Geometric and Electronic Structures of Silicon Oxide Clusters

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A systematic study on the geometric and electronic structures of ground-state silicon oxide clusters (Si_nO_m, where n, $m = 1-8$) has been performed using molecular orbital and density functional theories. We find that most of the structures contain planar or buckled ring units. Pendent silicon atoms bonded only to a single oxygen atom are found in silicon-rich clusters. Oxygen-rich clusters have perpendicular planar rings, while silicon monoxide like clusters usually form a large buckled ring. Structures made up of tetrahedrally bonded units are found only in two clusters. Furthermore, the energy gap and net charge distribution for clusters with different silicon:oxygen ratios have been calculated.

Introduction

Silicon oxide plays important roles in many fields such as electronics, optical communications, and thin-film technology.[1,2] It is highly desirable that the atomic-scale structures of the various silicon polymorphs be better understood. The study of small silicon oxide clusters (Si_nO_m, with different m and n) should provide useful information pertaining to silicon surface oxidation and defects in bulk silicon. Interesting questions include (1) whether bulk structural motifs can be found in small clusters, (2) how oxide defects can be modeled at the atomic level, and (3) whether one can provide better evidence to support the more important experimental interpretations. Much interest has been generated in the investigations of Si_nO_m clusters theoretically and experimentally.[3–7,11–13] Theoretical studies on possible stable structures of $(SiO_2)_n$ ($n = 1-8$, 18) clusters were reported by Harkless et al. using molecular dynamics and an additive pair interaction potential.[5] They found that (1) the small silicon dioxide clusters bear no structural resemblance to the crystalline SiO_2 polymorphs and (2) there is indication of the occurrence of valences +3 and +5 for the silicon atoms on the surface of bulk crystalline silica phases. Neutral and charged $(SiO)_n$ ($n = 3-5$) clusters and their photoemission spectra (PES) have been studied by Chelikowsky using the pseudopotential method and Langevin dynamics.[12] There was good agreement between the simulated spectra and measured spectra. New buckled structures were also revealed for Si_4O_4 and Si_5O_5 clusters. On the other hand, Nayak et al. have theoretically studied the $(SiO_2)_n$ ($n = 1-6$) and Si_3O_m ($m = 1, 3, 4$) clusters.[11] They discussed the electronic properties including binding energy, ionization potentials, and HOMO–LUMO gap, as well as their dependence on cluster size and silicon:oxygen ratio. Theoretical investigations were also carried out on doubly negative Si_2O_m ($m = 4, 5$) clusters using Hartree–Fock and configuration-interaction theories.[7] In a series of experimental and theoretical reports, Wang et al. discussed the PES and structures of $(SiO)_n$ ($n = 3-5$), $(SiO_2)_n$ ($n = 1-4$), $Si(SiO_2)_n$ ($n = 2, 3$), and Si_3O_m ($m = 1-6$) clusters.[4,6,13] Large changes in the geometry after the neutral clusters are ionized have been revealed, and a Si_3O_4 cluster has been proposed to model oxygen-deficient defects in bulk silicon oxide.[4,6,13]

Interests in silicon oxide clusters have been renewed after the recent synthesis of nanomaterials, particularly silicon nanowires, because of their potential applications in future nanotechnologies. Experiments in our laboratory have shown that the yield of silicon nanowires will be greatly enhanced if silicon oxide is present during the synthesis.[8] In addition, silicon nanoparticles or silicon nanoclusters embedded in SiO_2 films are the origin of the photoluminescent (PL) peaks. Their relationship has been clearly observed by high-resolution transmission electron microscopy (HRTEM) recently.[9,10] Detailed studies on silicon oxide clusters with various Si:O ratios should provide crucial information with regard to the design and growth of silicon nanosized structures. However, the silicon oxide cluster systems studied previously are mainly $(SiO)_n$, $(SiO_2)_n$, and Si_3O_n with limited variations of "n", and thus are far from sufficient for such a purpose.

