel detector and Omni III lens with an 800 $\mu$m aperture. A model 04-548 X-ray source provided either Al or Mg K$\alpha$ X-rays. The analytical instrumentation was mounted in a Perkin Elmer model 41N test chamber in the standard configuration providing a base pressure of $8 \times 10^{-11}$ Torr. Samples were cleaned in a preparation chamber with base pressure of $4 \times 10^{-11}$ Torr and dosed in a small chamber with a $2 \times 10^{-10}$ Torr base pressure pumped by a turbomolecular pump and a titanium sublimater. Both the preparation and analytical chambers were pumped with a combination of ion pumps and titanium sublimaters. All chambers were interconnected by gate valves so that samples could be transferred *in situ* from the dosing chambers to the analytical chambers.

Vacuum ultraviolet (VUV) photoemission spectroscopy was performed at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The spectrometer and beam line have been previously described.[9,10] The acceptance solid angle was a cone of 86° width around the sample normal. The incident light was p polarized and 64° from normal. All core-level spectra were taken at $h\nu = 170$ eV, the incident photon energy which was determined to maximize surface sensitivity while not causing intensity differences in the Si 2p core level peaks caused by cross-section effects. Photon energy resolution was 0.2–0.3 eV and the resolution of the analyzer was set between 0.1 and 0.15 eV. Valence band spectra were also collected at 170 eV, but the energy resolution of the analyzer was set to 0.5 eV. Base pressure in the analyzer and preparation chambers was $1 \times 10^{-10}$ Torr while base pressure in the dosing chamber was $2 \times 10^{-10}$ Torr.

Si(100), Si(111), and Ge(100) samples were obtained from Virginia Semiconductor. Well-oriented wafers (<1/4° misorientation) were employed. Silicon samples were cleaned by resistive heating to 1050 °C in UHV. The ordering of the 2×1 and 7×7 reconstructions was checked by observation of the surface states for experiments at NSLS. Samples at Brown were cleaned in the same manner and confirmed as clean by absence of O 1s, C 1s, or any other non-silicon derived core level. The Ge(100) sample was cleaned by resistive heating to 500 °C combined with Argon ion bombardment. Interfaces were prepared by exposing a cleaned Si(100) surface to the vapor pressure of the $H_8Si_8O_{12}$, $H_{12}Si_{12}O_{18}$, or $H_{14}Si_{14}O_{21}$ in a dynamically pumped chamber ($4 \times 10^{-7}$, $2 \times 10^{-7}$, and $3 \times 10^{-8}$ Torr, respectively). Exposure times of 20 min proved to give saturating coverages in all cases. Core-level Si2p photoemission data from the NSLS were treated in the following manner. A measured secondary electron background spectrum was subtracted, an additional smooth background, followed by the removal of the $Si2p_{1/2}$ spin–orbit component, all by standard methods.[9] XPS spectra from Brown were utilized as measured.

Mass spectra were obtained using a UTi 100c quadrupole mass spectrometer (0–200 amu) mounted 10 cm from the sample. Temperature measurements were made by infrared pyrometry. Extended Hückel and INDO calculations were carried out using the CAChe set of computation programs developed by Tektronix. Distances and angles for $H_8Si_8O_{12}$ were taken from the literature.[11]

## Results

**$H_8Si_8O_{12}$ Derived Interface.** The spectrum of the $H_8Si_8O_{12}$ (1) derived interface is shown in Figure 1 along with the least-squares decomposition of the spectrum into its five constituent peaks.[4] The peak at lowest binding energy (BE) corresponds to bulk silicon (BE ~99.6 eV) and has been defined as having a BE of zero (0.0) for convenience in comparing to literature results. The three features at BE shifts of 1.04, 2.19, and 3.64 eV relative to bulk silicon are readily apparent from distinct peaks in the spectrum. The fifth component, at a shift of 0.4 eV, is manifested by an asymmetric tailing to the high BE side of the bulk peak. This peak has been included on both numerical and *a priori* chemical grounds. Numerically, far worse fits were obtained if this peak was left out. For the bulk peak to fit the leading edge of the spectrum accurately, the feature at 1.04 eV was required to have a physically unreasonable full width at half maximum (fwhm) of greater than 1 eV, substantially larger than previous assignments for peaks in this region in the amorphous thermal oxide,[9,10] and even then fits were poor. Chemical motivations also support inclusion of a peak at a shift of ~0.4 eV. It is difficult to imagine a mechanism for strong attachment of **1** to the surface other than the addition of a Si–H bond across a surface dimer site, leaving an attached cluster and a chemisorbed hydrogen atom. Chemisorbed hydrogen derived from water has been observed at a BE of 0.3 eV in past studies.[9] In the present work, the Si-H was initially fixed to 0.3 eV; however the total variance of the fits is not very sensitive to small changes in the position of this peak and upon relaxing the constraints it consistently shifted to ~0.4 eV. The chemisorption mechanism proposed here is analogous to that exhibited by $SiH_4$ on Si(100).[12] To sum-

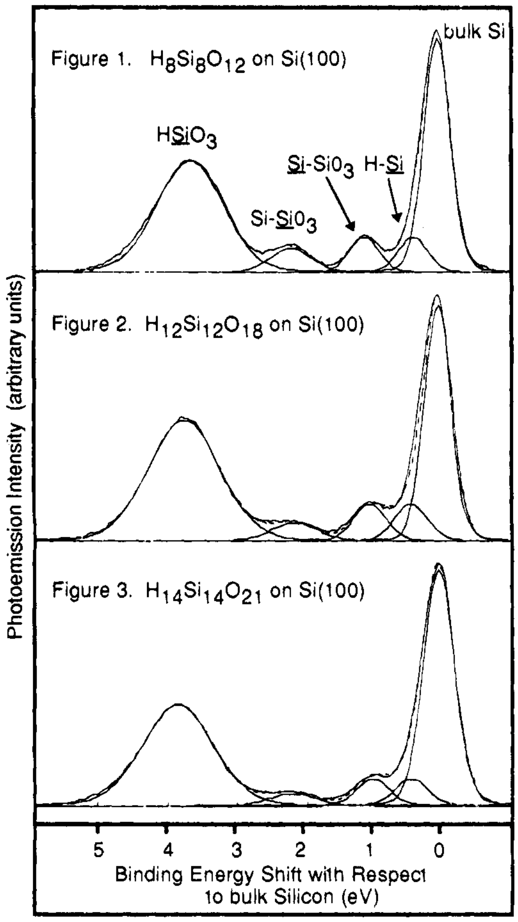


Figure 1. $H_8Si_8O_{12}$ on Si(100)

