Oxidation of silicon surfaces[a]

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We have carried out theoretical studies (generalized valence bond) for chemisorbed O atom and O_2 molecule on Si(111) surfaces using clusters of atoms to model the surface. For the perfect surface we find that O_2 molecule binds to a single surface Si with an Si–O bond length of 1.68 Å (bulk $SiO_2 R_{Si\text{–}O} = 1.61$ Å), an Si–O–O angle of 116°, and an O–O bond distance of 1.32 Å. We have also calculated the shifts in the Si(2p) and O(1s) core level energies for chemisorbed O and O_2 on the surface. The Si(2p) shift is + 1.1 eV (higher binding energy) for the O atom and + 1.5 eV for O_2, in agreement with the shifts observed for low oxygen exposure by Spicer and co-workers.

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I. INTRODUCTION

The initial steps in the oxidation of Si(111) surfaces has been a topic of considerable interest for 20 years. A large number of experimental studies has shown that the exposure to O_2 of a clean Si(111) 2 × 1 surface leads to two regimes of chemisorption[1]: at first there is a fast process of chemisorption until a saturation level is reached (oxygen exposures of about 10^{-4} to 10^{-2} Torr s), corresponding to formation of, at most, a few monolayers. This phase is followed by a slow formation of a macroscopic oxide layer (dominated by diffusion of O_2 through the oxide and reaction at the silicon/oxide interface).

We present here theoretical studies of states that may be involved in the initial steps of the first regime of oxidation. Using a finite cluster of atoms to model the surface, we have carried out *ab initio* calculations of the energetics and optimum geometries for O and O_2 chemisorbed on the surface. In addition, we have calculated experimental observables (primarily those associated with photoemission experiments) related to such chemisorption states.

In Sec. II we summarize our results, comparing with experiment where appropriate, and suggest a model for the early states of oxidation. A more detailed description of the methods and results is given in Sec. III.

II. SUMMARY OF RESULTS

A. Surface Si

For the 1 × 1 perfect Si(111) surface we find that the surface Si atom relaxes inward by 0.14 Å with respect to the bulk terminated surface. Each surface atom has a singly-occupied surface orbital (75% p character) pointing perpendicular to the surface. The calculated absolute IP from this orbital is 5.95 eV. Thus, from the absolute position of the valence band maximum[2] (VBM), 5.15 eV, we find the dangling bond orbital bound by 0.80 eV. This compares favorably with the experimental values[2] of 0.5 to 0.8 eV.

We have calculated the Si(2p) core level ionizations of both the surface Si and of bulk Si and find (see Table I) that the surface Si leads to shifts of +0.29, +0.20, 0.05, and −0.30 eV (positive means higher binding energy). There are four levels since the core hole may be parallel (σ) or perpendicular (π) to the surface normal, and since the core hole and dangling bond orbital may be coupled to high (triplet) or low (singlet) spin. These results are in excellent agreement with the observed splittings on the 2 × 1 surface[3]: +0.16, −0.14, −0.37 eV.

B. Geometries of chemisorbed oxygen

The calculated geometries for O atom and O_2 molecule chemisorbed on the perfect Si(111) surface are shown in Fig. 1. These geometries will be discussed further in Sec. III, but it should be noted that the SiOO bending mode for chemisorbed O_2 (peroxy radical) is very flat with an energy change of only 0.013 eV for 10° of change in bond angle. Thus, at room temperature the angular motion of the peroxy radical varies, at least, from 106° to 126°.

We also considered the possibility of a zwitterion O_2 species[4] on the surface, but found this to be of high energy (1.7 eV above the peroxy radical species) so that such states should not be expected to be observed.

TABLE I. Si(2p) core ionizations Si(111) surface. All energies in eV, positive shift means larger binding energy.

	Theory		Experiment[a]	
	1 × 1		2 × 1	7 × 7
Shift (with respect to bulk)[b]	+0.29, +0.20, +0.05, −0.30	+0.40, +0.22	+0.16, −0.14, −0.37	−0.7
Cluster	H_3Si–Si(SiH_3)–SiH_3	H–Si(H)–H		

[a] Ref. 3.
[b] The absolute IP calculated for the bulk is 105.39 eV.

