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Oxygen adsorption on small Si clusters: a full-potential linear-muffin-tin-orbital molecular-dynamics study

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Abstract

Using the full-potential linear-muffin-tin-orbital method, we have performed molecular-dynamics simulations for oxygen adsorption on Si_n ($n = 1-7$) clusters. It is found that Si_1 , Si_2 and Si_3 can react with the O_2 molecule directly to form small SiO_2 , Si_2O_2 and Si_3O_2 molecules. For the Si clusters with more than four Si atoms, the O_2 molecule cannot be adsorbed on them directly, due to the potential barrier for dissociative chemisorption of O_2 . In contrast, atomic oxygen favours reactions with all the silicon clusters considered here. The formation of strong Si–O bonds makes the structures of the small Si clusters obviously distorted and their stabilities decreased. As for the fragmentation, the processes from Si_nO_2 to $\text{Si}_{n-2} + 2\text{SiO}$ are found to be energetically favourable. The theoretical investigations can help us to understand the existing experimental results.

1. Introduction

Oxidation of silicon is probably one of the most important chemical reactions in the microelectronics industry. The importance of this reaction has motivated numerous surface science studies on the oxidation of single-crystal silicon surfaces of various orientations. If the current miniaturization trend continues, the minimum device component will approach the scale of nanometres containing a few tens of atoms in the near future. Thus, the study of silicon clusters is particularly relevant to the understanding of the structure and reactions in electronic materials applications. The reactivity of silicon clusters has been found to be different from that of bulk silicon [1]. The chemical reactions of silicon clusters with water [2, 3], acetylene [2], ethylene [4–9], ammonia [2, 10–15], oxygen [2, 9, 16] and carbon monoxide [1, 18–20] have

been studied experimentally. It has been revealed that silicon clusters containing fewer than 70 atoms are much less reactive than bulk silicon surfaces.

The reactions of ionic silicon clusters with O_2 have been studied previously. Creasy and co-workers [2] have studied the reactions of silicon cluster cations containing up to six atoms with oxygen. The ions were formed directly by laser vapourization of solid silicon, followed by trapping of the ions in a Fourier transform mass spectrometer and reaction with O_2 . Their study suggested that this reaction would etch the cluster, two silicon atoms at a time, all the way down to Si_2^+ or Si^+ . Jarrold *et al* have investigated the chemical reactions of ionic silicon clusters, Si_n^+ ($n = 10-65$), with oxygen using selected ion drift tube techniques [16, 17]. For clusters containing fewer than 29 atoms, the main products were found to be Si_{n-2}^+ and two SiO molecules. Each reaction of an oxygen molecule with the silicon cluster results in the loss of two silicon atoms in two SiO molecules. For clusters with more than 35 atoms the dominant product is $Si_nO_2^+$, arising from chemisorption of O_2 onto the cluster. In the transition region between 29 and 35 atoms a significant amount of $Si_{n-1}O^+$ is also observed; this product arises from evaporation of only one SiO molecule from the oxidized clusters. The notable feature of the oxidation reaction in the clusters is their large exothermicities but generally slow rates. The most dramatic characteristic is that its rate constant decreases by a factor of three between $n = 3$ and 4. Unfortunately, the mechanism of the reactions has not been clearly understood.

Some theoretical studies have been performed on the reactivity of silicon clusters. Krack and Jug [21] have studied ammonia adsorption with neutral Si_5 and Si_{10} clusters using the semiempirical molecular orbital (MO) method SINDO1 and the *ab initio* program Gaussian 90. Using the DV- X_α method, we have further studied the nature of NH_3 molecular adsorption and dissociation on neutral Si_n ($n = 5-7$) and Si_{10} clusters [22, 23]. We have also performed full-potential linear-muffin-tin-orbital molecular-dynamics (FP-LMTO-MD) studies for NH_3 , H_2O and CO adsorption on Si_n ($n = 5-7$) clusters [24-26]. However, to the best of our knowledge, there have been no theoretical studies of oxygen adsorption on silicon clusters. For deeper and more complete understanding of the physical and chemical properties of silicon clusters, such theoretical study does have scientific importance.

In this work, we study oxygen adsorption on neutral Si_n ($n = 1-7$) clusters by the FP-LMTO-MD method. Although experimental attention is focused more on the study of chemistry of cluster ions or cations, it is appropriate to study adsorption on neutral clusters, which is, in many cases, more scientifically interesting in terms of the different behaviours of clusters and extended surfaces.

