

First-principles studies on the reactions of O₂ with silicon clusters

S. F. Li

Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei-230031, People's Republic of China

X. G. Gong^{a)}

Surface Physics Laboratory and Department of Physics, Fudan University, Shanghai-200433, People's Republic of China and Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei-230031, People's Republic of China

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The reactions of an O₂ molecule with the neutral and positively charged Si_n ($n=3-16$) clusters are studied with first-principles calculations. Neutral Si_n ($n=4,5,6,7,10,14$) and charged Si_n⁺ ($n=4,5,6,7,13,15$) clusters show higher inertness to O₂ molecule adsorption, which is in good agreement with experimental results. Both charge transfer and hybridizations between Si and O play an important role in the dissociative adsorption of O₂ molecule. We find that the spin triplet-single conversion of O₂ molecule is always accompanied with O₂ dissociatively chemisorbed on the Si_n clusters. © 2005 American Institute of Physics. [DOI: 10.1063/1.1885465]

I. INTRODUCTION

Silicon clusters have been the subjects of many experimental and theoretical investigations,¹⁻¹⁹ because the size of microelectronic devices will approach nanoscale in the next decade¹ if the current miniaturization trend can continue. These studies have shown that silicon clusters have much different physical and chemical properties from that of silicon bulk. Recently, some efforts have been made to build silicon nanotubes or nanowires^{20,21} as well as some stable silicon quantum dots²²⁻²⁵ based on the silicon clusters for their potential applications. It is well known that a stable oxide layer on the surface of the bulk silicon prevents further oxidation, however, much less is known about the oxidation process if the size of the device is reduced to nanometer scale. Therefore, it is important to study the silicon clusters interacting with an oxygen molecule.

The structures of silicon clusters, especially for small Si_n ($n \leq 7$),^{8,15-19} have been well determined. Some of them have been confirmed by Raman²⁶ and infrared²⁷ (IR) spectroscopies of matrix-isolated species, and vibrationally resolved photoelectron spectroscopy of gas-phase anions.²⁸ The geometrical and electronic structures of the larger cluster ($n > 8$)^{2,3,5,8-11,15,19,29} have also been studied by theoretical calculations. The shape of the larger Si_n ($n > 20$) clusters has been obtained by measuring the mobilities for their ions.^{12,30,31} For the reactivity of low-dimensional silicon structures, experiments have been performed to examine the reactions of pure silicon clusters or bare surfaces with ethylene,^{30,32-36} acetylene,³⁷ water,^{37,38} ammonia,^{37,39,40} and oxygen,^{35,37,41,42} respectively. These results showed that the pure silicon clusters in the range of 2-70 atoms have much less reactivity than bare bulk silicon surfaces. It has been found that O₂ can etch smaller Si_n⁺ ($n \leq 6$) clusters,³⁷ two silicon atoms at a time, all the way down to Si₂⁺ or even Si⁺. The

reactivity of large Si_n⁺ ($n=10-65$) clusters with respect to O₂, studied with selected ion drift tube techniques,⁴¹ was found to depend on the sizes of the clusters. An oxygen molecule reacting with silicon clusters, of which the number of atoms is less than 29, takes away two silicon atoms from the cluster, and the main products are Si_{n-2}⁺ and two SiO molecules. For the Si_n⁺ ($n > 35$) clusters, the dominant product is Si_nO₂⁺ with molecular chemisorption of O₂. In the transition region ($29 \leq n \leq 35$) between 29 and 35 atoms, a significant amount of Si_{n-1}O⁺ is observed, which is due to etching only one silicon atom to form a single SiO molecule at a time. Recently, the stability of silicon cluster ions has been studied by O₂ etching,⁴² and the results suggest that Si_n⁺ ($n=4,6,9,13,14,23$) and Si_n⁻ ($n=18,21,24,25,28$) clusters have very high stability. Generally, the low sticking probability for O₂ on these clusters indicates less reactivity than that of silicon bulk surfaces. However, to our knowledge, the theoretical study on the reaction of silicon cluster with O₂ is very much limited; we are still very far from fully understanding the physics and chemistry of the reactions even for small silicon clusters.⁴³

In this work, we study the reaction of O₂ molecule with neutral and positively charged Si_n clusters using first-principles calculation; due to the difficulties in searching the atomic structures of large clusters, we constrain our calculations only for $n=3-16$. The rest of the paper is organized as follows: In Sec. II, the calculation details are briefly described. Section III presents the results and discussions. Finally, the summary and conclusions are given in Sec. IV.

