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Infrared Study of $H_{10}Si_{10}O_{15}$ Chemisorbed on a Si(100)-2×1 Surface

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Reflection−absorption infrared spectroscopy of the model interface derived from $H_{10}Si_{10}O_{15}$ on Si(100)-2×1 is presented. The spectra obtained are compared to the $H_8Si_8O_{12}$-derived model interface and discussed in terms of the soft X-ray photoemission spectroscopy obtained for cluster-derived interfaces.

I. Introduction

Detailed chemical characterization of the Si/SiO_2 interface has become an increasingly important problem as the length scales of transistor devices have shrunk to the molecular level.[1] In an effort to elucidate structural details of this interface, we have developed a program which spectroscopically characterizes model thin films containing known chemical moieties.[2] Here, we present the first surface infrared spectroscopy of a model Si/SiO_2 interface derived from $H_{10}Si_{10}O_{15}$, a spherosiloxane cluster, chemisorbed on Si(100)-2×1. This work complements previous X-ray photoemission spectroscopy (XPS) performed on this interface model.[2d]

Figure 1a shows the Si 2p core-level spectrum of $H_{10}Si_{10}O_{15}$ chemisorbed on Si(100)-2×1. For comparison, the spectrum of $H_8Si_8O_{12}$ is shown in Figure 1b. Ratioed integrated areas are listed above each spectrum. As discussed elsewhere, the integrated intensity of the curve fit peaks is consistent with the cluster binding to the surface via a single vertex.[2] Note that the $H\underline{Si}O_3/O_3\underline{Si}{-}Si$ ratio changes as expected given the different cluster sizes. This trend has also been observed in model studies utilizing $H_{12}Si_{12}O_{18}$, $H_{14}Si_{14}O_{21}$, and $HSi(OCH_2CH_2)_3N$.[2b,c] Despite the good experimental agreement obtained over five separate model systems, the Si 2p core-level assignments applied to these model systems have been questioned in a series of papers taking a theoretical approach to the first-principles calculation of core-level shifts.[3] Most controversial is the peak observed with a binding energy shift of 1.0 eV for the Si 2p core level, assigned as an $O_3Si{-}\underline{Si}$ group on the Si(100)-2×1 surface. This dimer-derived silicon has a first-neighbor coordination sphere of four silicon atoms: one from the vertex of the cluster, one from the other silicon of the dimer pair, and two from the first subsurface silicon layer. Assignment of this photoemission feature, shifted by 1.0 eV from bulk silicon, as a $O_3Si{-}\underline{Si}$ fragment requires that the oxygen second neighbors are needed for accurate prediction and interpretation of X-ray photoemission core-level spectroscopy.[4] In general, the notion that second-neighbor effects are important for core-level spectroscopy is well documented in the literature.[5] However, the first-principles calculations performed (local density approximation to density functional theory, LDA−DFT) only support that the first-neighbor shell contributes in a significant fashion to the observed binding energy shifts.[3] These key differences in interpretation led to important differences in the structural interpretation of the silicon/silicon oxide interface region in common devices such as metal oxide semiconductor field effect transistors or MOSFETs.[6−9]

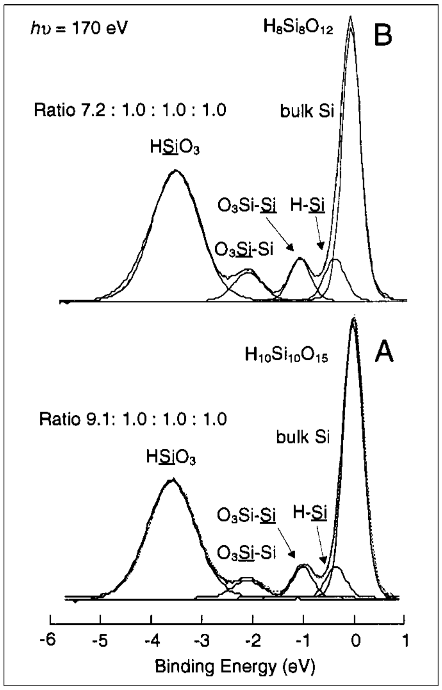

Figure 1. X-ray photoemission spectroscopy (Si $2p_{3/2}$ core levels) of (A) $H_{10}Si_{10}O_{15}$ and (B) $H_8Si_8O_{12}$ chemisorbed on Si(100)-2×1. The relative peak areas for all peaks but bulk silicon are provided.

