AIP | The Journal of Chemical Physics

A theoretical study of the initial stages of Si(111)–7×7 oxidation. II. The dissociated state and formation of SiO4

Boris Schubert, Phaedon Avouris, and Roald Hoffmann

Citation: J. Chem. Phys. 98, 7606 (1993); doi: 10.1063/1.464700
View online: http://dx.doi.org/10.1063/1.464700
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v98/i9
Published by the American Institute of Physics.

Additional information on J. Chem. Phys.

Journal Homepage: http://jcp.aip.org/
Journal Information: http://jcp.aip.org/about/about_the_journal
Top downloads: http://jcp.aip.org/features/most_downloaded
Information for Authors: http://jcp.aip.org/authors

ADVERTISEMENT

Downloaded 07 Dec 2012 to 128.253.229.242. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

A theoretical study of the initial stages of Si(111)–7×7 oxidation. II. The dissociated state and formation of SiO_4

Boris Schubert
Department of Chemistry and Materials Science Center, Cornell University, Ithaca, New York 14853

Phaedon Avouris
IBM Research Division, T. J. Watson Research Center, Yorktown Heights, New York 10598

Roald Hoffmann
Department of Chemistry and Materials Science Center, Cornell University, Ithaca, New York 14853

(Received 25 August 1992; accepted 11 January 1993)

In a preceding paper (referred to as part I) we presented a theoretical study of the initial stages of the oxidation of the Si(111). Specifically, we discussed the structure of the molecular precursors and the stable products, using approximate molecular orbital calculations of the extended Hückel type. In this contribution (part II) we propose pathways which lead from one oxygen chemisorption configuration to another. A scheme is constructed to account for the reaction sequence from the clean Si(111) surface to molecular precursors, through dissociated states and finally to SiO_4 units which are precursors for bulk-like SiO_2.

I. INTRODUCTION

As pointed out in paper I,[1(a)] understanding the process of silicon oxidation would provide insight into the character of the Si/SiO_2 interface. In paper I we introduced the theoretical technique and discussed the molecular precursor state. We identified the *paul-para*[1(b)] and *grif* structure as the major stable precursor and the *bridge* structure as an unstable precursor which dissociates to give the *ins-rest* structure (the structural designations are defined in Fig. 1). In this paper we explore the reaction pathway of the silicon oxidation that eventually leads to the formation of SiO_4 units. In Sec. II we identify the most likely stable oxidized structures as a function of coverage. In Sec. III we show how SiO_4 units, which are necessary for building SiO_2, are generated on the Si(111) surface.

Before discussing the oxidation process we briefly introduce the structure of the reconstructed Si(111) surface and the unit cell used in our calculations.

The structure of the 7×7 Si(111) reconstruction is described by the DAS (dimer adatom stacking fault) or Takayanagi model.[2–5] The reconstructed Si(111) surface contains the top layer Si atoms, so-called adatoms, second layer rest atoms (with dangling bonds which are not saturated by bonding to an adatom), corner holes, two different stacking patterns and dimers. A full view of the reconstructed surface is given in paper I. Oxidation of this complex structure is not going to be simple.

Theoretical calculations are also difficult since the unit cell of the stable 7×7 cell is very large. Goddard, Redondo, and McGill,[6] Chen, Batra, and Brundle,[7] Bhandia and Schwarz,[8] and Ciraci, Ellialtioglu, and Erkoc[9] used different simplified unit cells and came to different conclusions regarding the main oxygen species on the surface during Si(111) oxidation.

We have performed extended Hückel[10] tight-binding[11] *slab* calculations with weighted H_{ij}'s.[12] Five double layers were used and the unit cell was composed of a 2×2 adatom model for the Si(111) surface which includes a rest atom (see Fig. 2). At the bottom layer, hydrogen saturates the dangling bonds (Si–H: 1.48 Å). In comparison to the real 7×7 unit cell we neglect the effect of the dimers, corner holes, and of the stacking fault. Although these, especially the stacking fault and corner holes, do play a significant role in the oxidation (see Refs. 13–15 and conclusion), we think that the 2×2 unit cell is a fairly good representation for the reactive sites of the 7×7 unit cell, since the dangling bond bearing adatoms and rest atoms are the dominant sites for Si(111) surface chemistry. The parameters of the calculation are given in the Appendix.

Figure 1 shows most of the Si–O configurations discussed in this contribution. It can be seen that some involve molecular oxygen[6,16–19] either attached to one Si atom or as a bridge between two Si atoms (peroxy bridge). Other geometries are derived from adsorbing atomic oxygen on top of top-layer Si atoms[18,20–22] or inserting atomic oxygen into a bond between the adatom and a first layer silicon (adatom backbond).[9,19,23–25] In the following they are referred to as *clean*, *grif* (for Griffith),[26] *paul* (for Pauling),[27] *para* (from parallel to the surface), *trival* (one oxygen is trivalent), *bridge*, *ins* (from inserted), *ad*, *rest*, *ins-ad*, *ins-rest*, *ins-ad-rest*, and *sio4*. In the absence of a systematic nomenclature of adsorbate sites, these terms are at least descriptive.