Figure 2. $H_{12}Si_{12}O_{18}$ on Si(100)

Figure 3. $H_{14}Si_{14}O_{21}$ on Si(100)

Incident Photon Energy is 170 eV
$Si2p_{3/2}$ Core levels shown

---

[9] Himpsel, F. J.; McFeely, F. R.; Morar, J. F.; Taleb-Ibrahimi, A.; Yarmoff, J. A. In *Proceedings of the 1988 Enrico Fermi School on Photoemission and Absorption Spectroscopy of Solids and Interfaces with Synchrotron Radiation*; North Holland: Varenna, 1988.

[10] Himpsel, F. J.; McFeely, F. R.; Taleb-Ibrahimi, A.; Yarmoff, J. A. *Phys. Rev. B.* **1988**, *38*, 6084–6096.

[11] Auf der Hyde, T. P. E.; Bürgi, H.-B.; Bürgy, H.; Törnroos, K. W. *Chimia*, **1991**. *45*, 38–40.

[12] Gates, S. M.; Greenlief, C. M.; Beach, D. B. *J. Chem. Phys.* **1990**, *93*, 7493–7503.

Figures show the appropriate cluster bound to a surface dimer by one vertex. A hydrogen atom is also shown attached to the dimer.

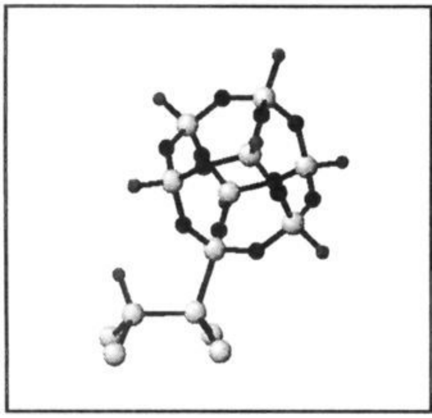


**Figure 4.** $H_8Si_8O_{12}$ on Si(100)

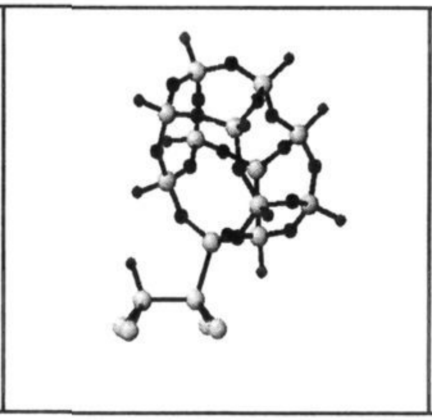


**Figure 5.** $H_{12}Si_{12}O_{18}$ on Si(100)

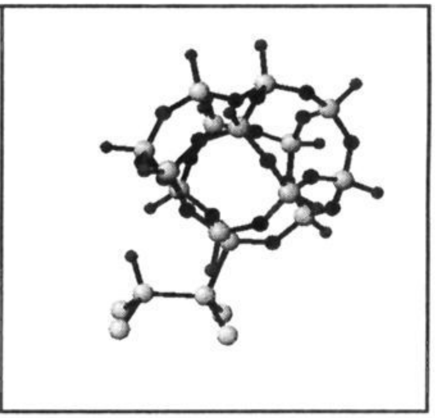


**Figure 6.** $H_{14}Si_{14}O_{21}$ on Si(100)

marize, the observed data and its least-squares decomposition for the $H_8Si_8O_{12}$ (**1**) derived interface resulted in the assignment of five component peaks at shifts of 0.0 (defined), 0.4, 1.04, 2.19, and 3.64 eV. A single O 1s core level was observed at 533.0 eV.

Assignment of the five peaks shown in Figure 1 to specific chemical moieties followed in a straightforward fashion. As discussed above, the bulk Si peak could be directly assigned by the observed binding energy and the inclusion of a Si−H peak was integral to the fitting process. The remaining three peaks, all clearly present in the spectrum, were assigned specific chemical identities based on their integrated intensities and binding energy shifts. The feature at 1.04 eV derives from the surface atom to which the cluster is attached ($\underline{\mathrm{Si}}-\mathrm{SiO_3}$). The small shift compared to the cluster derived Si photoemission peaks is a consequence of having no direct bonds to oxygen. Given the mechanism proposed for chemisorption, the feature should possess the same intensity as the surface $\underline{\mathrm{Si}}-\mathrm{H}$ derived feature. This condition was imposed on the fit as a subsidiary condition. Upon fitting the spectrum in this fashion, the $\underline{\mathrm{Si}}-\mathrm{H}$ and $\underline{\mathrm{Si}}-\mathrm{SiO_3}$ derived peaks had fwhm within 0.05 eV of the bulk silicon feature, consistent with previous observations in the cases of water chemisorption and the amorphous $Si/SiO_2$ interface.[9,10] The feature at 2.19 eV was assigned to the vertex Si of the cluster ($\mathrm{Si}-\underline{\mathrm{Si}}\mathrm{O_3}$). The final feature, the one of highest binding energy in the Si 2p spectral region, was assigned to the $\mathrm{H}\underline{\mathrm{Si}}\mathrm{O_3}$ cluster units. Although both the $\mathrm{H}\underline{\mathrm{Si}}\mathrm{O_3}$ and $\mathrm{Si}-\underline{\mathrm{Si}}\mathrm{O_3}$ moieties are formally $Si^{3+}$, significantly different chemical shifts are not unexpected in the context of simple ideas about electronegativity or electronic structure. Initial state effects, the differing electronegativity of Si and H (1.7 and 2.2, respectively), would be expected to shift the $HSiO_3$ peak to higher binding energy. Final state effects, the greater ability of the Si lattice to donate charge to stabilize the core hole state, would be expected to lower the observed binding energy of the $\mathrm{Si}\text{-}\underline{\mathrm{Si}}\mathrm{O_3}$ peak.

