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Stable tetrahedral structure of the silica cluster $(\mathrm{SiO_2})_{10}$

M. W. Zhao,* R. Q. Zhang,† and S. T. Lee
Centre of Super-Diamond and Advanced Films (COSDAF) & Department of Physics and Materials Science,
City University of Hong Kong, Hong Kong SAR, China

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We report an extremely energetically favorable tetrahedral structure of the $(\mathrm{SiO_2})_{10}$ cluster predicted by density-functional calculations. This structure is predicted to have an electronic energy gap lower than its isomers reported early and bulk α-quartz, highly localized frontier orbitals at the nonbridging oxygen atoms, a unique IR spectrum, and a propensity to assemble into a variety of higher-dimension structures. This structure, if synthesized, is expected to not only provide a new porous material, but also to have potential applications, particularly in surface technology.

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I. INTRODUCTION

Silica clusters have attracted considerable attention because of their important technical applications in nanoelectronics and optics. Experimentally, silica clusters can be synthesized through different methods, including combustion, plasmas, thermal reactors, evaporation-condensation, and gas-phase reactions in flames.[1–4] It has been revealed that silica clusters display different electronic and optical properties from the surface of bulk materials in many experiments, ranging from light adsorption[5] to photoluminescence.[6–8] The localized states appearing at the band tail and the narrowing of the band gap revealed in photo absorption are mainly attributed to the structural defects, such as nonbridging oxygen (NBO) created in the growth of silica clusters.[5] Similar to $\mathrm{SiO_2}$ glass, the NBOs in silica clusters may dominate the visible and near ultraviolet (UV) absorption.[9] These unique electronic and optical properties of silica clusters make them promising candidates for building silica-based nanodevices. In order to understand these properties, the determination of stable geometries of silica clusters is highly desirable. Theoretical studies on small silica clusters indicate diverse morphologies quite different from the network of silicon-centered corner-sharing $\mathrm{SiO_4}$ tetrahedra of bulk silica, where six-membered rings (6 MRs) are found to be the most frequent. According to density-functional (DF) calculations, for $n<7$, silica cluster $(\mathrm{SiO_2})_\mathrm{n}$ chains, formed by edge-sharing two-membered rings (2 MRs) terminated at each end by a NBO, are predicted to be the most thermodynamically stable form, favored over all other such stoichiometric silica clusters that compose of three- or four-membered rings (3,4 MRs).[10,11] The linear chain can be further scrolled to a molecular ring by joining the NBOs at both ends of the chain which outweighs the energetic disadvantage of strain needed to form the molecular ring for large clusters. High-level DF calculations show such fully coordinated silica clusters to be energetically more stable than the corresponding linear chains as $n>11$.[12] However, due to the high intrinsic internal strain existing in 2 MRs,[13–16] this molecular ring is unfit for modeling relatively large clusters. Recently, using highly-efficient DF calculations we revealed that silica clusters with a configuration of linked 3MRs are energetically more favorable than the fully coordinated molecular rings of the same size as $n>25$. The high thermal stability, low intrinsic internal strain, and good extendibility to three-dimensional networks of these new structures make them reasonable models of strained extended silica systems and useful precursors for new bulk-silica polymorphs with tubular or porous morphologies.[17] Apart from these possible configurations, elongated and compact types of structures in silica clusters $(\mathrm{SiO_2})_\mathrm{n}$ for n ranging from 12 to 46 were also investigated using plane-wave DF calculations. The structural transition from an elongated to a compact structure is predicted to occur at the point of $n=38$.[18] Both elongated and compact types of silica clusters contain large-membered rings, including 4MRs and 5MRs, apart from 2MRs.

Here, we report a structure of $(\mathrm{SiO_2})_{10}$ cluster having edge-sharing 3MRs with each silicon atom being fully coordinated. DF calculations show that this tetrahedral morphology is energetically more favorable than its isomers reported so far. This cluster, if synthesized, may have potential applications in building a film with special electronic and optical properties.