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(1) For examples, see: *The Physics and Chemistry of SiO_2 and the Si−SiO_2 Interface,* 3rd ed.; Massoud, H. Z., Poindexter, E. H., Helms, C. R., Eds.; The Electrochemical Society; Pennington, NJ, 1996; and references therein.

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The model interface derived from $H_{10}Si_{10}O_{15}$ and Si(100)-2×1 has previously been characterized by high-resolution X-ray photoemission studies (Figure 1a).[2d] However, the controversy that has erupted over the proper approach to interpreting photoemission spectra at silicon/silicon oxide interfaces has called into question the photoemission assignments made for this $H_{10}Si_{10}O_{15}$-derived model interface. Because the assignments are not consistent with the LDA−DFT-based predictions for the binding energy shifts of the Si 2p core levels, it has been suggested that contamination such as water must be present or that the clusters must have adopted some other struture on the surface leading to the formation of surface Si−O bonds.[3] In an attempt to address the issues of contamination and surface binding mode, reflection−absorption infrared spectroscopy (RAIRS) studies of the $H_{10}Si_{10}O_{15}$-derived model interface have been performed. RAIRS allows direct observation of the cluster vibrational modes and is, therefore, an excellent complement to X-ray photoemission studies. In addition, it offers a highly sensitive probe of potential water and/or hydrocarbon contamination.

II. Experimental Section

Details of the ultrahigh vacuum (UHV) experimental apparatus and RAIRS technique are explained elsewhere.[14] Briefly, RAIRS was performed with a Bio-Rad FTS-40 FTIR spectrometer. Because silicon is highly transparent in the IR spectral region of interest, specially prepared samples,[10] with an internal $CoSi_2$ mirror, were used for these experiments. The preparation of these samples has been discussed in detail elsewhere.[11] Thin films were synthesized by first resistively flashing the Si(100) substrate to ~1050 °C, followed by back-filling the chamber with the molecule of interest. The base pressure of the chamber without a gas load was $<5 \times 10^{-10}$ Torr. The cluster, a white solid that sublimes at room temperature, was introduced to the chamber via a bellows-sealed Nupro valve. During dosing, the pressure was typically 2×10^{-8} Torr. Experiments typically involved taking a background spectrum, performing the desired chemisorption, and then taking a second spectrum. All single-beam spectra represent a signal averaging of 256 scans taken with 8-cm^{-1} resolution. Each spectrum required about 90 s to complete.

III. Results and Discussion

A RAIRS spectrum of $H_{10}Si_{10}O_{15}$ chemisorbed on Si(100)-2×1 is shown in Figure 2a. For comparison, Calzaferri's solution IR spectrum of $H_{10}Si_{10}O_{15}$ in CCl_4 can be seen in Figure 2b.[12] Both spectra show intense features at roughly 890, 1180, and 2270 cm^{-1} and are assigned as $\delta(H-SiO_3)$, $\nu_a(Si-O-Si)$, and $\nu(H-SiO_3)$, respectively. This correlation suggests that the $H_{10}Si_{10}O_{15}$ cluster is largely intact on the silicon surface. However, additional peaks not observed for the free molecule are now observed at 817, 859, 915, 1054, and 1108 cm^{-1}. The features at 859 and 915 cm^{-1} can be explained using symmetry arguments and referencing to similar systems. The free $H_{10}Si_{10}O_{15}$ cluster has the D_{5h} symmetry. However, once the cluster is chemisorbed to the surface, the symmetry is lowered, breaking the degenerate $H-SiO_3$ bending modes into three resolved features. This effect is similar to that previously observed by Calzaferri et al. for a variety of $R(H_7Si_8O_{12})$ species in solution[12] and for $H_8Si_8O_{12}$ chemisorption on Si(100)-2×1.[13,14] The lowering of the symmetry is also related to the appearance of additional features at lower wavenumber for the $\nu_a(Si-O-Si)$-derived modes. In particular, both previous solution work and theoretical calculations support the presence of the additional bands observed at 1108 and 1054 cm^{-1}.[12,13] Note that we can rule out the possibility that these bands arise from a cluster physisorbed to the surface, as low-temperature studies have shown that such clusters volatilize at temperatures lower than 20 °C.[13,15]