The relative integrated intensity of the five peaks is 1.2:1.2: 1:7.4, in quite good agreement with the proposed structure shown in Figure 4. The ideal set of ratios for **1** bound via a single vertex to the surface is 1:1:1:7 corresponding to one each $\underline{\mathrm{Si}}-\mathrm{H}$, $\underline{\mathrm{Si}}-\mathrm{SiO_3}$, and $\mathrm{Si}-\underline{\mathrm{Si}}\mathrm{O_3}$ units and seven $HSiO_3$ units. While it is geometrically possible for more than one cluster vertex to react with the surface Si dimers, producing a cluster which is multiply rather than singly attached to the surface, this does not occur to any measurable extent. If the cluster was attached by two vertices a peak ratio of 1:1:1:3 would be expected while attachment by four vertices generates fours peaks of equal intensity. The data clearly support the monoattached structure and not any multiply attached structure. Although there are three types of $HSiO_3$ fragments by symmetry in a monoattached cluster of **1**, it is not surprising that the energy difference of these fragments is less than the ~0.1 eV resolution of the photoemission experiment. The potential 1:3:3 ratio of $HSiO_3$ fragments is thus observed as a single peak in the photoemission spectrum.

A single O 1s core level is observed at a BE of 533.0 eV (relative to Si 2p defined as 99.8 eV) and is assigned to the twelve oxygen atoms present in **1**. Potential contamination from water was tested by purposely exposing a sample to water. Dosing the surface with enough **1** to generate only partial coverage ($4 \times 10^{-7}$ Torr for 10 s), followed by exposure to $5 \times 10^{-8}$ Torr of $H_2O$ for 10 s, generates an *asymmetric* feature in the O 1s region derived from both **1** and water. This feature was fit with both an O 1s core level from water (532.5 eV for surface bound hydroxide) and an O 1s core level deriving from the cluster (533.0 eV) in a 1:1.9 ratio respectively. A separate experiment in which a clean Si(100)-(2×1) surface was dosed with $1.0 \times 10^{-7}$ Torr of $H_2O$ for 2 min confirmed that the surface bound hydroxide should come at 532.5 eV. Exposing a surface treated with a saturating dose of **1** ($4 \times 10^{-7}$ Torr for 20 min) to $5 \times 10^{-8}$ Torr of $H_2O$ results in no change in the O 1s core-level features.

We have not been able to propose any other structure consistent with the core-level data. Any other binding mechanism, including all reasonable modes of partial cluster decomposition, must involve additional oxidation of the surface and reduction of the cluster. The species deriving from such reactions will place spectral features in the area between the bulk Si peak and the $HSiO_3$ derived peak. No such features are present in the spectrum. Particularly interesting is the lack of features in the range normally assigned to $Si^{2+}$ derived moieties (1.75 eV). Given the lack of additional states present in the regions generally assigned to the decomposition species expected (0.4 to 3.6 eV), we believe partial or total decomposition scenarios can be safely dismissed. Additional support that the clusters are intact comes from thermal decomposition studies. Upon heating to 600 °C for 2 min, peaks appeared at ~1.7 eV and ~2.6 eV, exactly in the regions conventionally assigned to $Si^{2+}$ and $Si^{3+}$, respectively. A dramatic reduction in the $HSiO_3$ intensity accompanies the growth of these peaks, exactly the type of change expected for the decomposition of the proposed interface structure.

Intrigued by the ability to synthesize a silicon/silicon oxide interface of well-defined geometry and thickness, we explored the use of two other spherosiloxane clusters, $H_{12}Si_{12}O_{18}$ (**2**) and $H_{14}Si_{14}O_{21}$ (**3**). Unlike $O_h$-**1** in which all Si–H bonds are geometrically equivalent, $D_{2d}$-**2** and $D_{3h}$-**3** have two and three types of Si–H groups, respectively. The two bond types in **2** are in a 2:1 ratio while the three bond types in **3** are in a 3:3:1 ratio. Thus, while the reaction of any vertex of **1** will yield the same surface species, reactions utilizing **2** and **3** will generate interfaces containing a mixture of at least two and three types of cluster binding, respectively. In addition, the different geometries of **2** and **3** require consideration once again of the possibilities of multiple vertex attachment and the partial or total decomposition of the initial cluster structure.

**$H_{12}Si_{12}O_{18}$ and $H_{14}Si_{14}O_{21}$ Derived Interfaces.** The spectrum of the $H_{12}Si_{12}O_{18}$ (**2**) derived interface, along with its least-squares decomposition into five peaks, is shown in Figure 2. The fitting of the spectrum was performed in an analogous manner to that indicated for the interface derived from **1**. Once again, proper fitting of the leading edge of the spectrum, combined with a physically reasonable line width for the peak at ~1 eV, confirmed numerically that an additional peak in the region expected for a Si–H moiety was necessary for a meaningful fit. The resulting fit gave peaks at shifts of 0.40, 1.03, 2.09, and 3.66 in a 1.5:1.5:1:10.9 ratio, respectively. These were assigned as corresponding to $\underline{Si}$–H, $\underline{Si}$–$SiO_3$, Si–$\underline{Si}O_3$, and $H\underline{Si}O_3$ functionalities in direct analogy to the assignments made for **1**. The ratio of the integrated areas corresponds to an interface in which **2** has bound to the Si(100) surface by one vertex as shown in Figure 5. Ideally, the ratio for a monoattached cluster is 1:1:1:11 while that for a cluster attached via two vertices would be 1:1:1:5. The data support binding by one vertex to the surface. As mentioned above, if the two different Si–H bonds of **2** react with the surface in a purely statistical fashion, then the spectrum is a mixture of two different cluster geometries. There is no hint of this in the spectrum, and it is expected that these energetic differences are beyond the ability of this experiment to resolve. Once again, the $HSiO_3$ units are not all identical by symmetry; however at the energy resolution of the experiment all eleven (or 22 for two symmetrically inequivalent cluster binding modes) are observed in the same region and assigned as one peak.

