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Structure of the thinnest most stable semiconducting and insulating nanotubes of SiO_x ($x=1,2$)

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The ability of silica to form different phases can be used to stabilize its nanostructures. Here we explore the stability of thin nanotubes of SiO_x ($x=1$ and 2) using *ab initio* calculations with the generalized gradient approximation for the exchange-correlation energy. We find that the pentagonal nanotubes are energetically most stable. The pentagonal SiO nanotube is a semiconductor with the largest calculated band gap of 0.90 eV, which is close to the value for bulk Si. The SiO_2 nanotubes are, however, insulating similar to bulk silica and could be promising as the thinnest insulating layers for nanodevices. Our results demonstrate that we can get the most important circuit elements for nanoelectronics, namely semiconducting, as well as insulating nanotubes based on silicon in the subnanometer regime.

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I. INTRODUCTION

Silica is an important material for research due to its wide range of applications in microelectronics, optical fibers, catalysis, and biological systems[1] as well as its ubiquitous presence in the environment. It has the flexibility to exist in different phases in bulk and this makes it interesting to realize different nanostructures. Recently, various nanostructures of silica have been studied with promising applications. Experimentally amorphous silica ribbons with 80 nm width, 20–40 nm height, and up to 500 μm in length were prepared by hydrolyzing SiCl_4 at highly oriented pyrolytic graphite surfaces and were found to be important as conduits for light.[2] Silica nanowires and helical nanosprings (80 to 140 nm in diameter and up to 8 μm in length) have been synthesized with a chemical vapor deposition technique[3] and these may have potential applications in nanomechanical and nanoelectronmagnetic devices, as well as in composite materials. Silica nanospheres can be synthesized in the size range of 45 to 8 nm.[4,5] Dispersal of extremely small tin oxide nanocrystals on the surface of silica nanospheres have been shown to produce improved sensors as well as catalytic behavior.[4,6]

Among the various nanoforms of silica, nanotubes are potentially important not only in electronics but in catalysis and bioanalysis also. This is due to the availability of the inner and outer surfaces of the nanotubes. Generally, silica nanotubes are synthesized within the pores of porous alumina membrane templates and by dissolving the alumina template single silica nanotubes can be recovered.[7] In another way nanotubes can be formed by agglomeration of nanospheres of silica.[6] Recently, a different way of producing silica nanotubes has been discussed, in which silicon nanowire arrays are transformed into silica nanotube arrays through a thermal oxidation-etching approach.[8] These nanotubes keep the orientation of the original silicon nanowire arrays and are proposed to be useful for fabrication of single nanotube sensors and nanofluidic systems. Besides silica, nanotubes[9] as well as nanowires[10] of SiO have also been synthesized. Using an ordered nanochannel-array of anodic alumina as templates, nanotubes,[9] and nanowires with a uniform diameter of 30 nm have been synthesized. These are observed to grow out of each pore of the anodic alumina templates. Like silica, these nanowires and nanotubes of SiO are proposed to have prospective applications in the semiconductor and catalysis industries. Theoretically cagelike and elongated structures have also been predicted.[11–13] Calculations[12] with model potentials have been performed to study the effects of water interaction on the stability of SiO_2 clusters in the form of a finite hexagonal nanotube.

The structures and electronic properties of experimentally produced nanotubes are not well understood. The electronic properties of thin nanotubes are of special interest for the miniaturization of electronic devices. At the nanoscale these could be very different from bulk and exhibit strong stoichiometry dependence. *Ab initio* studies on these systems can provide vital information on the electronic properties, which could be decisive for further developments in this versatile field. We explore the stability of the thinnest infinite nanotubes, keeping approximately the tetrahedral arrangement around Si atoms that is ideally required in all these phases and study their electronic properties. We present results of a comprehensive study on the structural and electronic properties of thin nanotubes of SiO_x ($x=1$, 2), which show that the thinnest, most stable nanotubes have pentagonal structures. Moreover, the SiO nanotubes are found to be semiconducting while the SiO_2 nanotubes are insulating quite similarly to bulk.