II. COMPUTATIONAL DETAILS AND MODELS

DF calculations were performed using the *Gaussian 98* package,[19] and a Becke-type three parameter and hybrid exchange-correlation functional, namely B3LYP.[20,21] The validity of DF calculations in reproducing the properties of silica clusters obtained from both experimental studies and other high-level calculations has been demonstrated in many previous studies.[10–12] Cluster geometries were first relaxed with an efficient *ab initio* code known as SIESTA,[22,23] and then further optimized at the B3LYP/6-31G* level without any symmetry constraints. Single-point calculations at the B3LYP/6-311+G* level based on the optimized geometries at the B3LYP/6-31G* level were performed to obtain the energetic order of the isomers at $n=10$ with a higher accuracy. Binding energies were calculated from the difference between the total energy of a cluster and the energy of the corresponding isolated triplet-state O and Si atoms at the same level.

We conducted a careful systematic search for the energetically favorable configurations of silica clusters $(\mathrm{SiO_2})_\mathrm{n}$ (n

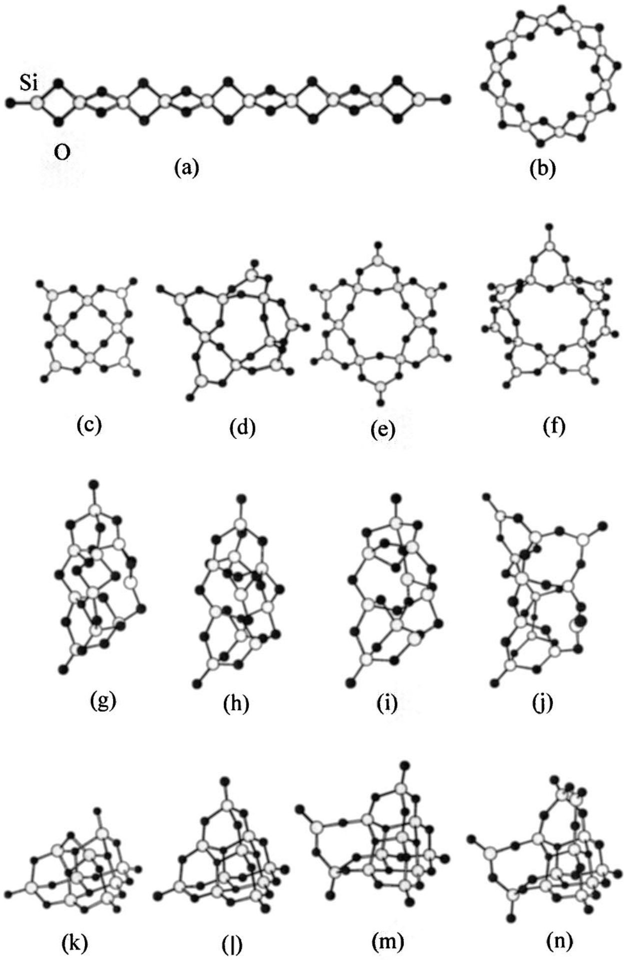

FIG. 1. Geometries of silica clusters $(SiO_2)_n$ optimized at B3LYP/6-31G* level of theory: (a) 2MR-based chain for $n=10$; (b) molecular ring based on 2MRs for $n=10$; (c)–(f) 3MR-based molecular rings (for $n=8$, 10, 12, and 14); (g)–(j) elongated structures (for $n=9$, 10, 11, and 12), and (k)–(n) tetrahedral-like structures (for $n=9$, 10, 11, and 12).

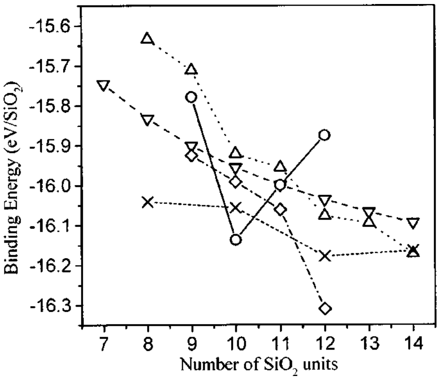

FIG. 2. Binding energies of silica clusters with different structures, 2MR-based linear chain [Fig. 1(a) for $n=10$] (down triangles), 2MR-based molecular ring [Fig. 1(b) for $n=10$) (up triangles), molecular ring based on 3MRs [Figs. 1(c)–1(f)] (crosses), elongated configuration [Figs. 1(g)–1(j)] (open diamonds), and 3MR-based tetrahedra [Figs. 1(k)–1(n)] (opened circles), as a function of the number of SiO_2 units contained.

