Atomic oxygen in silicon: The formation of the Si—O—Si bond

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We study the equilibrium atomic configuration of atomic oxygen in silicon. We calculate the total energy of a cluster of silicon atoms before and after the incorporation of atomic oxygen. The energy is calculated for various atomic configurations to obtain the stable one. The equilibrium atomic distribution involves the separation of the silicon atoms forming a covalent bond to accommodate the oxygen atom. Analysis of the charge distribution reveals the break of the covalent silicon–silicon bond which is replaced by a Si—O—Si puckered bond. A careful analysis of the energy spectrum as well as of the charge-density matrix in the equilibrium configuration indicates the similarity between the new Si—O—Si bond formed and the basic chemical unit of SiO_2. Analysis of the rotational and vibrational modes around the defect is in good agreement with infrared-absorption measurements.

I. INTRODUCTION

Oxygen is probably the most common impurity in silicon. It is present interstitially,[1] substitutionally,[2,3] and forms different aggregates[4] in crystalline silicon. Extreme care has to be taken to remove it from the surface[5,6] and it is regularly present in amorphous samples. There are, therefore, various different situations in which atomic oxygen is present in silicon. Although clearly each specific configuration requires a specific treatment to understand it, all these situations share a common fact which is the gain in energy when forming the energetically stable Si—O—Si bond. Simple energetic considerations[7] indicate that it is even energetically favorable to break a covalent silicon–silicon bond and form a Si—O—Si bridge bond as in SiO_2. Previous total-energy calculations[8] indicate that this is indeed the case although the equilibrium atomic configuration was not fully established.

In this work we have established the equilibrium configuration of atomic oxygen in perfect crystalline silicon by minimizing the total energy with respect to the coordinates of the various atoms involved. The results indicate again the break of the covalent Si—Si bond by atomic oxygen. This breaking mechanism is the essential feature of atomic oxygen in silicon as an interstitial impurity as well as in the oxidation process. Therefore, we will concentrate here on the analysis of both the atomic and electronic structures around the stable atomic configuration of atomic oxygen in the otherwise perfect silicon lattice.

In this work we study in detail the new bond formed after the incorporation of oxygen at the atomic equilibrium configuration. To this purpose we have calculated the total energy for different atomic configurations to obtain the equilibrium configuration of an oxygen atom interacting with a Si_8H_{18} cluster formed by seven tetrahedrally oriented Si—Si bonds. We will show that clusters of this size can account very well for the electronic structure of crystalline silicon. Also a careful analysis of the charge distribution in the new Si—O—Si formed bond and a comparison with the SiO_2 charge distribution in the α-quartz structure is presented.

This work is organized as follows. In Sec. II we describe the method used in the calculation. In Sec. III we show the results of the calculation and the equilibrium atomic configuration found is discussed. A careful analysis of the new Si—O—Si bond is made. A detailed comparison with the Si—O—Si bond of SiO_2 follows. An analysis of the infrared absorption due to the presence of oxygen is made. Finally, in Sec. IV the main conclusions of our work are drawn.

II. METHOD OF CALCULATION

The calculations are performed in finite clusters of atoms in order to work in real space and use quantum chemistry techniques in view of the difficulties of dealing with oxygen when using solid-state methods.[9–11] Since the bonds involved in the problem are localized we will see that this approach provides us with the most relevant information. We first consider an isolated oxygen atom and a cluster formed by eight silicon atoms and 18 hydrogen atoms included to saturate the dangling bond as is customarily done in cluster calculation to avoid the problems of nonsaturated bonds. The eight silicon atoms are tetrahedrally oriented as in the diamond crystal structure and they are intended to represent the local configuration in crystalline silicon. To calculate the electronic structure and the total energy we eliminate the core electrons by assuming atomic pseudopotentials[12] of the form

$$V_{ps}(r) = -Z/r + \sum_l P_l W_l(r) , \quad (1)$$

where Z represents the net charge of the atom excluding the valence electrons. P_l is the operator projection over the wave functions of angular momentum l, and $W_l(r)$ is a radial function characteristic of the atom involved