II. METHOD

The calculations were performed within the *ab initio* density functional theory using the ultrasoft gradient-corrected Vanderbilt type pseudopotentials.[14] The optimizations were performed[15,16] without any symmetry constraints, within the generalized gradient approximation[17] (GGA) for the exchange-correlation functional. The valence electron wave functions were expanded using a plane wave basis set with a kinetic energy cutoff of 396 eV. We have done test calculations to show the convergence of energy with respect to cutoff energy. Since for Si the 396 eV is already quite large, we

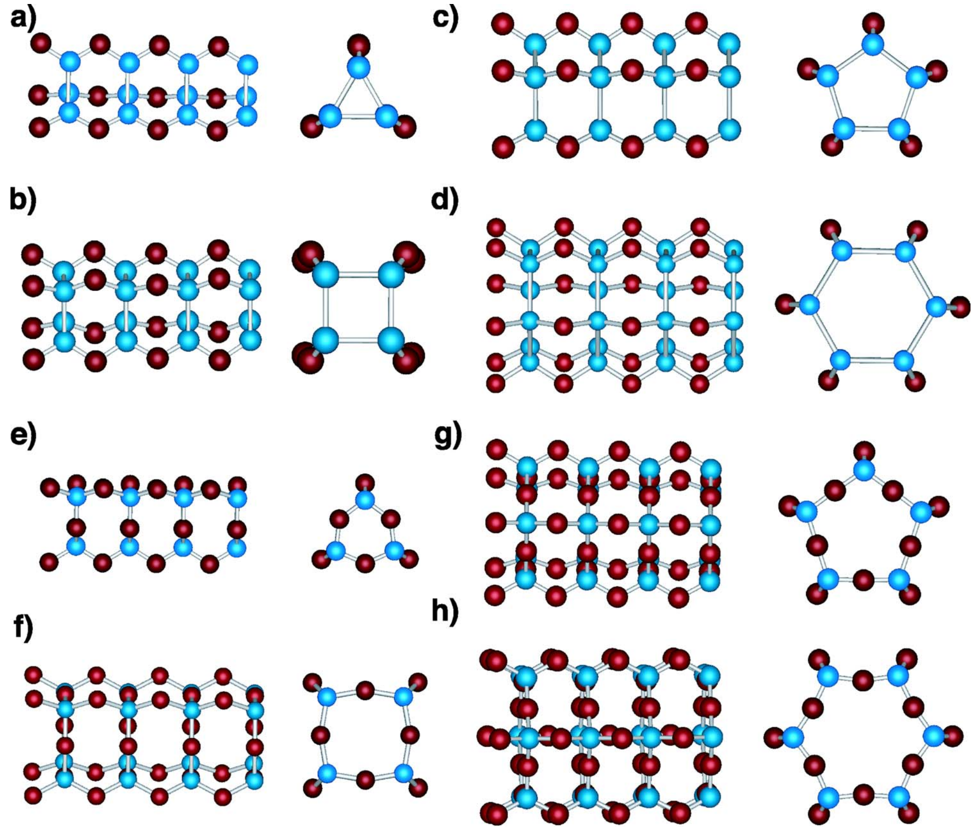

FIG. 1. (Color online) Optimized unit cells of SiO nanotubes viewed along and perpendicular to the axis of the nanotubes: (a) $Si_{12}O_{12}$ triangular, (b) $Si_{16}O_{16}$ tetragonal, (c) $Si_{20}O_{20}$ pentagonal, and (d) $Si_{24}O_{24}$ hexagonal rings of Si, connected by oxygen atoms. Note that the oxygen atoms in (b) are not aligned; this is due to a symmetric twist in the structure. The corresponding optimized unit cells of infinite SiO_2 nanotubes are shown in (e)–(h). In these nanotubes every Si atom is connected with four oxygen atoms.

studied oxygen dimer with the cutoff energy of 396 eV and with an increased cutoff energy of 496 eV. No gain in binding energy (BE)/atom was observed until the fourth decimal place. The total energies per atom were well converged within 0.001 eV/atoms with respect to the variation in the cut-off energy, even for the nanotubes. The Brillouin zone integrations were carried out using 15 *k*-point sampling along the nanotube direction. Test calculations show that no significant gain in the BE is obtained by increasing the number of *k* points. The periodic boundary conditions (PBC) were applied in the *z* direction (along the nanotube length). Sufficient vacuum space was kept in the *x* and *y* directions to create an infinite one-dimensional system. The distances between the outermost atoms of a nanotube and its corresponding nearest neighbor in the periodic replica in *x* and *y* directions were taken to be more than 12 Å, which is sufficient to avoid any significant interactions between the replicas. Increased distance, like 15 Å between the replicas, does not change the geometries and energies of the system. All the test calculations were performed on a SiO triangular nanotube. The cell lengths of all the nanotubes were optimized along the nanotube axis.