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FIG. 1. Calculated geometries of the O atom and the O_2 molecule chemisorbed on the perfect Si(111) surface. The electronic structure is schematically shown. A circle (O) represents a p-type orbital pointing perpendicular to the plane of the paper; a symbol of the form (8) represents a p-type orbital parallel to the plane of the paper. The number of electrons is indicated by the number of dots in each orbital.

TABLE III. O and O_2 chemisorption on Si(111) surfaces. O(1s) core ionizations. All energies are in eV, all values are referred to the free O_2 molecule.[a]

Shift	O_1	O_2		
SCF	−4.87	−6.24	−8.32	−8.3
Koopmans Theorem	−3.5	−4.6	−4.6	−6.9
Cluster	O_2–O_1–Si ($\bar{H}$ $\bar{H}$ $\bar{H}$)		O–Si ($\bar{H}$ $\bar{H}$ $\bar{H}$)	$\bar{H}$–Si–O–Si–$\bar{H}$ ($\bar{H}$ $\bar{H}$ $\bar{H}$ $\bar{H}$)

[a] Calculated value 545.20 eV, allowing localization of all orbitals.

C. Si(2p) core levels for chemisorbed oxygen

Binding of O or O_2 to the surface Si (see Table II) shifts the surface Si(2p) core level by +0.98 and +1.08 eV for O atom and by +1.48 and +1.58 for O_2 molecule. Each case leads to two shifts due to the asymmetric environment[21] for the Si (2p) hole; the π state (parallel to the surface) has the smallest shift for both O and O_2. The splitting due to the singlet vs triplet coupling of the core hole and the radical (singly-occupied) orbital of the oxygen is less than 0.01 eV for both cases. In both cases the oxygen pulls charge from the Si, shifting the core level to deeper energy.

Experimentally it is observed that formation of a bulk oxide leads to a shift[5] of +4.5 eV and that there are two intermediate phases observed in regime I of oxidation. For very low exposures (regime Ia) there are two shifted Si(2p) lines[6] at + 0.9 eV and +1.4 eV, while at slightly higher exposures (regime Ib) there is a new Si(2p) line[6] at 1.8 eV.

Our results (1.1 and 1.5) compare well with the observed shifts in regime Ia, and we suggest that in this region both chemisorbed O atom and O_2 molecule may be present. Of course, it is also possible that the 1.4 eV feature is the peroxy radical form of O_2 at a perfect surface site but that the 0.9 eV feature is a chemisorbed O_2 at a defect or step site.

D. O(1s) core levels

Referencing all O(1s) ionization potentials to that of the free O_2 molecule, we find that the chemisorbed O_2 leads to two levels at −4.87 eV and −6.24 eV (weaker binding energies), where the larger shift is for the outer oxygen. Such a small chemical shift difference (1.3 eV) is difficult to detect experimentally since the line widths are ~2.5 eV. However, Rowe *et al.*[7] have compared the asymmetry of O(1s) and Si(2p) for monolayer coverages of O_2 on Si(111) to obtain two O(1s) lines of approximately equal intensity shifted by 0.7 to 0.9 eV. The calculated average O(1s) shift of chemisorbed O_2 of 5.5 eV is in reasonable agreement with the value of ~6.0 eV obtained by Chen *et al.*[8] and Rowe *et al.*[7] Although not conclusive, these comparisons support the existence of chemisorbed O_2 in the peroxy radical form on Si(111).

For chemisorbed O atom, the calculated O(1s) level is at −8.32 eV with respect to the free O_2 molecule. Such large shifts have not been detected experimentally, indicating that such species may not exist in very large concentrations.

Tables II and III show that the Si(2p) shift for chemisorbed O_2 is larger than the corresponding one of chemisorbed O (1.5 eV vs 1.0 eV), whereas the O(1s) shifts go in the opposite direction (−5.5 eV for O_2 and −8.3 eV for chemisorbed O). This is due to the fact that the O_2 molecule pulls more charge out of the Si atom than the O atom does, leading to a larger shift for the Si(2p). This charge, however, is distributed between the two oxygens of the O_2, leading to smaller O (1s) shifts than in the chemisorbed O atom.

TABLE II. O and O_2 chemisorption on Si(111) surfaces. Si(2p) core ionizations. All energies are in eV, all values are referred to the bulk Si 2p ionization.