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TABLE I. Pseudopotential parameters (in atomic units) of oxygen and silicon.

	l	α	C_1	n_1	C_2	n_2	C_3	n_3
Oxygen	0	10.373 870	1.647 681	−1	45.078 280	0		
	1	25.320 090	−7.790 734	0				
Silicon	0	3.829 150	4.904 820	−1	−10.484 250	0	103.050 060	2
	1	2.734 040	1.663 490	−2	16.009 870	2	6.435 280	4
	2	1.554 080	−1.455 460	0				

$$W_1(r)=\exp(-\alpha r^2)\sum_i C_i r^{n_i} , \quad (2)$$

where the constants C_i, α_i, and n_i for the different atoms involved in the calculations are given in Table I.

For the atomic valence electrons we approximate their wave functions by contracted Gaussian orbitals of single-ζ type such that each orbital $\varphi_j(r)$ is formed by a sum of primitive Gaussian functions (four for oxygen and silicon and one for hydrogen). The values of the exponents and coefficients used in the calculations are shown in Table II. These parameters as well as the pseudopotential parameters are obtained from optimized atomic calculations. The fact that only one Gaussian function for hydrogen works properly is due to the fact that the hydrogen atoms are intended to act as saturators more than as actual hydrogen atoms. The forthcoming results prove the correctness of this choice.

The calculation of the electronic structure as well as the total energy is done in the restricted Hartree-Fock approximation in such a way that the matrix elements of the Fock operator F between atomic basis orbitals are given by

$$F_{ij}=H_{ij}^{\text{core}}+\sum_{k,l} P_{kl}(\langle ij \mid kl \rangle - 0.5\langle ik \mid jl \rangle) , \quad (3)$$

where P_{kl} are the matrix elements of the density matrix

$$P_{kl}=2\sum_{n=1}^{\text{occ}} c_k^n c_l^n , \quad (4)$$

and $\langle ij/kl \rangle$ stands for the two-electron integral of the form

$$\langle ij \mid kl \rangle = \int \int d^3r_1\, d^3r_2 \varphi_i(\mathbf{r}_1)\varphi_j(\mathbf{r}_1)\varphi_k(\mathbf{r}_2)\varphi_l(\mathbf{r}_2)/\mid \mathbf{r}_1-\mathbf{r}_2 \mid . \quad (5)$$

The sum in Eq. (4) runs over all the occupied molecular orbitals $\Psi_n=\sum_i c_i^n\varphi_i(\mathbf{r})$.

The calculation is performed self-consistently in such a way that we have an accuracy in the energy of 10^{-6} hartree. In the calculation we keep the two-electron Coulomb and exchange integrals larger than 10^{-6} hartree. In some cases smaller integrals were kept in the calculation, obtaining negligible differences. Once self-consistency is obtained for a given atomic configuration the total (electronic plus nuclear) energy is given by

$$E_T=0.5\sum_{\substack{i,j\\ i\neq j}} Z_i Z_j/\mid r_i-r_j \mid +0.5\sum_{i,j} P_{ij}(F_{ij}+H_{ij}) . \quad (6)$$

Before we incorporate atomic oxygen in the system we assume that the silicon atoms keep the tetrahedral coordination. We allow the variation of the distance between the atoms to obtain the equilibrium atomic configuration. It should be noticed that in Ref. 8 it was assumed that the Si-Si distance was the nominal 2.35 Å. We obtain, at the equilibrium configuration, that the Si-Si distance for the central bond is 2.47 Å whereas the bond distance for the outer Si—Si bonds is 2.49 Å. These distances are about 6% larger than the experimental crystalline Si-Si distance. However, they are very close to the values for crystalline silicon reported in calculations[13] based in the same Hartree-Fock method and for the same (or similar) basis functions. More important than the bond distance is the charge distribution which is well accounted for in the calculation (see Ref. 8) being similar to that obtained both experimentally and theoretically[14] in crystalline silicon. In particular a proper sp^3 hybridization is obtained. The s, p_x, p_y, and p_z populations of the central silicon atoms are 1.40 and 0.90, 0.88, and 0.90 electrons, respectively. Moreover, the s and p populations of the outer silicon atoms are 1.37 and 2.65 electrons, respectively.

