Chemisorption of Atomic Oxygen on Si(100): Self-Consistent Cluster and Slab Model Investigations

Inder P. Batra, P. S. Bagus, and K. Hermann[a]

IBM Research Laboratory, San Jose, California 95193

The dissociative chemisorption of oxygen on Si(100) is studied with use of an *ab initio* multiconfiguration self-consistent-field cluster approach and a self-consistent field pseudopotential slab simulation. The cluster calculations show, for the first time, that the dissociative adsorption of an oxygen molecule is *exothermic* by ~ 3 eV thus providing strong support for atomic chemisorption. Furthermore, atomic oxygen in the first-layer bridging positions is found to be modestly more stable than in the on-top configuration; stable adsorption at both sites is possible.

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Whereas it is generally believed that the chemisorption of oxygen on metals is dissociative, the situation on semiconductor surfaces has been controversial.[1-7] Two different models for molecular chemisorption have been proposed: (i) a molecular peroxide bridge model,[4] and (ii) a molecular peroxy radical[7] model. Dissociative chemisorption models[1, 5-9] have treated atomic oxygen above, in, and below the surface silicon atoms. Much of the experimental[8] and theoretical[9] work on oxidation of silicon surfaces has been reviewed recently with the conclusion that a dissociative chemisorption is more likely. However, the evidence for this conclusion is indirect.

In this paper, the dissociative chemisorption model is explored further. We report energy-minimized geometries and provide information about the absolute binding energies of possible surface sites. It is shown that dissociative chemisorption is energetically quite favorable thus providing strong support for the chemisorption of atomic oxygen rather than O_2 molecules. We also present bond lengths and vibrational frequencies obtained from slab and cluster models. Based on our results a reasonable interpretation of the recent electron-energy-loss spectroscopy (EELS) data[8] is proposed.

In the cluster-model calculations we studied three different high-symmetry sites for chemisorption of atomic oxygen on Si(100). These were as follows: (1) The on-top site represented by an $Si_3(1, 2)H_6O$ cluster which contains three Si atoms: the first-layer adsorption-site atom and its two second-layer nearest neighbors. (2) The bridge site represented by an $Si_6(2, 4)H_{12}O$ cluster which contains two first-layer Si atoms closest to the adsorbate in the bridge site; for each of these atoms, their two second-layer nearest neighbors are included. (3) The center (fourfold) site which is represented by an $Si_7(4, 2, 1)H_8O$ cluster which has four silicon atoms in the top layer; the two second-layer Si atoms are each shared by two surface-layer atoms and one third layer is a shared neighbor of the two second-layer Si atoms. The numbers in parenthesis indicate the number of Si atoms in each layer. The H atoms are used to terminate the bonds of the Si atoms which extend into the crystal; their use for embedding provides an sp^3 hybridization for the "bulk" atoms. The Si-Si distances and orientations were taken from the bulk crystal geometry, so that the clusters represent an unrelaxed and unreconstructed Si(100) surface. There are two possible geometries for a bridge site above an unreconstructed Si(100) surface. We have considered the geometry where the dangling bonds of the surface Si atoms are directed toward the center of the site. For this site, there is the maximum possibility to form covalent chemical bonds with an adsorbed O atom. Our clusters are shown in Fig. 1.

For the bare substrate clusters, each surface atom was assumed to have two dangling bonds. The electrons in these open-shell orbitals were coupled to have parallel spin. This was done for computational convenience and because the finite clusters considered are not sufficiently large to represent the surface bands formed on Si(100). When an O atom is placed at either the on-top or bridge site, it is also assumed to be sp^3 hybridized and to form polarized covalent bonds with the surface Si dangling-bond orbitals. Thus the on-top site Si_3H_6 cluster leads to a $^1A_1$ state and the bridge site $Si_6H_{12}O$ is $^3B_1$. There is no natural hybridization for O in the center site and we investigated several states in order to determine the cluster ground state which was found to be $^7B_2$.

All-electron *ab initio* wave functions were calculated for the Si_mH_nO clusters. It is known that

self-consistent-field (SCF) wave functions have limitations for describing the strongly polarized, or ionic, bonds formed between metals and oxygen.[10,11] Thus we have used multiconfiguration SCF (MCSCF) wave functions based on the complete active space SCF method developed by Roos, Taylor, and Siegbahn.[12] We have included a limited amount of electron correlation with the MCSCF in order to correct the most serious deficiencies of the SCF wave functions. The MCSCF wave functions are sufficiently flexible so that the Si_mH_nO clusters dissociate to the ground states of the separated components, Si_mH_n and O. The position of the O atom was varied normal to the surface leading to an interaction-potential curve as a function of the normal coordinate $r_\perp$. With this curve the equilibrium distance of O from the Si surface, $r_\perp = R_\perp$, and the vibrational frequency, ω_e, for motion of O normal to the surface were obtained keeping the Si lattice rigid. The O binding energy, D_e, was taken as the difference between the energy of Si_mH_nO at $R_\perp$ and the sum of the energies of the separated substrate cluster and oxygen atom.

