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Heterogeneous nucleation of oxygen on silicon: Hydroxyl-mediated interdimer coupling on Si(100)-(2×1)

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Infrared spectroscopy and *ab initio* quantum chemical cluster calculations are used to study the decomposition of water on the clean Si(100)-(2×1) surface at low temperature. Using this combined approach we are able to show that the initial surface is actually comprised of an array of isolated and intra-row coupled dimers. The latter are coupled by a hydrogen bonding interaction between OH groups that reside on the same end of adjacent dimers in a dimer row. We find that this interdimer bonding is ~2 kcal/mol more stable than the isolated dimer case. These findings are postulated to have a significant effect on subsequent oxygen agglomeration. [S0163-1829(98)52944-X]

The phenomenal progression in microelectronics miniaturization has now reached the point where gate oxide thicknesses of ~10 Å are being grown for the 60 nm transistors that will be the standard at the end of the next decade. Consequently, the need for precise understanding and control of the Si/SiO_2 interface homogeneity is of paramount importance. However, despite the plethora of studies of this critical interface over the past thirty years, remarkably little is known about the growth of the first monolayer (which will comprise $\frac{1}{3}$ of the total oxide thickness in a 10 Å film). This dearth of detailed information about the microscopic oxidation processes results largely from the absence of both suitable experimental probes with the requisite sensitivity and theoretical approaches with sufficient accuracy at reasonable computational cost. Recently, these limitations have been overcome and the pathways for initial oxygen insertion and agglomeration have been identified.[1,2] In short, it was found that for the model H_2O/Si(100)-(2×1) system, oxidation occurs inhomogeneously leading to the formation of epoxide species at temperatures above 800 K.[2] Notably, while the *intra*dimer reactions leading to O insertion were identified, the mechanisms of heterogeneous nucleation at such low temperatures remain unclear.

In the present work we have utilized broadband infrared (IR) spectroscopy in combination with comprehensive *ab initio* quantum cluster calculations to study the long-range coupling between dissociated water molecules. We are able to show that, upon exposure to water, the dimer structure of the clean surface is transformed into an array of ''isolated'' and ''coupled'' dimer units, with the coupling occurring by the interaction of neighboring surface hydroxyl groups. We propose that such interdimer coupling facilitates the subsequent transfer of oxygens between dimers and that the coupled dimer units consequently act as nucleation sites for oxidation. This work demonstrates that the evolution of a complex, heterogeneous semiconductor interface can be characterized in microscopic detail, suggesting that a rational approach to interfacial growth may be attainable in the near future.

Infrared spectroscopy has proven to be very sensitive to the chemical environments of SiO-H bonds, making it ideal for studying the initial stages of the water-induced growth of oxide films. We have utilized the high resolution intrinsic to infrared spectroscopy and achieved sensitivity to the entire 500–4000 cm^{-1} spectral region of interest, using an external transmission geometry and a state of the art FT-IR spectrometer (Nicolet 860 equipped with a broadband MCT-B detector, operated at 4 cm^{-1} resolution). This broadband sensitivity, coupled with precise temperature and purge gas flow control, allows not only identification of the stretching modes of H-containing species (e.g., Si-H, O-H), but also simultaneous observation of the low-frequency modes associated with the related H-*X* bending motions as well as the stretching modes of heavier atoms (e.g., Si-OH, Si-O-Si). This provides multiple experimental ''check-points'' for our theoretical treatment.

Figures 1(a)–1(c) show the spectra obtained after adsorbing low coverages of water on the Si(100)-(2×1) surface at 220 K, while Figs. 1(d)–1(i) are the analogous spectra at intermediate and high (saturation) coverages, respectively. Focusing first on the low-coverage limit, the principal absorption bands can be generically assigned to the Si-OH, Si-H, and SiO-H stretching modes by reference to the existing literature, as follows: ν(Si-OH):790–820 cm^{-1}, ν(Si-H):~2090–2100 cm^{-1}, and ν(O-H):3650–3690 cm^{-1}. The lowest frequency band at ~600–630 cm^{-1} has not previously been observed for the H_2O/Si(100)-(2×1) system, as it lay beyond the frequency range accessible in all prior studies.[3–5] However, by reference to recent work on both Si-H surface[2,6] and bulk (defect) species,[7] features in this spectral range can be broadly ascribed to Si-H bending vibrations. The central point here is that we are able to clearly resolve a *multiplicity* of discrete features within each of the above bands which, when viewed in concert, can be unequivocally interpreted in terms of an interdimer coupling-induced renormalization of the normal modes, as described below.

