

CH<sub>3</sub>OD in FR neon, with the total mole fraction of the methanol species being 0.05%. The fitted Lorentzian line parameters are listed in Table I. These results can be used to determine if the deuterated subunit occupies either the donor or acceptor position in the mixed dimer, assuming there is little interaction between the two C-O stretches within the complex.

Comparison of the transition frequencies of the mixed dimer with frequencies observed for (CH<sub>3</sub>OH)<sub>2</sub> and (CH<sub>3</sub>OD)<sub>2</sub> reveals that the mixed dimer has a definite configuration with respect to the subunits. If the donor and acceptor C-O stretches are assigned to the 1052- and 1026-cm<sup>-1</sup> bands, respectively, the mixed dimer transitions will enable us to assign where the CH<sub>3</sub>OH and CH<sub>3</sub>OD reside in the dimer. These dimer assignments were first made by Kabisch and Pollmer<sup>9</sup> and have been supported by solvated alkali-metal-ion studies carried out in this laboratory.<sup>10</sup> Examination of the band near 1027 cm<sup>-1</sup> in the mixed dimer spectrum shows that it lies nearest the acceptor peak in the (CH<sub>3</sub>OH)<sub>2</sub> VP spectrum, after subtraction of the contamination from (CH<sub>3</sub>OD)<sub>2</sub>. This strongly suggests that the acceptor position in the mixed dimer is occupied by CH<sub>3</sub>OH. Similarly, comparison of the 1053-cm<sup>-1</sup> mixed dimer band with the donor peaks of (CH<sub>3</sub>OD)<sub>2</sub> and (CH<sub>3</sub>OH)<sub>2</sub> shows that the donor position is very likely occupied by CH<sub>3</sub>OD. This configuration is expected for the mixed dimer, since it would have a lower zero-point energy compared to the other possible configuration. This was observed in a matrix isolation study of (HF)(DF) by Hunt and Andrews.<sup>11</sup> However, matrix effects have been shown to exclude some observed gas-phase structures, as shown by Andrews et al.<sup>12</sup> This preferred structure is possible especially at the expected temperature of the dimer; time of flight measurements show a translational temperature of 6 K. If the expansion conditions were different so that the dimer would be somewhat warmer, the production of the other mixed dimer might be possible, as observed<sup>13-15</sup> with (H-

F)(DF) and (DF)(HF).

It is also possible to estimate the relative amounts of CH<sub>3</sub>OH and (CH<sub>3</sub>OH)<sub>2</sub> in the molecular beam by measurement of the signals at *m/e* ratios respective of the species of interest. With the presence of only the monomeric and dimeric species in the molecular beam, the identification of the contributions of various compounds appearing at a given mass can be made quite easily. In the case of (CH<sub>3</sub>OH)<sub>2</sub>, it was shown<sup>3</sup> that this species fragments under electron impact ionization to *m/e* 33. It is also known that the trimer can appear at this mass, causing the spectral contamination mentioned earlier. With the trimer and larger clusters absent in the molecular beam, the species contributing signals to *m/e* 33 are (CH<sub>3</sub>OH)<sub>2</sub> and the carbon-13 isotopomer of CH<sub>3</sub>OH. The contribution of the C-13 isotopomer can be estimated by measuring the signal at *m/e* 32, which is due to the carbon-12 species of CH<sub>3</sub>OH. After subtraction of this component of the signal at *m/e* 33, the result is divided by 2 times the signal at *m/e* 32 to give the relative amount of (CH<sub>3</sub>OH)<sub>2</sub> to the monomer in the molecular beam. The factor of 2 arises from an assumption that the electron impact ionization cross section for the dimer is twice as large as for the monomeric species. With this method, a lower limit of (CH<sub>3</sub>OH)<sub>2</sub> relative to the monomer at the dimer/monomer only conditions is estimated to be ~1%.