2. Method

The FP-LMTO method [27-30] is a self-consistent implementation of the Kohn-Sham equations in the local-density approximation [31]. In this method space is divided into two parts: nonoverlapping muffin-tin (MT) spheres centred at the nuclei and the remaining interstitial region. LMTOs are augmented Hankel functions, and are augmented inside the MT spheres, but not in the interstitial region [32, 33]. In order to derive a force theorem, we attempt to differentiate the LDA Kohn-Sham total energy directly, but the expression derived is extremely complicated. To avoid this, we chose the Harris energy functional. It has been shown that the Harris energy is equal to the Kohn-Sham energy at self-consistency [29, 30]. In the LMTO method, one thing we must do is to calculate the interstitial-potential matrix elements:

$$V_{ij}^I = \int_I \phi_i(x) V_I(x) \phi_j(x) dx \quad (1)$$

where I is the interstitial region, V_I is the interstitial potential, i and j are the abbreviations for νL and $\nu' L'$, respectively, and ϕ_i is an LMTO envelope function centred at site ν with angular momentum L . L is the abbreviation for the angular-momentum quantum numbers (l, m). In different methods, we handle V_{ij}^I in different ways. In the FP-LMTO method for clusters, Methfessel and Schilfgaard [29, 30] used nonoverlapping MT spheres. They retained non-spherical potential terms inside the MT spheres, but expanded the interstitial potential $V_I(x)$ in a different set of atom-centred Hankel functions. In order to obtain the interstitial-potential matrix elements, we need an accurate representation, valid in the interstitial region, of the product of two Hankel functions centred at the same or at different sites. That is, we require an expansion of the form

$$\phi_i^* \phi_j = \sum_k C_k^{ij} \chi_k(x) \quad (2)$$

where k represents $(\nu L \alpha)$, the index α runs over different localizations (i.e. kinetic energies) and the χ_k are functions of the charge density Hankel function set. C_k^{ij} are expansion coefficients. The interstitial-potential matrix element V_{ij}^I then reduces to a linear combination of integrals of the functions χ_k multiplied by the interstitial potential. Because the interstitial potential itself is also expanded in functions of the type χ_k , the desired interstitial integral has now been expressed as a linear combination of integrals of products of pairs of Hankel functions; i.e., the three-centre integral has been reduced to a sum of two-centre integrals. Because the products are smooth functions, the coefficients in equation (2) can be adjusted until the best fit of the values and slopes of the right-hand side to the values and slopes of the products is obtained on all spheres simultaneously by a tabulation technique between the surfaces of the spheres. In the cluster method, the expansion is first calculated for two atoms arranged along the z axis and the coefficients are tabulated as a function of the interatomic distance. For general geometry, the expansion is obtained by rotating the tabulated fit using the rotation matrices and the spherical harmonics. The tabulated fit is made by direct numerical integration and can be made as accurate as desired [28]. The exactness of the total energy depends on the approximation one makes for the exchange–correlation part. The LDA exchange–correlation energy is given by

$$E_{xc}[\rho(r)] = \int \rho(r) \epsilon_{xc}[\rho(r)] d^3r \quad (3)$$

where $\epsilon_{xc}[\rho(r)]$ is the LDA exchange–correlation energy density. Inside the MT spheres, ϵ_{xc} is easily evaluated numerically for each point on the radial mesh. In the interstitial region, we perform the nonlinear local operations $\epsilon_{xc}[\rho(r)]$, and fit these to a series of atom-centred, overlapping Hankel functions. The exchange–correlation energy density ϵ_{xc} may thus be expressed in the same way as the charge density. Direct numerical integration on a mesh can be used. The force expression for the FP-LMTO method can be obtained by the Harris energy function [27, 28]. For a selected-size cluster, we can obtain the different stable structures as follows. Starting with a population of candidate structures, we relax these candidates to the near local minimum. When the optimization of one structure is being carried out, no restriction is imposed. We set up one time-step (1.0 au). All atoms are allowed to relax at each time-step. At the same time, the eigenvalue problem is solved exactly and the output density is admixed to the input density in the usual way. The nuclei are then moved according to the forces using the Verlet algorithm. When an atom is moved, we have a simulated annealing process by introducing a friction term directly proportional to the total momentum of the atom in the force acting on the atom. We then decompose the mixed density, move each partial density along with its atom, and re-overlap at the new geometry. After many iterations, the maximum of the forces is less than 0.002 (au), the largest velocity component of any atom falls below 35 m s^{-1} (corresponding to a temperature of about 2–5 K) and the total energy remains nicely