In the O-H stretching region, three discrete absorptions at 3655, 3676, and 3682 cm^{-1} are observed at the lowest coverage. The presence of *three* distinct features is confirmed by reference to the spectrum obtained for the same surface but with a fraction of the sites ''blocked'' by adsorption of

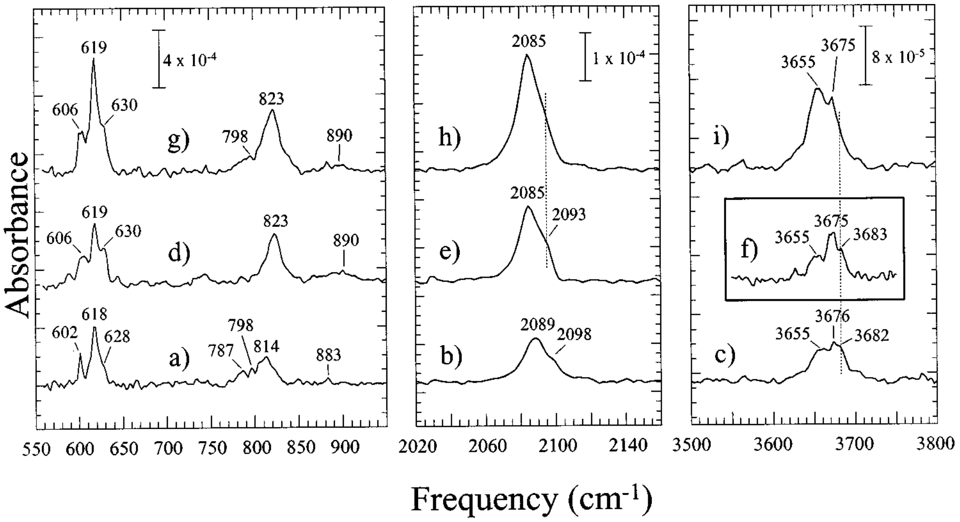

FIG. 1. External transmission infrared spectra for the Si(100)-2×1 surface following exposure to varying doses of H_2O at 220 K. (a)–(c) Low coverage; (d)–(e) intermediate coverage; and (g)–(i) high (saturation) coverage. (f) was obtained by pre-exposing the clean surface to atomic deuterium at 220 K to block a fraction of the surface sites, prior to saturating the surface with H_2O.

atomic deuterium prior to the H_2O exposure [Fig. 1(f)]. Some information can be gleaned about the state of the surface by analysis of these modes alone by the following naïve argument: the appearance of *three* distinct bands in a given spectral region is either due to the presence of three distinct isolated adsorbate structures or to the coexistence of single isolated dimer species (1 mode) and the same species in a coupled dimer pair (2 modes). Now, it is important to recall that only one reaction product is known for reaction of water on the dimerized Si(100)-(2×1) surface: the formation of Si-H and Si-OH groups by dissociative attachment of a water molecule on a single dimer unit.[1–5,8] Therefore, by the preceding analysis, the multiple vibrational bands must result from an interadsorbate interaction. Indeed, the presence of a low-frequency O-H feature at 3655 cm^{-1}, shifted down in frequency by $\sim$20–30 cm^{-1} from the two other bands is suggestive of a hydrogen bonding type of interaction, which is known to lead to a lowering in frequency for the ''donor'' O-H group.[9] Notably, previous theoretical and experimental work has suggested the possibility of such interdimer interactions. For instance, ESDIAD studies[10] showed that OH groups were oriented perpendicular to the dimer bond, which was attributed to either hydrogen bonding between adjacent OH fragments or to a dative-bond type interaction between the oxygen lone pair on one dimer and a dangling bond on another. Similarly, theoretical calculations[8] have indicated that this kind of bonding leads to stabilization by a few kcal/mol.