Further details (e.g., replacement of atoms due to insertion of an oxygen in the adatom backbond, O–O distances, choice of parameters) are discussed in paper I.

II. THE STABLE STRUCTURES

In this section we want to identify the main stable configurations formed for low (e.g., 0.2 L O_2) and medium (e.g., 2.5 L O_2) O_2 exposure (1 L$=10^{-6}$ Torr s). Higher exposures (>10 L O_2) will be considered in the next section.

 0021-9606/93/097606-07$06.00 © 1993 American Institute of Physics

Downloaded 07 Dec 2012 to 128.253.229.242. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

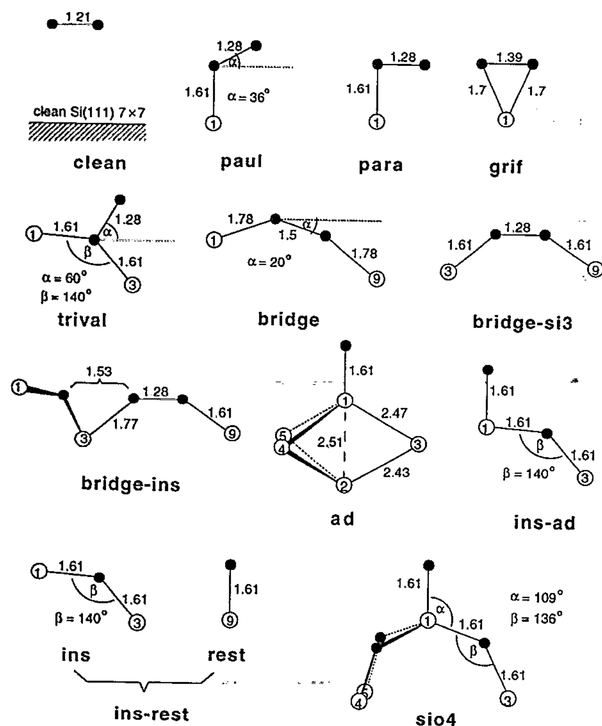


FIG. 1. The Si–O configurations discussed in this contribution (solid circle: O, open circle: Si). Si_1 is the adatom; Si_9 is the rest atom. *clean* stands for the clean surface and an O_2 molecule without any interactions with the surface. *ins-ad-rest* (the only structure not shown) consists of *ins-ad* and *rest* in one unit cell. For *ad*, also a bit of the Si arrangement close to the adatom is displayed.

It is now generally accepted that *at room temperature* the chemisorption of O_2 on Si surfaces is dissociative. Even at very low coverages oxygen breaks the Si(adatom)–Si backbonds to form Si–O–Si bridges (see *ins, ins-ad, trival, bridge-ins, ins-rest,* and *sio4* in Fig. 1) similar to SiO_2. It was already pointed out by Goddard, Redondo, and McGill[6] that the driving force for this insertion process is probably a strong Si–O bond replacing a weakened O–O bond on the surface. Most results indicate that at least one insertion takes place during stabilization. However, it is not clear what the structure of the most stable configuration is.

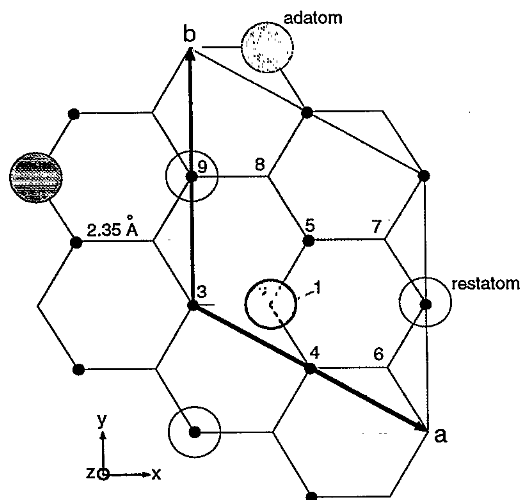


FIG. 2. Top view of the 2×2 unit cell (shadowed area) used for our extended Hückel calculations. The numbering of the Si atoms is also indicated. The small circles refer to the up position of the puckered hexagon. The two lattice vectors **a** and **b** of the overlayer structure are 3.84 Å long.

By comparing experimental scanning tunnel microscopy (STM) results[13,28] to extended Hückel calculations, in previous work we were able to identify[29] the stable and dominant Si–O configuration (dark sites in STM, stage 2) to be given by configuration *ins-ad* and the bright sites in stage 2 as the *ins* structure. We will keep in mind that while these are likely candidates, there must also be a reasonable reaction pathway from the precursors described in paper I to the two stable product configurations named above.

In choosing configurations as candidates for molecular precursors we ask the following questions:

(I) Does the density of states (DOS) match with the ultraviolet photoemission spectroscopy (UPS) or STS spectra?

