

New Model of the Initial Stages of Si(111)-(7 × 7) Oxidation

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By combining scanning tunneling microscopy (STM) and ultraviolet photoelectron spectroscopy, we show that the adsorption of single O₂ molecules on Si(111)-(7 × 7) produces essentially molecular sites, seen as bright individual sites in STM topographs, which are stable at room temperature. Atom-resolved STM studies also reveal that these molecular sites react very efficiently with further O₂ and H₂O molecules. This is shown to account for the saturation at low exposure of the molecular site density and for the apparent decay lifetime of these molecular sites. [S0031-9007(96)00224-4]

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There has been a continuing interest in studying how molecules adsorb and react on semiconductor surfaces. Over the past few years, the interaction of oxygen molecules with silicon surfaces has emerged as a case study and as such has been investigated by a large variety of experimental techniques [1–10] and theoretical methods [11–13]. Despite this large effort, the adsorption and reactivity of oxygen on silicon surfaces is still controversial and no clear model has emerged so far. Until recently it was considered [5–8,14] that the adsorption of O₂ on Si(111)-(7 × 7) surfaces at room temperature is essentially dissociative and is preceded by a short-lived molecular precursor. Detailed atom-resolved studies using the scanning tunneling microscope (STM) [8,9,15,16] have been performed on O₂ exposed Si(111)-(7 × 7) surfaces. Assuming that the molecular precursor was too short lived to be observed with the STM, stable adsorption sites seen as bright and dark sites in STM topographs have been assigned to various dissociated states of O₂ on Si(111)-(7 × 7) [8,9,15,16]. However, several authors [17–19] recently reported much longer lifetimes of the molecular precursor at room temperature ranging from 50 to 1500 min. This put into question the model of dissociative adsorption and the resulting interpretation of STM experiments. This also raised questions about the discrepancies between the various lifetime measurements of the molecular states.

In this paper, we propose a markedly different model of the initial stages of Si(111)-(7 × 7) oxidation based on new results obtained by combining STM and UPS (ultraviolet photoelectron spectroscopy) studies. According to this new model, the low coverage adsorption of O₂ on Si(111)-(7 × 7) is essentially molecular. This gives rise to molecular adsorption sites, seen as bright sites in STM topographs, which are quite stable at room temperature. The key point is that these molecular sites, although thermodynamically stable, react very efficiently with further O₂ and H₂O molecules hitting the silicon surface. When increasing the O₂ exposure, the reactivity of these O₂

molecular sites with further O₂ molecules leads to complicated reacted sites which appear grey in STM topographs. It will be shown that the reactivity of adsorbed O₂ with H₂O molecules from the residual gas accounts for the apparent finite lifetime of the molecular sites.

The STM from Omicron Vakuumphysik GmbH is operated in a UHV chamber having a base pressure well below 5×10^{-11} Torr. An adjoining preparation UHV chamber ($p < 5 \times 10^{-11}$ Torr) is used to prepare and clean tungsten tips and silicon samples before they are transferred under vacuum to the STM. Gas dosing (typically 1×10^{-9} Torr during a dose) of silicon samples is performed *in situ* on the STM. During dosing, the tip is retracted by about 2 μm such that the same area of the sample can be imaged before and after gas exposure. This ensures that perfectly cleaned surfaces are studied and that all the observed reacted sites are due to gas exposure. UPS is performed in a separate UHV experimental setup which has been described elsewhere [17]. All the reported UPS spectra are recorded with *p* polarization at an energy $h\nu = 40.8$ eV using the synchrotron radiation from Super-Aco in Orsay as a linearly polarized photon source. In all experiments, the Si(111) sample of *n* type, phosphorous doped (1 Ω cm), was heated up for degassing to 700 °C for several hours by resistive heating and then flashed at 1100 °C for 30 s in order to get a clean Si(111)-(7 × 7) surface.