The calculated values of $R_\perp$, D_e, and ω_e are given in Table I. The D_e for the on-top and bridge sites are rather large, ~4 eV; the bridge site is more stable by ~0.5 eV. This is consistent with the fact that there is a natural hybridization for the bonding of O with the surface Si dangling bonds at these sites. However, this hybridization is not possible at the center site. This explains why the D_e for the center site is

rather small, ~0.3 eV. The O to Si surface distance for the bridge site is $R_\perp = 0.06$ Å, whereas in the on-top and center sites O stabilizes above the surface at $R_\perp = 1.64$ Å and $R_\perp = 0.96$ Å, respectively. For the on-top site, ω_e is the largest; for the bridge site, it is smaller by a factor of 3; while for the center site, ω_e is rather small. The differences among the ω_e arise, in major part, from the different O-Si coordination and bond angles for the different sites.[13,14]

We also investigated the on-top and bridge sites for chemisorbed oxygen on the Si(100) surface using a slab model. The fourfold center site was not considered because the cluster calculations indicated that the bonding is not likely to be strong. We used a repeating slab geometry whose repeat unit consisted of five layers of Si (in their ideal bulk positions) with a monolayer of oxygen on either side and an equivalent of five Si layers of empty space. The calculations were performed with the self-consistent pseudopotential method[15-17] with nonlocal norm-conserving ionic pseudopotentials.[17] This method has been successfully applied to chemisorption of Cl[18] on silicon.

We calculated the total energy as a function of the vertical distance, $r_\perp$, of oxygen above the Si surface plane for both the on-top and the bridge sites. From this curve, we obtained the equilibrium normal distance, $R_\perp$ (and hence the Si-O bond length d), and the normal vibrational frequency, ω_e, assuming a rigid substrate lattice. For the on-top site, we found $R_\perp = 1.76$ Å, $d = 1.76$ Å, and $\omega_e = 1081$ cm^{-1}. For the bridge site, our slab calculated values are $R_\perp = 0.96$ Å, $d = 2.15$ Å, and $\omega_e = 530$ cm^{-1}. The calculated interatomic distance for the on-top site is in good agreement with the value obtained by Goddard,
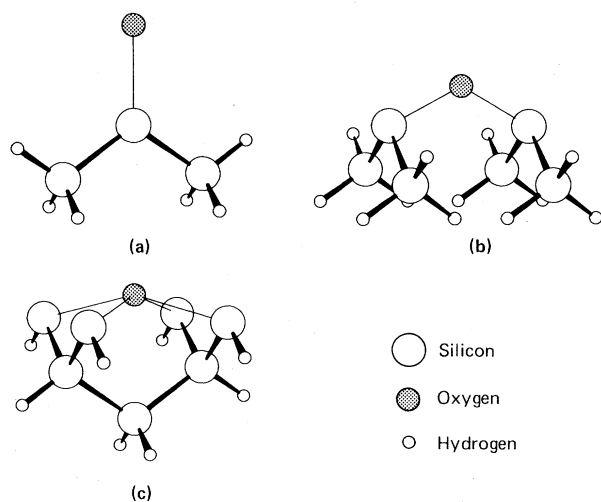

FIG. 1. A perspective view of clusters used to model (a) the on-top site, (b) the bridge site, and (c) the center site for oxygen chemisorption on the Si(100) surface.

TABLE I. Calculated adsorption properties, $R_\perp$ (in angstroms), D_e (in electronvolts), and ω_e (in inverse centimeters), for atomic oxygen at the on-top, bridge, and center sites of Si(100). The table also contains values (in angstroms) for the respective nearest-neighbor Si-O distance d in the equilibrium position.

	$R_\perp$	d	D_e	ω_e
On-top site				
$Si_3(1,2)H_6O$	1.64	1.64	3.81	866
Bridge site				
$Si_6(2,4)H_{12}O$	0.06	1.92	4.28	288
Center site				
$Si_7(4,2,1)H_8O$	0.96	2.88	0.27	106

Silicon   Oxygen   Hydrogen

Redondo, and McGill,[7] 1.69 Å, and also with our cluster value of 1.64 Å. We find the bridge site to be more stable, by ~0.35 eV, than the on-top site in good agreement with the cluster results.