The experiment was repeated using $H_{14}Si_{14}O_{21}$ (**3**) as the cluster source. In this instance a 1.6:1.6:1:12.7 ratio of peaks was observed at 0.4, 0.95, 2.12, and 3.75 eV, respectively. We believe this is most consistent with an interface consisting of monoattached clusters of **3** (as shown in Figures 3 and 6) combined with an increased amount of adventitious oxidation of the surface. No differentiation of the three possible cluster binding modes via the three different Si–H bonds was observed and the thirteen (or 3 × 13 = 39) $H\underline{Si}O_3$ peaks were fit as a single peak.

In making these assignments, greatest emphasis was placed on the observed ratio between the Si–$\underline{Si}O_3$ and $H\underline{Si}O_3$ fragments. Note however that the intensities for the $\underline{Si}$–H and $\underline{Si}$–$SiO_3$ peaks are clearly greater than required for an interface consisting of no other species than monoattached **2** or **3**. We have observed in experiments with **1** that water contamination affects the observed intensity for $\underline{Si}$–H and $\underline{Si}$–$SiO_3$ (since the Si–H and Si–OH peaks for water directly overlap) while not changing the observed ratio between the vertex peak and the rest of the cluster. As the vapor pressure of the clusters decreases, competition from chamber and sample derived background becomes more problematic. We have identified the contamination as deriving from the samples and believe it is related to residual water. Spectral features clearly deriving from water are present at 0.4 and 1.0 eV in the spectra before the *in situ* purification techniques are used, yet the $H\underline{Si}O_3$ to Si–$\underline{Si}O_3$ ratios remain constant. For this reason, we are confident that the 1:10.9 and 1:12.7 ratios are a good indicator of monovertex binding.

**Table 1.** Summary of Observed Shifts for Clusters 1, 2, and 3 (eV)

| cluster | $H\underline{Si}$ | $\underline{Si}-SiO_3$ | $Si-\underline{Si}-O_3$ | $H\underline{Si}O_3$ |
|---|---|---|---|---|
| $H_8Si_8O_{12}$ (**1**) | 0.4 | 1.04 | 2.19 | 3.64 |
| $H_{12}Si_{12}O_{18}$ (**2**) | 0.4 | 1.03 | 2.09 | 3.66 |
| $H_{14}Si_{14}O_{21}$ (**3**) | 0.4 | 0.95 | 2.12 | 3.75 |

The assignments of specific peaks to species present in each interface are summarized in Table 1. The absolute agreement of $\underline{Si}$–H shifts at 0.4 eV is an artifact of setting values as consistently as possible for comparison between the three clusters. In fitting many of these spectra, the fit was not very sensitive to the exact placement of this peak, and unrestrained values varied from 0.35 to 0.42 eV. Similarly, variation was noted in the $\underline{Si}$–$SiO_3$ and Si–$\underline{Si}O_3$ features. In general, fitted peaks varied somewhat in position with respect to the spectral features and the values reported in Table 1 reflect the full range of variance, generally less than 0.1 eV. Variance within a set of fits for a particular type of cluster (say **1** for example) was less than 0.05 eV. We are not certain if chemical differences between the clusters induced the greater variance in the location of a particular chemical moiety, as this is right at the edge of the spectral resolution for the experiment. There is a distinct trend for the $H\underline{Si}O_3$ groups toward higher binding energy which would be consistent with the larger clusters isolating some $HSiO_3$ fragments from surface inductive effects. This suggests that we are close to being able to resolve at least a few of the $HSiO_3$ units which must have differing energy levels by symmetry.

The spectroscopic fate of the unreacted surface silicon dimers is a very interesting question. These appear at a BE shift of −0.5 eV on a clean Si(100)-(2×1) surface. Partial oxidation of the silicon surface should shift the dimer peaks toward the bulk feature and could possibly obscure it. It is also possible that significant reconstruction occurs and the dimers are essentially gone, replaced by some other species. In the spectrum for the interfaces derived from **2** and **3**, some of the unreacted dimers appear to have reacted with species such as water to give rise to additional oxidation products. The spectrum would require one water per every two clusters.

**Additional Studies on All Three Interfaces.** Valence band spectra for the interfaces derived from **1**, **2**, and **3** were collected with a photon energy of 170 eV. A direct comparison of the three spectra is provided in Figure 7. All three spectra share the common feature of a peak of greatest intensity at 7.8 eV. This peak is readily assigned to the oxygen lone pairs of the clusters in analogy to previous spectra of silicon oxides.[13] Another clearly defined feature occurs in the 3–4 eV range and is assigned to the bulk silicon bands. Additional cluster derived peaks, quite distinct from bands present in thin films of thermally grown oxides, occur in the range from 9.2 to 16.7 eV. Assigning these states to specific molecular orbitals has proven difficult. Extended Hückel and ZINDO calculations performed on the model complex $(H_3Si)H_7Si_8O_{12}$ indicated that Si–H and Si–O derived bonding orbitals should come in this range. A grouping of oxygen "lone pair" and weakly bonding orbitals consistent with the peak at 7.8 eV was observed. For

---

(13) Hollinger, G.; Berignat, E.; Chermette, H.; Himpsel, F.; Lohez, D.; Lannoo, M.; Bensoussan, M. *Philos. Mag. B* **1987**, *55*, 735–746.

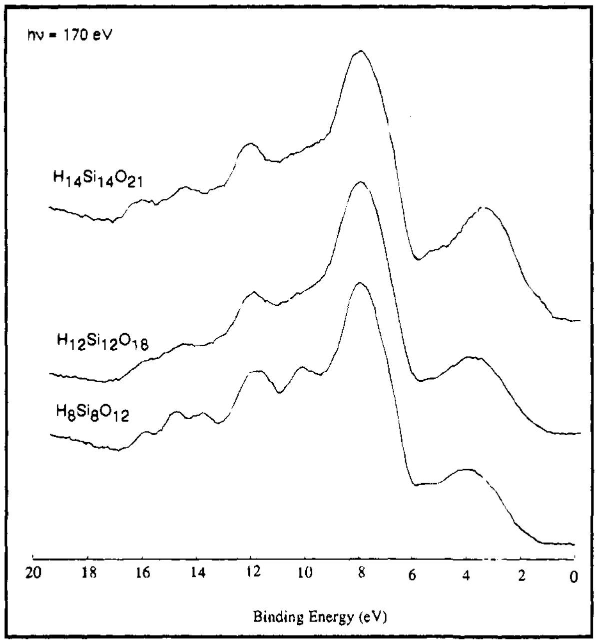


**Figure 7.** Valence bands for the three cluster derived interfaces.

the model complex, the HOMO was Si–Si based as expected; however the valence spectrum is not amenable to identifying the cluster–surface Si–Si based bond in a direct fashion. Unfortunately, recent *ab initio* and semiempirical calculations performed on $H_8Si_8O_{12}$ do not help to resolve these issues.[14]