The charge distribution (see Ref. 8) is very similar to other calculations of clusters[15] and of crystalline silicon.[16] Even the results obtained using very different[14] methods of calculations and basis functions give results similar to ours. It is remarkable that our results for a finite cluster of atoms give charge distribution similar to the experimental one for crystalline silicon. The similarity between the outer Si—Si bond and the central one indicates the correct role played by the hydrogen atoms as saturators to simulate the rest of the crystalline silicon lattice. It should be pointed out that although the equilibrium position is 6% off the experimental one, the stretching forces between the silicon central atoms are well accounted for in the calculation. The force-constant parameter obtained is 1.6×10^5 dyn cm^{-1} which is within the range of the values fitted to obtain the silicon crystal's phonon dispersion relations. This emphasizes the correct description of the covalent

TABLE II. Exponents and coefficients (in atomic units) of the atomic wave functions of oxygen and silicon.

Orbital	Exponent	Coefficient
O(2s)	5.799 125	−0.137 734
	1.298 338	0.292 953
	0.547 297	0.531 222
	0.226 132	0.302 855
O(2p)	12.655 163	0.068 201
	2.953 693	0.274 403
	0.886 188	0.482 324
	0.259 961	0.416 022
Si(3s)	2.649 877	0.202 103
	1.637 220	−0.429 090
	0.236 353	0.671 680
	0.087 377	0.480 558
Si(3p)	1.630 182	−0.023 793
	0.333 686	0.390 174
	0.122 415	0.545 199
	0.047 150	0.192 726

silicon–silicon bond and the stability of the equilibrium configuration since the force constant involves the second derivative of the total energy versus atomic separation.

III. INCORPORATION OF OXYGEN

After we have obtained the correct bonding and hybridization for the Si_8H_{18} cluster in its equilibrium atomic distances, we add to it an oxygen atom. To obtain the equilibrium atomic configuration (or at least one close to it) we calculate the total energy for different atomic distributions. As a result of complexity of the problem we allow atomic displacements within the following constraints (see Fig. 1).

(i) Silicon atoms other than those labeled 1 and 2 in Fig. 1 as well as the hydrogen saturators are kept fixed at the bare-cluster equilibrium atomic separation described above, throughout the process of oxygen incorporation. This is intended to simulate the silicon lattice in the infinite network. The perturbation of the electronic structure around these atoms will indicate the correctness of this approximation.

(ii) Oxygen is first allowed to move in the plane formed by the silicon atoms labeled 5, 1, 2, and 6 in a symmetric position with respect to the silicon atoms 1 and 2. Motion out of plane and towards one or the other silicon neighbor will be allowed later.

(iii) Silicon atoms labeled 1 and 2 are allowed to relax along the original bond formed by them.

We have solved the self-consistent problem as in the case of the Si_8H_{18} cluster for various positions of the oxygen and silicon atoms compatible with the above constraints. We obtain a minimum total energy for an angle θ between the original Si—Si bond and the new Si—O one of 9°, while the Si-O distance is 1.62 Å. At this point oxygen is allowed to move off its symmetric position, either being closer to one of the silicon atoms or being off plane. When oxygen is moved in plane but out of its symmetric position the energy increases, indicating that the symmetric position is the stable one. When oxygen is moved out of plane to the other symmetric configuration with respect to the outer silicon atoms, the total energy difference is within numerical uncertainty (less than 10^{-5} hartree). Therefore we cannot assess which is the stable configuration, indicating that oxygen can rotate almost freely around the broken Si—Si bond. In the forthcoming study we take the in-plane position to analyze the charge distribution of the new bond formed because the differences between the charge distributions of these atomic configurations are negligible.