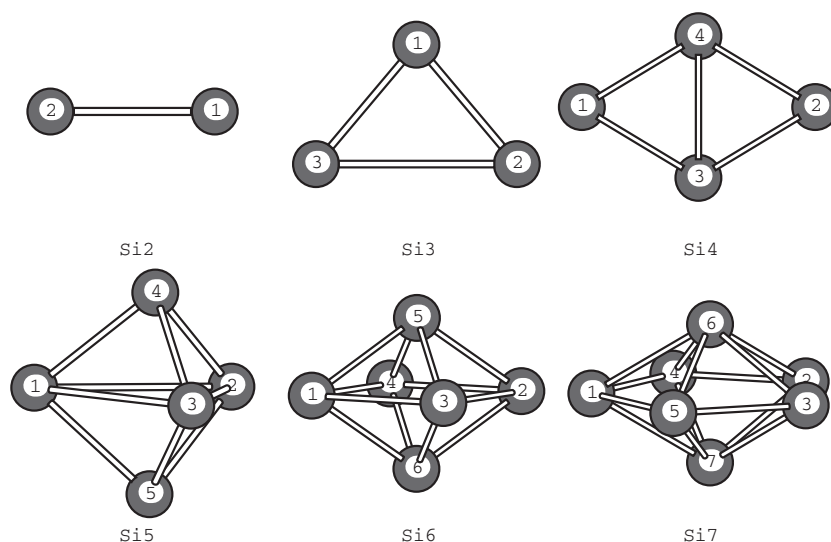


Figure 1. The ground-state structures of Si_{2-7} clusters.

constant because the system remains close to self-consistency. The process is stopped when the self-consistency condition is met. The variations in the total energies are less than 0.01 eV.

3. Results and discussion

In this paper, MT sphere radii for Si and O are taken as 2.0 and 1.0 au, respectively, so all MT spheres do not overlap. The LMTO basis sets include s, p and d functions. In this section, we shall present the results for oxygen atom adsorption on small Si_n ($n = 3-7$) clusters. Attempts have also been made at oxygen molecule adsorption on small Si clusters. However, no signs are found that the oxygen molecule can be adsorbed. We shall discuss mainly how the Si clusters adsorb the oxygen atom although O atoms and Si atoms can be combined into a series of Si_nO_m clusters [34]. Based on our FP-LMTO-MD study, the ground-state structures of Si_n ($n = 2-7$) clusters are the dimer (D_{2h}), isosceles triangle (C_{2v}), rhombus (D_{2h}), trigonal bipyramid (D_{3h}), tetragonal bipyramid (D_{4h}) and pentagonal bipyramid (D_{5h}) (see figure 1). These are in good agreement with earlier theoretical results in [35–40]. The ground-state structures of small ($n \leq 7$) silicon clusters (except for $n = 5$) have been confirmed by experiments [41].

As reported in our previous papers, some small molecules (H_2O , NH_3 , C_2H_2 , C_2H_4 and CO) are easily adsorbed on the apex atoms of the Si clusters [22–26]. For oxygen atom adsorption, there are similar trends of reactions found. Figure 2 shows their geometrical structures. Figure 3 illustrates the adsorption energy per O atom versus the number of silicon clusters (the thick curve corresponds to two O atoms adsorbed on the Si clusters).

The stabilities of the small molecules (SiO , SiO_2 , Si_2O and Si_2O_2) are illustrated as follows. For the SiO molecule formed from a Si atom and an O atom, our calculated Si–O bond length is 1.62 Å, which is very close to its common Si–O bond of 1.61 Å in the SiO molecule [43]. The SiO molecule is specially stable. Its binding energy is 10.81 eV, which is larger than the binding energy of the Si_2 cluster (4.06 eV) and the O_2 molecule (8.89 eV). Two O atoms and a Si atom may form a SiO_2 in two forms: linear structure and planar structure. However, the linear structure (O–Si–O) is 1.10 eV more stable than the triangular structure. The two Si–O bonds in the linear structure are both 1.62 Å, whereas the two Si–O bonds in the triangular