III. RESULTS AND DISCUSSION

The thinnest possible nanotubes were constructed with triangular, tetragonal, pentagonal, and hexagonal cross sections. For SiO nanotubes the unit cells consisted of one-dimensionally stacked four rings of Si connected by oxygen atoms. However, for SiO_2 nanotubes each ring consisted of alternating Si and O atoms such that each Si had four nearest neighbor oxygen. A larger unit cell (Fig. 1) was chosen to allow for possible changes in the structure. After optimizations it was found that one ring is adequate to represent the unit cell. The optimized structures are highly symmetric (Fig. 1) and all Si (O) atoms are ideally coordinated with four (2) atoms. The Si-Si and Si-O bond lengths (Table I) in all the SiO nanotubes are nearly the same, irrespective of the geometries. Their values are also close to those in bulk silicon (2.35 Å) and quartz (1.60 Å),[18–20] respectively. The Si-O-Si and O-Si-O angles (Table I) are nearly the same (≈113°)

TABLE I. The BE in eV/atom, Si-Si and Si-O bond lengths (Å), and O-Si-Si and O-Si-O bond angles (°) for the infinite SiO nanotubes.

System	BE	Si-Si	Si-O	O-Si-Si	O-Si-O
$Si_{12}O_{12}$ (triangular)	5.52	2.42	1.67	118.32	113.75
$Si_{16}O_{16}$ (square)	5.67	2.40	1.67	116.60, 109.43	113.26
$Si_{20}O_{20}$ (pentagonal)	5.72	2.42	1.67	108.56	113.54
$Si_{24}O_{24}$ (hexagonal)	5.71	2.42	1.67	105.68	113.60

TABLE II. The BE in eV/atom, Si-O (oxygen atom within the ring) and Si-O′ (oxygen atom connecting Si atoms in neighboring rings) bond lengths (Å), O-Si-O and O′-Si-O bond angles (°) for SiO_2 infinite nanotubes.

System	BE	Si-O	Si-O′	O-Si-O	O′-Si-O
$Si_{12}O_{24}$ (triangular)	6.50	1.63	1.64	108.24	107
$Si_{16}O_{32}$ (square)	6.53	1.61	1.64	109.40	113.26
$Si_{20}O_{40}$ (pentagonal)	6.54	1.60	1.64	107.55	109.54
$Si_{24}O_{48}$ (hexagonal)	6.54	1.61	1.65	105.68	113.60

and are close to the value (109.47°) for the tetrahedral angle. However, the O-Si-Si angles differ in different geometries. In the nanotube with a tetragonal cross section, there are two O-Si-Si bond angles (116° and 109°). This induces strain and results in a slight symmetric twist in the structure [Fig. 1(b)]. The O-Si-Si bond angles in the pentagonal nanotube [Fig. 1(c)] are closest to the tetrahedral angle, indicating the least deviation from the preferred tetrahedral bonding. Accordingly, the BE of the pentagonal nanotube is the maximum among all the nanotubes we have studied. It shows that the pentagonal nanotubes are the most stable.