$=7-14$). We first considered four structures that have been reported before to be energetically favorable. The first two are based on 2MRs: linear chain [Fig. 1(a)] and ring [Fig. 1(b)], which have been revealed to be the energetically favorable structures for silica clusters $(SiO_2)_n$ $(n<7)$[10,11] and $(SiO_2)_n$ $(n>11)$.[12] The third model is based on 3MR-based rings [Figs. 1(c)–1(f)].[17] Buckled chain structures based on 3MRs were not considered since it has been shown to be energetically unfavorable.[17] The fourth is the so-called elongated model [Figs. 1(g)–1(j)] which has been predicted to be also energetically favorable.[18]

In searching for energetically more favorable structures, we analyzed the formation principles of the previously-revealed energetically favorable structures, including the above-mentioned ones. It is clear that the reductions of the fraction of NBOs and the internal strain are the key factors to minimize the energy cost so as to make the structure more favorable. For instance, the geometry with D_{3h} symmetry (containing a 3MR) for a small silica cluster Si_3O_6 is energetically less favorable than its isomer with D_{2d} symmetry (consisting of two linked 2MRs) by 0.71 eV,[11] mainly due to the higher fraction of NBOs in the D_{3h} configuration. However, this energetic disadvantage could be outweighed by the lower intrinsic internal strain existing in 3MRs for larger clusters,[13–16] especially when a ring or more compact structure is formed. By considering these factors, we further constructed a new kind of structures based on 3MRs, which have tetrahedral-like configurations containing edge-sharing 3MRs [Figs. 1(k)–1(n)]. We find that the new structures have a minimum number of NBOs and reasonable atomic coordinates at $n=10$ and thus could be expected to be energetically very favorable at that particular size.

III. RESULTS AND DISCUSSION

The binding energies per (SiO_2) unit of silica clusters constructed with these models as a function of cluster size are shown in Fig. 2. Clusters with both a 2MR-based linear chain and a ring have a binding energy that decreases monotonously with increasing size at different rates. As $n>11$, 2MR-based ring structures become energetically more stable than the corresponding chain configurations based on 2MR. The difference in energetic stability between ring and chain structures is 0.0214 eV/SiO_2 at B3LYP/6-311+G*//B3LYP/6-31G* level of theory, which is very close to the 0.024 eV/SiO_2 at B3LYP/6-311+G* level of theory.[12] However, our results clearly show that even for $n<11$ 2MR-based rings are energetically less favorable than their isomers constructed based on 3MRs and the elongated models. The variations of binding energy as a function of cluster sizes corresponding to different models cross as n varying from 7 to 14. For $n=8$, the structure containing 3MRs [Fig. 1(c)] is more stable. However, at $n=10$ the 3MR-based tetrahedra [Fig. 1(l)] becomes energetically more favorable than the others, including the chain isomer based on 2MRs [Fig. 1(a)] and molecular ring based on 3MRs [Fig. 1(d)]. The structural feature of the model indicates a high possibility for it to be used as a building block for functional mate-

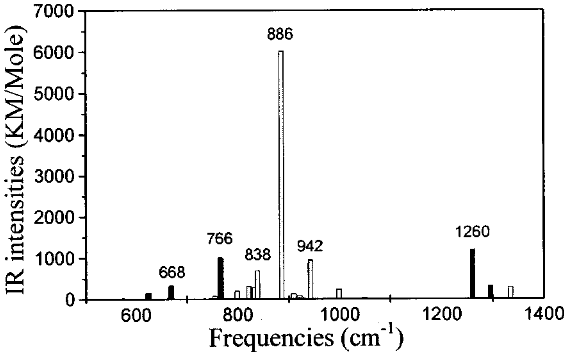

FIG. 3. The IR spectrum of $(SiO_2)_{10}$ cluster with tetrahedral structure (the black bars) and 2MR-based molecular chain (the gray bars).

rials. Such a possibility could not be seen from the elongated model [Fig. 1(j)], although it becomes energetically more favorable than other models at $n=12$.