It is also observed from the VP spectra of Figures 1C and 2A,B that the band line widths are not similar between isotopomers. A band contour analysis is presently under way to try to determine if the differences in the line shapes for the different isotopomers are due to VP lifetime differences, or significant rotational constant changes upon isotopic substitution. A measurement of the absolute photodissociation cross sections for the various isotopomers of (CH<sub>3</sub>OH)<sub>2</sub> is in progress to measure the change of the transition dipole moment upon complexation.

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## Elucidation of the Initial Stages of the Oxidation of Si(111) Using Scanning Tunneling Microscopy and Spectroscopy

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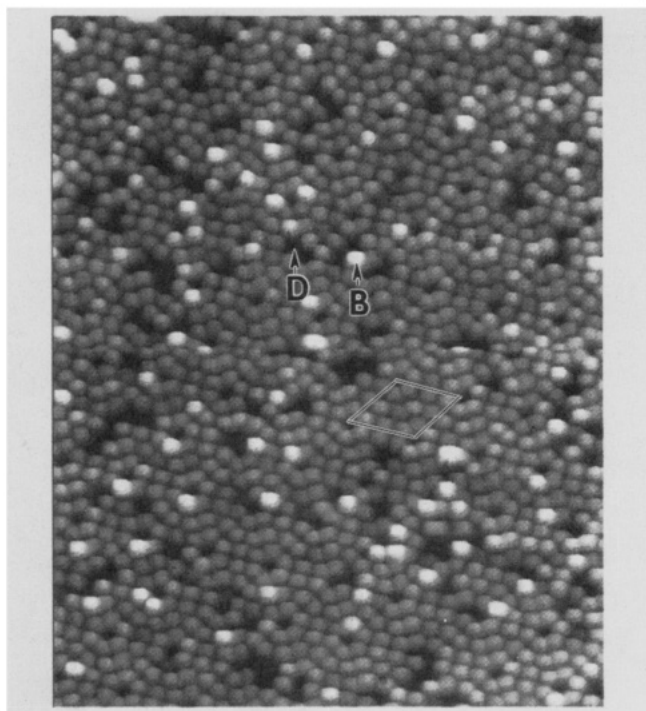
We use scanning tunneling microscopy, atom-resolved tunneling spectroscopy, and electronic structure calculations to determine the nature of the adsorption state of oxygen in the initial stages of the oxidation of Si(111). We are able to directly image two states of adsorbed oxygen. One of them is identified as a Si adatom site with one oxygen atom inserted in one of the back bonds, while the other involves an oxygen atom tying up the adatom dangling bond with, most likely, another oxygen inserted in one of the back bonds. As the coverage is increased toward the monolayer, the latter site becomes the dominant one.

### Introduction

The oxidation of silicon is perhaps the most important chemical reaction in the field of microelectronic materials, so it is not

surprising that it has been the focus of much attention. In particular, the nature of the bonding site of oxygen in the early stages of oxidation has been the subject of extensive study for the past 30 years. Many different configurations have been proposed including configurations where an O atom is inserted in Si-Si

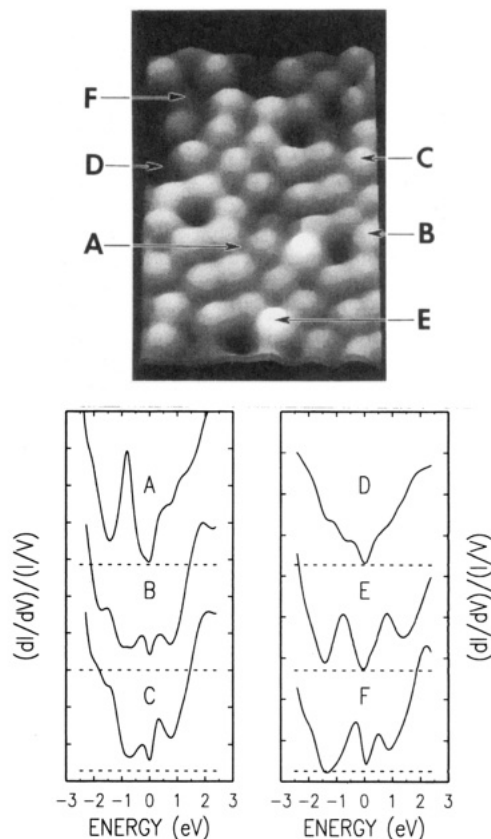
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**Figure 1.** Topograph of the unoccupied states of a Si(111)-7 $\times$ 7 surface after exposure to  $\sim 0.4$  langmuir of O<sub>2</sub> at 300 K (sample bias = +2 V). A 7  $\times$  7 unit cell containing 12 adatoms is outlined. Typical bright and dark oxygen-induced sites are indicated by B and D, respectively.

