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Stability of elongated and compact types of structures in SiO_2 nanoparticles

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The stability of elongated and compact types of structure in SiO_2 nanoparticles was studied using plane-wave density-functional theory. Calculations were carried out on small SiO_2 nanoparticles with 12–46 molecules. It is found that elongated structures are favored for particles consisting of less than 38 molecules of SiO_2. In contrast, nanoparticles containing more than 38 molecules favor the compact (spherical) structures. This indicates that the structural transition from elongated to compact structures occurs at a size of around 38 molecules. Several low-energy isomers of elongated types of structure for different sizes of SiO_2 nanoparticles have been characterized. The nanoparticles are found to consist of various types of silica rings (four-, five-, and/or six-membered rings), similar to vitreous silica in bulk. The elongated structures consist of rather regular and symmetric silica rings, while the compact structures consist of considerably distorted silica rings. In particular, the elongated structures consisting of five-membered rings with the top and bottom layers being connected in the form of four-membered rings are relatively stable, leading to very regular and symmetric structures. The elongated types of structures might be proposed for the atomic structures of silica nanowires.

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Silica nanoparticles are interesting because of their important technical applications in electronics and optics of nanodevices. It is also of fundamental importance to understand their properties. Structural defects formed on the surface of bulk materials are particularly important, since different types of structural defects on the surface mainly determine their unique surface properties, and therefore, influence the performance of the electronic and optical devices.[1,2] It has been shown that the electronic and optical properties of silica nanoparticles are different from those of the surface in bulk materials through experiments on light absorption,[3] FTIR spectra, and photoluminescence.[4–6] In particular, the structural defects lead to the narrowing of band gap and the formation of localized states within band tail, which were experimentally measured from light-absorption study of silica nanoparticles.[3] However, very few theoretical works have been done on silica nanoparticles despite the observed interesting properties.

The structural transition from elongated to compact structures has been experimentally observed in silicon clusters of intermediate size, Si_n $(20 \leqslant n \leqslant 25)$.[7] Theoretically, a variety of low-energy isomers has been found and the stability of the elongated versus compact types of structure has been extensively studied.[8] The structure transition of germanium cluster ions also appears to occur at around 70 atoms.[9] Recently, Ge nanoparticles with spherical shapes in the range of 28–300 atoms have been studied using a combination of empirical and first-principles molecular-dynamics techniques.[10] However, the structures, stability, and properties of silica nanoparticles and clusters have rarely been studied by both experimental investigation and atomic- and molecular-level calculations, because of the difficulties involved in SiO_2 cluster generation and in theoretical calculations of large cluster structures.[11] In the literature, magic numbers of silica clusters in solution with four and eight molecules have been reported,[11] and these magic numbers have led to an extensive study of atomic and molecular silica-based clusters.[12] However, efforts to study the molecular structures of silica clusters have been restricted to small size clusters consisting of less than 10 molecules.[13–15] Recently, silica nanowires have been synthesized in the form of amorphous materials,[16] similar to the crystalline semiconductor nanowires of Si and Ge.[17]

In the present study, we explore the stability of elongated and compact types of structures in SiO_2 nanoparticles using plane-wave density-functional theory (DFT). Calculations were carried out on small SiO_2 nanoparticles with 12–46 molecules. The effects of size, morphology, and different types of silica rings of nanoparticles on the minimum energies and their electronic and optical properties are discussed. Several low-energy isomers of the elongated types of structure for different size of SiO_2 nanoparticles were obtained and characterized.