(II) Does a reasonable pathway from the precursors exist?

(III) Does the DOS match with x-ray photoemission spectroscopy (XPS) data?

(IV) Are other criteria, such as overlap populations and charges, reasonable?

(I) Figure 3 shows the oxygen and $Si_1(p_z)$ DOS for the possible candidates. All the oxygen DOS's are within the energy range indicated by the two horizontal dashed lines and are therefore in agreement with the UPS spectra. Note, especially, that no DOS appears at 4 eV. This further supports the notion that the 4 eV peak derives exclusively from the precursor state, whereas the "7 eV peaks" have contributions from both the precursor and the stable product (see also paper I). This is also in agreement with calculations by Chen, Batra, and Brundle[7] and by Ciraci, Ellialtioglu, and Erkoc.[9] They found that the main DOS for different dissociated states is at about 7 eV.

Since all oxygen DOS curves are similar, we need another criterion to distinguish between these candidates, for instance, the $Si_1(p_z)$ DOS. It is known from STM and STS data[29] that the stable state reached after 0.2 L O_2 has a bit more dark sites (50%–70%) than bright sites and from UPS that only a very small fraction of the rest atoms have reacted. At 2.5 L O_2 exposure the surface is dominated by dark sites and the rest atom UPS peak begins to disappear. These observations suggest the *ins, ad, ins-ad, ins-rest* structures after the 0.2 L O_2 exposure, and the *ad, ins-ad, ins-ad-rest* structures for the 2.5 L O_2 exposure.

(II) In the preceding section we identified the *paul-para* and *grif* structures as the best candidates for the main precursors and *bridge* as an intermediate to *ins-rest.* The stable states must be related via plausible pathways to these molecular precursors. Probable pathways from precursors to dissociated states are shown in structure 1. Bold names or arrows indicate favored configurations or pathways.

Downloaded 07 Dec 2012 to 128.253.229.242. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

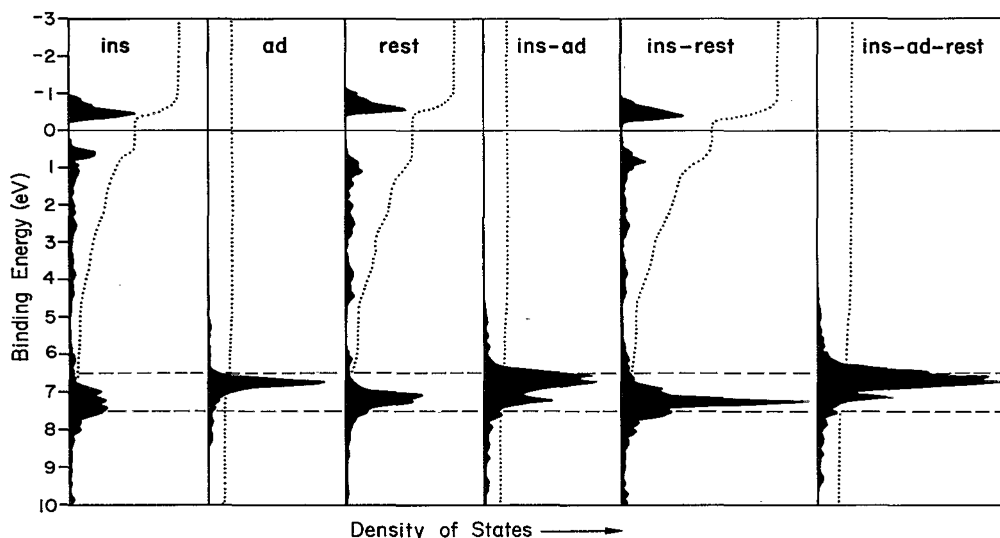
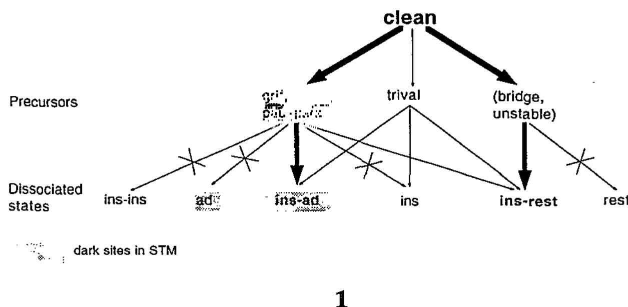


FIG. 3. DOS for the stable configurations. For the geometry see Fig. 1. The oxygen DOS is located mainly between 6 and 8 eV. The $Si_1(p_z)$ DOS (4 times magnified) accounts for the rest. The integration goes from 0% to 100% within each box. The horizontal dashed lines indicate the range of possible oxygen peaks judging from UPS data.

Note that this diagram represents the state of the surface in stage 2 (oxygen is dissociated), room temperature, ~0.2 L O_2 exposure.