bonds,<sup>1-6</sup> attached terminally to top-layer Si atoms,<sup>7-11</sup> or involving molecular forms of oxygen attached to a Si surface atom or bridging two Si atoms.<sup>12-14</sup> In the most recent comprehensive analysis of the problem it was concluded<sup>5</sup> that the stable initial state involves "a bridge-bonded oxygen atom between Si atoms in the first and second layer, respectively, with little influence on the dangling-bonds".

In the above studies, the problem of Si oxidation has been studied by using primarily valence- and core-photoelectron spectroscopy and surface vibrational spectroscopy. Preference for one adsorption model over another often has been based on the presence or absence of weak spectral peaks and satellites. The analytical techniques used provide information averaged over an area of the sample that usually includes more than 10<sup>12</sup> atomic sites. Under these conditions, it is difficult to associate particular spectral features with specific surface sites. Scanning tunneling microscopy (STM)<sup>5</sup> and atom-resolved tunneling spectroscopy (ARTS), on the other hand, allow the direct imaging of the surface with atomic resolution and the probing of the valence electronic structures of these atomic sites. In earlier work<sup>16,17</sup> we have shown



**Figure 2.** Top: Topograph of a region of the O<sub>2</sub>-exposed Si(111)-7 $\times$ 7 surface. The sites over which tunneling spectra have been obtained are labeled. Bottom: Atom-resolved tunneling spectra over the sites indicated in the topograph (top). Spectra A, B, and C are over clean restatom, corner-adatom, and center-adatom sites, respectively. Spectra D, E, and F are over oxygen-induced dark, bright, and perturbed (gray) adatom sites, respectively.

that these unique capabilities can be used to study the chemistry of the Si(111)-7 $\times$ 7 surface with atomic resolution. In these previous studies it was found that reactions with several different gases lead to the saturation of the dangling bonds and a reduction in the local density of states (LDOS) which, in turn, is observed as a "darkening" of the reacted site in STM topographs. In all cases studied it was found that restatoms are more reactive than adatoms and that center adatoms are more reactive than corner adatoms.

Here we apply the STM and ARTS techniques to the study of the initial stages of Si(111)-7 $\times$ 7 oxidation. Both O<sub>2</sub> and N<sub>2</sub>O are used as oxidizers. We find that exposure of Si(111)-7 $\times$ 7 to low doses of O<sub>2</sub> leads to the appearance of not only "dark" adatom sites but also of "bright" sites. Analogous behavior is observed with N<sub>2</sub>O, but at higher exposures. The bright sites show a preference for corner adatoms and the restatom sites are the least reactive. Using ARTS spectra and tight-binding electronic structure calculations we are able to identify the adsorption configurations corresponding to the two types of sites observed in the STM images and thus elucidate the nature of the oxygen adsorption site in the early stages of oxidation.

### Results and Discussion

Our experimental setup for obtaining STM topographs and atom-resolved tunneling spectra, as well as sample preparation procedures, have been described in detail elsewhere.<sup>16</sup> Similarly, information about the tight-binding calculations can be found in ref 18.