In order to understand the adsorption sites of O₂ on the reconstructed Si(111)-(7 × 7) surface, we performed a series of comparisons between the STM and UPS results. As previously observed [8,9], the STM reveals various adsorption sites which appear essentially as bright and grey reacted Si adatoms in STM topographs recorded with either +2 or -2 V on the sample (see Fig. 1). In addition, a few black sites (less than 10% of the total number of reacted sites) are also observed. Since it is not always easy to distinguish between grey and black sites, we will consider all together grey and black sites as dark sites. Bright and dark sites are not uniformly distributed on the surface.

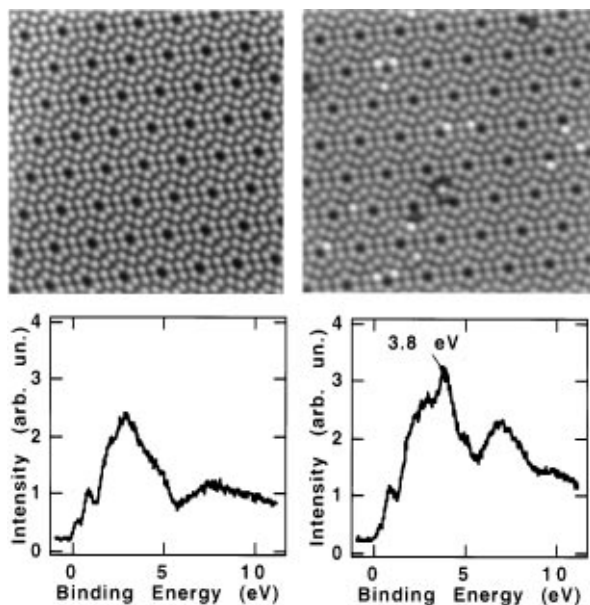


FIG. 1. Upper part: $190 \text{ \AA} \times 190 \text{ \AA}$ STM topographs of the same area of clean (left) and 0.1 L O₂ exposed (right) Si(111)-(7 × 7) surface (both +2.0 V sample bias; 1.0 nA tunnel current). Lower part: UPS spectra of clean (left) and 0.15 L O₂ exposed (right) Si(111)-(7 × 7) surface.

For bright sites we find a preference ratio of 1.1 to 1.6 for corner adatoms as compared to center adatoms and a preference ratio of 2.1 to 2.8 for the faulted half of the unit cells as compared to unfaulted ones. For dark sites the preference numbers are 0.9–1.3 and 1.4–1.6, respectively. These observations are in good agreement with those of Avouris, Lyo, and Boszo [8] and Pelz and Koch [9].

Both bright and dark stable sites in STM topographs have been previously assigned to dissociated states of O₂ on Si(111)-(7 × 7) [13]. Here we argue that bright sites are undissociated molecular states of O₂ whereas dark sites result from reactions of at least two O₂ molecules on the same site. Several experiments have been carried out which add weight to this statement. First of all, we recorded STM topographs of O₂ exposed Si(111)-(7 × 7) surfaces for various O₂ exposures ranging from 0.025 to 1 L (1 L = 1 langmuir). As seen in Fig. 2, the number of bright sites N_b relative to the total number of Si adatoms N_t of a given area rapidly increases as a function of the O₂ exposure and saturates at a value of N_b/N_t of about 0.1 for exposures higher than 0.6 L. This behavior of N_b/N_t exactly coincides with that of the intensity of the 3.8 eV “molecular” band in the UPS spectrum whose variation with the O₂ exposure is also shown in Fig. 2. In contrast the relative number of dark sites N_d/N_t increases continuously as a function of the O₂ exposure (see Fig. 2). The 3.8 eV band in the UPS spectrum (see Fig. 1) has been assigned to molecular states of O₂ by comparison with previous calculations [11–13]. The striking similarity between the N_b/N_t and UPS molecular band curves of Fig. 2 is clearly in favor of our assignment of bright sites as molecular states. Secondly, we performed cumulative