In this work, we explore the structures and electronic properties of Si_nO_m (n, $m = 1-8$) clusters by theoretical approaches. Both semiempirical molecular orbital and density functional (DFT) calculations were used to search for the ground-state structures, and the structural parameters, energy gap, and charge distribution are subsequently evaluated.

Theoretical Approach and Computation

The semiempirical molecular orbital PM3 method[14] has often been used to study the conformation of different molecular systems, especially those composed of the lighter elements such as those in the first two rows of the periodic table. The method is very efficient and able to produce reliable results. The PM3 method was first used to find all the potential ground-state structures. Afterward, a more accurate method, the density functional B3LYP, which adopts the Becke-type three-parameter density functional,[15] was used for further geometric optimizations to identify the lowest energy structure from the structures obtained in the PM3 calculation.

In this work, we have to deal with different configurations of many clusters with sizes ranging from a few to nearly 20 atoms. To achieve a balance between getting high accuracy and

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minimizing computational time in our first-principle calculation, a scheme involving the selection of economic basis set[16] is adopted in this work. We choose 3-21G for silicon atoms and 6-31G* for oxygen atoms in our calculation. Using this composite basis set, the predicted structures are the best in comparison with those obtained using the 3-21G or 6-31G basis set. The largest discrepancy of the bond lengths/bond angles predicted using the composite basis set from those using the standard 6-31G* basis set is below 0.03 Å/1.5° for the present silicon−oxygen systems. High-level single-point energy calculation with the standard basis set 6-31G* is further performed using the preliminary geometry parameters deduced from the result based on the composite basis set (6-31G*:O; 3-21G:Si). This economic scheme allows us to obtain the correct order of the energy of different isomers of a cluster and at the same time save CPU time and memory significantly, as compared with those using standard high-level 6-31G* and 6-311G*. In this way, binding energies of $(SiO_2)_n$ ($n = 1-4$) and dipole moments of $(SiO)_n$ ($n = 1, 4, 5$) determined using the economic scheme in Hartree−Fock, MP2, GGA, and B3LYP calculations are found comparable with those using higher-level basis sets such as 6-31+G* and 6-311G**.[17] In addition, geometric optimizations using the standard basis set 6-31G* for small Si_nO_m ($n + m < 10$) clusters have further confirmed the structures deduced using the composite basis set in B3LYP calculations. Therefore, we believe that the geometric structures and ground-state energies predicted by the present approach are sufficiently reliable to understand the various issues related to the gas-phase silicon oxide systems.

Geometric Structures of Silicon Oxide Clusters

We have made an exhaustive search for the ground-state structures of Si_nO_m (n, m = 1−8) clusters. It should be noted that the structures of Si_nO_m clusters with large n and small m such as Si_8O_m (m = 1−3), Si_7O_m (m = 1, 2), Si_6O_1, and Si_5O_1 have not been successfully found because of a convergence problem. On the other hand, Si_1O_8 and Si_2O_8 have been found to be energetically unfavorable and thus will not be discussed any further. Totally, we have worked on ground-state structures of 55 different compositions, and most of them have not been reported previously (less than 20 of them have been studied in previous work). Our systematic study would lead to conclusions on the trends of geometric structures of each type of silicon oxide cluster.

Although the predicted ground-state structures are different for various m and n, most of them contain a ring or several small rings. On the basis of their structural features and related properties, these clusters can be divided into three types: oxygen-rich clusters, silicon-rich clusters, and silicon monoxide like clusters (Si:O ratio equal or close to 1).