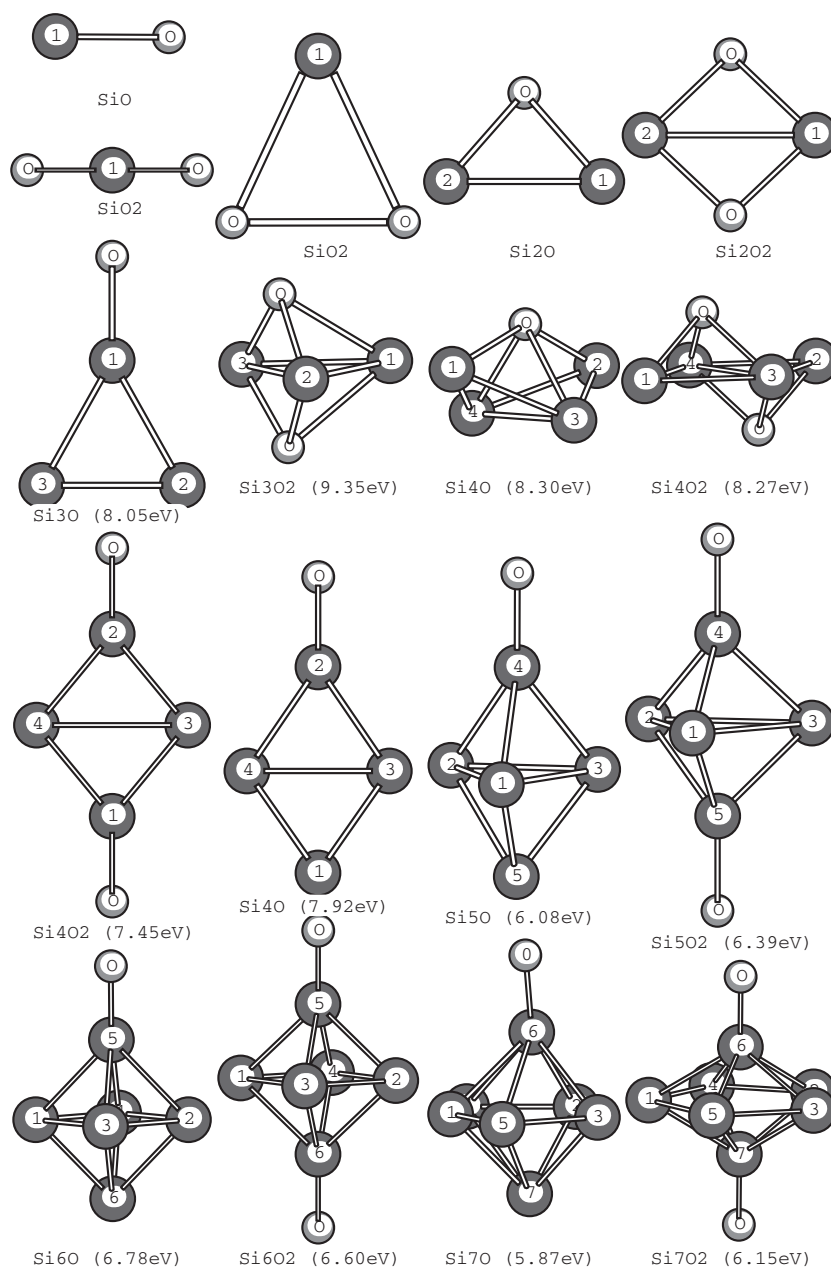


Figure 2. Geometrical structures of SiO, SiO₂, Si₂O and Si₂O₂ molecules and the adsorption structures of one O atom and two O atoms adsorbed on Si₃₋₇. The values below the Si₃₋₇ + O or Si₃₋₇ + 2O are their adsorption energies.

structure are 1.72 Å. Although there is an O–O bond of 1.58 Å in the triangular structure, the bond is weak compared with the O–O bond in the O₂ molecule (our calculated O–O bond length for O₂ is 1.23 Å, which is in agreement with its experimental value, 1.21 Å [42]).

Si₂O and Si₂O₂ molecules are a triangular ring and rhombus, respectively. The equilibrium Si–O bond length in Si₂O is determined to be 1.77 Å and the Si–O–Si bond angle to be 82.32°.