1

As shown in structure 1, we exclude configuration *ad*, since there is no reasonable pathway from the precursors discussed to this configuration. For the same reason *ins* is an unlikely candidate; most reasonable pathways lead to *ins-ad* or *ins-rest* (see also paper I and Ref. 30). But on the actual 7×7 surface, *ins* can be important at adatoms next to corner holes, due to different pathways possible.

In previous work[15] it was suggested that the stable state involves the insertion of *two* oxygens into the silicon backbonds (*ins-ins*, not shown in Fig. 1). Moreover, it was suggested that such a structure will appear dark in STM topographs of the unoccupied states of the sample. Our calculations on such a structure give a similar $Si_1(p_z)$ DOS as for *ins*. The main difference is that the adatom is more positive, which shifts some of the occupied Si_1 DOS above the Fermi level. Therefore, *ins-ins* definitely would appear as a very bright site in STM images of unoccupied states and can be excluded as being responsible for the dominant dark sites at exposures greater than 1 L O_2. The *ins-ins* configuration could, in principle, still play a role as a bright site at low coverages (0.2 L O_2). However, the total energy of the *ins-ins* structure is more than 5 eV higher than for an *ins-ad* or *ins-rest* structure.

For the bright sites, we have already identified the most promising candidate: the *ins-rest* structure. For the dark sites, we still have the *ins-ad* and *ins-ad-rest* structures to discuss. It is likely that *ins-ad* is the dark site at 0.2 L, whereas *ins-ad-rest* is the dark site at 2.5 L O_2. In support of this, the rest atom dangling bond disappears on going from 0.2 to 2.5 L.

Now we can understand what happens during the first 10 min at room temperature in the STM images: The molecular precursors *paul-para* and *grif* would dissociate. With respect to the dark sites no changes in the STM picture should be expected, since the product of dissociation (*ins-ad*) would also appear dark in STM topographs. This was discussed already in a previous publication.[29] For the bright sites, if the *trival* configurations dissociate to give *ins-ad* and *ins-rest* about 10% of the bright sites should turn dark to match the experimental results. So, at stage 2 (0.2 L O_2), we are left with a bit more of the dark sites (*ins-ad*) than bright sites (*ins-rest*). This matches the experimental ratio for (dark sites):(all reacted sites) of 50%–70%.[31]

At medium high coverages (e.g., at a few L O_2 exposure), structures such as *ins-ad-rest* should become increasingly more important and structures such as *ins-ad* or *ins-rest* will be strongly reduced. This will leave only a few adatom dangling bonds or bright sites. The dominant sites will now be dark (*ins-ad-rest, ins-ad*). This is what is found with STM.[13,29] Since the rest atom peak vanishes at higher coverages (S_2 in UPS, see paper I), it is plausible that *ins-ad-rest* is the main product.

At high coverages (>10 L), *sio4* should replace *ins-ad-rest* (see Sec. III below). This probably happens with a

Downloaded 07 Dec 2012 to 128.253.229.242. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

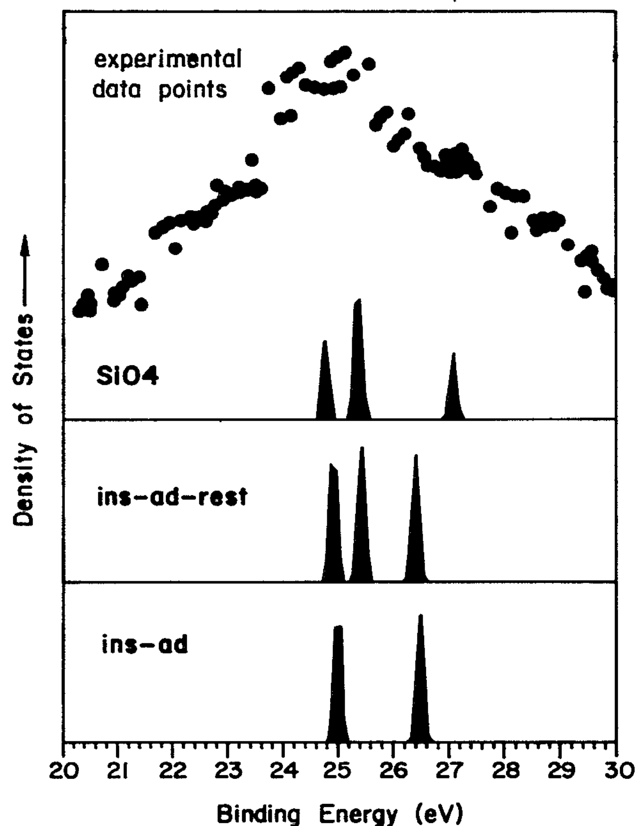


FIG. 4. O (2*s*) DOS for *ins-ad*, *ins-ad-rest*, and *sio4* compared to XPS data from Morgan *et al.* (Ref. 25).

different and lower sticking coefficient, as already indicated by some experiments.[19,32]