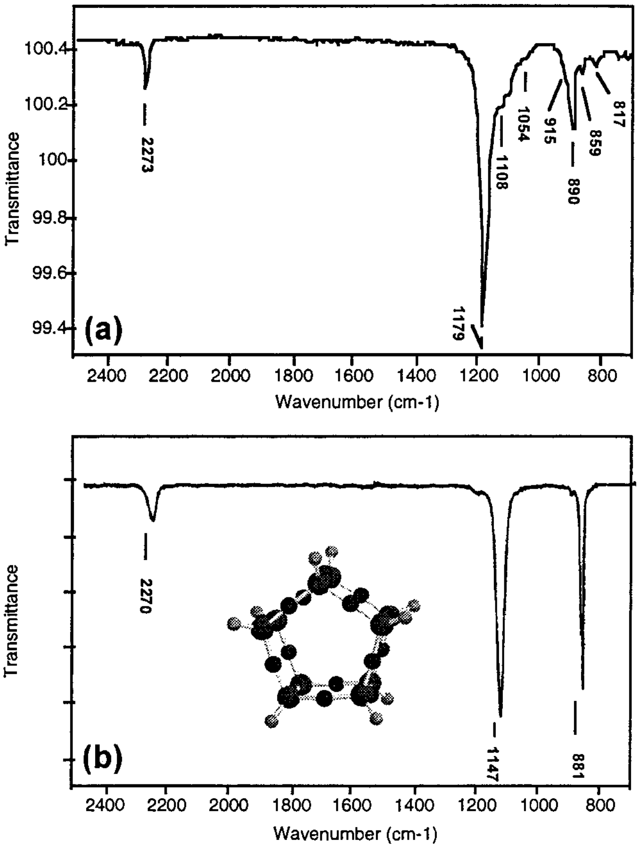

Figure 2. (a) RAIRS spectrum of $H_{10}Si_{10}O_{15}$ chemisorbed to a Si(100)-2×1 surface. (b) Solution IR spectrum of $H_{10}Si_{10}O_{15}$ (Calzaferri et al.).[17] $H_{10}Si_{10}O_{15}$ is shown as an inset in part b.

There are two more additional features of note in the RAIRS spectrum of the $H_{10}Si_{10}O_{15}$-derived model interface. First, the absence of a feature in the region 2070−2090 cm^{-1} is notable because we expect surface $\nu(Si-H)$ in this region based upon the single vertex activation hypothesis (Figure 3). This is also the same region where any water-derived $\nu(Si-H)$ should appear. Second, the feature observed at 817 cm^{-1} is unexpected on the basis of IR spectra of solution analogues[12] and normal-mode calculations for molecules in related systems.[13] The absence of the 2070−2090 cm^{-1} band and the presence of the