Oxygen-Rich Clusters. These are Si_nO_m clusters with m ≥ n + 2. Most of them possess rhombuses (rhombohedral rings) as illustrated in Figure 1. Our calculation shows that three to six oxygen atoms are connected to the silicon atoms in the smaller clusters. SiO_4 is a highly strained tetrahedron (O−Si−O angles equal to 59.2° or 139.1°). The oxygen-rich Si_2O_4 cluster contains a rhombus. The larger the cluster size, the more rhombuses the clusters contain. These rhombuses are arranged in a chain with adjacent ones perpendicular to each other. Si_5O_7 and Si_6O_8 clusters have a six-atom ring with alternate silicon and oxygen atoms. Such a ring is perpendicular to the adjacent rhombuses. The Si−O bond lengths in these rings vary largely. The actual lengths are influenced by the presence of other attached oxygen atoms. When an additional oxygen atom is
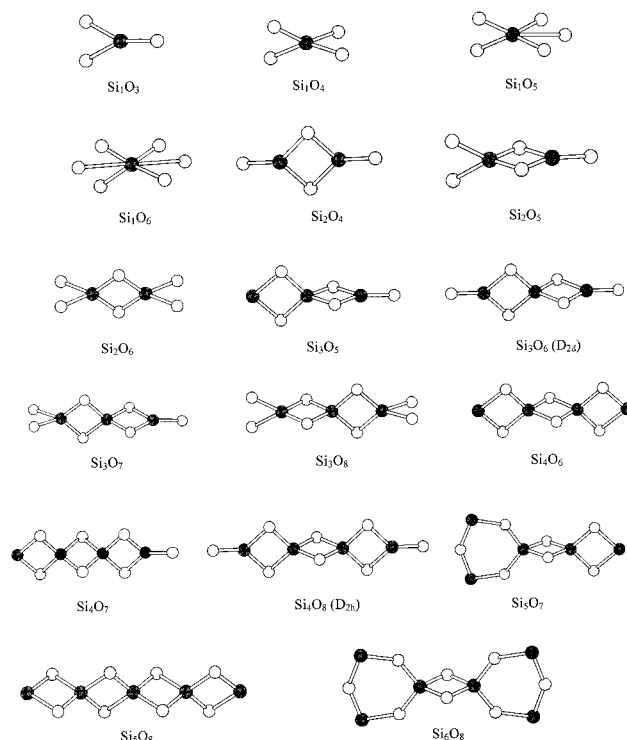
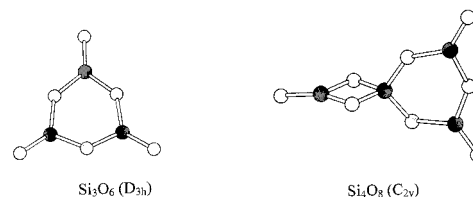**Figure 1.** Optimized structures of oxygen-rich clusters: ○, O; ●, Si.

Figure 2. Two isomers of Si_3O_6 and Si_4O_8 clusters: ○, O; ●, Si.

attached to a silicon atom in a rhombus, the resulting Si−O bond length is about 1.53 Å. When two oxygen atoms are attached, the Si−O bond length is about 1.66 Å. The bond angles of silicon in the rhombuses deviate greatly from 109.5° for a normal tetrahedron. However, some silicon bond angles in the hexagon rings of Si_5O_7 and Si_6O_8 are close to 109.5°. In summary, silicon atoms in oxygen-rich clusters can have coordination numbers of 2−6 and tend to show tetrahedral characteristics in larger clusters.