The DFT calculations were carried out using Vienna *ab initio* simulation program (VASP).[18] VASP is a plane-wave DFT code based on the local-density approximation and generalized gradient corrections (GGC) using the Perdew-Wang 91 functional.[19] In addition, the ultrasoft Vanderbilt pseudopotential[20] and spin polarization were used. The energy cutoffs were 20 Ry for the wave functions and 41 Ry for the augmented electron density. Our calculations were done on 12–46 molecule cells with a 10 Å vacuum size. The Brillouin zone of the cell was sampled only at the Γ point. Optimization of the structures was carried out using an iterative conjugate gradient minimization scheme. The DFT calculations underestimate the band gap energies when compared with experimental estimates. However, spin-polarized DFT calculations have been studied to satisfactorily represent both the geometrical structures and relative energy of different configurations for localized states by comparing DFT, Hartree-Fock (HF), Moller-Plesset perturbation (MP2), and Complete active space-self-consistent-field-results (CAS-SCF) calculations.[21–23]

In order to find fully reconstructed structures for silica nanoparticles, we used a combination of empirical and DFT-GGC techniques. For the compact type of structures, we started with perfect and amorphous bulk systems and cut the systems to obtain nanoparticles of three different sizes including 12-, 24-, and 45-molecules. We melted the nanoparticle by heating it up to 3000 K, 2700 K, and 2300 K for 10 000 ps using classical molecular dynamics with a Beest-Kramer-Santen (BKS) potential.[24] On the other hand, the elongated type of structures were obtained by sintering of nanoparticles. As a starting configuration, we used the lowest energy structures of spherical type of nanoparticles, six-, 12-, and 24-molecules. The replicate nanoparticles were placed in contact, i.e., at a distance equal to the nearest-neighbor distance and melted at 3000 K and 2000 K for 60 000 ps using classical molecular dynamics with a BKS potential. The temperature was then slowly decreased to 0 K. The final structures were then fully relaxed within the DFT-GGC until the interatomic forces were smaller than 0.001 eV/Å.

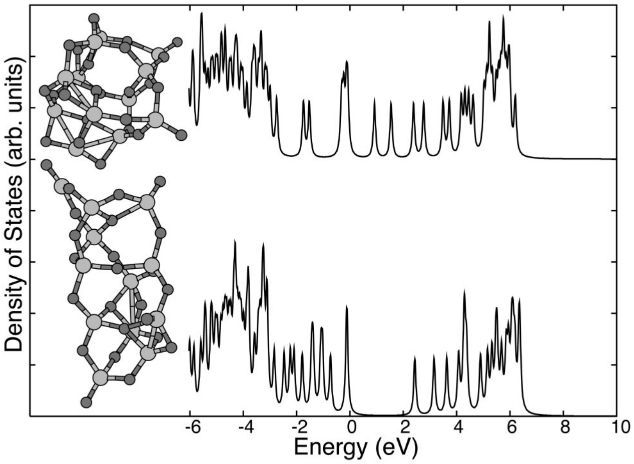

FIG. 1. The geometrical structures and density of states (DOS) of low-energy isomers containing 12 molecules of SiO_2 for the compact (top) and elongated (bottom) types of structures.

The geometrical structures of low-energy isomers of SiO_2 containing 12 molecules are shown in Fig. 1. The elongated type of structure given in Fig. 1 (bottom) has an energy approximately 0.10 eV per molecule lower than that of the compact type of structure shown in Fig. 1 (top). Several compact types of structure exist [refer to Fig. 1(a) showing the most stable one found for the compact types of structure]. For the compact types of structure, it was found that the more spherical and compact the nanoparticle, the more stable the structure. For both elongated and compact types of structures, the defects formed in the structure consist of dangling bonds on O atoms and high-fold coordinates due to Si-Si bonds. The structure is stabilized by forming a double bond from the dangling bond, which has a shorter bond length (approximately 1.48 Å) than that of a single bond (approximately 1.61 Å). The compact type of structure consists of eight overcoordinated Si atoms, while the elongated type of structure consists of four overcoordinated Si atoms. The electronic density of states (DOS) characterize the electronic and optical properties, in particular, the defect states locate around the Fermi level (0.0 eV). Figure 1 displays the DOS for the compact (top trace) and elongated (bottom trace) types of structures by using a Lorentzian broadening function of the discrete molecular eigenvalues with a broadening of 0.05 eV. The band gap is obtained as the difference between the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital). It is found that the elongated structure of small silica nanoparticles containing 12 molecules has a larger band gap energy, 2.5 eV, than the compact structure, 1.0 eV. This shows that the increase of defect concentration due to the overcoordinated Si atoms leads to the narrowing of the band gap energy. Note that DFT cannot be expected to give accurate band gap energies, but it can provide their trends. It is interesting to note that the different types of structure result in different electronic and optical properties.