(III) In the following we will test the above suggestions by comparing with further experimental results, such as the XPS data which monitor the position of the O (2*s*) levels.[25]

Figure 4 shows the O (2*s*) DOS for *ins-ad*, *ins-ad-rest*, *sio4*, and the original experimental data points obtained from Fig. 11 in Ref. 25. Morgan *et al.* assumed that there is only a single peak within this XPS band. We suggest that this band may contain several peaks. Since the XPS spectra were obtained after 250 L O_2, which is much more than a monolayer, we do not consider *ins-rest* anymore, but have included *sio4* (see the next section). It can be seen that all of the peaks could fit under the broad experimental curve. Ciraci, Ellialtioglu, and Erkoc[9] found the O (2*s*) peak for the *ins-ad* structure at exactly the same energy as we do.

(IV) An examination of the total energies shows that all configurations have substantial binding energies, although the on-top position is preferred over the inserted position.

Figure 5 shows clearly that in all configurations considered the Si–O overlap population is smaller in the case of an inserted oxygen than for oxygen on top of a Si atom. It also shows that *sio4* has a much stronger Si_1–$O_{on\ top}$ bond. This is because in *sio4* the Si_1 has moved far away from the silicon underneath it and can concentrate its p_z orbital towards the oxygen on top of it.

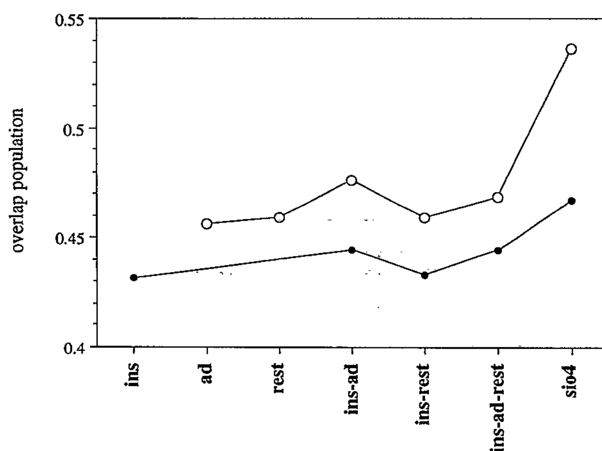


FIG. 5. Overlap population (OP) for all stable state configurations. Solid circle: mean of OP (Si_1–O_{ins}) and OP (Si_3–O_{ins}); open circle: OP (Si_1–O_{ontop} or Si_9–O_{ontop}), for *ins-ad-rest* the mean value of OP (Si_1–O_{ontop}) and OP (Si_9–O_{ontop}) was taken.

Figure 6 shows the charge transfer to the oxygen atoms for different configurations. The shadowed area in the middle marks all silicon atoms directly bonded to one oxygen. Si atoms below this area are not bonded directly to an oxygen and Si atoms above this area are bonded to two or four (in the case of *sio4*) oxygen atoms. As expected, the silicon atoms become more and more positive when bonded to more oxygen atoms. It is interesting to see that there is a difference between the effect of an inserted oxygen and of an oxygen on top. Obviously, the oxygen on top can more effectively obtain charge from the silicon, compared to the oxygen that is inserted (compare *ins* and *ad* for the adatom). One reason for this could be a better angular overlap.

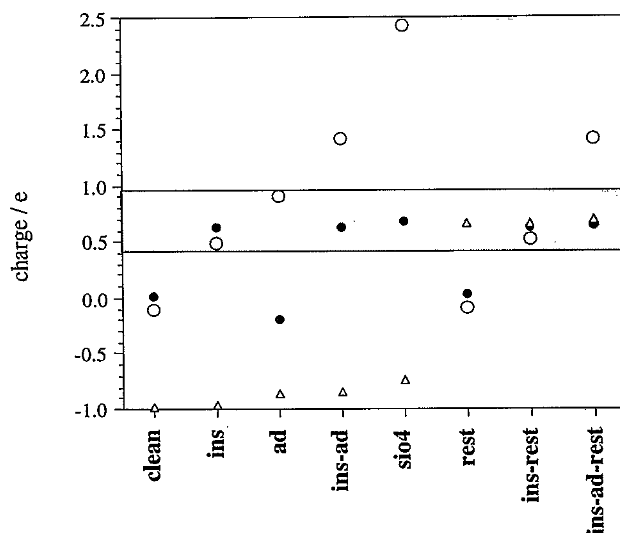


FIG. 6. Charges at different atoms for the configurations marked; open circle: adatom; solid circle: Si_3; triangle: rest atom.