Harkless et al. explored the structures of neutral $(SiO_2)_n$ ($n = 1-8$) clusters using the additive pair interactions potential model.[5] Nayak et al. calculated and discussed the geometry of $(SiO_2)_n$ ($n = 1-6$) clusters with density functional theory.[11] Our present results on $(SiO_2)_n$ ($n = 1-4$) clusters compare well with those from the above studies. The Si−O bond in SiO_2 is 1.54 Å, quite close to the value of 1.53 Å obtained by Nayak et al. The two geometric structures of the trimer $(SiO_2)_3$ discussed in their works are shown in Figures 1 and 2. In this study, the structure with D_{2d} symmetry is found to be energetically more favorable than the isomer with D_{3h} symmetry. Their energies differ by 0.71 eV. For the tetramer $(SiO_2)_4$ (also shown in Figures 1 and 2), the energy of the C_{2v} structure is 0.53 eV higher than that of the D_{2h} structure. The present work is in agreement with Nayak's study in which the energy differences are 0.69 and 0.53 eV for the trimers and tetramers, respectively.[11] Nayak et al. have ascribed the stability of these clusters to the preference of 4-fold coordination for silicon and 2-fold coordination for oxygen. This view is applicable to our study on oxygen-rich clusters. However, in the silicon-rich or silicon
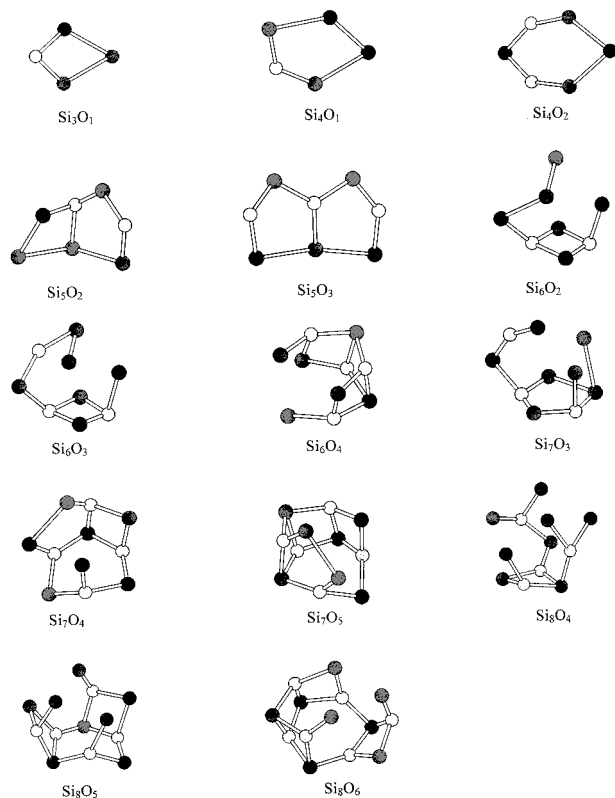
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Figure 3. Optimized structures of silicon-rich clusters: ○, O; ●, Si.

Figure 4. Optimized structures of SiO monoxide clusters: ○, O; ●, Si.

Figure 5. Optimized structures of $Si_{n-1}O_n$ ($n \leq 8$) clusters: ○, O; ●, Si.

monoxide like clusters where there are insufficient oxygen atoms to satisfy it, a 4-fold coordination for the silicon atom is rarely found. The 3-fold or 2-fold coordination of silicon and oxygen in these clusters is therefore a logical compromise and has been confirmed in this study.

Silicon-Rich Clusters. These are Si_nO_m clusters with m ≥ n + 2. Their ground-state structures are shown in Figure 3. For large clusters, pendent silicon atoms are found attached to either a ring or chain. For small clusters, the ring structure still dominates. The Si—O bond lengths range from 1.66 to 2.00 Å, while the Si—Si bond lengths range from 2.22 to 2.64 Å. Such a wide-range variation indicates that weak Si—Si and Si—O bonds exist in silicon-rich clusters, resulting in a high possibility of releasing some silicon atoms from the clusters. A silicon atom is found to have one to three neighboring atoms, while an oxygen atom has two or three. In fact, larger silicon-rich clusters can be viewed as being formed by the small Si_3O groups with their silicon atoms located at the corner connected to the adjacent groups. These clusters are energetically less favorable and are of unsaturated feature at their silicon atoms, suggesting that they may not be present in a significant amount in the gas phase. Unfortunately, no previous study is available for comparison.