Several low-energy isomers of silica nanoparticles containing 24 molecules are shown in the Fig. 2. Figure 2(a) shows a compact type of structure, whereas Figs. 2(b), 2(c), and 2(d) show three different elongated types of structure. The elongated structure of Fig. 2(b) is the most stable and has an energy lower by 0.11 eV per molecule than the compact structure in Fig. 2(a). Figure 2(b) consists of a six-membered ring and five-membered rings, with the top and bottom layers being connected in the form of four-membered rings. Figure 2(c) is composed of five-membered rings with the top and bottom layers being connected in the form of four-membered rings. On the other hand, Fig. 2(d) shows the connections between five-membered and four-membered rings with the top and bottom layers being connected in the form of four-membered rings. The total energy per molecule of Fig. 2(c) is higher by only 0.06 eV per molecule than that of Fig. 2(b), while that of Fig. 2(d) is higher by 0.20 eV per molecule. It is noted that the elongated structure consisting of five-membered rings with the top and bottom layers being connected in the form of four-membered rings is relatively stable and results in a regular and symmetric configuration. This suggests that such rather regular and symmetric structures could be formed for very small nanoparticles. Amorphous bulk silica has been shown to have various ring sizes.[25,26] Theoretical geometries of silica rings have been modeled by the semiempirical quantum molecular orbital methods named Austin model 1 (AM1) and parametric method 3 (PM3).[25,26] AM1 predicted that the five-membered ring is the most stable in amorphous silica, while PM3 predicted that the six-membered ring is the most stable.[25–27] However, our results show the different basis of silica nanoparticles formed by five-membered rings with the top and bottom layers being connected in the form of four-membered rings.

The low-energy isomers of the different types of elongated structure containing 22 molecules, which are obtained from Fig. 2(c), are shown in Fig. 3. The most stable isomer is given in Fig. 3(a), and the five-membered rings on both the top and bottom edges are considerably reconstructed and distorted, leading to high-fold coordination. Conversely, the five-membered rings in the middle are relatively regular and symmetric. This indicates that the structures of five-membered rings in elongated type of silica nanoparticles (except for the surface sides) might be stable and rather symmetric, although not perfectly symmetric. Other isomers corresponding to the structures without dangling bonds, with

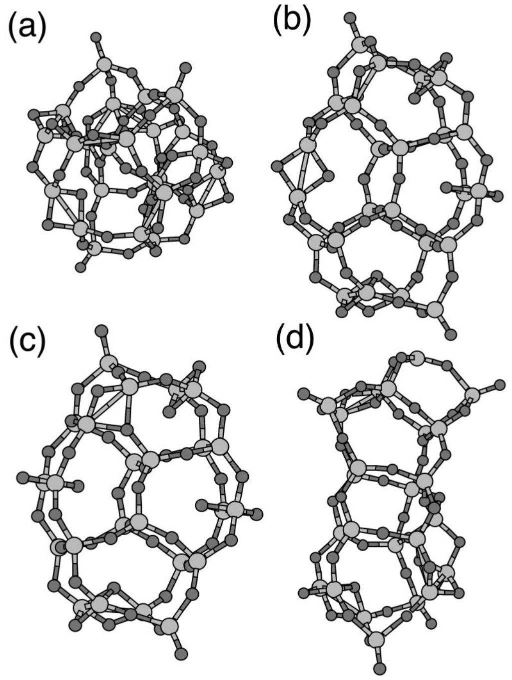

FIG. 2. The low-energy isomers of silica nanoparticles containing 24 molecules; (a) is the compact type of structure, and (b), (c), and (d) are three different elongated types of structure.