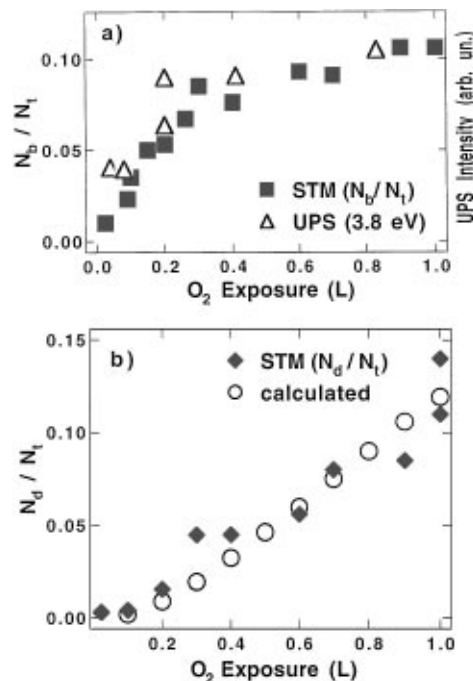


FIG. 2. (a) A graph showing the relative number of bright sites in the STM topographs N_b/N_t and the intensity of the 3.8 eV UPS molecular band plotted as a function of O₂ exposure in langmuirs. The two quantities have been normalized so as to agree at high O₂ exposure. The UPS data are taken from Ref. [17]. (b) A graph showing the relative number of dark sites in the STM topographs N_d/N_t and the calculated values of N_d/N_t from Eq. (2) setting $k_2 = 1.7L^{-1}$ and $k_3 = 0$.

exposures and with the STM examined the same area after an initial 0.2 L O₂ exposure and after an additional 0.2 L exposure. We found that after the initial O₂ exposure the observed bright sites are very reactive; during the second 0.2 L O₂ exposure they turn into grey sites with a probability of 0.34, whereas unreacted Si sites tend to become bright sites during the same exposure with a much lower probability of 0.044. These results are in good agreement with those reported by Pelz and Koch [9]. The saturation of the number of bright sites for O₂ exposures higher than about 0.6 L indicates that above this threshold the number of new bright sites is exactly compensated by the transformation of bright sites into dark sites via the reaction with additional O₂ molecules. The asymptotic behavior of N_b/N_t as a function of the O₂ exposure implies that all the STM bright sites are involved in this equilibrium reaction. Otherwise one would observe a slight increase in N_b/N_t with increasing O₂ exposure.

At this point we want to discuss whether all the dark sites originate from the reaction of bright sites with further O₂ molecules or whether some of them could be due to a direct adsorption of an O₂ molecule on a silicon adatom. For that purpose we recorded STM topographs with a very low O₂ exposure (0.025 L) in order to reduce secondary reactions on bright sites. We find a ratio of bright to dark sites, N_b/N_d , equal to 20. This indicates that the direct

mechanism for formation of dark sites, if it exists, has a very low probability as compared to the formation of bright sites. Most of the dark sites are thus considered to result from secondary reactions on bright sites. This model is further confirmed by a quantitative analysis of the results in Fig. 2. The kinetics of the O_2 adsorption can be described by the following equations:

$$dN_b/dL = k_1(N_t - N_b - N_d) - k_2N_b \quad (1)$$

and

$$dN_d/dL = k_2N_b + k_3(N_t - N_b - N_d), \quad (2)$$

where L is the O_2 exposure, k_1 , k_2 , and k_3 are the sticking coefficients for the formation of bright sites, the transformation of bright into dark sites, and the direct formation of dark sites, respectively. The coefficient k_2 is derived from the measured probability 0.34 (for an exposure of 0.2 L) for the transformation of bright sites into dark sites. This gives $k_2 = 1.7L^{-1}$. Using this value of k_2 , the best fit to the experimental values by Eq. (2) is found when $k_3 = 0$. This indicates that the direct formation of dark sites may be neglected. The slope of the N_b/N_t curve for low O_2 exposures is equal to k_1 [see Eq. (1)]. From Fig. 2 one can thus derive a value of k_1 equal to $0.25L^{-1}$.

An additional important question is whether or not all the bright sites in STM topographs are molecular sites. From the analysis of UPS spectra, Schubert, Avouris, and Hoffmann [13] demonstrated that at low O_2 exposures it is possible to have almost exclusively molecular states. Since we observed almost exclusively bright sites in STM topographs at low O_2 coverages, we conclude that there is a good correlation between molecular states and bright sites in STM topographs. Furthermore, ratios of molecular to nonmolecular states as high as 2 have been deduced from XPS measurements [13]. This is compatible with the results in Fig. 2 only by considering that virtually all the bright sites are molecular states.