Silicon Monoxide Like Clusters. Figure 4 illustrates the ground-state structures of silicon monoxide clusters, $(SiO)_n$. Among them, SiO is linear, while planar ring structures are found for both Si_2O_2 and Si_3O_3, and similar structures have been reported by Wang et al.[6] On the other hand, buckled-ring structures are found for Si_4O_4 and Si_5O_5. Two very competitive isomers have been obtained for Si_6O_6 and Si_7O_7. The first one follows the similar buckled-ring trend, and the second one has the configuration of a double-ring-like structure, connected to a third buckled rhombus (Si_8O_8 also shows such a structural feature). Wang et al. have predicted planar-ring structures for Si_4O_4 and Si_5O_5 clusters on the basis of their PES study.[6] On the contrary, buckled-ring structures were obtained for the same
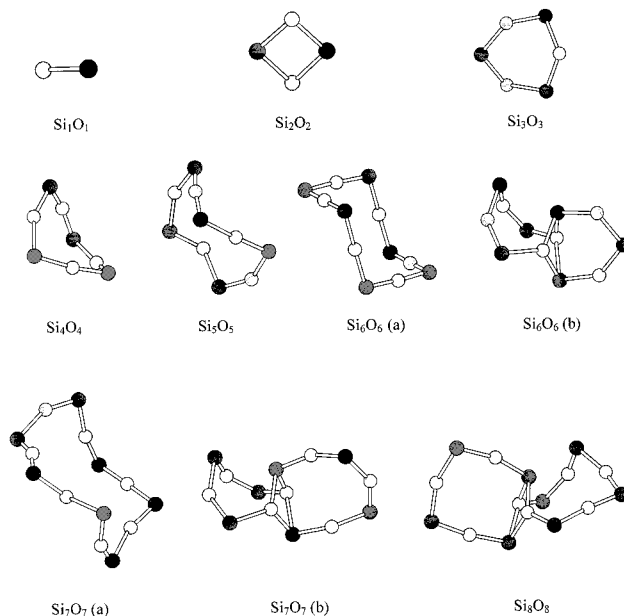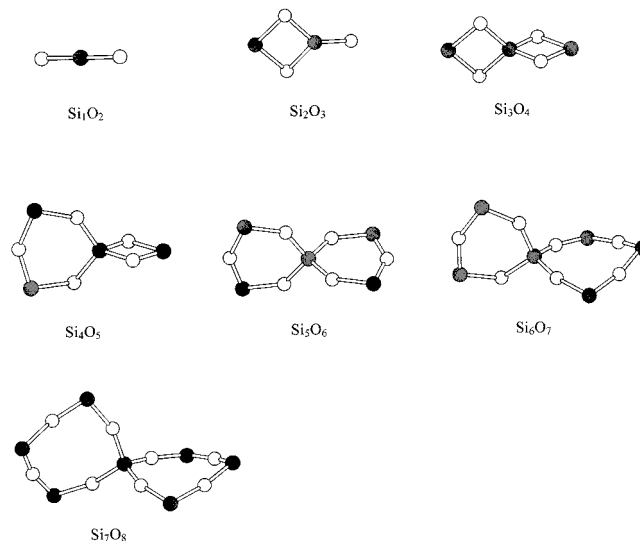
clusters in the study of Chelikowsky using the ab initio Troullier—Martins pseudopotential approach.[12] However, no previous reports can be found for larger clusters. It is noted that most Si—O bond lengths in these rings are from 1.6 to 1.8 Å. In addition, weak Si—O bonds with bond lengths from 1.91 to 2.06 Å are found in the rhombuses of Si_6O_6, Si_7O_7, and Si_8O_8. Their coordination number is found to be 2 for most of the silicon and oxygen. No tetrahedral structural units are found in these clusters.

The structures of $Si_{n-1}O_n$ clusters are shown in Figure 5. Except for SiO_2 possessing a linear structure and Si_2O_3 with an oxygen atom attached to one rhombus, the other clusters consist of two perpendicular rings similar to the $(SiO)_n$ ($n = 2-4$) clusters. The Si—O bond lengths in these rings vary from 1.65 to 1.75 Å. It is noteworthy that the exact tetrahedral angles are found in Si_5O_6 and Si_7O_8 involving a shared silicon atom and with Si—O bond lengths being 1.67 and 1.65 Å, respectively. The bulk motif is truly present in some small silicon clusters. The structural features of small clusters such as Si_1O_2, Si_2O_3, and Si_3O_4 revealed in this study are consistent with those from
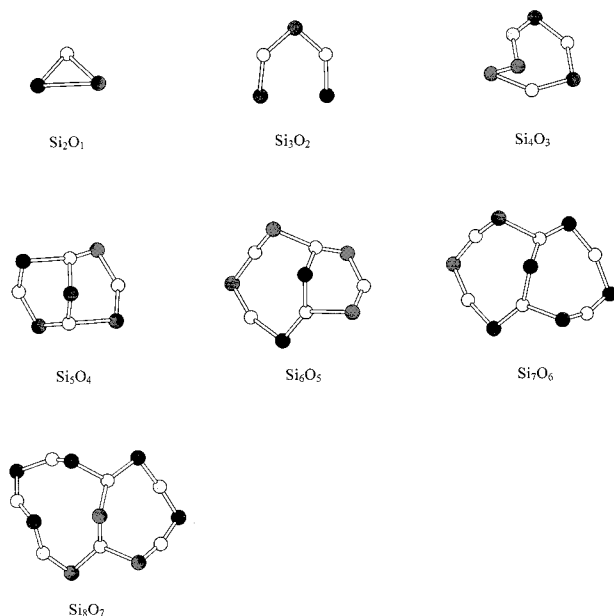
Figure 6. Optimized structures of Si_nO_{n-1} ($n \leq 8$) clusters: $\bigcirc$, O; $\bullet$, Si.