Further evidence in support of this hypothesis is obtained by inspection of the low-frequency 550–950 cm^{-1} spectral region. Once again, the low coverage spectrum shows three Si-O modes at 787, 798, and 814 cm^{-1} as well as three Si-H bending modes at 602, 618, and 628 cm^{-1}, consistent with the proposed interdimer coupling interaction. However, a more rigorous analysis is clearly required to definitively interpret these spectra; for this we have employed *ab initio* techniques using density-functional theory as described below. Before considering the results of this theoretical treatment we note, in passing, that as the coverage is increased (Figs. 1(d)–1(i)), the same modes are apparent, albeit with some changes in the relative intensity and frequency of several of the features: In the case of the OH stretch the two lowest frequency peaks at 3655 and 3675 cm^{-1} dominate at high coverage, as do the 619 and 2085 cm^{-1} modes in the Si-H bending and stretching regions, respectively. The Si-O modes undergo a more dramatic change, characterized by a shift of the highest-frequency mode from 814 to 823 cm^{-1}, leaving a shoulder at 798 cm^{-1}.

In order to investigate relevant energetics and vibrational frequencies associated with such interdimer coupling, we have performed first-principles calculations on model silicon atom clusters, based on Si_9, Si_{15}, and Si_{20} surface fragments. These clusters are large enough to ensure an accurate description of the adsorbate-adsorbate interactions on two neighboring surface sites, yet small enough to allow the highest level theoretical methodology to be employed. The truncated (bulk) Si-Si bonds are terminated by H atoms, so that the adsorption of two water molecules leads to the $2H_2O{:}Si_{15}H_{16}$ and $2H_2O{:}Si_{20}H_{24}$ model clusters used in this study. All calculations were performed using the gradient-corrected B3LYP density functional method with a 6-31G** polarized basis set on the first and second layer atoms as well as the adsorbate atoms, and a 6-31G basis set on the remaining atoms.[11,12] To elucidate the surface structure we investigated clusters representing all possible conformations of hydroxyl fragments: on unperturbed (isolated) dimers, as well as on dimers subject to intra-dimer, intra-row, and inter-row hydrogen bonding (Fig. 2). The geometry of these clusters (with corresponding adsorbed species) was optimized subject to physically motivated lateral constraints described elsewhere.[1,13] The characteristic surface vibrational modes were obtained by performing a harmonic vibrational analysis for the optimized degrees of freedom, with the computed frequencies subsequently corrected for anharmonic effects by applying an empirically determined correction for each mode type. Specifically, the appropriate corrections for the Si-H bending (-35 cm^{-1}) and stretching modes (-102 cm^{-1}) were *independently* determined by reference to previous studies,[1,2] whereas the Si-O and O-H corrections were evaluated from the highest frequency modes of each type observed

TABLE I. Summary of calculated and observed frequencies for the assigned structures. The O-H bending modes are not listed due to their negligible intensity. Parentheses indicate that a given mode is not the predominant contribution to an observed band for the cases where two modes are found to be degenerate. BB stands for broadband and indicates that there is spectral intensity over the relevant frequency range, although no discrete mode could be resolved.

Species	Mode	Theoretical Freq. (cm^{-1})	Experimental Freq. (cm^{-1})
(H, OH)	δ(Si-H)	604	602
(H, OH)	δ(Si-H)	617/620	618
	δ(Si-H)	627	628
	ν(Si-O)	783	787
	ν(Si-O)	814	814
	ν(Si-H)	2076	BB
	ν(Si-H)	2087	2089
	ν(O-H)	3656	3655
	ν(O-H)	3673	3676
(H, OH)	δ(Si-H)	612	612[a]
	δ(Si-H)	615	(618)
	ν(Si-O)	794	798
	ν(Si-H)	2084	BB
	ν(O-H)	3682	3682
(H,*)	δ(Si-H)	617	(618)
	δ(Si-H)	627	(628)
	ν(Si-H)	2100	2098
(OH,*)	ν(Si-O)	795	(798)
	ν(O-H)	3681	(3682)