II. CALCULATION DETAILS

Present calculations are based on the density-functional theory^{44,45} and plane-wave basis set,^{46,47} with spin-polarized generalized gradient approximations (GGA),^{48,49} as implemented in the code of VASP.⁵⁰ The wave functions are expanded in a plane-wave basis set with a cutoff energy of

^{a)}Electronic mail: xggong@fudan.edu.cn

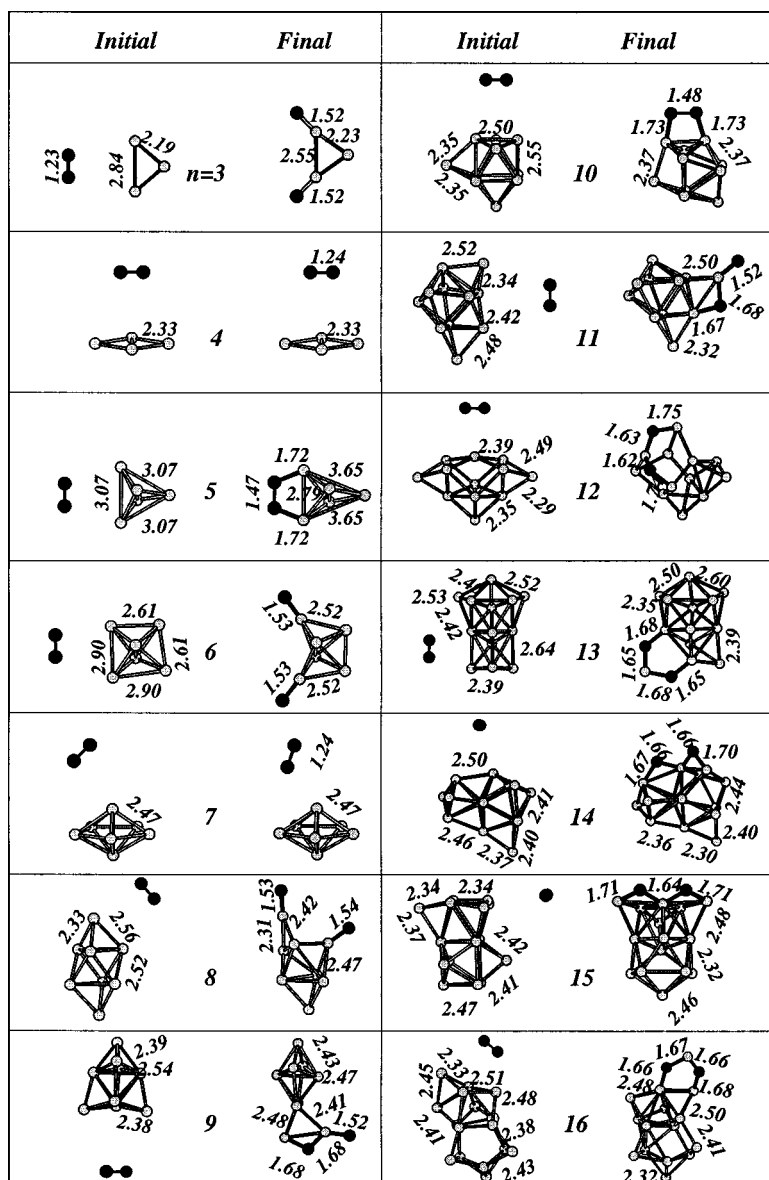


FIG. 1. The initial and the final structures for O_2 reacting with Si_n ($n=3-16$) clusters. The gray and black spheres denote silicon and oxygen atoms, respectively.

400 eV. The interaction of the valence electrons with the core is described by projector augmented wave (PAW) potential.^{51,52} The atomic positions are optimized by the conjugate gradient⁵³ (CG) method, with the force convergence up to 0.01 eV/Å.