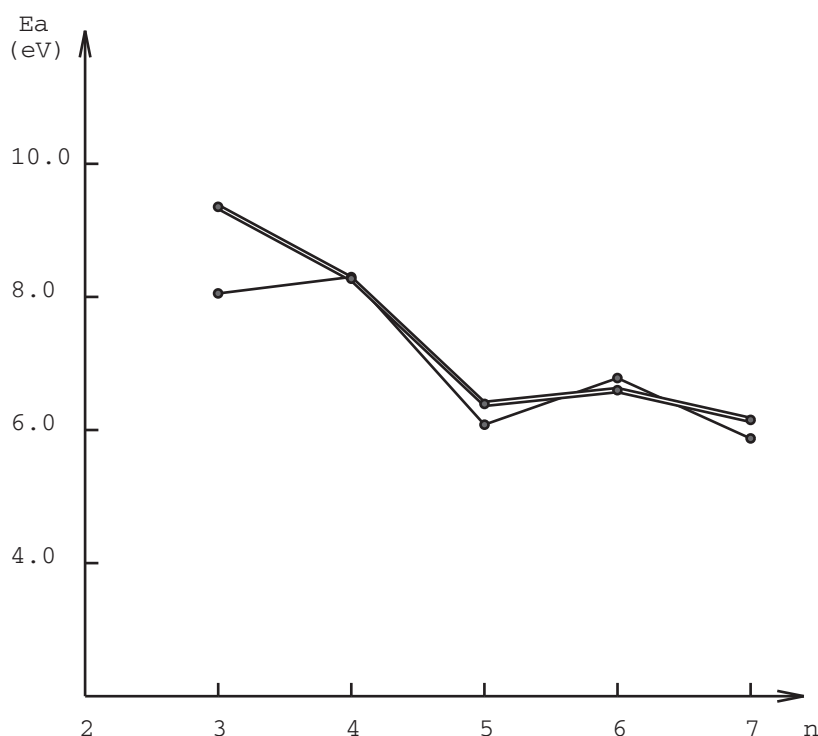


Figure 3. The adsorption energy per O atom (E_a) versus the atom number of the Si clusters. The thin curve corresponds to one O atom adsorbed on the Si clusters, while the thick curve to two O atoms.

The Si–O bond length in the Si_2O_2 and the O–Si–O bond angle are 1.76 Å and 87.2° as compared with 1.59 Å bond lengths and 109.5° bond angles in typical silicate glasses. Its binding energy is 25.01 eV, which is bound by 3.39 eV relative to two SiO molecules. In the process of the dynamics simulation performed on the structure of Si_2O_2 molecule when a Si_2 dimer and an O_2 molecule are put together, we find that the Si_2 dimer can fragment the O–O bond of the O_2 molecule, then form a stable rhombus. The Si–Si bond formed by the two Si atoms in the rhombus is still quite strong because the distance between them is only 2.54 Å. However, the distance between two O atoms in the structure is about 2.42 Å, which is twice the 1.23 Å bond length of the O–O bond in the O_2 molecule. Therefore, the two O atoms do not form an O–O bond. Figure 4 shows the process of formation of the Si_2O_2 molecule from Si_2 and O_2 dimers. All MT spheres for Si and O atoms in the initial structure (A) do not overlap. The bond lengths between the two Si and two O atoms correspond to those in the stable Si_2 and O_2 dimers, respectively. The final structure (F) is the stable structure of the Si_2O_2 molecule. Table 1 shows the geometrical parameters of the SiO and Si_2O_2 molecules obtained by the different methods (some are cited from [43]). Obviously, our calculated Si–O bond length is closer to the common Si–O bond length.

Now, we discuss oxygen atom O adsorption on Si_n ($n = 3-7$) clusters. Their adsorption energies per O atom (for Si_3-Si_7) are listed in table 2. When an O atom is adsorbed on the atop site of atom 3 in Si_3 , the Si–O bond length is computed to be 1.63 Å. The Si cluster stretches slightly along the Si–O direction, while it shortens in the other direction in parallel with its plan. The structural change suggests that the d_{12} ($= d_{13}$) bond length stretches, whereas the d_{23} bond length shortens. The Si_3O molecule is stable. But the adsorption of the O atom makes