The electronic structure is perturbed by the presence of oxygen in the manner reported in Ref. 8 as the analysis of the total electronic charge before and after oxygen is incorporated reveals. We observe again a dramatic disappearance of the original silicon–silicon bond which is substituted by a Si—O—Si puckered bond (see Fig. 2). The total charge transfer to the oxygen atom is 0.89 electrons which comes primarily from

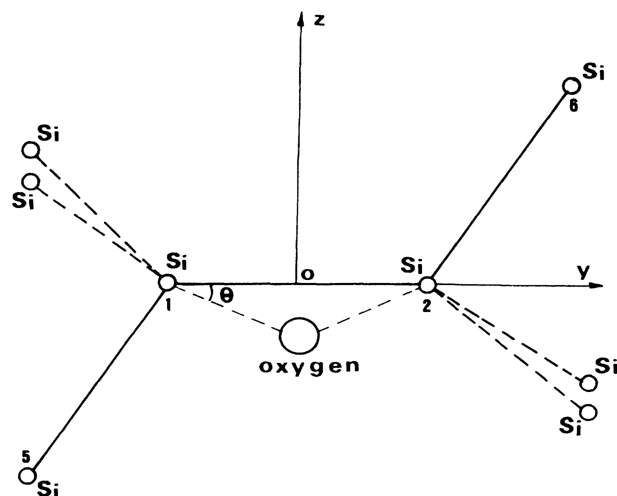

FIG. 1. Geometry and atomic configuration of the $O + Si_8H_{18}$ cluster.

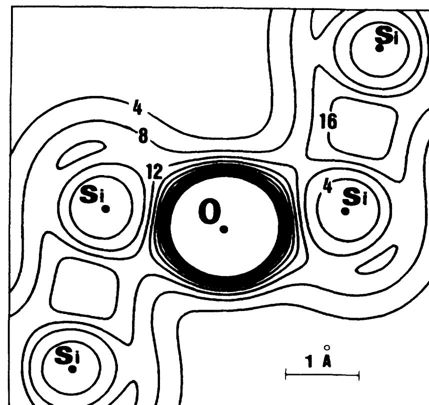

FIG. 2. Total electronic charge distribution (in units of the silicon unit cell) of the oxidized cluster at the equilibrium atomic configuration.

the destroyed silicon–silicon bond. The populations of the s, p_x, p_y, and p_z orbitals of oxygen are 1.77, 1.87, 1.39, and 1.86 electrons, respectively. On the other side the populations of the s, p_x, p_y, and p_z orbitals of the silicon atoms bonded to it are 1.25, 0.89, 0.50, and 0.87 electrons, respectively. The populations of the outer silicon atoms is very similar to that of the bare cluster before the incorporation of atomic oxygen. The above populations analysis reveals that the charge transfer is from the p_y orbitals of silicon and that these silicon atoms have a tendency to sp^2 hybridization compatible to the more planar structure due to the stretch of the original Si—Si bond by the presence of oxygen.

We are at this stage in a situation to address ourselves to the main problem we want to study in this work, namely, the character of the new Si—O—Si bond formed and to what extend this bond resembles the Si—O—Si bonding unit of SiO_2. To this end we have calculated the density of states projected into the oxygen atom. We define the local (projected) density of states associated to the orbital labeled i in the form:

$$N_i(E)=\sum_n \sum_j c_i^n c j^n S_{ij}\delta(E-E_n) , \quad (7)$$

where C_i^n are defined after Eq. (4), E_n are the eigenvalues, and S_{ij} is the overlap