Dense packing of **1**, **2**, and **3** results in roughly one cluster per two dimers as indicated by both model studies and molecular mechanics. Comparison of the integrated O 1s core levels of a **1** derived interface with a surface covered by a monolayer of water suggests that there is one cluster per three dimer sites. This coverage is consistent with the intensity ratio of cluster versus bulk silicon peaks observed in Figures 1–3. Evidence supporting a densely covered surface has been obtained via chemical probes. Exposure of an interface derived from **1** to $EtAuPMe_3$ for 5 min resulted in very little gold deposition as determined by the Au $4f_{7/2}$ core level. This result is identical to that observed for exposure of thin $SiO_2$ films on silicon to $EtAuPMe_3$, where gold is observed to deposit solely at defect sites present on the surface.[15] If the interface derived from **1** was not "monolayer" in nature, much more gold deposition would have been expected to occur. The interface was also observed to be quite oxidation resistant as compared to a normal silicon surface. After initial characterization, an interface derived from **1** was removed from vacuum and exposed to atmosphere for 15 min. Reanalysis of the Si 2p core levels did not show any evidence for ambient oxidation of the silicon surface. This strongly suggests that the surface is covered with a tightly packed layer of clusters. If areas of the surface were not covered, they would have been expected to oxidize upon exposure to the atmosphere and the effects would be readily observable in the Si 2p core levels. As mentioned earlier, the interface generated from **1** shows no reactivity, based on the O 1s core level, upon exposure to small amounts of water ($5 \times 10^{-8}$ Torr for 10 s). Since the interface generated from **1** appeared air-stable over short time periods, direct imaging of the interface via atomic force microscopy was attempted. However, air exposure and surface-induced tip damage complicated interpretation of the images obtained.[16]

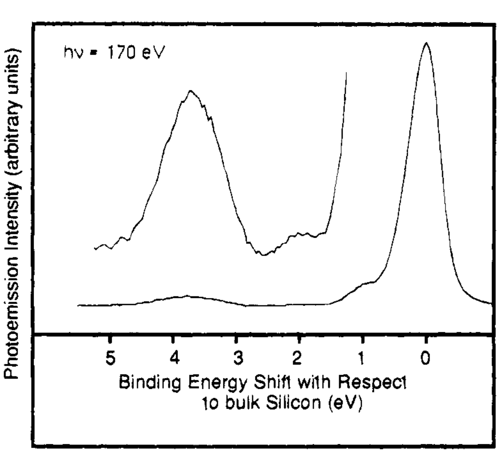


**Figure 8.** $H_8Si_8O_{12}$ on Si(111).

**The Reaction of $H_8Si_8O_{12}$ with Si(111) and Ge(100).** The reaction proposed for the three clusters with Si(100) is dependent on the presence of the Si dimers present in the 2×1 reconstruction.[17] The dimers perform addition reactions with a variety of substrates.[9,18] Changing the crystal face of silicon should affect the reaction. Exposing a Si(111)-(7×7) surface to $4 \times 10^{-7}$ Torr of **1** for 20 min resulted in a very small amount of cluster derived signal as shown in Figure 8. A small peak appeared at 3.8 eV, consistent with the $HSiO_3$ units of **1**. However, there was no significant signal derived from an activated cluster vertex at ~2.2 eV (the small feature seen at ~2.0 eV is in a 1:20 ratio with the $HSiO_3$ peak) . The $Si^{1+}$ peak is in fact larger than the cluster derived peak, indicating that other contaminants in the system ($H_2O$ for example) react in a more facile fashion with Si(111)-(7×7) than does **1**. It is possible that two reactive centers are required in close proximity for Si–H bond activation to occur. On the Si(100)-(2×1) surface, the dimers are separated by 3.85 Å while the Si-Si distance within the dimer is ~2.35 Å. These highly reactive sites protrude from the surface, making the reaction with a Si–H cluster bond a facile event. The Si(111)-(7×7) reconstruction[19] is generally noted to be less reactive than Si(100)-(2×1). Reactive sites on Si(111)-(7×7) were described in detail recently by Avouris.[6] The so-called rest atoms, while three coordinate, lie in the second layer and a successful reaction may be sterically difficult for a large cluster such as **1**. The center and corner adatoms, while both formally three coordinate, may in fact bond to a silicon directly below them in the lattice, reducing their reactivity.

Ge(100)-(2×1) seemed an ideal candidate for cluster reactions with **1** since the surface has the same structure as Si(100)-(2×1) reconstruction and the Si 2p core level region would be unobscured by bulk or surface derived silicon states. However, exposure of clean Ge(100) to **1** gave no hint of reaction as indicated by examination of the Ge 3d states, and the Si 2p states once again suggest that a small amount of **1** physisorbed on the surface.

---

[14] Earley, C. W. *J. Phys. Chem.* **1994**, *98*, 8693–8698.