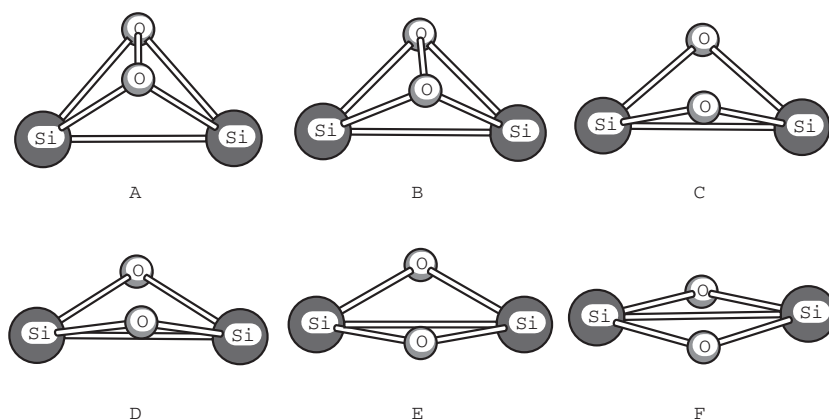


Figure 4. The process of formation of the Si_2O_2 molecule from Si_2 and O_2 dimers. The process is in the order A–F. The A and F structures are the initial and final structures, respectively.

Table 1. Geometrical parameters of the SiO and Si_2O_2 molecules obtained by different methods (bond length in Å bond angle in degrees).

Molecule	Method	Si–O	Si–Si	Angle O–Si–O
SiO	STO-3G	1.475	—	—
	3-21G	1.536	—	—
	3-21G*	1.496	—	—
	6-31G*	1.487	—	—
	FP-LMTO-MD	1.624	—	—
Si_2O_2	STO-3G	1.684	2.530	82.6
	3-21G	1.723	2.623	80.8
	3-21G*	1.682	2.489	84.5
	6-31G*	1.683	2.469	85.7
	FP-LMTO-MD	1.756	2.544	87.2

Table 2. Calculated adsorption energy (in eV, per atom) of oxygen atoms adsorbed on the Si_{3-7} clusters.

Structure	Si_3	Si_{4a}	Si_{4b}	Si_5	Si_6	Si_7
O	8.05	8.30	7.92	6.08	6.78	5.87
2O	9.35	8.27	7.45	6.39	6.60	6.15

the bond energies between Si atom 1 and Si atoms 2 and 3 decrease to 1.59 from 3.32 eV. This suggests that it easily fragments into a Si_2 dimer and a SiO molecule compared with its original Si_3 cluster. When an O_2 molecule is put on the atop site of the edge from Si atom 2 to its neighbouring atom 3, the O–O bond in the O_2 molecule will be broken to form a $\text{Si}_3 + 2\text{O}$ structure, as shown in figure 2. The process of formation of the Si_3O_2 molecule from the Si_3 trimer and O_2 dimer is similar to that of the Si_2O_2 molecule. Two Si atoms 2 and 3 and two O atoms in the Si_3O_2 molecule are almost on the same plane, forming a rhombus. The distance between Si atom 1 and the other Si atoms increases. Si atom 1 easily departs from the other two Si atoms. Their geometrical parameters are listed in table 3.

For Si_4 clusters, the oxygen atom could be adsorbed on the different active sites. The adsorption on the atop site of the plane of Si_4 leads to three-dimensional structures. Adsorptions

Table 3. Optimized molecular geometrical parameters (Å) for free Si₃ and Si₄ clusters, Si₃ + O, Si₃ + 2O, Si₄ + O and Si₄ + 2O.

Structure	d_{23}	$d_{13} = d_{12}$	Si(1)–O	Si(3)–O
Free Si ₃	2.79	2.17	—	—
Si ₃ + O	2.21	2.25	1.63	—
Si ₃ + 2O	2.82	2.33	1.83	2.33
Free Si ₄	2.39	2.31	—	—
Si _{4a} + O	2.51	2.33	2.04	1.92
Si _{4a} + 2O	2.74	2.42	1.91	1.83
Si _{4b} + O	2.89	2.26	1.63	—
Si _{4b} + 2O	2.59	2.30	1.63	—

Table 4. Optimized molecular geometrical parameters (Å) for the free Si₅ cluster, Si₅ + O and Si₅ + 2O.

Structure	d_{12}	d_{14}	d_{15}	d_{45}	Si–O
Free Si ₅	3.04	2.30	2.30	2.96	—
Si ₅ + O	2.59	2.38	2.35	—	1.65
Si ₅ + 2O	2.94	2.32	2.32	3.17	1.65

Table 5. Optimized molecular geometrical parameters (Å) for the free Si₆ cluster, Si₆ + O and Si₆ + 2O.