reconstruction only on the bottom side, and without any modification in both sides are shown in Figs. 3(b), 3(c), and 3(d). The total energy per molecule of Fig. 3(b) is higher by only 0.29 eV per molecule than that of Fig. 3(a), while those of Fig. 3(c) and Fig. 3(d) are higher by 0.36 and 0.40 eV per molecule, respectively. It is found that the defect states near the Fermi level are removed and the width of the band gap is increased in the structures without dangling bonds and with decreasing overcoordinated bonds. On the other hand, less reconstructed structures show semimetallic band structures, as illustrated in Figs. 3(c) and 3(d). This suggests that formation of high-fold coordination and/or passivation of the dangling bonds associated with the edge sites lead to a lower energy structure, and strongly influence the electronic and optical properties of nanoparticles.

Figure 4 shows the DOS of spherical (dotted line) and elongated (solid line) types of structures in SiO_2 for relatively large systems with 45 molecules and 46 molecules, respectively. Most defects formed in SiO_2 nanoparticles consist of dangling bonds and high-fold coordination due to Si-Si bonds and overcoordinated O atoms. The structural defects in both the compact and elongated types of silica nanoparticles are formed on the surface, not in the core. Thus, the defect states in the band gap can be attributed to structural defects, dangling bonds and high-fold coordinations, on the surface for both the compact and elongated types of silica nanoparticles. The defect states near the Fermi level in both the valence and conduction bands for the elongated structure are less than those for the spherical structure even though the width of the band gap energy is very similar. The optical processes, which depend explicitly on the details of the DOS, should be different for different types of structures of silica nanoparticles. The spherical type of structure has a diameter of 1.6 nm, while the elongated type of structure has a ratio of 1:4 (0.6 nm:2.5 nm) in the diameters. The elongated types of structure consist of rather regular and symmetric silica rings, while the compact (spherical) type of structure consists of considerably distorted silica rings. For particles larger than of 38 molecules, the spherical structure is more stable than the elongated structure. The elongated structure has an energy higher by 0.09 eV per molecule than the spherical structure. In particular, the elongated configuration consists solely of five-membered rings with the top and bottom layers being connected in the form of four-membered rings, leading to a very symmetric and regular structure, except for the five-membered rings of the edge sites.

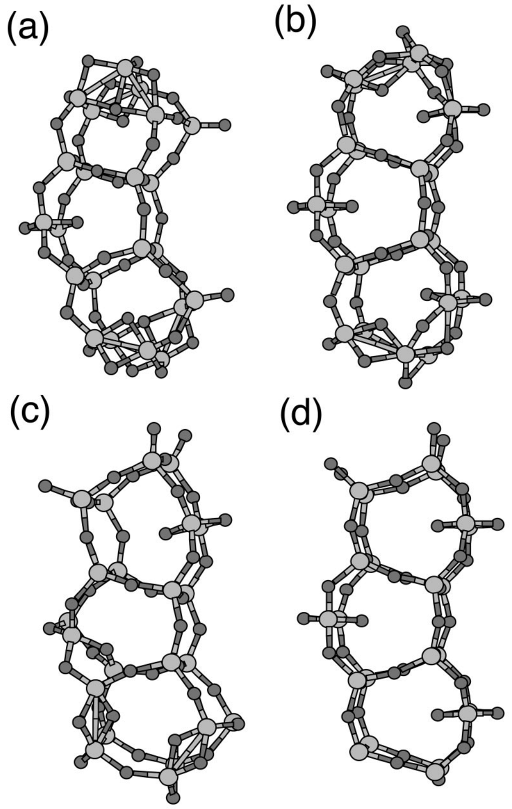

FIG. 3. The low-energy isomers containing 22 molecules consisting solely of five-membered rings with the top and bottom layers being connected in the form of four-membered rings.