[a] See text.

in this work. Consequently, the agreement between theory and experiment is forced for the 814 and 3682 cm^{-1} modes, but completely free for the other modes in these regions. Finally, we corrected for the overestimation of the splitting of the hydrogen-bonded ν(O-H) frequencies by the B3LYP density functional, by comparison of the calculated value for two H-bonded water molecules with the known experimental values for the same.[9]

Based on a comparison of the calculated vibrational frequencies with the experimental values (Table I), we conclude that the water-exposed Si(100)-(2×1) surface is comprised of a mixture of (i) single dimers with *isolated* hydroxyls groups, and (ii) ''paired'' dimers that are coupled by hydrogen bonding between OH groups on neighboring dimers in the same row of the reconstructed 2×1 surface.

Specifically, we find that the features at 602 cm^{-1} and 3655 cm^{-1} can only be assigned to the Si-H bending and OH stretching modes, respectively, of an intra-row coupled dimer pair (predicted frequencies: 604 and 3656 cm^{-1}). Without exception, for all other clusters studied, the analogous modes occur ~15–20 cm^{-1} higher in frequency (Table I). The pronounced lowering of the vibrational frequencies of these modes results from the hydrogen bonding of the two OH groups, which modifies both the force constants of the O-H groups and the local structure of participating Si dimers. The significant perturbation of the Si-H bending motion then necessarily arises due to its strong coupling to the Si-Si vibronic structure. A low-frequency Si-O stretching mode is also predicted for the coupled dimer at 783 cm^{-1}, which compares favorably with the experimentally observed feature at 787 cm^{-1}. The principal remaining modes associated with this coupled structure are predicted to be at 617/620, 627 cm^{-1} (Si-H bends), 2087 (Si-H stretch), and 3673 cm^{-1} (''acceptor'' O-H stretch), once again in excellent agreement with the observed modes at 618, 628, 2089, and 3676 cm^{-1}. An Si-H stretching mode is also predicted to occur at 2076 cm^{-1}, but with less than half the intensity of the 2089 cm^{-1} feature. Although no discrete mode could be resolved at this frequency, this is consistent with the presence of a broad tail to the low-frequency side of the Si-H band in the experimental spectrum.

In the absence of the aforementioned coupling, i.e., for dimers in which the hydroxyl groups are on opposing ends of neighboring dimers, one might expect modes of intermediate character (frequency). Such intuition is confirmed by rigorous theoretical analysis of the low-frequency modes, which predicts Si-H bending and Si-O stretching modes at 612/615 and 794 cm^{-1}, respectively, for the isolated dimer unit. The corresponding Si-H stretching and O-H stretching modes are predicted to be at 2084 and 3682 cm^{-1}. The presence of the Si-O and O-H modes in the experimental spectrum is quite clear (at 798 and 3682 cm^{-1}, respectively), but the 615 and 2084 cm^{-1} modes cannot be resolved due to the presence of the intense 618/2089 cm^{-1} features associated with the coupled dimer species at low coverage. Notably, some evidence was found for a mode at 612 cm^{-1} at low coverages, consistent with this analysis, although this feature is difficult to discern in the spectra in Fig. 1. Finally, the presence of intensity around 900 cm^{-1} is consistent with the predicted frequencies for the O-H bending modes (870–920 cm^{-1}) for the isolated and coupled dimers, although clearly no specific assignments can be made due to the low signal-to-noise ratio.

The only mode as yet unassigned is the weak shoulder at 2098 cm^{-1} on the Si-H stretching band. This feature is best accounted for by the Si-H stretch of an isolated dimer with a hydrogen on one end and a dangling bond on the other (theoretically predicted frequency 2100 cm^{-1}). Such an assignment is commensurate with previous scanning tunneling microscopy (STM) studies of this system, which have shown that the nominally ''saturated'' surface is actually comprised of 10–15% of dimers with only one end passivated.[14] These dimers are thought to form by ''disproportionation'' of a small fraction of the initial H-Si-Si-OH isolated dimers into H-Si-Si* (where* denotes a dangling bond) and *Si-Si-OH units. Importantly, the modes associated with the latter hydroxyl-containing dimer are indistinguishable from the analogous OH modes of the originating H-Si-Si-OH isolated dimer unit (Table I), so that only the H-Si-Si* structure would give rise to a distinct absorption, in accordance with our experimental observation.