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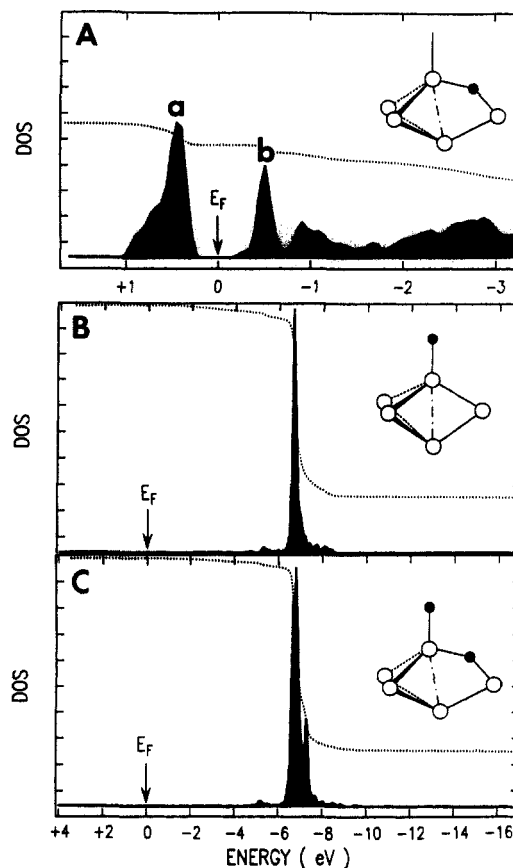
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In Figure 1 we show a topograph of the unoccupied states (sample bias = +2 V) of a Si(111)-7×7 surface after exposure to ~0.4 langmuir of O<sub>2</sub>. A 7 × 7 unit cell containing the 12 top-layer Si adatoms is outlined. Vacancies, so-called corner holes,<sup>19</sup> at the corners of the unit cell are clearly seen. Adatoms adjacent to these corner holes are referred to as corner adatoms while the rest of the adatoms are referred to as center adatoms.<sup>19</sup> The exposure to oxygen led to the appearance of two types of new sites: (A) dark sites, such as those marked D in Figure 1 and (B) bright sites such as those marked B. As can be seen from Figure 1, the bright atoms are located preferentially at corner-adatom sites. In this topograph, 55 bright atoms are located at corner- and 21 at center-adatom sites. The dark sites show little selectivity; there are 41 at corner sites and 34 at center sites. Oxidation with N<sub>2</sub>O also gives bright and dark sites. The exposures required are, however, almost 2 orders of magnitude higher. Moreover, bright atoms appear with higher selectivity on corner-adatom sites. Thus, an area of Si(111)-7×7 containing ~1600 adatoms after exposure to ~35 langmuirs of N<sub>2</sub>O yielded 28 bright sites, of which 23 were at corner adatoms, and 86 dark sites, of which 29 were on corner adatoms and 57 on center adatoms.

In addition to the topographic studies, we have performed detailed atom-resolved spectroscopic studies. Figure 2 shows a region of the reacted surface, and the various sites over which tunneling spectra have been obtained are indicated. Sites and spectra A, B, and C correspond to restatom, corner-adatom, and center-adatom sites in the Takayanagi et al. model<sup>19</sup> of the 7 × 7 surface, respectively. Negative energies denote occupied states while positive energies denote unoccupied states. In accord with previous results,<sup>17,20</sup> restatoms are characterized by a strong dangling-bond surface state at ~0.8 eV below  $E_F$ , while adatoms are characterized by states at ~0.3 eV above and below  $E_F$ . Site D is an O<sub>2</sub>-reacted dark site, E a O<sub>2</sub>-reacted bright site, while F is a "perturbed" adatom site. Only a few of the latter sites are formed, usually next to dark sites. The dark site spectrum (D) does not show the presence of dangling-bond surface states. The bright site spectrum (E), however, shows strong adatom-like surface states at ~0.8 eV above and below  $E_F$ ; i.e., its surface states are displaced by ~0.5 eV from the clean adatom surface states. Finally, the perturbed adatom spectrum shows only a change in the occupation of the surface states.