$$S_{ij}=\int d^3r\, \varphi_i(\mathbf{r})\varphi_j(\mathbf{r}) . \quad (8)$$

Results of the calculated local density of states at the oxygen atom (i.e., the sum of the local densities of its atomic orbitals) are given in Fig. 3. Also in this figure we show the calculated[17] density of states along with various experimental results of SiO_2. The calculation performed by Chelikowsky and Schluter[17] was done for crystalline SiO_2 in the α-quartz structure. A direct comparison between our results and those of SiO_2 reveals a good qualitative agreement except for the shape of the density of states at the energy region of peaks labeled A and A' in Fig. 3(a). The small peak between peaks labeled A and A' is due to the hydrogen saturators with a small weight at the oxygen atom as a careful analysis of the local densities of states at the different atoms of the cluster before and after the incorporation of oxygen reveals. It is remarkable that the local density of states is so similar to the density of states of SiO_2. The major difference being that the three peaks labeled A, B, and C in the calculation of crystalline SiO_2 have a double structure in the cluster calculation. This is indeed due to the difference in the local environment in both situations as the study of other clusters and SiO_2 indicates. In SiO_2 there are no Si—Si bonds and the interaction of the oxygen atom with the Si—Si back bonds in the impurity case is replaced by a completely different bonding between the oxygen atoms giving rise to a different energy distribution of the oxygen p-like states.

In order to make a more complete analysis of the new Si—O—Si bond formed we have analyzed (as in Ref. 17) the contribution to the charge distribution of the different peaks of the density of states. In our case since our spectrum is discrete we can separate the contributions to the charge density coming from the different eigenvalues E_n

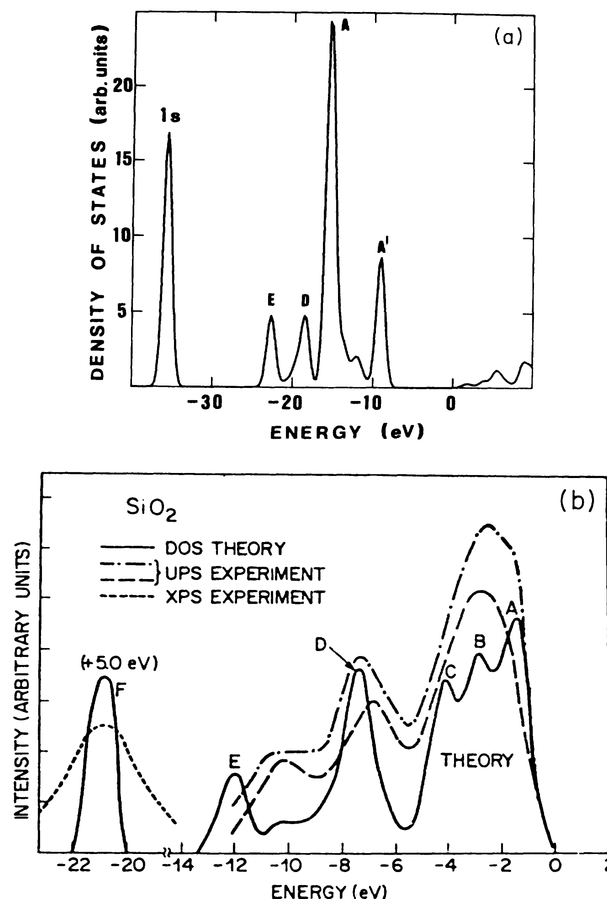

FIG. 3. (a) Local density of states at the oxygen atom in the equilibrium atomic configuration in the present cluster calculation. (b) Calculated and experimental densities of states for SiO_2 as shown in Ref. 17.

$$\rho_n(\mathbf{r})=\sum_{i,j} c_i^n c_j^n \varphi_i(\mathbf{r})\varphi_j(\mathbf{r}) . \quad (9)$$

The results of our calculations along with the results of Chelikowsky and Schluter for SiO_2 are shown in Figs. 4, 5, and 6 for peaks labeled A, D, and E, respectively.