The relative energy per molecule is shown in Fig. 5 as a function of the number of molecules. The empty squares and filled squares represent the compact (spherical) and elongated types of structure, respectively. As can be seen, the elongated structures are more stable for nanoparticles containing less than 38 molecules and the compact structures are more stable for nanoparticles containing more than 38 molecules.

In conclusion, the stability of elongated and compact types of structure in SiO_2 nanoparticles has been studied using plane-wave density-functional theory. It was found that the structural transition from elongated to spherical types of structures would occur at a size of around 38 molecules, similar to Si clusters of intermediate size in the range of 20

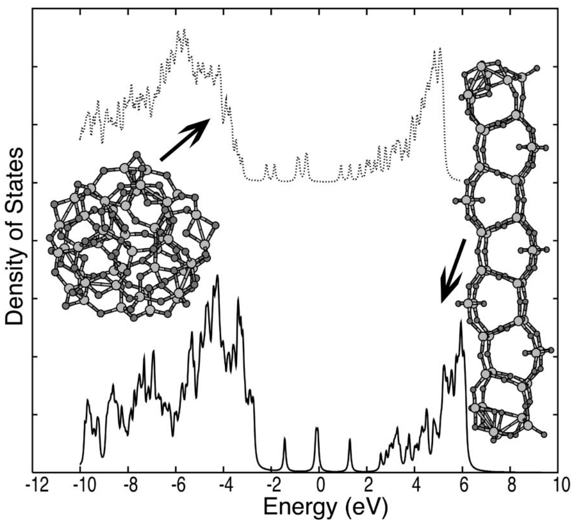

FIG. 4. Density of states for the spherical (dotted line) and elongated (solid line) types of structures in SiO_2 for relatively large systems with 45 molecules and 46 molecules, respectively.

$\leqslant n \leqslant 25$ in Si_n and[8] germanium cluster ions with 70 atoms.[9] The different types of structures cause the changes in the electronic properties and localization behavior of the states, leading to the changes in the optical processes. The results suggest that the elongated types of structure might be proposed for the atomic structures of silica nanowires synthesized using the laser ablation approach.[16]

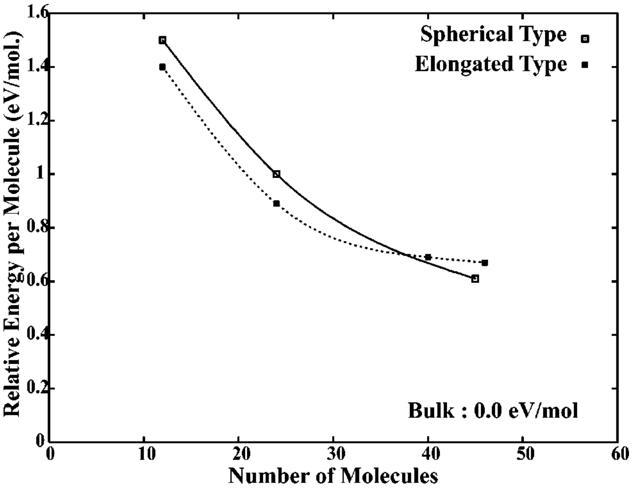

FIG. 5. Relative total energy per molecule as a function of the number of molecules.

The DFT calculations have been performed using the *ab-initio* total-energy and molecular-dynamics program VASP (Vienna ab-initio simulation program) developed at the Institut fur Theoretische Physik of the Technische Universitat Wien. This work was supported by National CRI Center for Nano Particle Control supported by the Ministry of Science and Technology, Korea. The calculations were carried out on a parallel IBM-RS6000 SP computer at Seoul National University.

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