	Theory			Experiment[a] (monolayer O_2)
Shift	+1.48, +1.58	+0.98, +1.08	+2.80	+0.9, +1.4
Cluster	O_2–O_1–Si ($\bar{H}$ $\bar{H}$ $\bar{H}$)	O–Si ($\bar{H}$ $\bar{H}$ $\bar{H}$)	$O\bar{H}$–Si ($O\bar{H}$ $O\bar{H}$ $O\bar{H}$)	

[a] Ref. 6.

E. Discussion of oxidation

Calculations and experiments at low exposure of O_2 are consistent with the formation of chemisorbed O_2 molecules having the form of peroxy radicals, as in Figs. 1 or 2(a). The question then is what happens next? Our calculations suggest rather large barriers to processes in which either oxygen of the peroxy radical species attacks the perfect surface. The oxidation could, of course, be initiated by defects or steps and then continued by defects or states produced by previous oxidation stages. However, our studies suggest one mechanism that could be important on the perfect surface.

From studies of zwitterions such as in Fig. 2(a), we find geometries favoring attack upon surface-subsurface Si–Si bonds. Thus the barriers for insertion of oxygen to yield species such as Fig. 2(b) will be sufficiently low to play a role in oxidizing the surface. Indeed, our calculations suggest that with creation of a valence band hole and a conduction band elec-

FIG. 2. (a) Peroxy radical and zwitterion models. (b) Mechanism for oxygen insertion into Si–Si bonds.

tron near the surface by band gap radiation, it may be energetically possible to form the zwitterion or superoxide states of Fig. 2, which could subsequently attack the surface, leading to species such as Fig. 2(b). Having formed an activated species such as in Fig. 2(b), the oxidation of the surface by adjacent chemisorbed O_2 molecules and by gas phase O_2 molecules may occur more rapidly.

If this zwitterion mediated oxidation of the surface is activated by band gap radiation, it might be possible to use this effect for some practical processes. Thus, using monochromatic light sources (e.g., lasers) with energies above the band gap might allow precisely controlled initiation of selective low temperature oxidations. The use of focused lasers might allow selective oxidation under UHV conditions of specific regions of surfaces, providing a means for better controlled studies of the mechanism of oxidation.

This mechanism could be tested experimentally by studying the rate of oxidation as a function of wavelength for light incident on the surface in the presence of O_2. An alternate experimental test is the study of the rate of oxidation upon carrier injection into the semiconductor. Some indications of such effects have been reported.[20]

III. CALCULATIONS

A. Wavefunctions

All calculations use *ab initio* methods [Hartree–Fock (HF) or generalized valence bond (GVB)] with all orbitals solved self-consistently. In many calculations, the core orbitals of the Si are replaced by *ab initio* effective potentials[9] (EP). Ionization potentials are calculated from self-consistent calculations on both the neutral and ion state and subtracting the total energies. [In some cases Koopmans theorem ionization potentials are quoted.] For the core ionizations [O(1*s*) and Si(2*p*)], the self-consistent solution for the ions required some care in selecting trial functions and in the initial iterative steps; however, in all cases self-consistent solutions without constraints were obtained. The basis sets were full double-zeta[9] for silicon and valence[10] double-zeta for oxygen. In addition, *d* functions ($\alpha_{Si} = 0.416$; $\alpha_O = 0.95$) were used in geometry calculations.

The geometry optimization for the chemisorbed O atom used GVB–CI wavefunctions, while the optimization for the chemisorbed O_2 used HF wavefunctions.

B. Surface models

In recent years we have carried out a number of studies of semiconductor surfaces where the surface is modeled by a cluster of atoms constructed by slicing out a finite portion of the surface and replacing every Si–Si bond by a bond to a hydrogen atom.[11–13] One problem with this approach is that a hydrogen atom is more electronegative than an Si, leading to some charge transfer effects that could bias the results. In the work reported here, we have modified the properties of the H atom so as to mimic an Si of the bulk crystal. This is done by constructing a model of a bulk silicon atom,

$$Si(Si\bar{H}_3)_4 \qquad (1)$$

and by modifying the properties of the hydrogen atoms, $\bar{H}$, so that the central Si atom is neutral.[14] Placing each $\bar{H}$ at the position of a bulk Si, we describe the $\bar{H}$ in terms of a scaled Slater 1*s* orbital[15] ($e^{-\zeta r}$) and choose the scale parameter ζ so that the central Si is neutral. The optimum scale factor is $\zeta = 0.2944$. Henceforth the $\bar{H}$ with this scale factor is referred to as siligen.