Figure 4 corresponds to an almost unperturbed $2p$ oxygen orbital indicating its nonbonding (lone-orbital) character of states associated to peaks A and A' of Fig. 3 (a similar charge distribution is obtained for the oxygen $2p_x$ orbital which weight is zero in the plane of Fig. 1). In Figs. 5 and 6 we obtain, as in SiO_2, the bonding orbitals between the silicon atoms and oxygen whose charge distribution indicates indeed the strong ionic character of the Si—O bond. In Fig. 5 the silicon p orbitals are involved whereas in Fig. 6 the silicon s orbitals are those involved as in SiO_2. The low-energy peak in the density of states corresponds to the oxygen $2s$ orbital in our impurity calculation as well as in SiO_2.

The remarkable similarities between our calculated charge distributions and those corresponding to α quartz (calculated using a complete different method) allow us

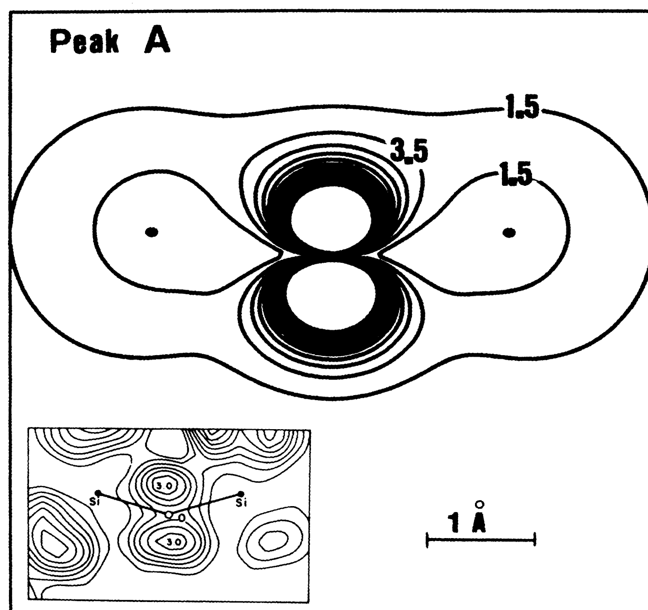

FIG. 4. Contribution to the charge density of the nonbonding orbitals corresponding to the enrgy range of the peaks A and A' of Fig. 3. At the inset the results of Ref. 17 for SiO_2 are shown.

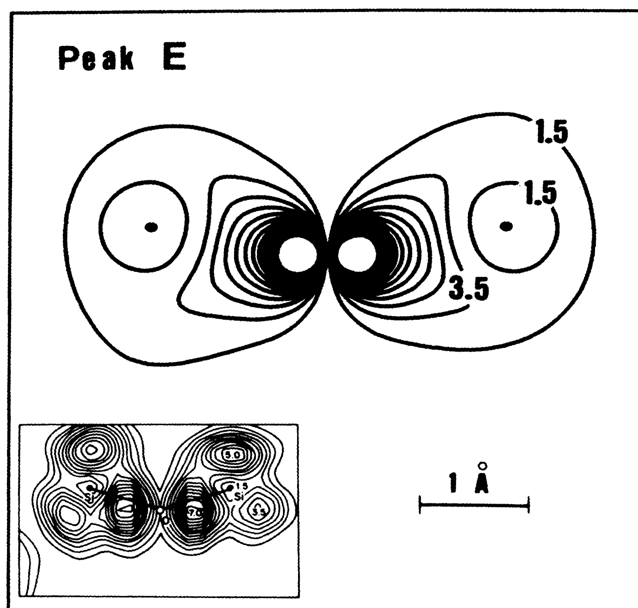

FIG. 6. Contribution to the charge density of the bonding orbitals (oxygen p like and silicon s like) corresponding to the energy range of peak E of Fig. 3. At the inset the results of Ref. 17 for SiO_2 are shown.

to conclude that the Si—O—Si bond formed by oxygen interstitially in silicon is very similar to that of SiO_2.