We can now go on to an important problem which has been much debated in the literature. This concerns the stability of the molecular adsorption sites. Since we have shown that bright sites are molecular sites, one should then be able to follow the possible instability of individual molecules by recording STM topographs of the same area of surface over very long periods of time. This is illustrated in Fig. 3 where bright sites are shown to have turned into dark sites after 6 h. After several such measurements, the measured lifetime of bright sites is found to be very long (mean value of the order of 1000 min) and to vary from sample to sample and from exposure to exposure. It should be mentioned here that a similar behavior was observed while monitoring the time evolution of the 3.8 eV molecular band in the UPS spectrum [17] (see illustration in Fig. 3). Therefore we propose that the apparent decay of the molecular sites in the STM and UPS experiments could be due to the interaction with contaminants from the residual gas. A small amount of various gases was introduced and the

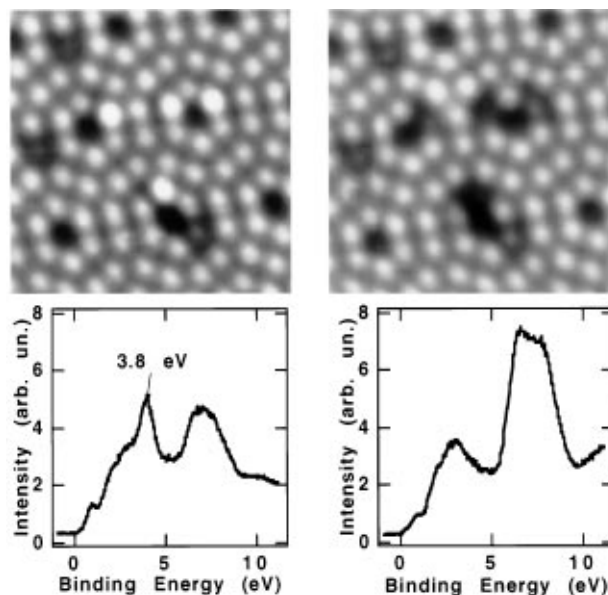


FIG. 3. Upper part: $70 \text{ \AA} \times 70 \text{ \AA}$ STM topographs of the same area of a 0.15 L O_2 exposed Si(111)-(7 \times 7) surface immediately after exposure (left) and 6 h later (right) (both +2.0 V sample bias; 1.0 nA tunnel current). Lower part: UPS spectra of a 0.3 L O_2 exposed Si(111)-(7 \times 7) surface immediately after exposure (left) and 6 h later (right).

result examined with the photoelectron spectrometer. A few langmuirs of H_2 or CO have no effect on the UPS spectra; however, a small amount (0.2 L) of H_2O has dramatic effects on both the STM topograph and the UPS spectrum, as shown in Fig. 4. A number of bright sites ($\approx 40\%$) turn dark whereas the intensity of the 3.8 eV