We use a big supercell with the size of 17 Å to make the interactions between the cluster and its periodic images negligible. For the charged clusters, a method proposed by Makov and Payne⁵⁴ is used to reduce the electrostatic interactions between the cluster and its periodic images. Due to the large supercell, only the Γ point is used for the summation of the Brillouin zone of the simulation cell.

The accuracy of the plane-wave basis set and the PAW potential is checked by calculating the ground-state properties of Si_2 and O_2 dimers. Both Si_2 and O_2 dimers are in spin-triplet state; the calculated bond lengths are 2.27 and 1.23 Å, respectively, which are in good agreement with experimental results⁵⁵ of 2.25 and 1.21 Å for a Si_2 dimer and an O_2 molecule, respectively.

In order to get Si_nO_2 structures, first, we have optimized the structures of the neutral and charged silicon clusters and

the isolated O_2 , respectively. Then the oxygen molecule is assumed at about 4.0 Å away from the silicon cluster for the following structure optimization. And we have considered various possible reaction paths (from 6 paths for small clusters to 15 paths for large clusters) by putting the O_2 around the silicon cluster with different sites and different O_2 orientations. By comparing the total energies of these optimized clusters, the final products of Si_nO_2 clusters for the barrierless reaction of O_2 on Si_n are obtained.

III. RESULTS AND DISCUSSIONS

A. The properties of Si_n and $Si_n^+(n=3-16)$ clusters

First of all, the ground-state structures of both neutral Si_n ($n=3-16$) clusters and their cations have been studied. Figure 1 shows all the calculated structures. We find that a C_{2v} triangle for Si_3 , a D_{2h} rhombus for Si_4 , a D_{3h} trigonal, D_{4h} tetragonal, and D_{5h} pentagonal bipyramids for Si_5 , Si_6 , and Si_7 , respectively, agree well with previous theoretical results.^{2,5,8,16-19} Present results show that Si_8 , Si_9 , Si_{10} , Si_{11} , Si_{12} , Si_{13} , Si_{14} , and Si_{15} are C_{2h} , C_{2v} , C_{3v} , C_s , C_{2v} , C_s , C_s , and

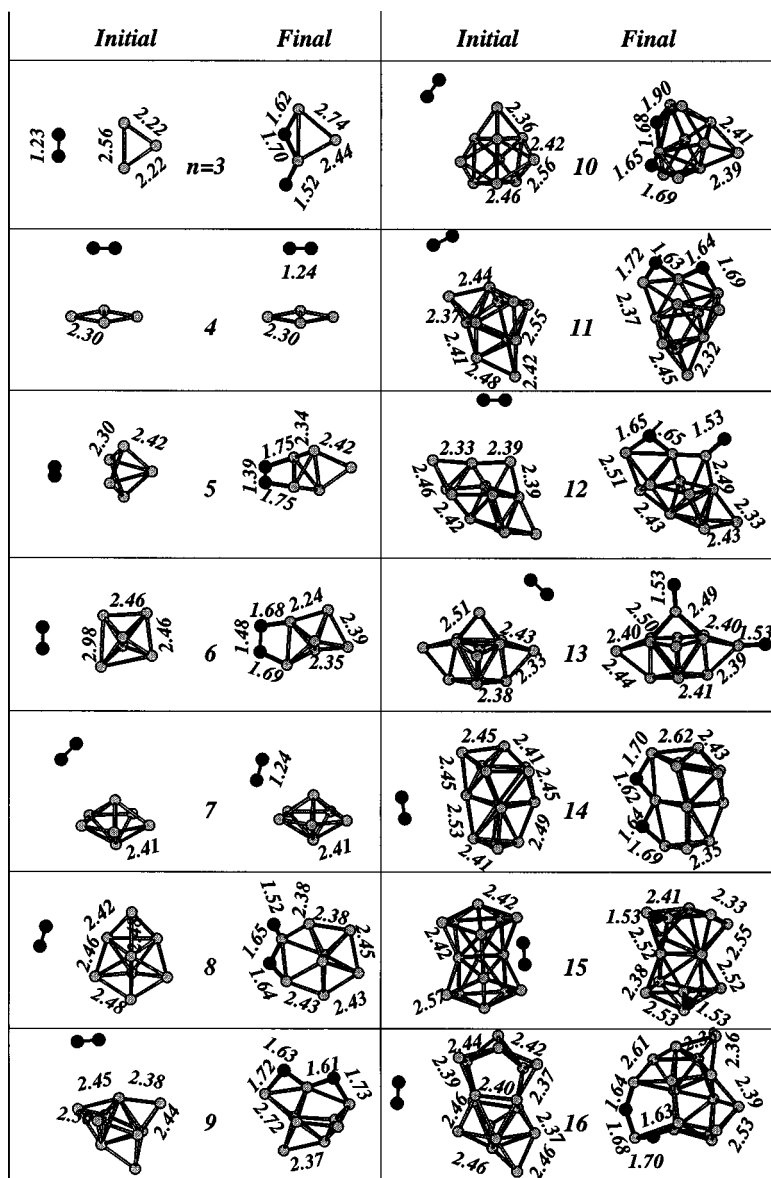


FIG. 2. The initial and the final reacted structures for O₂ on Si_n⁺ ($n=3-16$) clusters. The gray and black spheres denote silicon and oxygen atoms, respectively.

D_{3h} symmetries, respectively, which are in close agreement with the previous calculations.^{5,10} However, the optimized structure of Si₁₆ has a very low symmetry, similar to the C_{2h} structure obtained by Liu *et al.*⁵ but the present low-symmetry structure is slightly more stable. From Fig. 1, one can find that, within the small size range, the structures of Si_{n+1} ($n \leq 6$) can be derived from that of the Si_n clusters by adding one atom along the long edge site, i.e., edge-capping growth mode. While for large Si_n ($7 < n < 12$) clusters, the face-capping growth mode is preferred. For even larger clusters Si_n ($n > 12$), the growth format becomes more complicated.

Present calculations show that most of the Si_n⁺ ($n=3-16$) cation clusters (see Fig. 2) keep almost the same symmetry as that of the corresponding neutral clusters (see Fig. 1). However, some difference between the structures of neutral and cation Si₆ clusters has been observed. For Si_n⁺ ($n=8, 13, 15$) clusters, the obtained structures are obviously different from that of the neutral counterparts. The average nearest bond length of these cations is larger than that of the neutral counterparts.

Figure 3(a) illustrates the binding energies of the neutral and charged clusters, which approach to the binding energy of 4.63 eV of the crystalline Si.⁵⁶ As presented in Fig. 3(b), the ionization potentials (IPs), which are calculated by the energy difference between Si_n and Si_n⁺, decrease with increasing the size of the clusters. Two visible jumps can be observed at $n=7$ and $n=10$, which is an indication of higher stability. Figure 3(c) is the second-order difference of energies, $E_{n+1} - 2E_n + E_{n-1}$, indicating that the Si_n clusters with $n=4, 7, 10, 12, 15$ and the Si_n⁺ clusters with $n=4, 6, 7, 11, 13, 15$ are relatively more stable than their size neighbors. The different relative stability between the neutral clusters and their cations can be qualitatively attributed to two reasons. One could be that the charging has changed the electronic shell of the neutral clusters, thus the relative stability of these clusters can be changed. Another reason might be the change of geometry structures for some cations, such as Si_n⁺ ($n=8, 13, 15$) clusters. The clusters with high stability obtained in our calculations are in good agreement with the results of both experimental collision-induced dissociation fragments⁷ and mass spectra analysis.⁴²

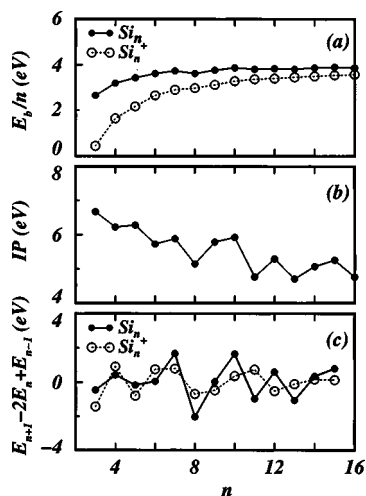


FIG. 3. The calculated properties for Si_n and Si_n^+ ($n=3-16$) clusters. (a) The binding energies per silicon atom E_b/n (eV), (b) The ionization potentials (IPs) of Si_n clusters, and (c) the second-order difference of the binding energies.

B. The reactions of O_2 with Si_n ($n=3-16$) clusters

We have calculated the adsorption energies of the Si_nO_2 clusters, $E_d = -[E(\text{Si}_n\text{O}_2) - E(\text{Si}_n) - E(\text{O}_2)]$, where $E(\text{Si}_n\text{O}_2)$, $E(\text{Si}_n)$, and $E(\text{O}_2)$ are the total energies of Si_nO_2 cluster, the Si_n , and O_2 , respectively. In fact, one can use E_d to qualitatively describe the reactivity of O_2 on the clusters. The calculated E_d has a strong dependence on the silicon cluster size, as shown in Fig. 4(a) and Table I. The present results show that an O_2 molecule can be physically adsorbed on Si_4 and Si_7 clusters with the adsorption energy less than 0.2 eV; meanwhile the structures of the reacted clusters are not affected by the adsorption of O_2 . It is also shown that O_2 can be molecularly chemisorbed on both Si_5 and Si_{10} clusters with about 2.2-eV adsorption energy which is much larger than the physical adsorption energy of 0.2 eV as mentioned above. While on all other clusters, O_2 prefers a dissociative

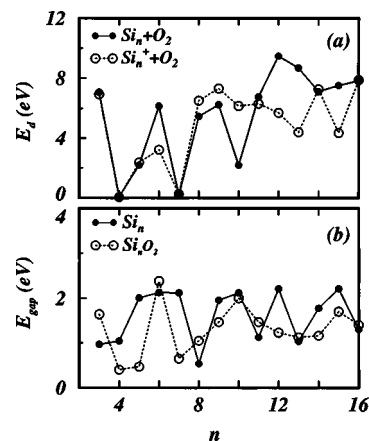


FIG. 4. (a) Adsorption energy E_d (eV) for O_2 on Si_n and Si_n^+ clusters; (b) HOMO-LUMO gap E_{gap} (eV) for Si_n and the reacted products Si_nO_2 clusters.

chemisorption with the adsorption energies more than 6.0 eV. In general, the adsorption of O_2 on larger Si_n ($n > 10$) clusters has larger adsorption energy. It is interesting to point out that the large clusters usually have small IPs, as shown in Fig. 3(b).

The adsorption sites of oxygen molecule are strongly correlated to the growth modes of silicon clusters. Since the small Si_n ($n \leq 7$) clusters follow the edge-capping growth mode, the favorite adsorption sites for O_2 reacting with Si_3 , Si_5 , and Si_6 are just for the axis of the O_2 parallel to the long edges of these clusters. While in large clusters where the face-capping growth mode is preferred, the adsorption sites for O_2 are the face sites.

Both the electronic and geometrical structures of Si_n clusters have been changed after O_2 dissociative adsorption. As shown in Fig. 4(b) and Table I, we compare the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) energy gaps of the Si_n clusters with that of the corresponding reacted products Si_nO_2 . It is clear

TABLE I. Some calculated properties for O_2 adsorption on Si_n and Si_n^+ ($n=3-16$). E_d (eV), E_{gap}^1 (eV), E_{gap}^2 (eV), and $\bar{R}_{\text{Si-O}}$ (Å) are adsorption energy, the energy gap (HOMO-LUMO) for bare Si_n and Si_n^+ clusters, the energy gaps for the final products Si_nO_2 (Si_n^+O_2) in Fig. 1 (Fig. 2), and the average nearest bond lengths of the Si-O bonds, respectively.

Size n	E_d (eV)		E_{gap}^1 (eV)		E_{gap}^2 (eV)		$\bar{R}_{\text{Si-O}}$ (Å)	
	$\text{Si}_n + \text{O}_2$	$\text{Si}_n^+ + \text{O}_2$	Si_n	Si_n^+	Si_nO_2	Si_n^+O_2	Si_nO_2	Si_n^+O_2
$n=3$	7.063	6.942	0.96	0.60	1.64	0.20	1.52	1.61
4	0.059	0.023	1.04	0.60	0.40	0.58
5	2.188	2.364	2.01	0.40	0.47	0.50	1.72	1.75
6	6.152	3.211	2.13	0.57	2.38	0.61	1.53	1.69
7	0.171	0.242	2.12	0.48	0.65	0.34
8	5.460	6.509	0.54	0.31	1.05	0.39	1.53	1.60
9	6.241	7.315	1.95	0.27	1.47	0.26	1.63	1.67
10	2.191	6.151	2.12	0.40	2.00	0.37	1.73	1.76
11	6.764	6.314	1.12	0.25	1.47	0.23	1.62	1.67
12	9.462	5.700	2.21	0.26	0.63	0.23	1.69	1.61
13	8.685	4.397	1.04	0.27	1.12	0.23	1.67	1.53
14	7.119	7.266	1.78	0.26	1.16	0.19	1.67	1.66
15	7.526	4.348	2.21	0.28	1.70	0.23	1.68	1.53
16	7.836	7.870	1.30	0.19	1.40	0.51	1.67	1.66

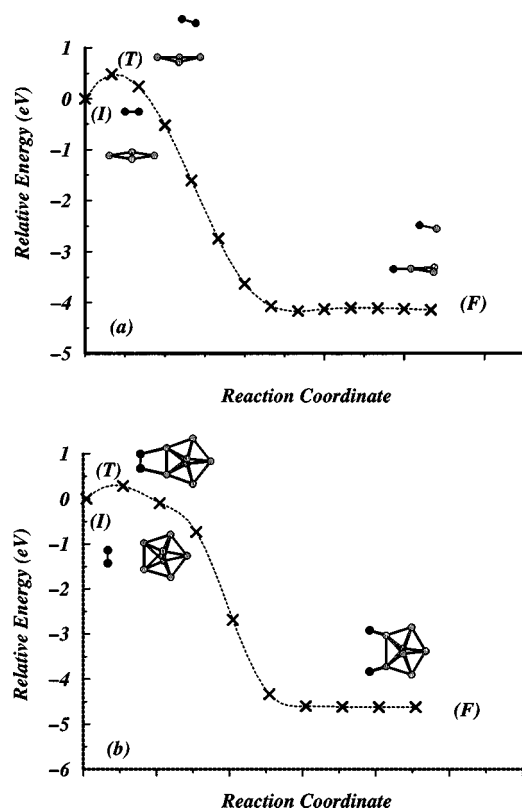


FIG. 5. The minimum-energy paths (MEPs) obtained by NEB method for O₂ dissociative chemisorption on Si₄ cluster (a) and Si₇ cluster (b): the initial adsorption configuration (I), the transition state (T), and the final products state (F). The energies of the initial states have been set as the reference for both Si₄O₂ and Si₇O₂. About 0.45 and 0.35 eV barriers are found for O₂ dissociatively to adsorb on Si₄ and Si₇, respectively.

that almost all the structures of the Si_{*n*} are changed after O₂ adsorption except for *n*=10, 13, 16. For almost all of the larger Si_{*n*} (*n*>7) clusters, after having reacted with O₂, the local geometrical structures of the silicon atoms binding with oxygen atoms are changed substantially, as shown in Fig. 1. Analysis of the nature of HOMO shows that HOMO are essentially contributed by Si atoms, and the occupied states of O atoms are well below the Fermi energy.

It is interesting to understand why Si₄ and Si₇ clusters are of high inertness with respect to the O₂ adsorption. We find that all Si atoms in the Si₄ cluster are in the *s*²*p*² configuration. Therefore, O₂ can hardly react with Si₄ directly since a reaction barrier must be overcome. To calculate this barrier, we have searched the minimum-energy path (MEP) for O₂ dissociation on Si₄ cluster using nudged elastic band (NEB) theory⁵⁷ [see Fig. 5(a)], obtaining a barrier of 0.45 eV. The inert character of Si₄ cluster to O₂ adsorption was also studied by Li *et al.* with full potential linear muffin-tin orbital (FP-LMTO) molecular-dynamics method,⁴³ but they estimated the barrier height to be as high as 0.8 eV, much higher than the present result, which might be due to different theoretical methods or the different MEP path. The high inertness of Si₇ cluster may be owing to its high symmetry of the pentagonal bipyramids. As have been discussed above, the edge-capping growth mode ends just at Si₇, which is energetically more stable than its neighbors in the sequence of the number of atoms in the clusters. An energy

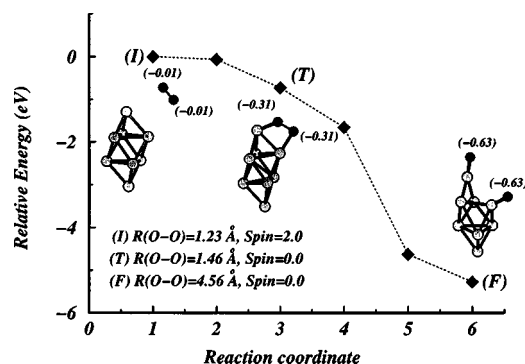


FIG. 6. Reaction coordinates for dissociative chemisorption of O₂ molecule on Si₈ cluster. The analysis of local electronic structure indicates that the net charge per oxygen atom is about 0.01, 0.31, and 0.63 *e* in the initial state (I), intermediate state (T), and final state (F), respectively. *R*_(O-O) (Å) is the distance between the two oxygen atoms. Spin-triplet to spin-singlet transition occurred in the transitional state with *R*_(O-O) around 1.46 Å.

barrier of 0.35 eV has been found from the MEP obtained by NEB method⁵⁷ [Fig. 5(b)] for O₂ dissociating on Si₇ cluster.

To understand the process of how an oxygen molecule oxidizes the silicon cluster, we have shown the reaction coordinates of O₂ on the Si₈ cluster in Fig. 6. With O₂ approaching to the cluster, the bond of O₂ is elongated step by step, from 1.23 Å in the initial state to 4.56 Å in the final product where the O₂ has been dissociated. The local structure close to the adsorption sites of oxygen atoms is strongly distorted, the bond between two silicon atoms is broken, while the other part of the structure does not change significantly.

Both charge transfer from silicon cluster to O₂ and the orbital hybridizations between the oxygen and the cluster states may play an important role in the process of O₂ dissociation. The present results show that, before O₂ dissociation, the charge transfer is about 0.3 *e* for each oxygen atom, and the interatomic distance between two oxygen atoms is less than 1.5 Å. While in the final product of Si₈O₂, each oxygen is charged more than 0.6 *e*. The Coulomb repulsive force weakens the bonding of these two oxygen atoms. From the density of state (DOS) presented in Fig. 7, one can find that in the initial state, there is almost no hybridization between O₂ and silicon atoms in the cluster, as O₂ is about 4 Å away from the cluster. However, in the intermediate states (see Fig. 7), the *p* orbital hybridizations between the oxygen atom and the silicon atom can be clearly seen. The DOS of the final state also clearly indicates the strong hybridization of Si-O bonds (Fig. 7). On the other hand, the formation of Si-O bonds is energetically favorable since the Si-O bond is stronger than the O-O bond.

We have noticed that the spin-triplet state of O₂ must be changed to spin singlet before it is dissociated in the reaction. As shown in Fig. 7, in the initial state, O₂ is in the spin-triplet state. In the intermediate state with the bond length of O₂ about 1.46–1.50 Å, the local spin state of O₂ has been changed to spin-singlet state. In the final state, some Si-Si bonds have been broken, some Si atoms are rebonded with oxygen atoms, and the cluster is entirely in the spin-singlet state. This is also true for all the Si_{*n*}O₂ clusters with O₂ dissociated. However, if the O₂ is molecularly