At this stage we can study the infrared absorption due to the presence of interstitial oxygen in an otherwise perfect silicon lattice. We can distinguish two kinds of contributions to the ir absorption, namely, absorption due to vibrational modes and absorption due to rotational modes. The rotational modes are due to the almost free rotation of the oxygen atom around the original silicon–silicon bond. Since we do not find any energy cost for this motion we can assume it is just a rigid rotator with energy levels given by

$$E_l = l(l+1)/2I, \quad l = 0,1,2 \ldots , \tag{10}$$

where I is the moment of inertia. The energy separation between the ground state and the first excited state is 32.6 cm^{-1} which compares very well with the experimental[1] value of 29.3 cm^{-1}. The infrared absorption due to vibrational modes can be calculated using standard methods like the cluster-Bethe lattice method.[18–20] In this case it is very difficult to obtain reliable force constants between the atoms from our total energy calculations. However, we have just calculated the stretching force constant between silicon and oxygen atoms obtaining the value of 4.9×10^5 dyn cm^{-1} which is very close to the value of 5.07×10^5 dyn cm^{-1} parametrized for SiO_2.[21] Results of this calculation[22] using a Born model for the potential between nearest-neighbor atoms gives a bending silicon split-off mode at 582 cm^{-1} and a stretching one at 1152 cm^{-1} whereas experimentally[23,24] they are found at 515 and 1106 cm^{-1}, respectively.

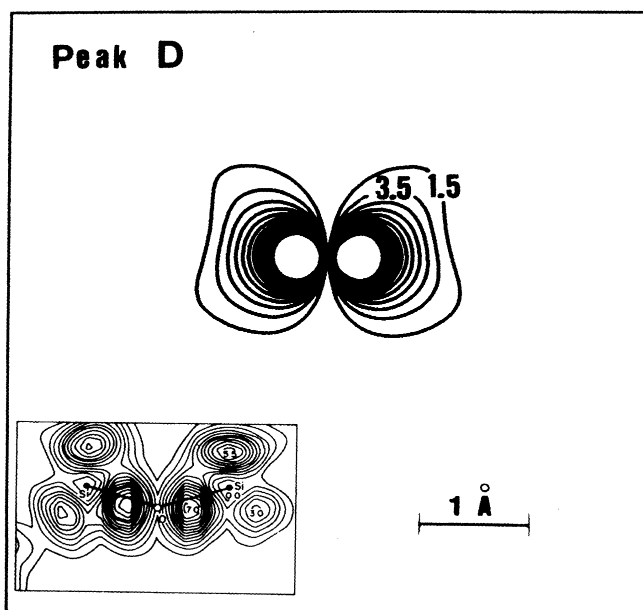

FIG. 5. Contribution to the charge density of the bonding orbitals (both silicon and oxygen p like) corresponding to the energy range of peak D of Fig. 3. At the inset the results of Ref. 17 for SiO_2 are shown.

IV. CONCLUDING REMARKS

By minimizing the total energy of finite clusters of silicon atoms we have obtained the equilibrium atomic configuration of atomic oxygen in silicon. We have calculated the total energy of a cluster of silicon atoms be-

fore and after the incorporation of atomic oxygen. The equilibrium atomic distribution involves the separation of the silicon atoms forming the original covalent bond to accommodate the oxygen atom forming a Si—O—Si puckered bond. A careful analysis of the charge distribution as well as of the variation of the total energy with the deviation from equilibrium allows us to conclude the following.

(i) A finite cluster of silicon atoms properly saturated with hydrogenlike atoms describes very well the local electronic distribution of crystalline silicon.

(ii) Although the total energy is not well accounted for in the Hartree-Fock calculations presented here its variations with respect to deviations from atomic equilibrium reproduce very well experimental force constants.

(iii) Interstitial atomic oxygen in silicon breaks the covalent silicon–silicon bond forming a new Si—O—Si bond. The atomic configuration is very stable but oxygen can rotate almost freely around the broken original silicon–silicon bond.

(iv) The eigenvalues distribution as well as the charge distributions are very similar to those of SiO_2.

(v) This first-principles calculation reproduces very well both rotation and vibrational modes due to the presence of oxygen as a comparison with infrared data indicates.

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