Downloaded 07 Dec 2012 to 128.253.229.242. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

To summarize, we propose that the reacted sites of stage 2 at, e.g., 0.2 L O_2 exposure most likely consists of about 50% *ins-rest* and 50% *ins-ad*. Since we find a little more dark than bright sites in the STM images, *ins-ad* should dominate slightly over *ins-rest.* At medium coverages (2.5 L O_2, only dark sites), *ins-rest* has to disappear. If all dangling bonds would be covered by oxygen, we would have 50% *ins-ad* and 50% *ins-ad-rest*, since the 7×7 unit cell has 2 times more adatoms than rest atoms. But, in fact, at a 2.5 L O_2 exposure we will have a oxygen coverage, at 300 K, of about 0.15 (Ref. 25) to 0.3 (Ref. 32), which would indicate a dominance of *ins-ad* over *ins-ad-rest*. This would leave some of the rest atoms dangling bonds still intact.

Finally, we should consider a structure (*ins-ins-ins*) which consists of three oxygen atoms inserted in the adatom backbonds. This structure looks like *sio4* (see Fig. 1) without the top oxygen. We do believe that the *ins-ins-ins* structure cannot represent the main dark site for the following reasons:

(a) STS measurements[29] of the main dark sites at stage 2 (0.2 L O_2 and higher coverage) indicate that no significant DOS exists within a range of ±3 eV from E_F. However, our calculations show a strong occupied Si_1 (p_z) peak at 1 eV below E_F.

(b) We have identified *paul-para* and *grif* as the main stable precursors (last section). They are responsible for the dark sites in stage 1. After dissociation, these configurations will lead to the structure *ins-ad* and not to *ins-ins-ins*.

(c) The main difference between *ins-ins* and *ins-ins-ins* is that for *ins-ins-ins* the adatom is moved up far enough to eliminate its interaction with the silicons in the next layer. Therefore, the $Si_1(p_z)$ orbital can establish a very strong and localized dangling bond at 1 eV. Compared to *ins*, the DOS at 1 eV increases by a factor of 5. If one of the main reactions would be the conversion from *ins* to *ins-ins-ins*, the peak at 1 eV should significantly increase in the UPS spectra. On the contrary, it is found to decrease.

Although *ins-ins-ins* cannot represent the majority of the dark sites, it can account for these dark sites which result from the subsequent reaction of some bright sites. The most plausible pathway to *ins-ins-ins* is to insert an oxygen molecule in the remaining backbonds of *ins*.

III. THE FORMATION OF SiO_4 UNITS

We now consider what happens if we continue to expose the Si(111) surface to more O_2. At higher exposures (>10 L O_2 at 300 K or about 1 L O_2 at 100 K) the sticking coefficient changes drastically[19,25,32] and we expect the *sio4* species to enter the reaction scheme and play an increasingly important role. Early measurements using gas volumetry already showed that the first adsorption process is fast, followed by a slow sorption process.[33,34] Many groups have assumed that configurations such as *ad*, *ins*, *ins-ad*, or *ins-ad-rest* would be sufficient to passivate the surface. We suggest that the real passivation may begin one step later—*after* formation of the SiO_4 units.

Let us consider the *sio4* structure in more detail.

(a) First, as can be seen from Fig. 1, the *sio4* structure is almost identical to the SiO_4 units in bulk SiO_2, which is the final product of oxidation. In SiO_2, the mean Si–O distance is 1.61 Å, the silicon is surrounded by an oxygen tetrahedron, and the Si–O–Si angle is 144°;[35] the geometry of *sio4* is almost the same. The only difference is that the Si–O–Si angle is 136° instead of 144°. In Fig. 1 the surface is not reconstructed (the adatom is moved up by almost 1 Å) Therefore, the main driving force for reconstructing the (111) surface at the adatom site has vanished. By structuring the surface slightly and shifting the $Si_{3,4,5}$ atoms 0.1 Å sideways, we would get an angle of 140°. Thus, it is easy to accomodate an SiO_4 unit without excess strain at the adatom site.

(b) Since the process of insertion of an oxygen atom into an adatom backbond is a favorable event on the Si(111)–7×7 surface, it may appear easy to insert more than one oxygen atom at the same adatom site. Some authors have indeed suggested[15,25] inserting two oxygens to form *ins-ins*. This configuration, however, is unfavorable due to surface stress (see the discussion in the preceding section). However, by inserting *three* oxygens in the three adatom backbonds the stress is relieved and one recovers the threefold symmetry characterizing the adatom site.

(c) As expected for a low stress structure, the binding energy is substantial for *sio4*. As compared to the clean surface plus two oxygen molecules, the system gains ∼20 eV by forming *sio4* (see also Fig. 7). Compared to one of the stable states (*ins-ad*, which would be the precursor for *sio4*) plus one oxygen molecule, the predicted gain in energy is very large, ∼10 eV (Fig. 7).

(d) The reaction pathway leading to *sio4* is rather obvious. Since it is unfavorable to have two oxygens inserted in the adatom backbonds (see last section), we have to insert two oxygen atoms at the same time. Starting from *ins-ad*, we can insert two oxygen atoms from a single oxygen molecule simultaneously in the remaining two adatom backbonds, by dissociating the oxygen molecule.