First we will consider possible oxygen-bonding configurations that may exemplify the characteristics of the bright sites. As we have discussed, saturation of a dangling bond should lead to a reduction of LDOS at the dangling-bond energy, unless the bonded group itself has low-lying levels at the same energy. We have observed the latter case in molecular adsorption.<sup>17,21</sup> Studies of Si oxidation at low temperatures have provided evidence for a molecular precursor.<sup>6</sup> However, the lifetime of this molecular precursor is too short to account for the bright sites seen here, which are stable under ultrahigh vacuum (UHV) conditions. Moreover, bright sites also are observed with N<sub>2</sub>O as an oxidizer.

Atomic oxygen directly bonded to an adatom dangling bond does not introduce low-lying states (see following discussion) and thus cannot be responsible for the development of bright sites. Therefore, the bright sites must involve oxygen not directly bonded to the dangling bond but influencing it indirectly, e.g., through a charge-transfer mechanism. The model in which an oxygen atom is inserted in one of the adatom back bonds is the most likely candidate (see inset in Figure 3A). To help understand the electronic structure of such a site we have performed extended Hückel tight-binding slab calculations. Five double layers were used and the unit cell was composed of a 2 × 2 adatom model for the Si surface which includes a restatom. Previous calculations on oxidation have used unit cells containing only an adatom;



**Figure 3.** Tight-binding calculations of the local density of states at the adatom site for various oxygen adsorption configurations. The configurations are shown schematically in the insets, where a circle indicates a silicon atom and a full circle an oxygen atom. Positive energies indicate unoccupied states while negative energies indicate occupied states.

however, it has been shown<sup>16,22,23</sup> that adatoms and restatoms are coupled so that in order to probe charge-transfer processes both types of sites have to be included. In these calculations, we have computed LDOS over the adatom site so that we can directly compare it with the STM results. The LDOS spectrum near  $E_F$  for a configuration with an oxygen in the adatom back-bond is shown in Figure 3A. The LDOS peak a above  $E_F$  corresponds to the Si adatom dangling bond and is essentially empty, due to charge transfer to the oxygen atom. Our calculations indicate the transfer of ~0.5 electrons to the adjacent oxygen. This is in agreement with a previous calculation<sup>4</sup> which gives a charge transfer of 0.6 electrons. At the clean 7 × 7 surface an adatom participates in the formation of a weak bond with the Si atom directly below it.<sup>16,22,23</sup> Our calculations give an overlap population of ~0.3 for this bond compared to 0.75 for a typical Si-Si bond. The introduction of the O atom displaces the adatom both laterally and vertically, and thus disrupts this subsurface bond (overlap population ~0.1) and increases the localization of the dangling bond on the adatom. The brighter appearance of adatoms with an oxygen inserted in one of their back bonds is then readily explained as due to the fact that the dangling bond is empty due to charge transfer to the oxygen, and because it is more localized on the adatom. We believe that the unoccupied states peak in spectrum 2E is to be correlated with theoretical peak a, discussed above, in the model of an O inserting into an adatom-Si bond. The occupied peak observed at -0.8 eV correlates with the calculated peak b, mainly of back-bond character. This is exactly the same behavior that was observed in the chemisorption<sup>24</sup> and segregation<sup>25</sup> of boron on Si(111). It was found that boron

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substitutes for the Si directly below the adatom and by charge transfer empties the Si adatom dangling bond. As in the present case of oxidation, the presence of boron led to a shift of the dangling bond away from  $E_F$  most likely due to the change in the s-p composition of the dangling-bond state.

Next we consider the preference of the bright atoms for the corner-adatom site. The fact that each corner adatom interacts with two Si dimers while a center adatom interacts with only one dimer in the  $7 \times 7$  unit cell, and the peculiar geometric arrangement around the corner holes,<sup>19</sup> lead to differences in the strain energy associated with the two types of adatom sites. Calculations<sup>26</sup> suggest that the corner adatom is the most strained site. Most likely then, strain energy considerations determine the site selectivity.