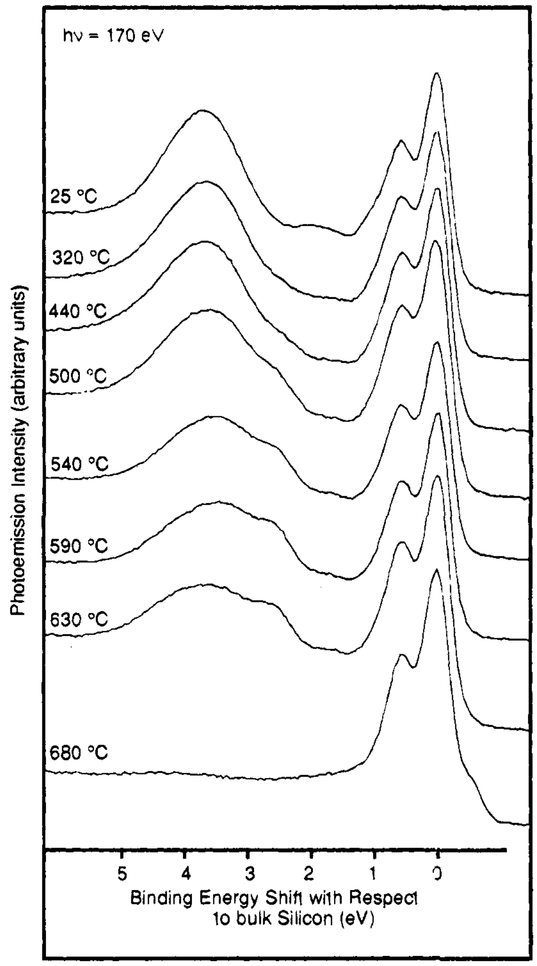
[15] (a) Banaszak Holl, M. M.; Seidler, P. F.; Kowalczyk, S. P.; McFeely, F. R. *Appl. Phys. Lett.* **1993**, *62*, 1475–1477. (b) Seidler, P. F.; Kowalczyk, S. P.; Banaszak Holl, M. M.; Yurkas, J. J.; Norcott, M. H.; McFeely, F. R. *Mat. Res. Soc. Symp. Proc.* **1993**, *282*, 359–364. (c) Banaszak Holl, M. M.; Seidler, P. F.; Kowalczyk, S. P.; McFeely, F. R. *Inorg. Chem.* **1994**, *33*, 510–517.

[16] Makan, S.; Musselman, I. H.; Banaszak Holl, M. M., unpublished results.

[17] (a) Hamers, R. J.; Tromp, R. M.; Demuth, J. E. *Phys. Rev. B* **1986**, *34*, 5343–5357. (b) Sugihara, K.; Sakai, A.; Kato, Y.; Akama, Y.; Shoda, N.; Tokumoto, H.; Ono, M. *J. Vac. Sci. Technol.* **1991**, *B9*, 707–710.

[18] For example see: (a) Bronikowski, M. J.; Wang, Y.; McEllistrem, M.; Chen, D.; Hamers, R. J. *Surf. Sci.* **1993**, *298*, 50–62. b) Kugler, Th.; Thibaut, U.; Abraham, M.; Folkers, G.; Göpel, W. *Surf. Sci.* **1992**, *260*, 64–74.

[19] Takayanagi, K.; Tanishiro, Y.; Takahashi, M.; Takahashi, S. *J. Vac. Sci. Technol. A* **1985**, *3*, 1502–1506.



Raw Si 2p Core levels, spectra have not had Si $2p_{1/2}$ core levels stripped.

**Figure 9.** $H_8Si_8O_{12}$ thermal decomposition.

**Thermal Decomposition Studies.** Si 2p core level spectra for the decomposition of an interface derived from **1** are shown in Figure 9. The primary features of the spectra derived from **2** and **3** are very similar. As the temperature increased, the total intensity derived from $H\underline{Si}O_3$ fragments decreased and a new spectral feature at ~2.7 eV appeared. The ratio of the cluster based features (all but the bulk peak) vs the bulk peak remained constant to ~600 °C. Conventional XPS experiments following both the O 1s and Si 2p core levels confirmed that the interface region is undergoing structural changes, but not losing silicon or oxygen atoms. Between 600 and 700 °C, we noticed a loss of ~40% of the O 1s core level intensity before all material evaporated off of the surface, regenerating the Si-(100)-(2×1) reconstruction. The valence band spectra rapidly lose the distinct cluster based features between 14 and 16 eV and by 320 °C are essentially identical to those observed for thermally grown thin films of silicon oxide.[13] Analysis of volatile products by mass spectroscopy shows hydrogen evolution by 500 °C, consistent with the normal desorption temperatures seen for hydrogen on Si(100)-(2×1).[12] The onset of hydrogen evolution occurs concurrent with the appearance of the new Si 2p core level feature at 2.7 eV.

## Discussion

Synthesis of solid–solid interfaces in which the geometric structure is known on the atomic level has been a daunting task. We have utilized an approach in this work relying on preformed clusters and single crystalline substrates of known reconstruction. The silicon/silicon oxide interfaces derived from the reactions of $H_8Si_8O_{12}$ (**1**), $H_{12}Si_{12}O_{18}$ (**2**), and $H_{14}Si_{14}O_{21}$ (**3**) with Si(100)-(2×1) represent a first step towards achieving the capability of atomic scale control of structure for the Si/$SiO_2$ interface. Equally important, the interfaces synthesized contain a spectroscopically assignable arrangement of silicon oxide moieties. The oxidation states and ring sizes present at the interface have been controlled, and in the case of ring size purposely modified. By choice of cluster, the interface thickness was also controlled. The oxide films formed are about 10, 12, and 14 Å thick for **1**, **2**, and **3**, respectively, based on the size of the cluster chosen.[20]

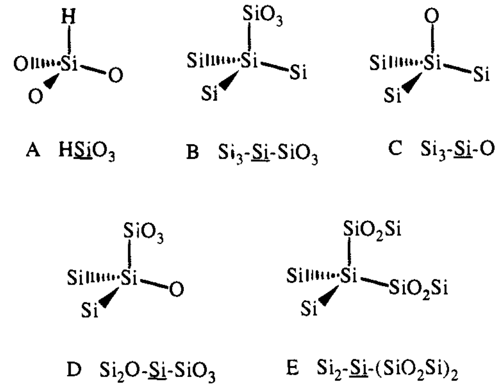


**Figure 10.** Interface fragments.

The interfaces discussed in this paper are unique structurally, but also serve as very interesting model systems for developing and refining photoemission as a technique for the study of Si/$SiO_2$ interfaces. In the cluster derived interface models, specific chemical species can be directly identified with spectral features present in the Si 2p core level spectrum. For the Si/$SiO_2$ interface, the assignment of a specific structural fragment to a given binding energy value is difficult because the exact nature of the surrounding chemical milieu is quite important. However, some generalization is worthwhile. Two species which we believe can be usefully assigned are shown in Figure 10. Fragment **A**, $H\underline{Si}O_3$, was observed in this study to appear at a BE shift of 3.7 ± 0.1 eV.