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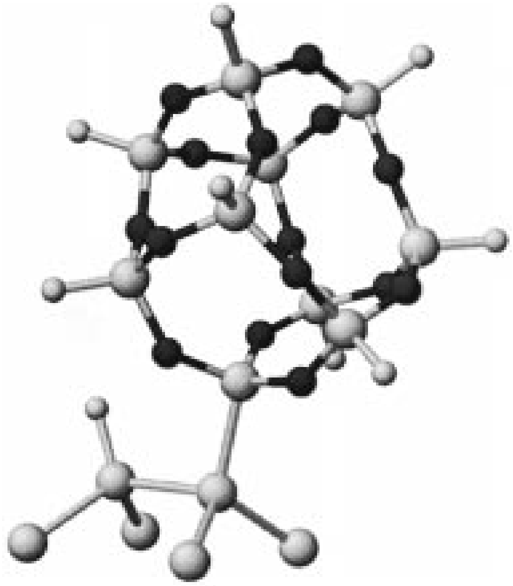

Figure 3. $H_{10}Si_{10}O_{15}$ chemisorbed via one vertex to a truncated Si(100)-2×1 surface illustrating simple Si−H bond activation.

817 cm^{-1} band may be related and will be discussed in conjunction with co-dosing experiments of water/$H_{10}Si_{10}O_{15}$.

Water contamination is always a concern when attempting to study Si(100)-2×1 surfaces. In these studies, it has been of particular concern because water chemisorbed on silicon is known to give a Si 2p core-level shift of ~1.0 eV from bulk silicon for the surface *Si*−OH moiety. Great care was taken with the photoemission experiments to try to avoid this problem, and a number of experiments, including the use of clusters of varieties of vapor pressures and clusters that contained no oxygen, were performed in an attempt to rule out water contamination.[4] RAIRS studies were able to conclusively rule out water contamination for the $H_8Si_8O_{12}$-derived model interface[14] however, typical dosing pressures used for $H_{10}Si_{10}O_{15}$ are approximately an order of magnitude lower than those used to dose $H_8Si_8O_{12}$. Therefore, a careful examination of this issue for the $H_{10}Si_{10}O_{15}$ system was in order. As mentioned above, no evidence for chemisorbed water, which dissociates to give Si−H and Si−OH moieties, is present based upon the expected ν(Si−H) at ~2090 cm^{-1}.[16] However, the feature present at 817 cm^{-1} is very close to the location expected for ν(Si−OH).[16] An example of water chemisorbed on Si(100)-2×1 can be seen in Figure 4, spectrum a, with the expected ν(Si−H) at ~2090 cm^{-1} and ν(Si−OH) at 816 cm^{-1}. The coverage is roughly 50% of the available surface sites. Treatment of the same surface with a saturation dose of $H_{10}Si_{10}O_{15}$ results in spectrum b. The main features noted for the chemisorption of $H_{10}Si_{10}O_{15}$ on clean Si(100)-2×1 are present including ν(H−SiO$_3$) at ~2275 cm^{-1}, ν_a(Si−O−Si) at 1167 and 1060 cm^{-1}, and δ(H−SiO$_3$) at 887 cm^{-1}. Comparison of Figure 4b and Figure 2a indicates that in the presence of water the splitting of the cluster δ(H−SiO$_3$) modes is significantly reduced. The shoulder at 915 cm^{-1} essentially disappears, and the distinct peak at 859 cm^{-1} is severely attenuated (compared to Figure 2). The difference of spectrum a and spectrum b is shown as Figure 4c. The difference spectrum highlights that the band at 816 cm^{-1} actually decreases in intensity, suggestive of a reaction occurring between the surface hydroxyls and the clusters, especially since no attenuation is seen for the water-derived ν(Si−H) at 2089 cm^{-1}. These spectra serve to highlight the fact that when water is present, we observe both the ν(Si−H) and ν(Si−OH) features. In addition, the presence of water causes a distinct change in the δ(H−SiO$_3$) features.