For $(SiO_2)_{10}$, the calculations at the level of B3LYP/6-311+G*//B3LYP/6-31G* show that the 3MR-based tetrahedra [Fig. 1(l)] and the molecular ring [Fig. 1(d)] are more stable than the 2MR-based chain, which was expected to be the most stable configuration of $(SiO_2)_{10}$ cluster in literatures, by about 0.29 eV/SiO_2 and 0.226 eV/SiO_2, respectively. The stabilization of these structures is mainly attributed to the less strain involved in 3MRs compared with 2MRs.[13–16] Although the molecular rings based on 3MRs contain more NBOs than the 2MR-based chain and ring structures, the advantage can be outweighed by the lower strain in the 3MR-based structure. The tetrahedral structure of $(SiO_2)_{10}$ has an additional advantage over the 3MR-based ring, in which each silicon atom is fully coordinated and is therefore more stable by about 0.064 eV/SiO_2 in binding energy. Four overcoordinated oxygen atoms are involved in the tetrahedra with a Si—O bond length of 1.802 Å that is longer than other Si—O bonds (from 1.573 to 1.749 Å). There are four NBOs in the corners of the tetrahedra with a bond length of 1.515 Å. It is noteworthy that the chemical environment of NBOs in the tetrahedra ($\equiv$Si—O·) is different from that of NBOs in the 2MR-based chain ($=$Si$=$O), which may result in different electronic and optical properties. In addition, silica clusters for $n=9$, 11, and 12, constructed following the tetrahedral configuration, have higher binding energy per SiO_2 unit than the tetrahedral $(SiO_2)_{10}$ cluster (Fig. 2) due to the 2MRs and higher fraction of NBOs involved in these clusters. Therefore, the $(SiO_2)_{10}$ is an exceptional cluster in this model, and may exist in silica clusters generated by combustion or other methods because of its higher energetic stability.

The $(SiO_2)_{10}$ cluster with a tetrahedral structure possesses IR bands characteristically distinct from those of the 2MR-based chain. The calculation of harmonic frequencies of the $(SiO_2)_{10}$ 2 MR-based chain [Fig. 1(a)] at the B3LYP/6-31G* level gives three prominent modes (886, 942, and 838 cm^{-1}), whereas for the tetrahedral structure [Fig. 1(l)] the prominent modes are 1260, 766, and 668 cm^{-1}, as shown in Fig. 3. The mode at 1260 cm^{-1} is of relatively high intensity at high frequency, and thus can be treated as the signature of the tetrahedral structure of $(SiO_2)_{10}$. In addition, the IR bands of tetrahedral $(SiO_2)_{10}$ cluster are quite different from those of dehydrated silica surfaces obtained from infrared measurements (908, 888, and 932 cm^{-1}),[24] indicating that this structure is unlikely to be created on the surface of silica through surface reconstruction. However, our simulations revealed that a similar configuration could be obtained through annealing the structure cut from bulk α-quartz, suggesting a higher probability of generating this cluster through combustion or plasma.

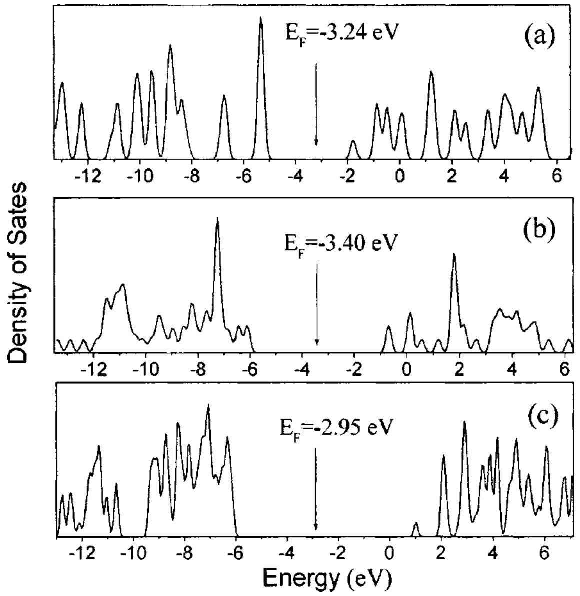

FIG. 4. The density of states (DOS) of (a) $(SiO_2)_{10}$ cluster with tetrahedral structure [Fig. 1(a) (l)], (b) $(SiO_2)_{10}$ with 2 MR-based molecular chain [Fig. 1(a)], and (c) bulk α-quartz. The Fermi levels (E_F) are also presented.