One significant finding of the present work concerns the binding energy of adsorbed oxygen atoms. At the on-top bridge sites, the MCSCF calculated cluster D_e is sufficiently large that the dissociative adsorption of O_2 is *exothermic*. Half the binding energy of the O_2 molecule, ~2.6 eV, is considerably smaller than the ~4-eV binding at these sites. Furthermore, the correlation in our MCSCF model is limited; in particular, the O atom is significantly negatively charged at the on-top and bridge sites and our model does not give an accurate value for the O electron affinity.[19] We expect that a more accurate calculation will lead to even larger values for D_e in these sites. Oxygen bonded molecularly to the Si(111) surface (in the peroxy radical form) has been calculated by Goddard, Redondo, and McGill.[7] They report a bonding energy of 2.2 to 2.5 eV per O_2 molecule. We take the Si(111) value as a guide to the binding energy for the Si(100) surface. This is less than the ~3-eV gain in energy due to two oxygen atoms chemisorbed on the silicon surface. Thus the dissociative adsorption of oxygen is likely to be favored. As discussed below, this conclusion is more definitively supported by our interpretation of the EELS data. We also find that adsorption at the bridge site is more stable than at the on-top site from both the cluster and the pseudopotential slab calculations. The cluster results have the bridge site more stable by 0.47 eV and the pseudopotential slab results by 0.35 eV. Given the small differences between D_e for these sites and the possibility of barriers to O atom motion, it is quite possible that O will be adsorbed at both these sites. This is consistent with our interpretation of the EELS vibrational data[8] to be given below. Finally oxygen is weakly bound at the center site and we would not expect stable adsorption at this site. It may, however, be an intermediate during dissociative adsorption.

The results of our cluster and slab model calculations also provide a reasonable interpretation for the EELS data.[8] At the lowest exposure, 10 L [1 L (langmuir)$=10^{-6}$ Torr sec], of O_2 to Si(100) at 700 K, two major EELS peaks were reported.[8] The largest one is at 1060 cm^{-1} and the second at 370 cm^{-1}. There are three other peaks, at intermediate energies, with considerably less intensity. In the high-exposure regime (10^3–10^4 L) there are three loss peaks at 1180, 830, and

500 cm^{-1}. It is very likely that the 1060-cm^{-1} loss peak has shifted to 1180 cm^{-1} and the 370 cm^{-1} has shifted to 500 cm^{-1} with increasing exposure. The intermediate loss peak at 830 cm^{-1} is prominent only at high exposures. In the low-exposure regime, it is appropriate to correlate the loss peaks with the cluster calculated frequencies; slab results are more suited at high exposures. The cluster ω_e for the on-top site is 866 cm^{-1}. It seems reasonable to identify this vibration at the on-top site with the EELS 1060 cm^{-1} loss. The cluster result for the bridge site is $\omega_e = 288$ cm^{-1} which can be ascribed to the 370-cm^{-1} EELS loss. The low-intensity intermediate peaks may be associated with adsorbed O_2, or O atoms in an initial or intermediate stage of oxidation of Si to form SiO_2. At high exposures, our two slab calculated frequencies of 1080 cm^{-1} (top site) and 530 cm^{-1} (bridge site) account rather nicely for the observed frequencies at 1180 and 500 cm^{-1}. The intermediate loss peak at 830 cm^{-1} could arise from oxygen which has penetrated the Si lattice. Alternatively, the 830 cm^{-1} might be due to O adsorption in the bridging between first- and second-layer silicon atoms as proposed by Ibach, Bruchmann, and Wagner.[8]

The O-Si bonding involves a considerable charge transfer from Si to O which leads to an O(1s) core shift. These core shifts from the free O atom are calculated to be 4.3, 3.0, and 0.3 eV to lower binding energy for the bridge, top, and center sites, respectively. They are obtained using Koopmans' theorem. Since the final-state relaxation may be quite different for a free O atom and for O/Si(100), the absolute values of the shifts are not likely to be particularly accurate. However, the 1.3-eV difference between O adsorbed in an on-top and a bridge site is likely to be reasonable since the final-state effects may be similar between these sites. The shifts between the adsorption sites are consistent with the different amounts of charge transfer from Si to O. The estimates given by a Mulliken population analysis for the O ionicity are -1.25, -0.7, and -0.2 electrons for the bridge, on-top, and center sites, respectively. The predicted difference between the on-top and bridge sites could be used to determine if both sites are indeed occupied through examination of O(1s) x-ray photoemission data. Such data may also be relevant for determining whether the center site is occupied.

(a)Permanent address: Institut für Physik B, Tech-

nische Universität Clausthal-Zfd. and Sonderforschungs-bereich 126, Clausthal/Goettingen, West Germany.

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