previous studies.[6,13] However, no information can be found for large clusters in this class in the literature.

The structures of Si_nO_{n-1} clusters are shown in Figure 6. A triangular structure is the most favorable for Si_2O_1, while Si_3O_2 forms an asymmetric pentagon and Si_4O_3 forms a buckled ring with one Si–Si bond of 2.41 Å. Furthermore, larger clusters are composed of two buckled rings where the Si–O bond lengths range from 1.67 to 1.96 Å.

In short, the small rings, especially a planar four-atom ring or rhombus (Si_2O_2), a planar six-atom ring (Si_3O_3), and a buckled eight-atom ring (Si_4O_4), are the basic building blocks of the ground states of the Si_nO_m clusters.

Electronic Structures of the Silicon Oxide Clusters

Energy Gaps and Discussion on Luminescence from Silicon Oxide. The highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of small silicon clusters have been considered as important factors in explaining the recent nanoparticle-related photoluminescence of SiO_2 films embedding silicon nanocrystals.[9,10] Although conventional theoretical approaches such as Hartree–Fock and DFT cannot describe accurately the HOMO–LUMO gap, they did provide qualitative information for interpreting or predicting luminescent properties of nanosized materials.[18,19] Figure 7 exhibits the HOMO–LUMO gap of all the silicon clusters as a function of the oxygen content. Other than minor fluctuations, an overall upward trend is apparent across the whole region. This trend indicates that the HOMO–LUMO gaps tend to be smaller for oxygen-deficient clusters. The difference in the gap among these small clusters may have a significant influence on the optical properties of materials with embedded silicon nanoparticles. When there are silicon particles in the SiO_2 films, the local stroichiometry will be altered by these nanoparticles. Oxygen-deficient clusters can be formed in these areas, keeping a rather small HOMO–LUMO gap. As assumed by Naysk et al.,[11] when the value of the gap decreases to that corresponding to visible light with decreasing oxygen content, photoluminescence will be possible and probable. Thus, nanoparticles and some photoluminescence peaks can be correlated.

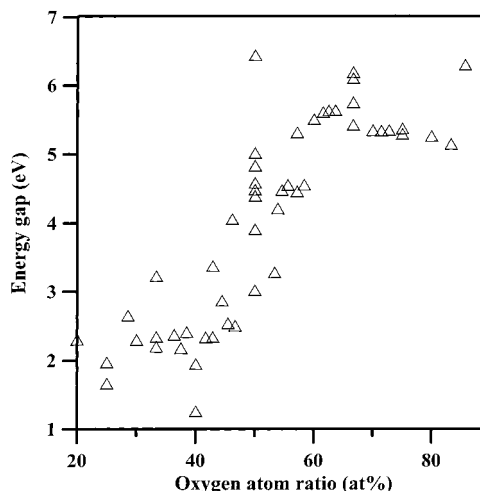A remarkable difference exists in silicon monoxide like clusters. For example, Si_1O_1 has the largest gap and Si_5O_5 has

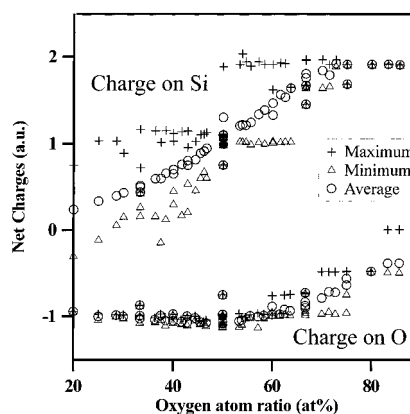**Figure 7.** HOMO–LUMO gap of Si_nO_m (n, $m \leq 8$) clusters.