In bulk SiO_2, SiO_4 tetrahedra are connected in different ways in different phases so that in all cases O-Si-O angles are close to the tetrahedral angle while the Si-O-Si angles are not so rigid. Their values in quartz and α-cristobalite are $\approx 146°$ but become 180° in β-cristobalite. In SiO_2 nanotubes, there are two nonequivalent oxygen atoms: one lying in the ring that we represent by O and the other denoted as O′ that bridge the rings. The bond angles at Si atoms lie close (Table II) to the tetrahedral angle. This is achieved by keeping O atoms outside the Si ring for the triangular and tetragonal nanotubes, but these are nearly aligned in the pentagonal nanotubes, whereas for the hexagonal nanotube the O atoms fall within the Si ring [see Figs. 1(e)–1(h)]. This feature of the hexagonal nanotube has also been observed in finite nanotubes.[12,21] The Si-O′-Si angle between the rings is $\approx 117°$ but within a ring Si-O-Si angles are 132.79, 160.61, 178.85, and 170.72°, respectively, for the triangular, tetragonal, pentagonal, and hexagonal nanotubes. Therefore, similar to bulk, bond angles at oxygen atoms vary significantly, but for the pentagonal nanotubes, the deviations from the ideal angles (as in cristobalite) are minimum and this makes it again energetically the most favorable among the SiO_2 nanotubes also [Fig. 1(f)]. Details of the optimized structures and the BEs are given in Table II.

The bond angles in SiO_2 nanotubes (Table II) give an indication that around Si atoms one can construct predominantly sp^3 hybrids whereas around the oxygen atoms it can be sp or sp^2-sp^3 type. Like bulk α quartz there are two slightly different Si-oxygen bond lengths: ≈ 1.61 Å within a ring and 1.64 Å between the rings (Table II). These are very close to the experimental values in bulk α-quartz.[18] Since the Si-O′-Si angles remain nearly the same for all geometries, the Si-O′ bond length is nearly constant. However, Si-O bond length is longer in the triangular nanotube as the Si-O-Si angle is much smaller than 180°. In other nanotubes the angles become closer to 180° and the overlap between the sp hybrid orbital of O and the sp^3 hybrids around Si increases making the bond slightly shorter. In general the different geometrical arrangements of SiO_4 tetrahedra in nanotubes lead to different bond angles around oxygen atoms compared to bulk. The BEs of SiO_2 nanotubes are significantly higher than the values for the SiO nanotubes and are about 97% of the calculated[19,20,22] value of the most stable α-quartz bulk phase, giving a strong possibility of the experimental realization of these thin nanotubes.

The electronic structures of these nanotubes show that the SiO nanotubes are semiconducting. This feature is common to all the nanotubes irrespective of their cross sections. The band gap is the largest (0.90 eV) for the pentagonal nanotube [Fig. 2(a)] and it is close to the value for bulk silicon. The SiO_2 nanotubes are, however, insulating [Fig. 2(b)]. The band gaps in all these nanotubes are of the order of 6 eV. This is 85% of the theoretical band gap of α-quartz[19] (≈ 7 eV), which is less than the observed experimental value of 9.6 eV due to the known underestimation in GGA.

The band structures, as well as the total and partial densities of states (DOS) of the pentagonal nanotubes, are shown in Fig. 2 using the effective unit cells Si_5O_5 and Si_5O_{10} for SiO [Fig. 2(a)] and SiO_2 [Fig. 2(b)] nanotubes, respectively. In general the peaks in the total DOS correspond to the peaks in the partial DOS of Si and oxygen, representing a typical feature of covalent bonding in these nanotubes. The partial DOS of the two types of oxygen atoms are different, indicating the difference in the bonding nature as was explained above. Apart from covalency, it can also be inferred from the DOS that charge transfer takes place from Si to oxygen atoms. In Fig. 2(b) the states near the top of the valence band arise mostly from oxygen atoms and the weight in the partial DOS of Si is significantly lower than for oxygen. The spikes in the DOS are due to the van Hove singularities.

The total charge density in SiO nanotubes [Fig. 3(a)] is concentrated around each bond again supporting the covalent bonding character. There is a strong concentration of charge on oxygen atoms, also due to two lone pairs. Considering the difference between the self-consistent charge density of a nanotube and the overlapping charge densities of the Si and oxygen atoms at the respective positions, we find excess of charge [Fig. 3(b)] around oxygen atoms. This is because of the polar bonding arising due to the difference in the electronegativities of Si and oxygen. Charge is depleted [Fig. 3(c)] on top of the Si and the bottom of the oxygen atoms, indicating sharing of charge between the oxygen and Si atoms. For SiO_2 nanotubes, there is a stronger build up of charge on the bridging (O′) atoms compared with O within a ring [Fig. 3(d)]. This feature can be observed more clearly in the isosurface of the excess of charge [Fig. 3(e)]. The depletion of charge [Fig. 3(f)] has mostly taken place from the top of the Si atoms and the bottom of the O atoms as in the SiO nanotubes. Thus the bonding in these nanotubes is mixed covalent-ionic type consistent with bulk silica.