(e) The O (2*p*) DOS is peaked 6 to 7 eV, similar to all other stable configurations displayed in Fig. 1. The O (2*s*) DOS spectrum is shown in Fig. 4 and is consistent with experimental XPS results.[25]

(f) The overlap populations for both the $Si–O_{ins}$ and $Si–O_{ontop}$ bond increase significantly when forming *sio4* (see Fig. 5); this is one reason for the stability of this SiO_4 unit.

All results discussed above favor the formation of *sio4*. However, expect the insertion of the oxygen molecule simultaneously in the two remaining adatom backbonds to

Downloaded 07 Dec 2012 to 128.253.229.242. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

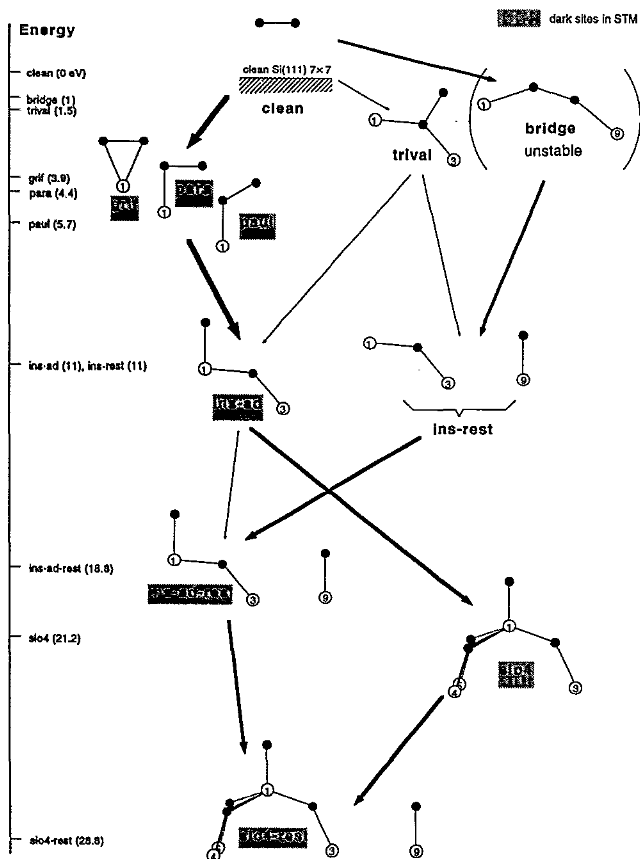


FIG. 7. The oxidation of Si(111): Initial stages, summary (for precursor states see part I of this contribution).

have a kinetic barrier. It will also be more difficult for an oxygen molecule to find the correct geometrical position for this reaction, compared, for instance, to the formation of the *paul* configuration. In the former case, especially the oxygen atom on top of the Si is expected to repel the incoming oxygen molecule. This will lead to a decrease of the sticking coefficient. Since experimental results show a drastically smaller sticking coefficient at exposures higher than about 10 L at 300 K, or 1 L at 100 K, we expect *sio4* to begin to form at these exposures. This is reasonable, since this exposure corresponds to half a monolayer (following Refs. 19 and 25) or to one monlayer (following Ref. 32). These coverages would correspond to two or four oxygen atoms per 2×2 unit cell. We expect SiO_4 to form at three oxygens per 2×2 unit cell (this is the amount needed to form the *ins-ad-rest* structure).

IV. CONCLUSION

In summary, we suggest that the initial stages of the oxidation of Si(111) roughly follow the scheme shown in Fig. 7.

The energies shown reflect the binding energies with respect to the clean surface. The thickness of the connecting lines indicates the relative importance of the specific reaction pathway.

TABLE I. Summary of the extended-Hückel parameters used in this contribution. The (a) H_{ii} values for oxygen are used for all Si–O configurations. In addition, we have used the (b) H_{ii} values for all configurations that do not contain molecular oxygen.

Atom	Orbital	(a) H_{ii} (eV)	(b) H_{ii} (eV)	ζ_1
O	2*s*	−30.0	−32.3	2.275
	2*p*	−13.6	−14.8	2.275
Si	3*s*	−17.3		1.383
	3*p*	−9.2		1.383
H	1*s*	−13.6		1.300

These results were obtained using a 2×2 unit cell which includes adatoms and rest atoms. We should remember that the 7×7 unit cell includes other structural features, such as the stacking fault and corner holes. These may have an influence on the oxidation chemistry of Si(111). For example, it has been shown that the faulted half of the 7×7 unit cell has a higher overall electron density,[36] and is the site of preferred oxygen attack.[13,15] The detailed role of these geometrical features remains to be studied in larger scale calculations.

ACKNOWLEDGMENT

We thank the Deutscher Akademischer Austauschdienst for the award of a NATO postdoctoral fellowship for B.S., and the Office of Naval Research for its support of the work at Cornell.

APPENDIX

Table I gives the extended Hückel parameters used.