Thus, it is clear from analysis of the vibrational spectrum that the low-coverage water-exposed Si(100)-(2×1) surface can be predominantly assigned to a mixture of isolated and coupled dimer units. This finding is further supported by consideration of the relevant energetics. The relative stabilities of all the possible configurations shown in Fig. 2 have been investigated, with the dimer coupling along each row [Fig. 2(d)] found to be 1–2 kcal/mol more stable than either

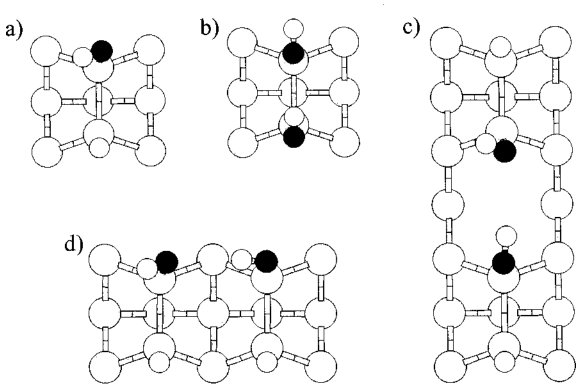

FIG. 2. Models of the different clusters investigated in this work: (a) Isolated dimer; (b) doubly hydroxylated ''isolated'' dimer; (c) coupled dimer (inter-row); and (d) coupled dimer (intra-row).

isolated dimers [Fig. 2(a)] or coupling between dimer rows [Fig. 2(c)]. The presence of two H's on one dimer and two OH's on another [Fig. 2(b)]was also found to be ~2 kcal/mol less stable than the intra-row coupled dimer configuration. In addition, since the intra-row hydroxyl interaction proposed above requires only a minor change in the orientation of the ''internal'' hydroxyl compared to the other possible configurations, it is likely to be both thermodynamically *and* kinetically favored. Final confirmation of the mixed composition of the surface layer comes from STM studies of the $H_2O/Si(100)$-(2×1) surface,[15] which have shown that the OH groups align along the dimer rows, for limited spans of two dimers. These features were separated by extended regions of ''isolated'' dimers (comprised of OH groups on opposing ends of neighboring dimers in a row), with no evidence being found for the 2-OH dimer structure [Fig. 2(b)], consistent with the preceding analysis.

The changes observed on increasing the exposure are worthy of some further consideration. The fact that the majority of the features are largely unchanged over the entire coverage range is an indication that the basic composition of the overlayer does not change significantly. In particular, the absence of a further shift of the lowest frequency OH stretching mode is definitive proof that there is no change in the extent of hydroxyl-mediated interdimer coupling (e.g., to include a third coupled dimer) as the coverage is increased, given that O-H frequency for water trimers is downshifted by ~12 cm^{-1} relative to that for H_2O dimers.[9] We therefore propose that these frequency shifts arise from changes in the extended structure of the overlayer, although an accurate description of this phenomenon is lacking at this time.

In summary, our work establishes that the dissociation of water molecules on the Si(100)-(2×1) surface at ~220 K acquires a thermodynamically stable configuration wherein hydrogen bonding between two hydroxyl groups on adjacent dimers on the same row predominates. We anticipate that this coupling of neighboring OH's may have a profound influence on the mechanism of subsequent oxygen insertion as the temperature is raised. It has recently been shown that the first step in water-induced oxidation is the formation of single and doubly oxygen inserted dimer units—reminiscent of the initial surface composition described here. We therefore speculate that the single oxygen insertion reactions occur on ''isolated'' dimers, whereas the coupled dimers lead to the facile production of the doubly inserted dimers. If so, the arrangement of the initial coupled and isolated dimer units essentially dictates the nucleation sites for subsequent agglomeration and, hence, the ultimate interfacial homogeneity. Consequently, controlling the adsorption process would be of significant interest to the technological community, providing clear motivation for further studies of this system.

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