Admittedly, the chemical environment remained quite similar in all cases. However, given that the BE shift of stoichiometric $\underline{Si}O_2$ is quite similar, 3.9 eV, one would not expect the value for $HSiO_3$ units in a $SiO_2$ matrix to be very different. In somewhat different language, we expect the dielectric behavior of $SiO_2$ and the spherosiloxane clusters to be similar. A decrease in the observed binding energy shift value would be expected for fragment **A** if all three oxygens were bound directly to the bulk silicon. Based on simple electronegativity arguments discussed earlier, one could expect a shift to ~3.0 eV. This is mere speculation, but the value is similar to that proposed for $H\underline{Si}O_3$ fragments by Hattori et al.[21] Our data strongly argue against binding energy shift assignments of ~2.5 eV for $HSiO_3$ fragments in a $SiO_2$ medium. We observe fragment **B** at 1.00 ± 0.05 eV. This is a significant departure from past assignments which would have placed the central silicon at ~0 eV shift from the bulk.[9,10,22] Since the $H\underline{Si}O_3$ shift at 3.7 eV is comparable

---

[20] Bürgy, H.; Calzaferri, G. *J. Chromatog.* **1990**, *507*, 481–486.

[21] (a) Hattori, T. *Thin Solid Films* **1991**, *206*, 1–5. (b) Ogawa, H.; Terada, N.; Sugiyama, K.; Moriki, K.; Miyata, N.; Aoyama, T.; Sugino, R.; Ito, T.; Hattori, T. *Appl. Surf. Sci.* **1992**, *56–58*, 836–840.

[22] An extensive review of Grunthaner's and others work on the $SiO_2$/Si interface as well as a summary of the Si–O ring size discussion is contained in the following: Grunthaner, F. J.; Grunthaner, P. J. *Mater. Sci. Rep.* **1986**, *1*, 65–160.

**Table 2**[a-c]

| cluster | BE shift | fwhm (eV) | 8-membered rings | 10-membered rings |
|---|---|---|---|---|
| $H_8Si_8O_{12}$ (**1**) | 3.64 | 1.2 | 6 | 0 |
| $H_{12}Si_{12}O_{18}$ (**2**) | 3.65 | 1.2 | 4 | 4 |
| $H_{14}Si_{14}O_{21}$ (**3**) | 3.75 | 1.2 | 3 | 6 |

[a] Reference 1a. [b] Reference 1b. [c] Reference 1c.

to the $SiO_2$ shift of 3.9 eV (implying similar initial and final state effects), we believe that this assignment is not restricted to a surface silicon attached to a cluster vertex, but that it should be fairly accurate for the generalized fragment **B** in which the three lower silicons are part of the bulk crystal and the silicon attached to three upper oxygens is part of an amorphous $SiO_2$ lattice.

The distribution of Si–O ring sizes near the interface region has also been a matter of discussion. Grunthaner et al. have published a series of papers on this subject describing the interpretation of photoemission spectra in terms of the size of Si–O rings present in the interface region.[22,23] Data were treated with a resolution enhancement routine which deconvolved the typically ~1 eV fwhm "$Si^{4+}$" peak of interface silicon oxide photoemission spectra into several peaks. These peaks were assigned to differing ring sizes of Si–O present at the interface. The spherosiloxane cluster based model systems allow a direct study of the effect of Si–O ring size on observed photoemission results. Table 2 gives the fwhm and binding energy shift for the interfaces derived from **1**, **2**, and **3**, for the $H\underline{Si}O_3$ feature.

As can be seen from Table 2 or by inspection of Figures 1, 2, and 3, the width of the $HSiO_3$ feature does not show any observable change with cluster utilized. A cluster containing all eight-membered rings (**1**) gives a peak of identical width to those containing both eight- and ten-membered rings (**2** and **3**). As noted earlier, there may be a trend in binding energy shift for the $HSiO_3$ fragments. However, this is not correlated with ring size as both **2** and **3** contain eight- and ten-membered rings. While structural inhomogeneites and varying ring size are no doubt present in the $Si/SiO_2$ interface region, this study of three different model interfaces provides a strong argument against any observable effect in the photoemission spectra of silicon oxide systems due to ring size variations.

Many models have been advanced for the structure of the $Si/SiO_2$ interface. Photoemission is but one of many experimental techniques which have been employed. Several models, however, have taken the photoemission data as one of the primary guidelines for model construction and are based upon two foundations. The first is the observation of three intermediate interfacial oxide features in the Si 2p core level spectrum, exhibiting binding energy shifts of approximately 1, 1.7, and 2.5 eV, with respect to the bulk Si substrate peak. The second is the interpretation that these features arise from Si atoms bound directly to one, two, and three oxygen atoms, respectively, without regard to any other structural details. This interpretation implicitly asserts that the effect of second nearest neighbors on the core level binding energies is always negligible. The observation, in all three cluster derived interfaces, that the surface silicon to which the cluster vertex is attached (the central Si of fragment B) is shifted by over 1 eV directly contradicts this assumption. This Si atom is formally $Si^0$, all of its nearest neighbors are silicon atoms, and by the assignment rules given above it would be assumed to be unshifted from the bulk. The consequences of this observation for previous models, and model building generally, are twofold. First, it shows in the most concrete manner that there is an additional structural moiety, $Si_3{-}\underline{Si}{-}SiO_3$ (**B**), which can contribute to the 1 eV shifted peak in the spectra of the thermal oxide interfaces, in addition to the $Si_3{-}Si{-}O{-}$ (**C**) moieties. Either of these moieties at the interface, or any admixture of the two, must be regarded in themselves as being equally compatible with the experimental observations. Second, the establishment that there is one type of second-nearest-neighbor configuration which can produce chemical shifts fully as large as those caused by a change in formal oxidation state necessitates a reevaluation of the previous photoemission based models, as all of these models contain a large number of $Si^0$ species bound to oxidized Si atoms. Unfortunately, for this task we lack the firm experimental grounding we have for our first assertions above, and instead must rely upon inferences drawn from carefully chosen model systems, coupled with arguments based upon group electronegativities.[24] While the details of this reanalysis have been presented by us elsewhere,[25] these are the principle conclusions based largely upon the model interfaces presented in this paper.