The tetrahedral $(SiO_2)_{10}$ cluster, as shown in Fig.1(l) also possesses a smaller energy band gap than those of both 2MR-based chain [Fig. 1(a)] and α-quartz, as revealed in our calculations using the SIESTA (Fig. 4). The band gaps of the tetrahedral $(SiO_2)_{10}$, the 2MR-based chain structure, and α-quartz are 2.81, 4.75, and 6.61 eV, respectively.[25] Although theoretical calculations predict a smaller band gap of α-quartz than the experimental value 9.2 eV,[26] it is believed that the trend of band gaps from theoretical calculations is valid. Since the electronic density of states (DOS) characterizes the electronic and optical properties, the tetrahedral $(SiO_2)_{10}$ clusters with a small band gap may possess different electronic and optical properties from those of α-quartz and other isomers. Further analysis shows that the highest occupied molecular orbital (HOMO) of tetrahedral $(SiO_2)_{10}$ cluster is highly localized on the four NBOs at the corners of the tetrahedra, making these regions highly reactive centers. Recently, theoretical and experimental studies have revealed that the oxygen dangling bond $\equiv$Si—O·, which is often denoted as a nonbridging oxygen hole center (NBOHC), usually dominates the absorption spectrum of irradiated silica by its well-known optical absorption bands at 2.0, 4.8, and 6.8 eV.[9,27] We notice that the chemical environment of the NBO in tetrahedral $(SiO_2)_{10}$ cluster [Fig.1 (l)] is quite similar

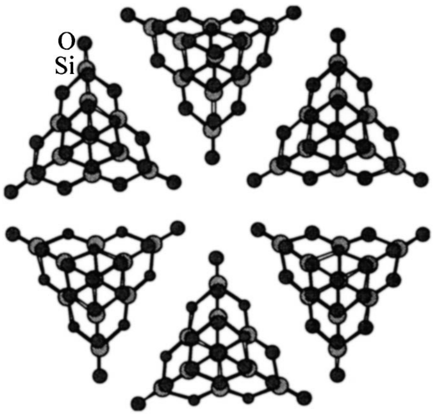

FIG. 5. The predicted structure (top view) of 3MR-based tetrahedral $(SiO_2)_{10}$ clusters deposited orderly on the surface of a substrate.

to that of NBOHC. We therefore conjecture that the NBOs in tetrahedral $(SiO_2)_{10}$ clusters may also result in the visible and near ultraviolet (UV) absorption spectrum similar to irradiated silica.

The high reactivity of NBOs in tetrahedral $(SiO_2)_{10}$ clusters makes the clusters easily bind to the surface of a substrate, such as silicon, forming a film of $(SiO_2)_{10}$ clusters. A highly ordered structure, such as a hexagonal structure, as shown in Fig. 5, may be formed, probably via the interactions between cluster and substrate and between clusters themselves. These aligned tetrahedral clusters in the film would act as a matrix sensor because of their unique electronic and optical properties. This kind of film, if synthesized, may have wide applications in nanoscience and technology.

IV. CONCLUSION

We have proposed here a structure mode of $(SiO_2)_{10}$ cluster that was found to be energetically more favorable than its isomers reported in earlier studies. We conjecture that the film composed of this cluster may have a potential application as microsensors due to its unique electronic and optical properties.

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*On leave from Faculty of Physics, Shandong University, Jinan, Shandong 250100, China.

†Email address: aprqz@cityu.edu.hk

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ployed was generalized gradient approximation (GGA) in the form of Perdew, Burke, and Ernzerhof. The basis sets were double-ζ plus polarization orbitals (DZP). The charge density was projected on a real space grid with an equivalent cutoff 100 Ry. Silica clusters were initially relaxed at the temperature of 500 K for 1.0 ps using a Nose algorithm, then cooled down to 0 K, and finally optimized by a conjugate gradient approach. The thickness of the vacuum layer around these clusters was set to 10 Å to exclude the interaction between clusters in the neighboring unit cells.

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