The bright sites, although interesting, are not representative of the main oxidation process. The dark sites are more representative. As the  $O_2$  or  $N_2O$  exposure is increased, the dark sites grow in numbers and eventually destroy the  $7 \times 7$  reconstruction, leading to a rough, oxidized surface. This behavior is clearly seen in the topographs reported recently by Leible et al.<sup>11</sup> We find that the dark sites remain dark for both negative and positive sample bias, indicating that the adatom dangling bond is saturated by a group that does not have any occupied or unoccupied states near  $E_F$ . Saturation of the dangling bond by an oxygen atom satisfies this criterion. As can be seen in Figure 3B, the LDOS at the adatom site for the case where a single oxygen is attached to the adatom, or when one oxygen atom is on top of the adatom and the other is inserted in its back bond (Figure 3C), have no states that can be imaged by the STM. There are several questions that need to be answered regarding the nature and origin of these dark sites: (A) Which of the above two configurations corresponds to the actual structure of the dark sites? (B) How are the dark sites formed? (C) What is their relation to the bright sites?

The STM/ARTS results alone do not allow us to discriminate between structures 3B and 3C. However, comparison of our computed total DOS (not shown) for the different adsorption structures with published valence photoelectron spectra<sup>6</sup> obtained in the early stages of oxidation show better agreement for structure 3C. In particular, a double-peak structure at about 6.8 and 7.5 eV in these spectra suggests the presence of bridge-bonded oxygen. The mechanism by which structure 3C can be formed is easy to imagine. An  $O_2$  molecule bonds terminally on top of an adatom, and then rotates and inserts one O atom in the back bond while

leaving the other on the top site. From our data we can exclude another proposed mechanism for oxygen insertion in adatom back bonds. According to this mechanism<sup>6</sup> an oxygen molecule dissociates by interacting with both an adatom and a neighboring restatom. We have probed by ARTS restatom sites adjacent to dark and bright adatoms and have found that the restatom dangling bond is intact. We also have considered the adsorbate-substrate orbital symmetry correlation requirements for the above reaction. We find that the simultaneous interaction of  $O_2$  with an adatom and restatom is symmetry forbidden.

Finally, we can address the question of the relation between bright sites and dark sites. Are the dark sites formed from the bright sites by saturating the adatom dangling bond with an oxygen atom? Although with increasing  $O_2$  or  $N_2O$  exposure the bright sites are eventually eliminated, they do not appear to be the precursors to the dark sites. This can also be seen by considering the adatom site preference of the two types of sites. We have discussed already that bright atoms appear predominantly at corner-adatom sites. If the dark sites resulted from the reaction of the bright sites, then one may expect that the site selectivity will be preserved. However, as we saw, this is not the case. Dark sites show little site selectivity. In the case of  $N_2O$ -induced oxidation, the contrast is even sharper. Thus, it appears that dark and bright sites are formed largely independently and by different mechanisms. Moreover, the mechanism of dark site formation appears to be different in the case of  $O_2$  and  $N_2O$  oxidation.

### Conclusions

In conclusion, we have shown that structure 3A involving one oxygen inserted in the adatom back bond is indeed present in the very early stages of silicon oxidation at room temperature. This structure is assigned to the bright sites of Figure 1. However, it does not appear to be the majority species. The dominant species which grow with increasing oxygen exposure are represented by the dark sites which do not possess a dangling bond. On the basis of comparisons between valence photoelectron spectra and our calculated DOS spectra, we suggest that structure 3C with two oxygens, one in an on-top site and one inserted in the back-bond, is the majority species. Furthermore, we propose that this site is formed by a rearrangement process from a precursor produced by the attachment of an  $O_2$  molecule to the dangling bond of a single adatom.

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