In order to get an idea of the mechanical behavior of the most stable nanotube, we further calculated the Young's modulus of the SiO_2 pentagonal nanotube as it has been done for carbon nanotubes[23,24] and found it to have a value of around 350 GPa. This is much higher than the value for bulk

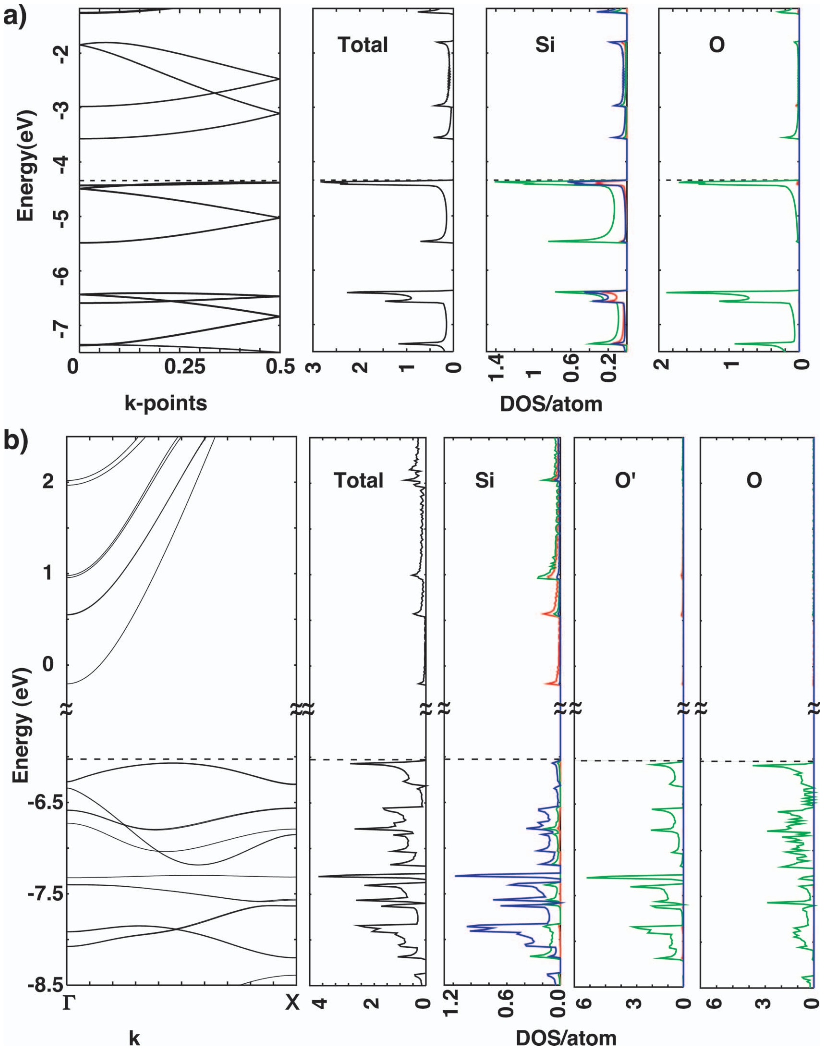

FIG. 2. (Color) Band structures and total and partial densities of states (DOS) of pentagonal infinite nanotube with the effective unit cell: (a) Si_5O_5 and (b) Si_5O_{10}. Only states near the top of the valence band and the bottom of the conduction bands have been shown. O′ and O correspond to the oxygen atoms at the bridge sites and in the rings, respectively, in SiO_2 nanotubes. The broken line shows the top of the valence band. The spikes in the DOS at the band edges arise due to van Hove singularities that represent the typical features of a one-dimensional system. Red, green, and blue lines represent contributions from s, p, and d orbitals. For clarity the scale for the partial DOS of Si has been changed.

quartz. Therefore this nanotube would also have good mechanical stability.