Structure	d_{12}	d_{15}	d_{16}	d_{56}	Si–O
Free Si ₆	2.72	2.35	2.35	2.69	—
Si ₆ + O	2.40	2.46	2.44	—	1.64
Si ₆ + 2O	2.46	2.41	2.41	—	1.64

on other sites result in planar adsorption structures. The adsorption energy of the three-dimensional structure is larger than that of its corresponding planar structures. It is found from table 3 that the oxygen atom adsorption makes the rhombus of the Si₄ cluster slacken. Our calculation indicates that the Si₄ cluster cannot bind O₂ molecules directly. However, it can bind two O atoms. This suggests that there is probably a potential barrier for the dissociative chemisorption of O₂. The calculated potential barrier height is about 0.8 eV.

For O atom adsorption on the Si₅, Si₆ and Si₇ clusters, similar trends have been found. The adsorption makes the two Si clusters lengthen along the direction connecting the O atoms to the centre of the Si clusters. Their Si–O bond lengths are almost the same (1.64–1.66 Å). For Si₇ + O and Si₇ + 2O, the adsorption makes the Si cluster slacken a little for the whole structure compared with the free Si₇. The geometrical parameters for the reactions of Si_{5–7} with O atoms are listed in tables 4–6. It is also found that Si_{5–7} cannot bind O₂ molecules. We have also calculated the potential barrier heights for Si_{5–7}. They are 0.2, 0.5 and 0.5 eV, respectively.

We note the following characteristics for oxygen adsorption on the small Si clusters. (1) For Si₁, Si₂ and Si₃, they can react with O₂ molecule directly to form small SiO₂, Si₂O₂ and Si₃O₂ molecules by dissociative chemisorption. (2) For the Si clusters with more than four Si atoms, O₂ molecules cannot be adsorbed on their surfaces directly. The potential barriers for dissociative chemisorption of O₂ make the reactions of Si clusters with O₂ slow. (3) When

Table 6. Optimized molecular geometrical parameters (Å) for the free Si₇ cluster, Si₇ + O and Si₇ + 2O.

Structure	d_{12}	d_{23}	d_{34}	d_{16}	d_{17}	d_{27}	d_{28}	d_{37}	d_{38}	d_{67}	Si–O
Free Si ₇	2.47	2.47	2.47	2.44	2.44	2.44	2.44	2.44	2.44	2.49	—
Si ₇ + O	2.27	2.34	2.63	2.43	2.41	2.95	2.90	2.45	2.48	—	1.63
Si ₇ + 2O	2.49	2.49	2.49	2.47	2.47	2.47	2.47	2.47	2.47	—	1.66

Table 7. Exothermicities calculated in the reactions of the Si clusters with O atoms (in eV).

Reactants	Products	Exothermicities
Si ₃ + O ₂	Si + 2SiO	2.08
Si ₄ + O ₂	Si ₂ + 2SiO	0.97
Si ₅ + O ₂	Si ₃ + 2SiO	1.40
Si ₆ + O ₂	Si ₄ + 2SiO	1.57
Si ₇ + O ₂	Si ₅ + 2SiO	1.40

an O atom is adsorbed on the Si clusters to form an Si–O single bond, it is as strong as that in the SiO molecule. However, when an O atom forms a Si–O multiple bond with many Si atoms, the Si–O bond lengths increase obviously.

The bond energies in the Si–O single bonds with almost the same bond lengths should be about the same as the Si–O bond in the SiO molecule. However, the calculated adsorption energy per O atom is less than the bond energy of 10.81 eV in the Si–O molecule; the difference is obviously remedied by the decrement of stability in the Si cluster. For small clusters, our calculations show that the oxygen adsorption results in their slackness in structure. As temperature increases, they would fragment. In order to understand the reactions between Si_n and O₂ and their fragmentation, we have also calculated the changes in energy in the fragmentation processes. We find that the processes from Si_n + O₂ to Si_{n-2} + 2SiO are all exothermic, indicating that they are energetically favourable. Table 7 shows their exothermicities. We noted that in the reactions between Si_n⁺ and O₂ the desorption of SiO from oxidized silicon surfaces has been observed above 975 K and at higher O₂ pressures [16, 44]. The conditions of higher temperature and pressures make the slack Si_n + O₂ structures fragment. However, in their ionic oxidation reactions, the reaction processes are quite slow experimentally, less than $4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. For clusters with fewer than 29 atoms the main products are Si_{n-2}⁺ and two SiO molecules. Since Si–O bonds (about 10 eV) are much stronger than Si–Si bonds (about 4–5 eV), the formation of an Si–O bond should supply enough energy to fragment the clusters very readily. However, in fact, the reactions with O₂ that are observed are quite slow. The rate decrease occurs between $n = 3$ and 4. What is the mechanism they relate to? Creasy and his co-workers [2] have proposed a four-centre mechanism to account for the slow reaction rates using orbital theory. Since the probability of forming the four-centre mechanism is low, the oxidation reactions occur slowly.