In the model presented by Himpsel, McFeely, Taleb-Ibrahimi,Yarmoff, and Hollinger (HMTYH), formal $Si^+$ species are assigned to the 1 eV shifted interface peak, even though it is also bound to a $-SiO_3$ group.[10] We contend that if an $Si_3{-}\underline{Si}{-}O{-}$ (**C**) moiety has a 1 eV shift, as we know from studies of water chemisorption, and $Si_3{-}\underline{Si}{-}SiO_3$ (**B**) has a 1 eV shift, then it is implausible to assume that $Si_2{-}\underline{Si}O{-}SiO_3$ (**D**) also has only a 1 eV shift. Instead, this moiety is a more plausible contributor to the peak at 1.8 eV shift. Most of the formal $Si^0$ bound to oxidized silicon in the HMTYH model (86%) may still be plausibly assigned a negligible chemical shift, even in light of our results (the shifts must be less than 0.2 eV given the observed fwhm of 0.3 eV for the bulk Si peak); however there is one feature, $Si_2{-}\underline{Si}{-}(SiO_2Si)_2$ (**E**), which has four second-nearest-neighbor oxygens as opposed to only three for $Si_3{-}\underline{Si}{-}SiO_3$ (**B**), and also has a slightly higher calculated group electronegativity. On these grounds we reassign this moiety to the 1 eV shifted feature. The net result of these reassignments is to change the predicted photoemission intensity distribution of the interfacial oxide peaks from 2:3:2, in tolerable agreement with the rough equality observed experimentally, to 1:5:2, in definite disagreement. Similar reassessments of compatibility with the photoemission also take place upon examination of models proposed by Grunthaner et al.[22] and others.[1,26,27,28] It is still possible to construct models which appear to be truly compatible with the photoemission spectra of the $Si(100)/SiO_2$ interface, and we have presented an example of one in ref 25.

---

(23) The original literature assigning ring sizes: (a) Grunthaner, F. J.; Grunthaner, P. J.; Vasquez, R. P.; Lewis, B. F.; Maserjian, J.; Madhukar, A. *Phys. Rev. Lett.* **1979**, *43*, 1683–1686. (b) Grunthaner, F. J.; Grunthaner, P. J.; Vasquez, R. P.; Lewis, B. F.; Maserjian, J.; Madhukar, A. *J. Vac. Sci. Tehnol.* **1979**, *16*, 1443–1453. (c) Vasquez, R. P.; Klein, J. D.; Barton, J. J.; Grunthaner, F. J. *J. Electron Spectrosc. Rel. Phenom.* **1981**, *23*, 63–81. (d) Grunthaner, F. J.; Lewis, B. F.; Maserjian, J. *J. Vac. Sci. Technol.* **1982**, *20*, 747–750.

(24) For lead references see: (a) Lindberg, B. J.; Hamrin, K.; Johansson, G.; Gelius, U.; Fahlman, A.; Nordling, C.; Siegbahn, K. *Phys. Scr.* **1970**, *1*, 286–298. (b) Lucovsky, G. *J. Phys.* **1981**, *C4*, 741–744. The group electronegativity calculations for the present paper use the Allred and Rochow scale.

(25) Banaszak Holl, M. M.; Lee, S.; McFeely, F. R. *Appl. Phys. Lett.* **1994**, *65*, 1097–1099.

(26) Ohdomari, I.; Akatsu, H.; Yamakoshi, Y.; Kishimoto, K. *J. Non-Cryst. Solids* **1987**, *89*, 239–248.

(27) (a) Ourmazd, A.; Taylor, D. W.; Rentschler, J. A.; Bevk, J. *Phys. Rev. Lett.* **1987**, *59*, 213–216. (b) Ourmazd, A.; Fuoss, P. H.; Bevk, J.; Morar, J. F. *Appl. Surf. Sci.* **1989**, *41/42*, 365–371.

(28) Herman, F.; Kasowski, R. V. *J. Vac. Sci. Technol.* **1981**, *19*, 395–401.

Notably, all of the above problems may be avoided by employing the formally $Si^0$ $Si_2-\underline{Si}-(SiO_2Si)_2$ (**E**) as the sole source of intensity for the 1 eV shifted feature of the interface spectra.

## Summary

Three structurally unique interfaces generated from the reaction of spherosiloxane clusters with Si(100) and their characterization via conventional and synchrotron photoemission have been presented. These interfaces represent a significant step forward in the rational design of solid/solid interfaces. In addition, the new interfaces constructed provide interesting models for the study of the $SiO_2$/Si interface. Spectroscopic assignments of all Si 2p photoemission features have been made in a straightforward fashion and the geometrical attachment of the clusters to the surface elucidated. The formal oxidation state model for assignment of photoemission spectra from silicon surfaces has been shown to work poorly for the cluster derived interfaces as well as the Si/$SiO_2$ interface. Consideration of second-nearest-neighbor effects and final state effects is critical for proper assignment of core level spectra in interfacial regions.

**Acknowledgment.** P. Agaskar, F. Feher, and W. Klemperer are thanked for their many helpful and encouraging discussions regarding silicon oxide cluster chemistry. Agaskar and Klemperer are especially thanked for their preparation of $H_{12}Si_{12}O_{18}$ and $H_{14}Si_{14}O_{21}$ clusters, which they graciously shared with F. Feher, who then generously shared them with us. Feher also provided initial samples of $H_8Si_8O_{12}$ which helped get the project off the ground. R. M. Stratt and B. A. Scott are also thanked for many helpful discussions. M.M.B.H. thanks the Petroleum Research Foundation, NSF, Surface Interface Inc., and IBM for financial support of this work. S.M. thanks the National Science Foundation for a summer REU fellowship. Portions of this work were carried out at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the Department of Energy (Division of Materials Science and Division of Chemical Sciences of the Office of Basic Energy Sciences).