Figure 8. Charge distribution of Si_nO_m (n, $m \leq 8$) clusters.

the smallest one, while other silicon monoxide like clusters possess gaps intermediate between them. However, the smallest gap of all is found in the Si_3O_2 cluster. Si_3O_2 is one of the Si_3O_m clusters proposed by Wang et al. to describe silicon surface oxidation and silicon bulk defect sites.[13] Our studies on the HOMO–LUMO gaps of Si_3O_m clusters can be used to understand the roles of these clusters with respect to the optical properties of bulk silicon. The gap variation with increasing oxygen percentage for Si_3O_m ($m = 1–6$) clusters also follows the overall trend of other silicon clusters. The calculated gaps for them are 1.86, 1.32, 4.65, 5.46, 5.79, and 5.92 eV, respectively, clearly showing the larger gap for oxygen-rich clusters. A similar trend has been found by Nayak et el. that the HOMO–LUMO gaps of Si_3O, Si_3O_4, and Si_3O_6, are, respectively, 1.19, 3.87, and 4.21 eV in calculations using a larger basis set at the generalized gradient approximation (GGA) level of theory.[11] Thus, our present study on the HOMO–LUMO gap of extensive silicon clusters can illustrate the gap dependence on composition.

Net Charge Distributions. Studies on the net charge distributions in these silicon clusters may provide useful information on building various force fields during the molecular mechanics/dynamics simulation of silicon oxide systems. Figure 8 shows the charge distribution on the silicon and oxygen atoms obtained in this work according to the Mulliken population analysis. The trend of charge distribution with various Si:O ratios in the silicon oxide clusters has been further confirmed in this work by those predicted via the theory of atoms in a molecule.[20] Our results of charge residing on each atom of each cluster are too large in amount to show here in their entirety. To show the

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trend of charge distribution with cluster composition, only representative indices such as maximum, minimum, and average charges are given here. As for the charges on silicon atoms, our result shows that there is a large variation of charges on the silicon atoms in silicon-rich clusters. The maximum and minimum charges on silicon atoms differ greatly in silicon-rich clusters, and this difference becomes smaller for silicon monoxide like clusters. For oxygen-rich clusters, the difference between the maximum and minimum charges increases again. Next, we discuss the charges on the oxygen atoms. They tend to be quite similar for silicon-rich and silicon monoxide like clusters. Only when the oxygen percentage gets above 50% does the difference between the maximum and minimum charges on the oxygen atoms become obvious. In silicon-rich clusters, the charges vary much more on silicon atoms than on oxygen atoms. The increase of the average charge with increasing oxygen percentage indicates that charge transfer from oxygen to silicon becomes more apparent in oxygen-rich clusters. The average charge on the oxygen atoms shows a minimum when the oxygen content is 50%. This shows that the charges on the oxygen atoms become most negative for silicon monoxide like clusters. It should also be noted that, in some silicon-rich or oxygen-rich clusters, negative charges can be found on some silicon atoms and positive charges on some oxygen atoms. This is contrary to what is observed for most other clusters.

Conclusion

The ground-state structures of small silicon oxide clusters contain small planar or buckled-ring units. Pendent silicon atoms may bond only to one oxygen atom in silicon-rich clusters. Oxygen-rich clusters have perpendicular planar rings, whereas silicon monoxide like clusters usually form a large buckled ring. The HOMO−LUMO gap tends to increase with the oxygen content. The charges residing on oxygen atoms are rather uniform, while the charges vary much more on silicon atoms.

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