Our calculations suggest that Si clusters with fewer than three atoms can react with an O₂ molecule, whereas Si clusters with more than four atoms cannot. This is related to the property of the chemical bonds. Atomic silicon has an s²p² valence configuration, whereas crystal silicon is expected to have an sp³ configuration. According to a simple Mulliken population analysis performed by Raghavachari [45], the atoms in the Si clusters have configurations different from s²p² and sp³ due to fractional charges at the HF/6-31G* level of theory. Some atoms with highest coordination number (such as atom 1 in Si₃, atoms 3 and 4 in Si₄ and two apex atoms in Si₅, Si₆ and Si₇) have a population of s^{1.63–1.68}p^{2.37–2.32}. However, the other atoms

have a configuration approximating to s^2p^2 . They are very close to atom-like. For the different selected-size clusters, the atoms appear to hybridize by varying amounts. According to orbital theory [46, 47], for a reaction to be allowed by orbital symmetry and occur with no barrier, the highest occupied molecular orbital (HOMO) of the electron donor must overlap well with the lowest unoccupied molecular orbital (LUMO) of the electron acceptor. For the O_2 molecule, the common molecule orbital is $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_x})^2(\pi_{2p_y})^2(\pi_{2p_z})^2(\pi_{2p_y}^*)^1(\pi_{2p_z}^*)^1$. The HOMO is a π^* antibonding orbital. The π^* antibonding orbital has two lobes on each O atom [47]. For Si_2 , two p_x orbitals on two Si atoms form a σ bond. Two p_y (or p_z) orbitals may overlap reasonably well with the π^* orbital of O_2 to form the Si_2O_2 molecule. For Si_3 , the bond (2.79 Å) between atoms 2 and 3 is weak compared with the bond (2.17 Å) between atoms 1 and 2. For convenience of discussion, the weak bond is not considered here. Thus, two p (p_x or p_y) orbitals on atoms 2 and 3 form divalent bonds with atom 1, respectively. The other two p_z orbitals may overlap well with the π^* orbital of O_2 , forming the Si_3O_2 molecule. For Si_4 , two divalent atoms 1 and 2 have a population of s^2p^2 . After they form divalent bonds with atoms 3 and 4, there are no remaining p-orbital electrons. On the other hand, two trivalent atoms 3 and 4 are hybridized. They probably produce two remaining sp-like hybrid orbital electrons. This type of hybrid orbital has one large lobe. Two hybrid orbitals are in two opposite directions due to the D_{2h} symmetry of Si_4 . One hybrid orbital would not overlap well with the π^* orbital of the O_2 molecule. Therefore, Si_4 cannot react with O_2 directly. For Si_{5-7} , all atoms are hybridized. They do not have any remaining p-orbital electrons. Even if there are probably sp-like hybrid orbitals, they would not overlap well with the π^* orbital of O_2 . It is concluded that Si_{4-7} clusters cannot bind O_2 directly. This explains our calculated results.

4. Conclusions

We have studied oxygen atom adsorption on Si_{1-7} clusters by the FP-LMTO MD method. According to our calculations, we can draw the following conclusions: firstly, the adsorption of the O_2 molecule on the Si_1 , Si_2 and Si_3 clusters is dissociative chemisorption. For the Si clusters with more than four atoms, there is a potential barrier for the dissociative chemisorption of O_2 . Secondly, O atoms can be adsorbed on the active sites of the Si clusters. Oxygen atom adsorption causes a significant distortion in the Si clusters and their decreased stabilities. Thirdly, the Si–O single-bond lengths range from 1.63 to 1.66 Å, which is close to the Si–O bond of 1.62 Å in the SiO molecule.

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