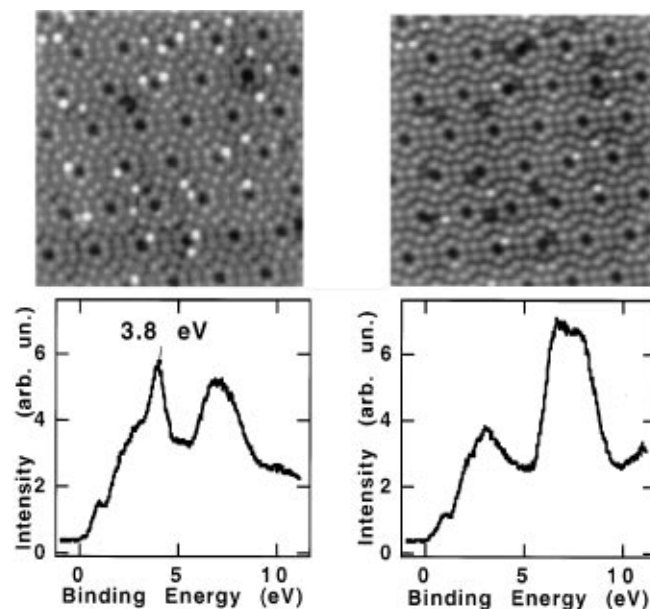


FIG. 4. Upper part: $150 \text{ \AA} \times 150 \text{ \AA}$ STM topographs of the same area of a 0.3 L O_2 exposed Si(111)-(7 \times 7) surface immediately after exposure (left) and after an additional 0.2 L H_2O exposure (right) (both +2.0 V sample bias; 1.0 nA tunnel current). Lower part: UPS spectra of a 0.3 L exposed Si(111)-(7 \times 7) surface immediately after exposure (left) and after an additional 0.2 L H_2O exposure.

molecular band in the UPS spectrum strongly decreases. The same H₂O exposure on clean Si(111)-(7 × 7) has no observable effect either on the STM image or on the UPS spectrum. This strongly suggests that the apparent time decay of the molecular sites is due to reaction of the adsorbed O₂ with water molecules from the residual gas in the UHV chamber. It is striking indeed to observe the exact similarity between the UPS spectra in Figs. 3 and 4, recorded a long time after O₂ exposure and after O₂ and H₂O exposures, respectively. From the results in Fig. 4, we deduce a reaction cross section of 52 Å² for a water molecule with a bright O₂ molecular site. With such a high reactivity, a partial pressure of 2 × 10⁻¹¹ Torr of H₂O is sufficient to produce a decay of the molecular sites with a lifetime of 270 min. It follows that the exact lifetime of O₂ molecular sites, which is considered here to be very long (>500 min) or infinite at room temperature, would be very difficult to measure even under ideal UHV conditions.

We note that the high reactivity of O₂ molecular sites with H₂O molecules may be interestingly related to the effects of trace amounts of water on the thermal oxidation of silicon in oxygen [20]. Although pressure and temperature regimes are quite different, the relative partial pressures are comparable. Our results seem to indicate that the enhanced reactivity may be observable over the whole pressure range (atmosphere to 10⁻¹¹ Torr) and that this reactivity has its origin at the molecular level. In other words the elementary reactions may well be similar in both experiments.

In conclusion, we propose here a new model for the low coverage adsorption of oxygen molecules on Si(111)-(7 × 7). We have shown that the adsorption of single O₂ molecules produces essentially only molecular sites which appear as bright sites in STM topographs. These molecular sites are quite stable at room temperature under extremely good UHV conditions. This contrasts with previous models in which the adsorption of single O₂ molecules was considered to be essentially dissociative with a short-lived molecular precursor. The previously observed short lifetime of molecular sites is possibly due to the adsorption of H₂O molecules from the residual gas on these highly reactive O₂ molecular sites. When increasing the O₂ exposure, these O₂ molecular sites react very efficiently with further O₂ molecules. This leads to the formation of complicated reacted sites which appear dark in STM topographs. The exact structure of the molecular (bright in STM) and reacted (dark in STM) sites is still an open question. From the UPS spectrum and its comparison with previous calculations [13] it seems reasonable to assign the molecular sites to the paul, para, or grif geometry [13] with the O₂ molecule bound to a single silicon adatom and the O-O bond essentially parallel to the surface. These molecular sites show up as bright sites in STM images obtained with both +2 and -2 V on the sample, suggesting that both unoccupied and occupied electronic states lie close to the Fermi level. This could not be confirmed by the DOS (density of states) calculations of Schubert, Avouris,

and Hoffmann [13]. We note, however, that the STM image contrast is not directly related to DOS considerations [21]. The assignment of the reacted (dark in STM) sites is even more problematic. The corresponding band in the UPS spectrum lies about 7 eV below the Fermi level. This was assigned by Schubert, Avouris, and Hoffmann [13] to various states of dissociated oxygen adsorbed on silicon adatoms. However, more complicated reacted sites involving two oxygen molecules should also be considered since we are sure that these reacted sites originate from the successive reaction of two molecules on the same silicon adatom. Further DOS calculations and spectroscopic experiments are required for clearly identifying the nature of these reacted sites.

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