[1](a) B. Schubert, P. Avouris, and R. Hoffman, preceding paper, J. Chem. Phys. **98**, 7593 (1993); (b) *paul-para* is a dynamic mixture between *paul* and *para*.
[2]G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, Phys. Rev. Lett. **50**, 120 (1983).
[3]R. J. Hamers, R. M. Tromp, and J. E. Demuth, Phys. Rev. Lett. **56**, 1972 (1986).
[4]Ph. Avouris and R. Wolkow, Phys. Rev. B **39**, 5091 (1989).
[5]K. Takayanagi, Y. Tanishiro, M. Takahashi, and S. Takahashi, J. Vac. Sci. Technol. A **3**, 1502 (1985).
[6]W. A. Goddard III, A. Redondo, and T. C. McGill, Solid State Commun. **18**, 981 (1976).
[7]M. Chen, I. P. Batra, and C. R. Brundle, J. Vac. Sci. Technol. **16**, 1216 (1979).
[8]A. S. Bhandia and J. A. Schwarz, Surf. Sci. **108**, 587 (1981).
[9]S. Ciraci, S. Ellialtioglu, and S. Erkoc, Phys. Rev. B **26**, 5716 (1982).
[10]R. Hoffmann, J. Chem. Phys. **39**, 1397 (1963).
[11](a) M.-H. Whangbo and R. Hoffmann, J. Am. Chem. Soc. **100**, 6093 (1978); (b) R. Hoffmann, Rev. Mod. Phys. **60**, 601 (1988).
[12]J. H. Ammeter, H.-B. Bürgi, J. C. Thibeault, and R. Hoffmann, J. Am. Chem. Soc. **100**, 3686 (1978).
[13]Ph. Avouris, I.-W. Lyo, and F. Bozso, J. Vac. Sci. Technol. B **9**, 424 (1991).
[14]H. Tokumoto, K. Miki, H. Murakami, H. Bando, M. Ono, and K. Kajimura, J. Vac. Sci. Technol. A **8**, 255 (1990).
[15]J. P. Pelz and R. H. Koch, Phys. Rev. B **42**, 3761 (1990).
[16]M. Green and A. Liebermann, J. Phys. Chem. Solids **23**, 1407 (1962).
[17]H. Ibach and J. E. Rowe, Phys. Rev. B **10**, 710 (1974).

Downloaded 07 Dec 2012 to 128.253.229.242. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

[18] G. Hollinger and F. Himpsel, Phys. Rev B **28**, 3651 (1983); J. Vac. Sci. Technol. A **1**, 640 (1983).

[19] V. Höfer, P. Morgan, W. Wurth, and E. Umbach, Phys. Rev. B **40**, 1130 (1989).

[20] R. Ludeke and A. Koma, Phys. Rev. Lett. **34**, 1170 (1975).

[21] A. J. Schell-Sorokin and J. E. Demuth, Surf. Sci. **157**, 273 (1985).

[22] M. Leibsle, A. Samsavar, and T.-C. Chiang, Phys. Rev. B **38**, 5780 (1988).

[23] F. M. Meyer and J. J. Vrakking, Surf. Sci. **38**, 275 (1973).

[24] H. Ibach, H. D. Bruchmann, and H. Wagner, Appl. Phys. A **29**, 113 (1982).

[25] P. Morgan, V. Höfer, W. Wurth, and E. Umbach, Phys. Rev. B **39**, 3720 (1989).

[26] From J. S. Griffith, Proc. R. Soc. London, Ser. A **235**, 73 (1956).

[27] End-on model from L. Pauling, Nature (London) **203**, 182 (1964).

[28] The "brightness" of surface sites in the STM depends on both topographic and electronic structure. Atoms which are situated higher than the other surface atoms or have an increased DOS (integrated from E_F to eV applied, $V=2$ eV in this case) will appear bright. The opposite conditions lead to dark sites.

[29] I.-W. Lyo, Ph. Avouris, B. Schubert, and R. Hoffmann, J. Phys. Chem. **94**, 4400 (1990).

[30] B. Schubert, D. Proserpio, and R. Hoffmann (unpublished).

[31] We should note that *ins-ad* is not the only possible structure responsible for the dark sites. Another possibility is an insertion of three oxygen atom in all adatom backbonds (*ins-ins-ins*), but for several reasons this configuration cannot play a major role (see discussion at the end of Sec. II).

[32] K. Edamoto, Y. Kubota, H. Kobayashi, M. Onchi, and M. Nishijima, J. Chem. Phys. **83**, 428 (1985).

[33] J. T. Law, J. Phys. Chem. Solids **4**, 91 (1958).

[34] M. Green and K. H. Maxwell, J. Phys. Chem. Solids **13** 145 (1960).

[35] A. F. Wells, *Structural Inorganic Chemistry*, 4th ed. (Clarendon, Oxford, 1975).

[36] M. Fujita, H. Nagayoshi, and A. Yoshimori, Surf. Sci. **242**, 229 (1991).

Downloaded 07 Dec 2012 to 128.253.229.242. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions