

First Principles Study on Si_nO ($n=14-18$) and $\text{Si}_{10-m}\text{O}_m$ ($m=1-8$)

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Abstract

Combining the full-potential linear-muffin-tin-orbital molecular-dynamics (FP-LMTO-MD) and the Amsterdam Density Functional (ADF) with TZ2P basis set in conjunction with self-consistent-field (SCF), we have studied the geometric features and stabilities of the Si_nO ($n=14-18$) clusters. The total binding energy E_{tot} , gap of HOMO (highest-occupied molecular orbital)-LUMO (lowest-unoccupied molecular orbital) E_g , dipole moment μ and total constant volume heat capacity $C_{\text{v}(\text{tot})}$ were also calculated. The results show that the one dopant oxygen atom tends to occupy the edge or the surface position in the middle size silicon clusters (Si_n , $n=14-18$). To further understanding the evolutionary tendency of the physical characteristics for the Si-O clusters with different composition, the $\text{Si}_{10-m}\text{O}_m$ ($m=1-8$) clusters were also studied using the same methods. It was found that the structures of the $\text{Si}_{10-m}\text{O}_m$ ($m=1-8$) clusters evolve from compact three dimensions to chain-like with increasing of the O proportion. The binding energy curve of $\text{Si}_{10-m}\text{O}_m$ clusters with different m shows a dip at $m=6$, which suggests that an optimal proportion of O and Si atoms may exist in the $\text{Si}_{10-m}\text{O}_m$ ($m=1-8$) clusters.

Keywords: Si-O clusters; Stable structure; Bonding energy

Introduction

Silicon and its oxides are important materials because of their wide application potential, such as light-emitting materia, [1-3] solar energy [4] and catalyst [5]. With the deeply understanding of the physical properties of the silicon oxide materials, more new application fields have been developed [6,7]. For example, the SiO_x -based resistive switching behavior provides a new use for traditional SiO_x materials [8]. In addition, the Si-O compounds are found to be very abundant in most dusty media in space, and thus important in astrophysical processes such as star and planet formation [9]. All these (potential) applications are closely related to the structures of these compounds, therefore a systematical study would be of great importance.

In recent years, the oxide silicon was investigated in both experiment [1,4,5,10-13] and theory [10-21] for its broad prospect in the application. Desjardin and co-workers [1] studied oxidation of Si (111)-(7×7) surface by STM. They found that the low coverage O_2 molecules absorbed on the surface could form more stable structures at room temperature. Very recently, Kinahan et al. [4] revealed the quantitative relationship between the coverage of site-specific oxygen and a decrease of the Si (111)-(7×7) surface stress in tensile by the same method. Wang et al. [5] studied the Si_3O_y clusters using anion photoelectron spectroscopy and *ab initio* calculation. They presented that the Si_3O_4 may be a model structure for oxygen defect sites in bulk SiO_2 .

On the other hand, the features of the Si-O clusters are the key points in the study of the Si-O systems. Kinds of Si-O clusters such as Si_mO_n ($m, n=1-8$) [10,11], Si_nO ($n=3-5$) [12], Si_mO_n ($m=1-5, n=1, 2m+1$) [14], Si_nO_n ($n \geq 5$) [17], Si_6O_n ($n=1-12$) [19], Si_7O_n ($n=1-14$) [20] and SiO_n ($1 < n \leq 6$) [21] were studied by first principle calculations. Many new possible structures of these clusters were drawn and numerous unfamiliar features of them were investigated. Based on the quantum-mechanical calculations, Zhang et al. [10] studied the O-ratio-dependent features of the Si_mO_n ($m, n=1-8$) clusters. They found that energetically the most favorable small Si-O clusters have O atomic ratios at about 0.6. James [12] found that the structure of the ground state Si_3O_3 cluster is planar and the lowest energy structures of Si_4O_4 and Si_5O_5 are non-planar rings. Lu and coworkers [17] obtained the results that the binding energies of Si_mO_n ($m=1-5, n=1,$

$2m+1$) clusters increase with the number of oxygen atoms, and the dissociation energies of these clusters are strong relative to the O and Si atoms ratio in one cluster. In addition, some researches focused on the $(\text{SiO}_2)_n$ nanoclusters [15,16,18]. A number of ringed, tube-like, cage shape, columnar and disk-like nanostructures based on SiO_2 unit were illustrated in detail.

We studied oxygen molecule and one O atom adsorption on Si_n ($n \leq 13$) clusters by the FP-LMTO-MD method [22-25] and ADF program [26] and the lowest energy structures for these clusters were given [13,27]. The calculated results show that there is a potential barrier of dissociative chemisorption of O_2 when the Si clusters have more than four atoms. Moreover, it is found that the edge or the surface of the host Si clusters is the favorable adsorption sites for one O atom.

In this work, we investigated one oxygen atom adsorption on the middle size silicon clusters (Si_n , $n=14-18$) and the $\text{Si}_{10-m}\text{O}_m$ ($m=1-8$) clusters using combination of the FP-LMTO-MD and ADF program. Our main purpose is to find the lowest energy structures of these clusters, and to explore the geometry and physical properties in the evolutionary procedure of the Si-O clusters with various compositions. Some new the lowest energy structures for these Si-O clusters were found. The total binding energy for $\text{Si}_{10-m}\text{O}_m$ ($m=1-8$) clusters decrease, and then increase with the increasing of the ratio of Si:O.

Methods

The initial structures of the Si_nO ($n=14-18$) clusters are constructed through an oxygen atom being absorbed on the positions of the lowest energy silicon clusters [28] which are given by previous studies.

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Geometrical optimization algorithm is performed on the initial structures without any symmetry constraints by the FP-LMTO-MD method. For the $\text{Si}_{10-m}\text{O}_m$ ($m=1-8$) clusters, a huge number of initial atomic conformations are randomly sampled within a real three-dimensional box, or cage, or ball structure. Moreover, several chain-like initial structures of the $\text{Si}_{10-m}\text{O}_m$ ($m=1-8$) clusters are also prepared.

After that, we choose the three lowest energy structures of each Si-O clusters in two types as candidates and re-optimize these selected structures by using the ADF program [26] version (2007.01) with TZ2P [29] basis set in conjunction with self-consistent field (SCF). The TZ2P basis using in ADF is an all-electron basis with triple-zeta quality for valence region. The frozen-core approximation for the inner-core electrons is used. The orbitals up to 2p for silicon and 1s for oxygen are kept frozen. An accessional STOs (Slater Type Orbitals) basis set including s, p, d, f, and g-type is used to fit the molecular density and hence to present the Coulomb and exchange potentials more accurate. The combined self-consistent-field (SCF) is converged to a value of 10^{-6} . For both two types' clusters, the frequencies of them are computed using numerical differentiation of gradients in slightly displaced geometries.

Furthermore, the cationic and anionic clusters corresponding to each neutral candidate are also calculated. Using the ADF program, such calculations can be performed by altering the charge state in the input file for a given cluster.

Results and Discussions

Existing imaginary frequencies indicate that the given molecular structure is unstable. Our calculated results show that there are no imaginary frequencies in the energy minima structures for both two types' Si-O clusters. It suggests that our obtained the lowest energy structures are stable.

Si_nO ($n=14-18$) clusters

The three lowest energy structures for the Si_nO ($n=14-18$) clusters are shown in Figure 1. The number 0 and the sign +, - in parentheses represent the neutral, cationic and anionic clusters respectively. The three isomers are labeled as *a*, *b* and *c* in order of decreasing stability. For example, (0,-) *a* indicates that the labeled structures are the most stable structure for neutral and anionic clusters. The calculated results for each neutral Si_nO ($n=14-18$) cluster are listed in Table 1, which include the total binding energy (E_{tot} , in eV), electron affinity (EA, in eV), ionization potential (IP, in eV), the gap of HOMO-LUMO (E_g , in eV), dipole moment (μ , in Debye), and total constant volume heat capacity ($C_{v(\text{tot})}$, in cal/mol·K).

For the Si_{14}O cluster, their isomers are formed by an O atom being adsorbed to different sites of the ground state Si_{14} cluster [6,28]. The $\text{Si}_{14}\text{O}(0)\text{a}$ structure with Cs symmetry lies 0.23eV energetically below the $\text{Si}_{14}\text{O}(0)\text{b}$ structure. Both of the structures $\text{Si}_{14}\text{O}(0)\text{b}$ and the $\text{Si}_{14}\text{O}(0)\text{c}$ have C_1 symmetries. The energy difference between them is only 0.01eV. Our calculated result shows that the largest energy difference between the adsorption structures with the same host Si structure can be up 0.8 eV.

For Si_{15}O isomers, the symmetries of the lowest two binding energy Si_{15}O clusters are both C_2 , while for third one is C_3 . The most and second stable structures of them are formed by the second lowest energy structure of pure Si_{15} cluster [28] absorbing an impurity oxygen atom at the different edge sites for a Si triangular pyramid unit. While, for the third stable Si_{15}O cluster, the O atom connects three Si atoms

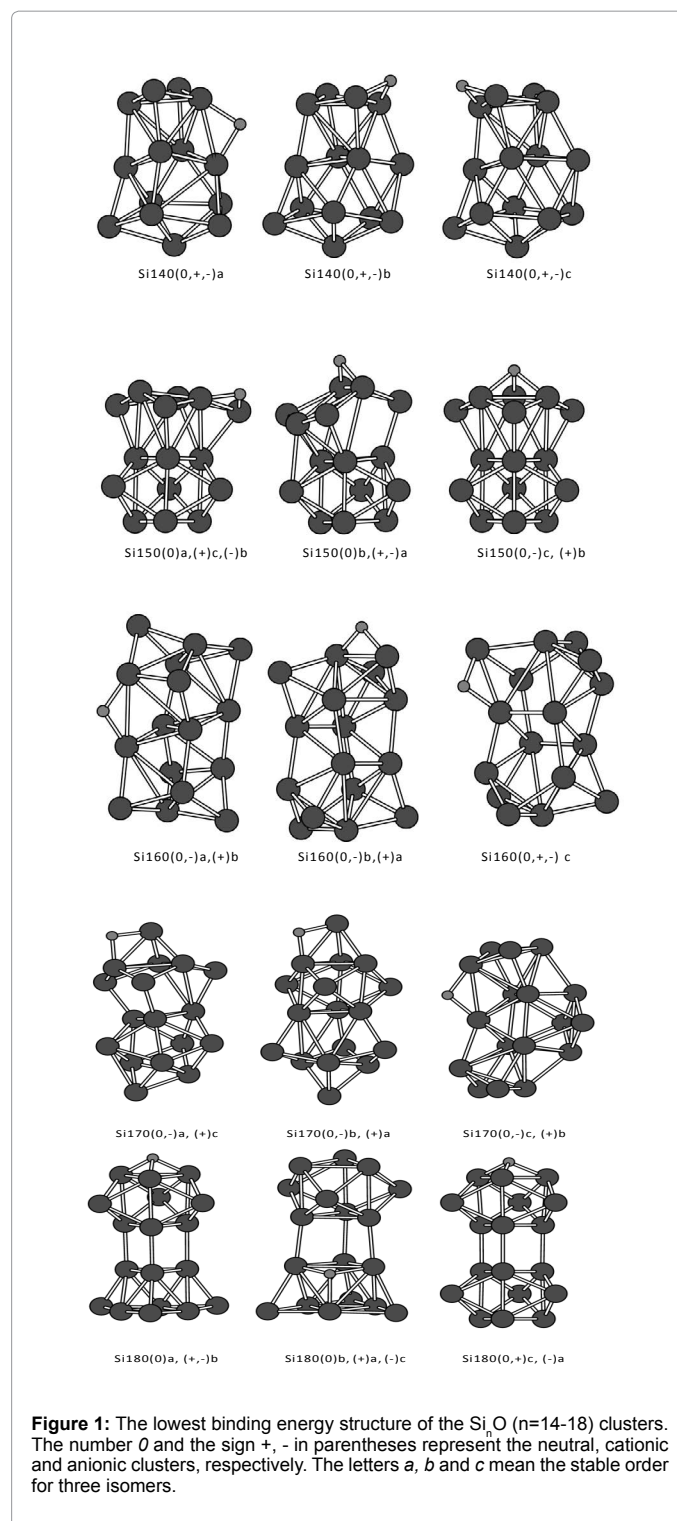


Figure 1: The lowest binding energy structure of the Si_nO ($n=14-18$) clusters. The number 0 and the sign +, - in parentheses represent the neutral, cationic and anionic clusters, respectively. The letters *a*, *b* and *c* mean the stable order for three isomers.

to form a triangular pyramid and lays on the apex site of the pyramid, as shown in Figure 1. The similar adsorbed sites of O atom also can be found in other Si_nO ($n=14-18$) clusters (shown in the Figure 1 and 2). The energy of the cluster $\text{Si}_{15}\text{O}(0)\text{a}$ is about 0.73eV and 0.84eV more stable than $\text{Si}_{15}\text{O}(0)\text{b}$ and $\text{Si}_{15}\text{O}(0)\text{c}$, respectively.

The three lowest binding energy structures of Si_{16}O cluster are C_2 symmetries. Comparison of the structures for the Si_{16}O [6, 28] and Si_{16}O

| structure | E _{tot} (eV) | EA (eV) | IP (eV) | E _g (eV) | μ | C _v |
|-----------|-----------------------|---------|---------|---------------------|------|----------------|
| Si14oa | -69.58 | 2.61 | 6.76 | 1.30 | 1.03 | 71.38 |
| Si14ob | -69.35 | 2.61 | 6.94 | 1.40 | 1.20 | 72.00 |
| Si14oc | -69.34 | 2.48 | 7.00 | 1.69 | 1.02 | 71.98 |
| Si15oa | -74.90 | 1.60 | 8.11 | 1.85 | 2.37 | 76.92 |
| Si15ob | -74.17 | 2.66 | 7.11 | 1.56 | 0.42 | 76.51 |
| Si15oc | -74.06 | 2.44 | 7.23 | 1.78 | 2.19 | 76.74 |
| Si16oa | -78.72 | 2.86 | 6.58 | 0.94 | 0.84 | 80.73 |
| Si16ob | -78.65 | 2.78 | 6.48 | 0.72 | 1.27 | 80.99 |
| Si16oc | -78.49 | 2.81 | 6.68 | 0.92 | 0.91 | 80.87 |
| Si17oa | -83.45 | 3.05 | 7.13 | 1.21 | 0.72 | 86.54 |
| Si17ob | -83.44 | 2.90 | 6.86 | 1.27 | 0.12 | 86.72 |
| Si17oc | -83.06 | 2.63 | 6.53 | 1.08 | 1.55 | 86.85 |
| Si18oa | -87.61 | 2.51 | 6.79 | 2.03 | 3.25 | 92.28 |
| Si18ob | -87.58 | 2.50 | 6.72 | 1.54 | 4.47 | 91.64 |
| Si18oc | -87.54 | 3.08 | 7.01 | 1.05 | 1.96 | 93.21 |

Table 1: The total binding energy (E_{tot}, in eV), electron affinity (EA, in eV), ionization potential (IP, in eV), the gap of HOMO-LUMO (E_g, in eV), dipole moment (μ, in Debye), and total constant volume heat capacity (C_v(tot), in cal/mol K), for the three lowest energy structures of Si_nO (n=14-18) clusters.

cluster shows that the impure O atom will result in the compact pure cluster becoming loose. The distortion arising from the O atom doping is more significant for Si₁₆O clusters than for other Si_nO (n=14,15,17 and 18) clusters.

The three Si₁₇O clusters shown in the Figure 1 are C_s symmetries, which are formed by one O atom being absorbed to the lowest and the third lowest Si₁₇ clusters [6, 28]. The difference of binding energy for the first and second stable structures is only 0.01eV. For the third stable isomer, the absorbed O atom leads the two ends of the pure Si₁₇ cluster slightly bend to the center.

For the Si₁₈O isomers, the O atom performs as a trigonal face-capping atom. The symmetries for three lowest binding energy clusters are C_{3v}, C_{2v} and C_{3v} in energy order. After the O atom is adsorbed, slight distortion occurs in the host silicon structures. The energy difference of three low-lying isomers of pure Si₁₈ cluster is about 0.26 eV [6]. The absorption O atom reduces the difference to less than 0.07 eV. Hence, the three structures of Si₁₈O clusters can be regarded degenerate energetically.

Our calculated results reveal that the impurity oxygen atom is favorable to adsorb on the edge or surface site of the middle-size silicon clusters, the same phenomena also has been found in small-size Si_nO (n=1-13) clusters [27]. The Si atom with 3s²3p² electronic configurations, trends to through sp³ hybridization forming covalent bonds with other atoms. Meanwhile, the 2s²2p⁴ O atom has lone electron pair of p orbital besides two p single electrons and probably forms two or three bonds with neighboring atoms in the mixed clusters. This is the main reason why the doped oxygen atom usually occupy the surface or edge site to form three or two bonds in the Si_nO clusters (the analyses in details see our previous study [13,27]).

For the adsorption structures with edge-capping O atom, O atom bridges two Si atoms by two bonds, in which the lengths are from 1.64 to 1.79Å. The bond angles of the Si-O-Si are from 90.5 to 116.1 degree. For the surface adsorption, the O-Si bond lengths are around 1.83 Å and slightly longer than bonds in the edge-adsorption's case. Compared with the Si_n (n=14-18) clusters [6,28], the structures of the Si_nO clusters become loose. We think the main reason is that the parts of charges transfer from the surrounding Si atoms to doped O atom and the covalent bonds are formed between them.

The ionic clusters corresponding to the above neutral Si_nO (n=14-18) candidates with larger binding energies are also studied. The calculated results indicate that the neutral and ionic clusters show similar geometrical configurations and different stability orders. It is found from observing the positions of all atoms for a given Si_nO cluster that the differences of coordinates for the ionic and neutral clusters are less than 0.2Å. Such small difference is hardly to distinguish from the structural figures. So we use the same structure to describe the ionic and neutral cluster with similar motif. As shown in the Figure 1, the three lowest binding energy ionic and neutral Si₁₄O clusters have same energetic orders. While, when n>14, the energetic orders of ionic and of neutral Si_nO clusters are different. The energy gaps between HOMO and LUMO (E_gs) of ionic and of neutral SinO clusters are also different. For example, for the three Si₁₇O isomers at the lowest energy state, the E_gs of the neutral clusters are 1.21eV, 1.27eV and 1.08eV, while 0.23 eV, 0.36eV and 0.39eV for cationic isomers and 0.44 eV, 0.31eV and 0.32eV for anionic ones, respectively. We speculate that the electronic redistributions due to add or reduce one electron may contribute to the energy order and E_g changes.

We have also investigated the magnetism properties of the neutral and ionic Si_nO (n=14-18) clusters. It is found that the neutral clusters with even number of electrons have no magnetic moment because all the electrons are paired together in their respective molecular orbitals, whereas all the ionic clusters with odd number of electrons have the total magnetic moment of 1.0 μ_B, which is trivial, due to one unpaired electron. In addition, Mulliken population analyses imply that about 0.62e to 0.66e charge transfer from the silicon atoms to the oxygen atom.

Si_{10-m}O_m (m=1-8) clusters

Zhang and co-workers reported that the binding energies per O atom for Si₆O_n (n=1-12) increased with the numbers of O atoms at first, and then decreased when n>8 [19]. The similar tendency also was found in Si₂O_n (n=1-14) clusters [20]. The structural feature of Si_mO_n clusters strongly depend on the ratio of component Si and O atoms [14,19,20]. For small Si_mO_n clusters, the structural motif will transit from a disk-like structure to a double-oxygen-bridged rod structure [19].

In order to explicitly explore how the different ratio of Si:O effect on the structural evolution properties and physical characteristics for the SiO mixed clusters, the Si_mO_{10-m} (m=1-8) clusters are studied. The initial structures of them are given by unbiased global search (details see the method). More than 4000 candidates for each Si_mO_{10-m} clusters with different m are calculated, and the most stable structures of them are shown in the Figure 2. For all clusters, the bond lengths of O-O, Si-O and Si-Si fall between 1.52-1.65 Å, 1.67-1.71 Å and 2.31-2.95 Å, respectively. The shortest Si-O bond is the single Si-O bond in Si3O7 cluster.

For Si₉O cluster, the O atom is adsorbed on the edge site of the lowest energy Si₉ cluster [30], which excellently agrees with our previous results using different method [27]. To our knowledge, the ground-state structure of Si₈O₂ cluster has never been reported up to now. The Si₈O₂ cluster has C_s symmetry. It looks like a silicon crown being adorned with two O atoms jewels. When m≥3, the Si₃O₃-ring and Si₂O₂-rhombus structures formed in the ground state Si_mO_{10-m} clusters. With the ratio of O atom further increasing, the SimO10-m clusters trend to form the chain-like conformation. Our calculated lowest energy structures of Si₇O₃, Si₆O₄, Si₅O₅, Si₄O₆ and Si₃O₇ are in agreement with the findings of other groups [14,19,20]. The most stable structure for Si₂O₈ cluster consists of the two SiO₃ rhombuses

and one Si_2O_2 rhombus buckled-chain structure. The computation of frequencies shows that the structure Si_2O_8 is stable because no imaginary frequencies exist. We also calculated the SiO_9 clusters. The structures are unstable, therefore, the dissociated SiO_9 cluster does not be listed.

The Si_4O_6 cluster is the most stable in all the $\text{Si}_{10-m}\text{O}_m$ ($m=1-8$) clusters. The chain-like Si_4O_6 cluster with D_2 symmetry is formed by three Si_2O_2 -rhombuses sharing with two Si atoms. The lengths of Si-O bonds in the cluster are different. The lengths of Si-O bonds connecting the two ends Si atoms are 1.73 Å, which are longer than the other bonds' lengths (about 1.68 Å). Mulliken population analyses imply that the some charge transfer from silicon atoms to oxygen atoms. For neutral Si_4O_6 cluster, the dipole moment is zero due to symmetrical structure.

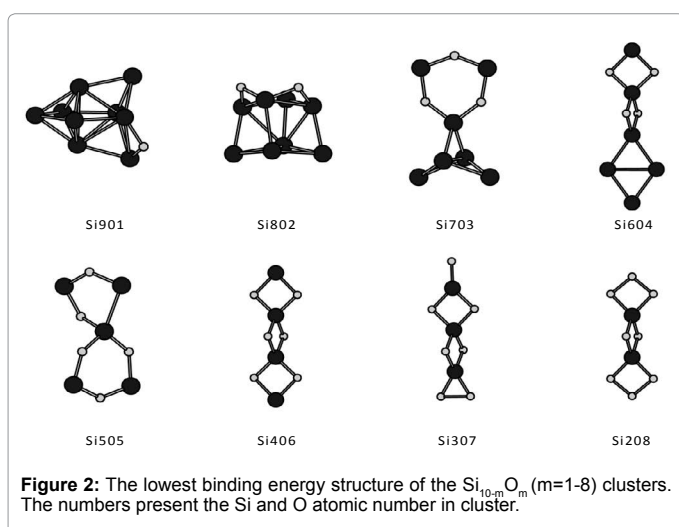


Figure 3 plots the total binding energies E_{tot} ($\text{Si}_{10-m}\text{O}_m$) versus the number of oxygen atoms. As opposed to the linear curve of the nitrogen atom and aluminum atom doped to Si clusters [31,32], the curve for the Si-O mixed cluster shows a valley. With the number O atom increasing, the E_{tot} ($\text{Si}_{10-m}\text{O}_m$) decreases linearly when $1 \leq m \leq 6$, and then goes up when $m > 6$. This is to say that the lowest binding energy structure for $\text{Si}_{10-m}\text{O}_m$ cluster with the ratio of 0.6 for O component, which is similar to the findings by Zhang's in the Si_mO_n ($m, n=1-8$) clusters [14]. On the one hand, comparing the $\text{Si}_{10-m}\text{O}_m$ clusters, there is a tendency that the structures of the $\text{Si}_{10-m}\text{O}_m$ clusters evolve from compact three dimensions to chain-like with increasing of the proportions for O components. On the other hand, the symmetries of these clusters increase with O when $m \leq 6$. Therefore, the energetic valley may suggest that the stability of the mixed Si-O clusters depends on the cooperation of the composition and structural properties.

The second different energy $\Delta_2 E$ (eV) is a sensitive quantity to reflect the stability of clusters. It is defined as $\Delta_2 E (\text{Si}_{10-m}\text{O}_m) = E_{\text{tot}} (\text{Si}_{10-(m-1)}\text{O}_{m-1}) + E_{\text{tot}} (\text{Si}_{10-(m+1)}\text{O}_{m+1}) - 2 E_{\text{tot}} (\text{Si}_{10-m}\text{O}_m)$. The $\Delta_2 E$ have the largest value at $m=6$, also indicates that the Si_4O_6 cluster is more stable than their neighboring clusters (Figure 4). In addition, the $\Delta_2 E$ also displays an even/odd alternating pattern as a function of cluster size. The clusters with even oxygen atoms present higher stability.

The energy gaps E_g between the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO) are showed in Figure 5. The highest peak occurs again at the Si_4O_6 cluster. The energy gaps also display a certain even/odd alternating pattern as a function of cluster size. All the evidences mentioned above suggest that the ratio 4:6 is the optimal proportion for the stability of the $\text{Si}_{10-m}\text{O}_m$ ($m=1-8$) clusters. Chu *et al.* found that when O ratio reaches to about 60% in a small Si-O clusters, the energy gaps of the clusters present the biggest value [11]. Such result is a convincing evidence to support our conclusion.

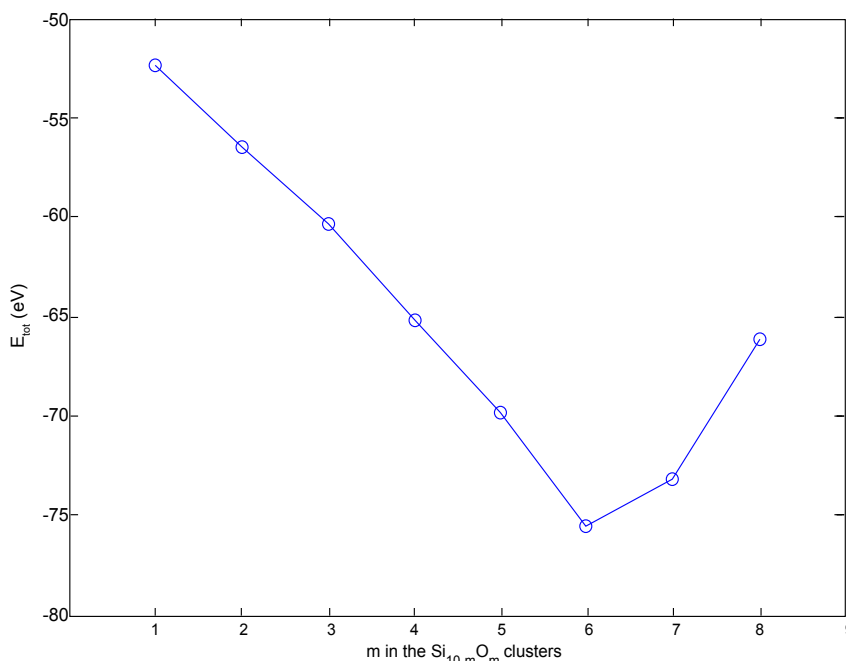


Figure 3: The total energies of the $\text{Si}_{10-m}\text{O}_m$ ($m=1-8$) clusters E_{tot} (eV) versus the atom number of O atom m.

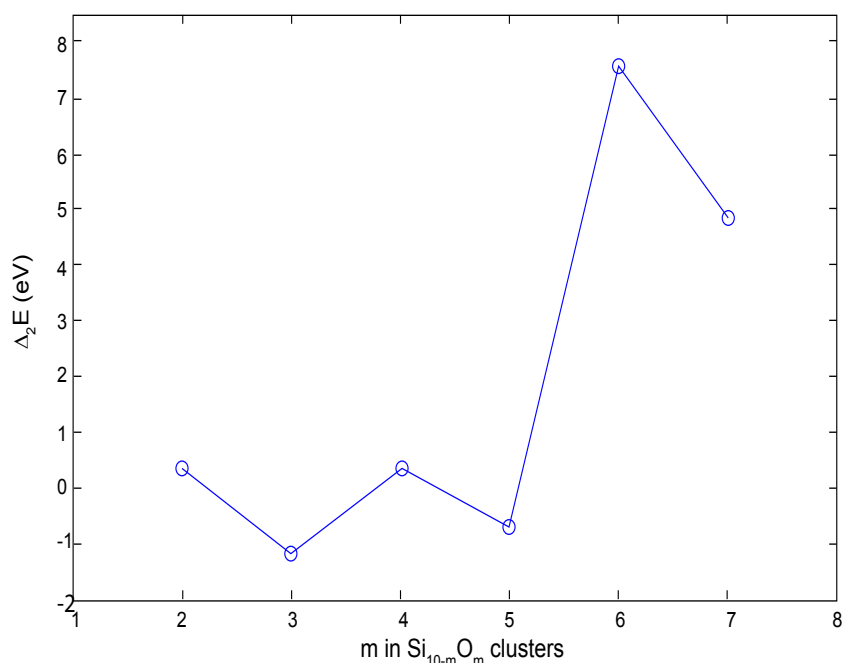


Figure 4: The second different energies of the $\text{Si}_{10-m}\text{O}_m$ ($m=1-8$) clusters $\Delta_2 E$ (eV) versus the atom number of O atom m.

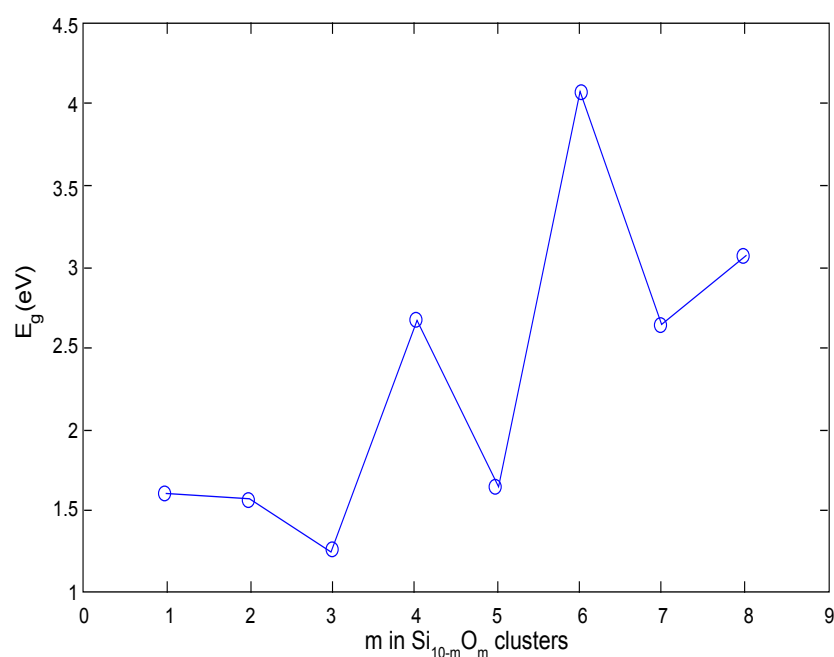


Figure 5: The energy gaps E_g s (eV) between the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO) of $\text{Si}_{10-m}\text{O}_m$ ($m=1-8$) clusters.

Furthermore, it is found that the rhombus Si_2O_2 unit is a basic structure of ground Si-O clusters [5,11,33,34]. Two rhombus Si_2O_2 units will buckle with each other by sharing a central Si atom to form a stable chain-like configuration. Such structural patterns are usually found in ground state Si-O clusters [5,11,13,19,20]. In other word, to form the stable buckled rhombus Si-O chain, for each added Si atom

needs two O atoms more. This may be the reason why the Si-O clusters with even oxygen atoms possess lower binding energy.

The heat capacities of the clusters are computed based on the ideal gas approximation omitting the electronic contribution. The heat capacity C_v is related to the number of degrees of freedom (DoF) of the cluster system. In ideal gas model, the nonlinear cluster with n atoms

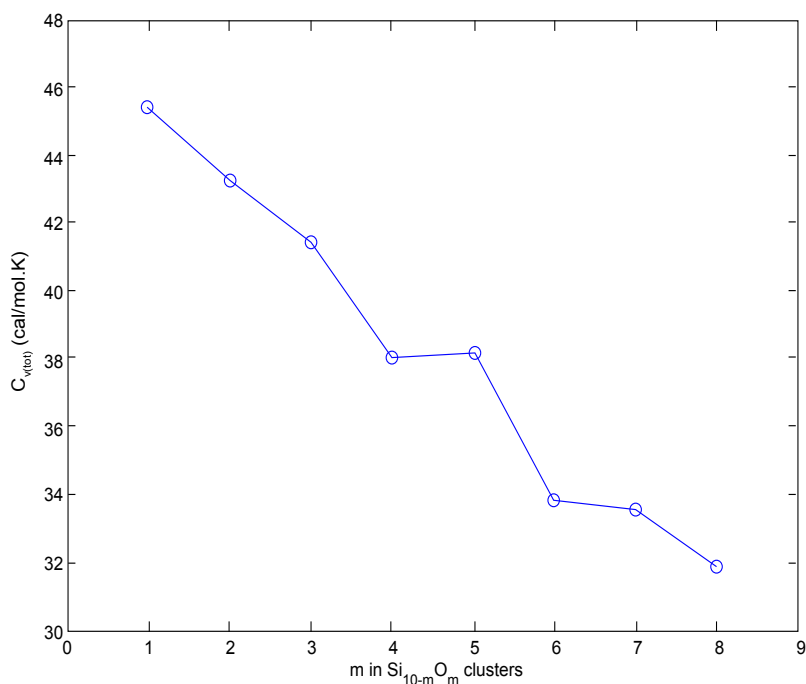


Figure 6: The total constant volume heat capacity (cal/mol.K) of $\text{Si}_{10-m}\text{O}_m$ ($m=1-8$) clusters.

has 3 translational, 3 rotational and $3n-6$ vibrational DoF. The molar heat capacity of the n -atom cluster is $[3+3+2(3n-6)]\cdot R/2$, where R is the ideal gas constant. For $\text{Si}_{10-m}\text{O}_m$ ($m=1-8$) clusters, the $C_{v(\text{tot})}$ equals to $27R$ (≈ 53.6 cal/mol.K). In our calculation, Si_9O cluster shows the largest heat capacity 45.4 cal/mol.K. The smaller $C_v(\text{tot})$ s with respect to the theoretical values may be due to the inactivation of some vibrational DoFs. According to the ideal gas model, the heat capacity of the cluster only relates to its atom number. Thus, the $\text{Si}_{10-m}\text{O}_m$ clusters would have similar value of the $\text{Si}_{10-m}\text{O}_m$ cluster. However, it is interesting that the $C_v(\text{tot})$ of $\text{Si}_{10-m}\text{O}_m$ cluster decreases gradually with the proportions of O atomic increases (See Figure 6). Observing the structural evolution of $\text{Si}_{10-m}\text{O}_m$ clusters, it is found that the structures of these clusters vary radically with the increasing of the ratio for oxygen: the whole structure for silicon-rich clusters transfer to the fragments consisted for oxygen-rich clusters. We assume that such structural changes may contribute to the decreasing of C_v with increasing of the O component's ratio for the $\text{Si}_{10-m}\text{O}_m$ clusters.

Conclusions

The Si_nO ($n=14-18$) and $\text{Si}_{10-m}\text{O}_m$ ($m=1-8$) clusters are investigated systemically by using the FP-LMTO-MD and the ADF with TZ2P basis set in conjunction with SCF. The calculated results suggest that the edge and surface adsorption structures are the favorable structures for the middle size silicon clusters doped an oxygen atom. For $\text{Si}_{10-m}\text{O}_m$ ($m=1-8$) clusters, their structures evolve from compact three dimensions to chain-like with increasing of the proportion of O. The Si_4O_6 cluster has the lowest bonding energy and the largest Δ_2E . It suggests that the conclusion which the small silicon-oxygen clusters have the optimal ratio of 0.6 for O component [14] is still correct in the $\text{Si}_{10-m}\text{O}_m$ ($m=1-8$) clusters. Whether the bigger Si-O clusters still have such optimal O ratio needs further study.

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References

1. Dujardin G, Mayne A, Comtet G, Hellner L, Jamet M, et al. (1996) New model of the initial stages of Si(111)-(7 x 7) oxidation. Phys Rev Lett 76: 3782-3785.
2. Yuan ZS, Zhu LF, Tong X, Li WB, Liu XJ, et al. (2002) Which is the most stable one in WSi_n ($n=1-4$)? A density functional investigation with pseudo-potential model. J Mol Struct: Theochem 229-237.
3. Ganji MD, Ahaz B (2010) First Principles Simulation of Molecular Oxygen Adsorption on SiC Nanotubes, Commun. Theor. Phys, 53: 742-748.
4. Kinahan NT1, Meehan DE, Narushima T, Sachert S, Boland JJ, et al. (2010) Site-specific evolution of surface stress during the room-temperature oxidation of the Si(111)-(7 x 7) surface. Phys Rev Lett 104: 146101.
5. L.-S. Wang, J.B. Nicholas, M. Dupuis, H. Wu, S.D. Colson, Si_3O_y ($y=1-6$) Clusters: Models for Oxidation of Silicon Surfaces and Defect Sites in Bulk Oxide Materials, Phys. Rev. Lett., 78, (1997) 4450-4453.
6. K.-M. Ho, A.A. Shvartsburg, B. Pan, Z.-Y. Lu, Cai-ZhuangWang, J. G.Wacker, J.L. Fye, M.F. Jarrold, Structuresofmedium-sized silicon clusters, Nature, 392, (1998) 582-585.
7. Ho MS1, Hwang IS, Tsong TT (2000) Direct observation of electromigration of Si magic clusters on Si(111) surfaces. Phys Rev Lett 84: 5792-5795.
8. Y.-F. Chang, P.-Y. Chen, Y.-T. Chen, F. Xue, Y. Wang, F. Zhou, B. Fowler, J.C. Lee, Study of polarity effect in SiO_x -based resistive switching memory, Appl. Phys. Lett., 101, (2012) 052111.
9. A.N. Witt, K.D. Gordon, D.G. Furton, Silicon Nanoparticles: Source of Extended Red Emission?, Astrophys. J., 501, (1998) L111-L115.
10. R. Zhang, T. Chu, H. Cheung, N. Wang, S. Lee, High reactivity of silicon suboxide clusters, Phys. Rev. B, 64, (2001) 113304.
11. T.S. Chu, R. Q. Zhang, H.F. Cheung, Geometric and Electronic Structures of Silicon Oxide Clusters, J. Phys. Chem. B, 105, (2001) 1705-1709.
12. J.R. Chelikowsky, Structural and electronic properties of neutral and charged silicalike clusters, Phys. Rev. B, 57, (1998) 3333-3339.
13. B.-X. Li, P.-L. Cao, Z. Ye, R.Q. Zhang, S.T. Lee, Oxygen adsorption on small