An estimate of the ζ for the siligen can be made by considering electronegativities (EN), defined as[16]

$$EN = (IP + EA)/2, \qquad (2)$$

where IP is the ionization potential and EA is the electron affinity. For bulk silicon the absolute IP[2] is 5.15 eV (top of the valence band relative to vacuum) and the band gap is 1.11 eV, so that an EA of 4.04 eV (bottom of the conduction band) leads to an EN of 4.60 eV. For a siligen with scale factor ζ,

$$IP = \zeta - \tfrac{1}{2}\zeta^2,$$

$$EA = \tfrac{3}{8}\zeta - \tfrac{1}{2}\zeta^2,$$

leading to

$$EN = -\tfrac{1}{2}\zeta^2 + \tfrac{11}{16}\zeta. \qquad (3)$$

Equating (2) and (3) leads to $\zeta = 0.32$, in reasonable agreement with the value from the cluster calculations.

The siligen represents the effects of binding to a bulk Si and consequently the Si–$\bar{H}$ bonds should polarize in response to changes or ionic bonds in the Si cluster. Indeed, the siligens seem to represent these effects very well, as indicated in Table IV. The $Si(Si\bar{H}_3)_3$ model yields an IP of 5.95 eV, in excellent agreement with experiment,[2] 5.6–5.9 eV, and even the $Si\bar{H}_3$ model is off by only 0.2 eV. In contrast, using real H atoms for $Si(SIH_3)_3$ leads to errors of over 2 eV (these latter results are correctable using a continuous dielectric model). From Mulliken population analyses of the chemisorbed O and O_2 clusters we do not expect very large dipole moments. It is not clear, however, that our clusters are large enough to reliably calculate work function changes due to chemisorption.

TABLE IV. Comparison of absolute dangling bond ionization potentials (eV) obtained by cluster calculations.

	Real H atoms			
	No cluster correction	Dielectric continuum correction	Siligens No cluster correction	Experiment[b]
Si–H, H, H	8.6	...	6.11	5.6–5.9
Si–SiH_3, Si H_3, Si H_3	7.9	5.9[a]	5.95	

[a] The final state (positive ion) is corrected for the polarization of a dielectric continuum lying outside the region of the cluster.
[b] Ref. 2.

C. Geometry optimizations

The optimum SiO distance is 1.69 Å and 1.68 Å for chemisorbed O and O_2 on Si(111). This value is similar but longer than that found in other oxygen systems,[17] i.e., $R_{Si-O} = 1.607$ Å in quartz and $R_{Si-O} = 1.633$ Å in

$$H_3Si-O-SiH_3$$

We previously[12] optimized the geometry of

$$H_3Si-O-O\cdot$$

using hydrogens rather than siligens. Using siligens, the Si–O length is longer by 0.05 Å, the O–O length is shorter by 0.05 Å, and the Si–O–O angle is 10° smaller. This indicates the importance of charge transfer in geometries.

Our calculations[18] show that in order to obtain the correct geometries it is necessary to include d-type basis functions on both the Si and O atoms. On the other hand, the geometries obtained by Hartree–Fock calculations are practically as accurate as those of the configuration integration calculations. The largest uncertainties appear in the calculation of angles, but these are probably due to the flatness of the energy surface.

D. Ionization potentials

In Table III we also show the results for the core O(1s) ionizations when Koopmans Theorem[19] is used. In this case we still observe a 1.1 eV splitting between the two O(1s) ionizations for the chemisorbed peroxy radical. There is no difference, however, between the radical O atom 1s ionization in the chemisorbed O_2 and that of the chemisorbed single O atom. As is well known, Koopmans Theorem results are not always trustworthy.