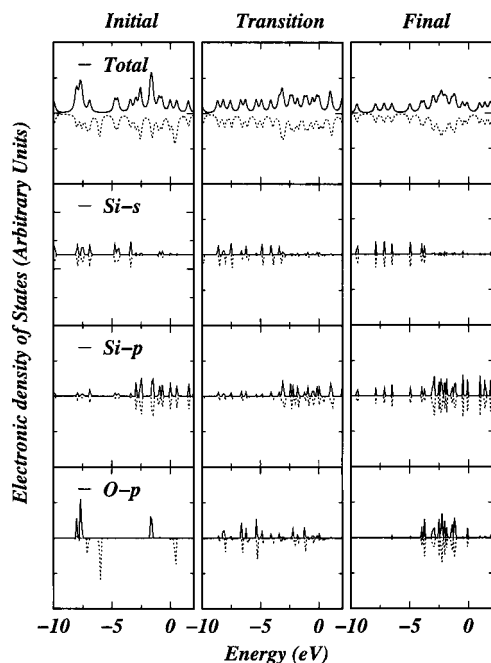


FIG. 7. The electronic density of states for O_2 reacting with Si_8 cluster. Initial, transition, and final correspond to the initial state (*I*), intermediate state (*T*), and reacted product state (*F*) in Fig. 6, respectively. Strong hybridizations between oxygen and silicon cluster in the intermediate state and the final reacted product can be observed.

chemisorbed, the spin-triplet state will not be changed. As all these calculations have only shown the ground-state properties, we did not pay much attention on how the spin flipped. In fact, if the spin-conserving condition is considered, a barrier should be overcome for the O_2 dissociation even on the Si_8 cluster.

C. O_2 adsorption on $Si_n^+(n=3-16)$ clusters

We have shown the initial adsorption sites for O_2 on $Si_n^+(n=3-16)$ and the corresponding reacted products in Fig. 2. The adsorption energies and HOMO-LUMO gaps are shown in Table I. Although there are some small structural differences between the cation clusters and the neutral clusters, the Si_n^+ clusters show growth modes very similar to that of the neutral clusters. Therefore, the adsorption sites for O_2 on Si_n^+ clusters are almost the same as that observed in the neutral clusters. However, the final structures for O_2 on $Si_n^+(n=3,6)$ are much different from their corresponding neutral counterparts. This strongly suggests that the charge on these silicon clusters changes the potential-energy surfaces for the Si_n and Si_nO_2 clusters.

Similar to neutral Si_n clusters, we find that both Si_4^+ and Si_7^+ clusters show low reactivity to the oxygen molecule indicating a high stability. The results for Si_4^+ are in close agreement with the experiment results.^{31,42} However, the experiment⁴² of Bergeron and Castleman did not show any evidence of high inertness of Si_7^+ cluster with respect to O_2 , although Si_7^+ cluster was found to be very abundant in the collision-induced fragment products.⁷ Such a contradictory for the reactivity of Si_7^+ is still not fully understood.

Generally, as observed in the neutral cluster, the larger Si_n^+ clusters are more reactive to the O_2 molecule. However,

compared with their neighboring clusters, both Si_{13}^+ and Si_{15}^+ clusters show less reactivity, i.e., higher stability. In fact, the high stability of Si_{13}^+ had already been found by Bergeron and Castleman,⁴² but up to now, the reason for the high stability is still unclear. Our results indicate that O_2 molecule can only be chemically adsorbed on one or two sites on Si_{13}^+ cluster; this suggests that the inertness of Si_{13}^+ cluster with respect to O_2 could be a geometric reason, i.e., the less possibility for O_2 molecule to stick on the surface of the cluster in the experiment⁴² with the presence of a constant flow of helium carrier gas.

IV. SUMMARY

The neutral Si_n and charged $Si_n^+(n=3-16)$ clusters reacting with O_2 have been studied with first-principles spin-polarized GGA calculations. The atomic structures and the reaction coordinates for a few clusters are obtained. We find that O_2 can be physically adsorbed on Si_4 and Si_7 , molecularly adsorbed on Si_5 and Si_{10} , and dissociatively adsorbed on all other studied Si clusters; however, the large clusters are generally more reactive. The charge transfer from silicon cluster to oxygen as well as the hybridization between the Si and O orbitals may play an important role in the dissociative adsorption of O_2 . For O_2 , the local spin state conversion from triplet to singlet as a key step for the dissociative adsorption is also observed. The neutral Si_n clusters with $n=4,5,6,7,10,14$, and the charged Si_n^+ clusters with $n=4,5,6,7,13,15$ show the high inertness character as to O_2 adsorption.

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