- Si clusters: a full-potential linear-muffin-tin-orbital molecular-dynamics study, *J. Phys.: Condens. Matter*, 14, (2002) 1723-1733.
14. W.C. Lu, C.Z. Wang, V. Nguyen, M.W. Schmidt, M.S. Gordon, K.M. Ho, Structures and Fragmentations of Small Silicon Oxide Clusters by ab Initio Calculations, *J. Phys. Chem. A*, 107, (2003) 6936-6943.
 15. E. Flikkema, S.T. Bromley, Dedicated Global Optimization Search for Ground State Silica Nanoclusters: $(\text{SiO}_2)_N$ ($N=6-12$), *J. Phys. Chem. B*, 108, (2004) 9638-9645.
 16. D. Zhang, M. Zhao, R.Q. Zhang, Two- and Three-Membered-Ring Hybrid Structures of Silica Nanoclusters, *J. Phys. Chem. B*, 108, (2004) 18451-18454.
 17. Zhang RQ, Zhao MW, Lee ST (2004) Silicon monoxide clusters: the favorable precursors for forming silicon nanostructures. *Phys Rev Lett* 93: 095503.
 18. Bromley ST, Flikkema E (2005) Columnar-to-disk structural transition in nanoscale $(\text{SiO}_2)_n$ clusters. *Phys Rev Lett* 95: 185505.
 19. Zang QJ, Su ZM, Lu WC, Wang CZ, Ho KM (2006) Oxidation pattern of small silicon oxide clusters: structures and stability of Si_6O_n ($n=1-12$). *J Phys Chem A* 110: 8151-8157.
 20. Q.J. Zang, Z.M. Su, W.C. Lu, C.Z. Wang, K.M. Ho, A first-principles study of oxidation pattern in magic Si7 cluster, *Chem. Phys. Lett.*, 430, (2006) 1-7.
 21. G. Forte, G.G.N. Angilella, V. Pittalà, N.H. March, R. Pucci, Neutral and cationic free-space oxygen-silicon clusters SiO_n ($1 < n \leq 6$), and possible relevance to crystals of SiO_2 under pressure, *Phys. Lett. A*, 376, (2012).
 22. O.K. Andersen, R.G. Woolley, Muffin-tin orbitals and molecular calculations: General formalism, *Mol. Phys.*, 26, (1973) 905-927.
 23. O.K. Andersen, Linear methods in band theory, *Phys. Rev. B*, 12, (1975) 3060-3083.
 24. M. Springborg, O.K. Andersen, Method for calculating the electronic structures of large molecules; helical polymers, *J. Chem. Phys.*, 87, (1987) 7125-7145.
 25. Methfessel M, van Schilfgaarde M (1993) Derivation of force theorems in density-functional theory: Application to the full-potential LMTO method. *Phys Rev B Condens Matter* 48: 4937-4940.
 26. ADF2007.01, SCM, Vrije Universiteit, Amsterdam, The Netherlands, 2007.
 27. Y.-H. Zhu, B.-X. Li, F.-S. Liang, J. Xu, Theoretical Study of Neutral and Ionic Si_nO ($n=1-13$) Clusters, *Int. J. Mod. Phys. B*, 23, (2009) 3729-3738.
 28. B.-X. Li, P.-L. Cao, S.-C. Zhan, Ground state structures of Si_n ($n=11-25$) clusters, *Phys. Lett. A*, 316, (2003) 252-260.
 29. Van Lenthe E, Baerends EJ (2003) Optimized Slater-type basis sets for the elements 1-118. *J Comput Chem* 24: 1142-1156.
 30. M.F. Jarrold, Nanosurface Chemistry on Size-Selected Silicon Clusters, *Science*, 252, (1991) 1085-1092.
 31. B.-X. Li, G.-Y. Wang, M.-Y. Ye, G.-C. Yang, C.-H. Yao, Geometric and energetic properties of Al-doped Si_n ($n=2-21$) clusters: FP-LMTO-MD calculations, *J Mol Struct: Theochem.*, 820, (2007) 128-140.
 32. W.-F. Ding, B.-X. Li, A first-principles study of $\text{Al}_n\text{Si}_{m-n}$ clusters ($m=6, 9, 10; n \leq m$), *J Mol Struct: Theochem.*, 897, (2009) 129-138.
 33. T. Morita, N. Takami, Nano Si Cluster-SiOx-C Composite Material as High-Capacity Anode Material for Rechargeable Lithium Batteries, *J. Electrochem. Soc.*, 153, (2006) A425-A430.
 34. Tamanai, H. Mutschke, J. Blum, G. Meeus, The 10 μm Infrared Band of Silicate Dust: A Laboratory Study Comparing The Aerosol and KBr Pellet Techniques, *Astrophys. J.*, 648, (2006) L147-L150.