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[1]See, for example, F. Meyer and M. J. Sparnaay, in *Surface Physics of Phosphors and Semiconductors*, edited by C. G. Scott and C. E. Reed (Academic, New York, 1975), p. 321; H. Ibach, K. Horn, R. Dorn, and H. Luth, Surf. Sci. **38**, 433 (1973).
[2]D. E. Eastman and W. D. Grobman, Phys. Rev. Lett. **28**, 1378 (1972); L. F. Wagner and W. E. Spicer, *ibid.* **28**, 1381 (1972); F. G. Allen and W. Gobeli, Phys. Rev. **127**, 150 (1962).
[3]F. J. Himpsel, P. Heimann, T.-C. Chiang, and D. E. Eastman, Phys. Rev. Lett. **45**, 1112 (1980).
[4]W. A. Goddard III (unpublished).
[5]F. J. Grunthaner, P. J. Grunthaner, R. P. Vasquez, B. F. Lewis, J. Maserjian, and A. Madhukar, J. Vac. Sci. Technol. **16**, 1443 (1979).
[6]C.-Y. Su, P. R. Skeath, I. Lindau, and W. E. Spicer, J. Vac. Sci. Technol. **18**, 843 (1981) and private communication.
[7]J. E. Rowe, G. Margaritondo, H. Ibach, and H. Froitzheim, Solid State Commun. **20**, 277 (1976); G. Margaritondo (private communication). A value of 532.0 eV is shown for the O(1s) peak for monolayer adsorption of O_2 on Si(111) [see Fig. 2]. Using the value of 5.15 eV for the position of the valence band maximum with respect to vacuum [Ref. 2] and the value of 543.1 eV for the O(1s) ionization in free O_2 [K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, *ESCA Applied to Free Molecules* (North-Holland, Amsterdam, 1971)] we obtain a shift of about −6.0 eV for chemisorbed O_2 on Si(111) with respect to free O_2.
[8]M. Chen, I. P. Batra, and C. R. Brundle, J. Vac. Sci. Technol. **16**, 1216 (1979). They observe a value of 532.0 eV for O (1s) of submonolayer O_2 on Si(111), leading to a shift of about −6.0 eV as discussed above.[7]
[9]A. Redondo, W. A. Goddard III, and T. C. McGill, Phys. Rev. B **15**, 5038 (1977).
[10]T. H. Dunning, Jr. and P. J. Hay, in *Modern Theoretical Chemistry: Methods of Electronic Structure Theory*, edited by H. F. Schaefer III (Plenum, New York, 1977), Vol. 3, p. 1.
[11]A. Redondo, W. A. Goddard III, T. C. McGill, and G. T. Surratt, Solid State Commun. **20**, 733 (1976).
[12]W. A. Goddard III, A. Redondo, and T. C. McGill, Solid State Commun. **18**, 981 (1976); A. Redondo, Ph.D. Thesis, California Institute of Technology (1976).
[13]W. A. Goddard III, J. J. Barton, A. Redondo, and T. C. McGill, J. Vac. Sci. Technol. **15**, 1274 (1978).
[14]Based on Mulliken populations [R. S. Mulliken, J. Chem. Phys. **23**, 1841 (1955)]. This should be an adequate measure of the charge at the central Si since its nearest neighbors are real Si atoms.
[15]The Slater orbital was described as a linear combination of three Gaussians ($e^{-\alpha r^2}$) according to the method described by Huzinaga [S. Huzinaga, J. Chem. Phys. **42**, 1293 (1965)].
[16]R. S. Mulliken, J. Chem. Phys. **2**, 782 (1934).
[17]L. E. Sutton, Ed., *Interatomic Distances, Supplement*, The Chemical Society (London), Special Publication No. 18 (1965); A. F. Wells, *Structural Inorganic Chemistry* 4th edition (Clarendon Press, Oxford, 1975).
[18]A. Redondo, W. A. Goddard III, and T. C. McGill (unpublished results).
[19]T. Koopmans, Physica **1**, 104 (1933).
[20]E. A. Irene and D. W. Dong, J. Electrochem. Soc. **125**, 1146 (1978); S. A. Schaefer and S. A. Lyon, J. Vac. Sci. Technol., these proceedings.
[21]For example, the cluster with four oxygens tetrahedrally distributed about the Si leads to a triply degenerate Si (2p) ionization (see Table II).