IV. SUMMARY

In summary we find that the optimal thinnest nanotubes of SiO_x $(x=1, 2)$ are pentagonal with the highest band gaps and subnanometer diameters. SiO nanotubes are semiconducting and, for the pentagonal nanotube, the gap is close to the value for bulk silicon making it interesting for nanoscale electronic devices. The SiO_2 nanotubes are insulating and could be useful as insulating covers on atomic wires. The mechanical properties of pentagonal SiO_2 nanotubes are

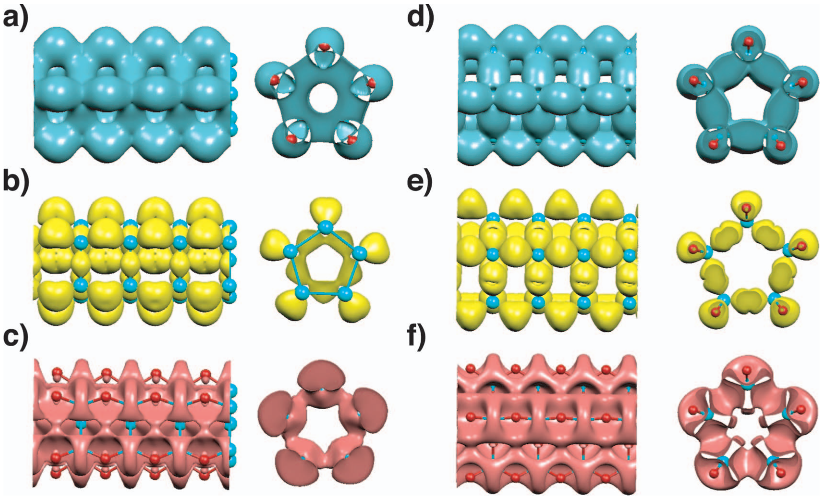

FIG. 3. (Color) Isosurfaces of (a) the total electronic charge density of SiO (with unit cell $Si_{20}O_{20}$), (b) the excess, and (c) the depletion of charge as compared to the overlapping charge densities of the Si_{20} and O_{20} at the respective positions. The buildup of charge seen on the oxygen atoms is due to the polar nature of Si-O bonds. The corresponding isosurfaces of infinite SiO_2 nanotubes (with unit cell $Si_{20}O_{40}$) are shown in (d)–(f).

found to be much superior compared with the bulk. The BE of this nanotube is 97% of the bulk calculated cohesive energy of silica, giving a strong indication for the experimental realization of this nanotube. A recent finding of smallest diameter (1.2 nm) nanowires of silicon[25] could prove to be a breakthrough in bringing down the diameter of the SiO$_x$ ($x=1, 2$) nanotubes. Oxidizing these nanowires and dissolving inner silicon could be a possible way to synthesize smaller diameter nanotubes of silica. Also Si$_x$O$_x$ ($x=3, 4$) cluster has ringlike structure,[26] and assembly of these clusters could be another viable way of producing nanotubes in the laboratory. By controlling the stoichiometry of oxygen atoms during the growth process it could be possible to grow either semiconducting or insulating nanotubes. Together with the metallic thin nanotubes[27,28] of silicon that have been formed experimentally,[29] these could be promising circuit elements for nanoelectronic based on silicon. The availability of both inner and outer surfaces in the nanotubes could also offer interesting possibilities for catalysis and bioanalysis.

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[21] The stability of these nanotubes is further checked by removing the constraint of periodic boundary condition. Studies on finite nanotubes with Si$_{nx}$O$_{nx-n}$ and Si$_{nx}$O$_{2nx-n}$ ($n=3$, 4, 5, and 6) stoichiometries for SiO and SiO$_2$ nanotubes show them to be structurally similar to the infinite nanotubes, except for the Si atoms at the end rings that are connected to O atoms only on one side. This leads to reconstruction of the end rings. However, the remaining rings preserve the symmetry, confirming further the inherent stability of these nanotubes.

[22] The calculated BE is more than the experimental bulk cohesive energy because of the overestimation in GGA. Similar results have been obtained using the same methodology for the bulk phases of silica (Ref. 19).

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