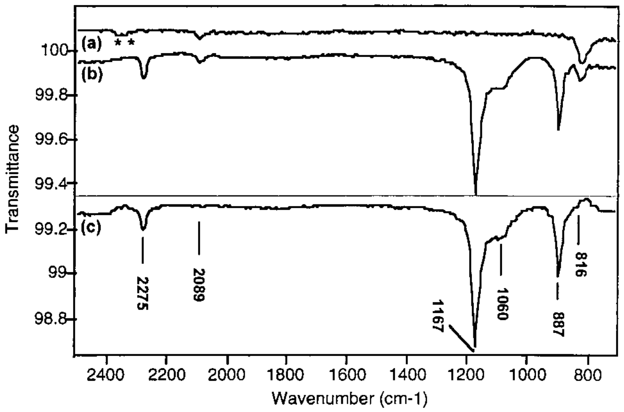

Figure 4. RAIRS spectra of co-dosing experiment of $H_{10}Si_{10}O_{15}$ and H_2O on Si(100)-2×1. (a) H_2O chemisorbed on Si(100)-2×1 (~0.5 monolayer, asterisks mark trace CO_2 in N_2-purged optics bench). (b) H_2O chemisorbed on Si(100)-2×1 (~0.5 monolayer) subsequently exposed to a saturating dose of $H_{10}Si_{10}O_{15}$. (c) Difference of b − a.

Overall, the RAIRS for $H_{10}Si_{10}O_{15}$ chemisorbed on Si(100)-2×1 is strikingly similar to that for $H_8Si_8O_{12}$ chemisorbed on Si(100)-2×1.[13,14] All of the features are similar in terms of frequencies and relative intensity ratios of the bands. This is not surprising, however, considering that the previously reported liquid IR spectra of these two clusters, as well as the IR spectra of their monosubstituted derivatives, are also quite similar.[12,17] It is quite interesting that both clusters generate a peak at 817 cm^{-1}. In our previous study,[14] we assigned this feature as δ(H−Si) based upon the frequency at which it appears and the fact that it shifts upon deuterium labeling of the cluster. This peak is tentatively assigned as a surface Si−H bending mode or a cluster Si−H bending mode. A detailed discussion of this peak was provided previously in our study of the $H_8Si_8O_{12}$-derived interface.[14] We had hoped that the RAIRS study of the $H_{10}Si_{10}O_{15}$-derived interface would provide significant help in assigning the band at 817 cm^{-1}. However, the striking similarity of all aspects of this spectrum with that of the $H_8Si_8O_{12}$ derived interface makes it impossible to make any progess in determining if the 817 cm^{-1} band is derived from surface or cluster Si−H.

IV. Conclusions

RAIRS of $H_{10}Si_{10}O_{15}$ chemisorbed on Si(100)-2×1 gives a spectrum consistent with an essentially intact cluster chemisorbed to the silicon surface. The spectrum obtained is very similar to that obtained for the chemisorption of $H_8Si_8O_{12}$ on Si(100)-2×1. On the basis of data from both experiments, we can definitively rule out water contamination as playing a signficant role in the spectroscopy obtained for these interfaces. Note the excellent signal-to-noise ratio obtained in the C−H stretching region as well and that no evidence of hydrocarbon contamination is observed either. The similarity of the RAIRS spectra for both cluster-derived interfaces is especially striking given the almost identical Si 2p core-level spectra obtained for both interfaces (Figure 1). The XPS spectra differ only in the

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relative area of the features at 2.1 and 3.6 eV, assigned as the cluster vertex bound to the surface $O_3\underline{Si}-Si$ and the unactivated $H\underline{Si}O_3$ moieties, respectively. The data support an identical chemisorption mode for the two clusters and are consistent with a cluster bound via a single vertex to the silicon surface as depicted in Figure 3. As discussed in detail in previous publications,[2,4−6,14] the sum of these data indicate that the formal oxidation state scheme for the assignment of Si 2p core-level spectra at silicon/silicon oxide interfaces is seriously flawed and should be abandoned in favor of an assignment scheme that explicitly takes into account longer range effects such as second neighbor.

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