Electronic properties of silica nanowires

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Abstract. Thin nanowires of silicon oxide were studied by pseudopotential density functional electronic structure calculations using the generalized gradient approximation. Infinite linear and zigzag Si-O chains were investigated. A wire composed of three-dimensional periodically repeated Si₄O₈ units was also optimized, but this structure was found to be of limited stability. The geometry, electronic structure, and Hirshfeld charges of these silicon oxide nanowires were computed. The results show that the Si-O chain is metallic, whereas the zigzag chain and the Si₄O₈ nanowire are insulators.

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1. Introduction

Nanochains of metals [1], as well as of carbon, semiconductors and organic materials [2, 3] have recently been the subject of experimental and theoretical studies. Similar chains of many other chemical elements and compounds have not been studied. Because of the present interest in nanotechnology these studies are important. Chains with particular properties are candidates for preparation of nanostructures with chosen applications. It is also possible to deposit chains on various substrates and to obtain one-dimensional conductors and quantum confinement.

There are many crystalline phases of bulk silica, for example, quartz, tridymite, cristobalite, keatite, coesite, and stishovite [4]. In addition, amorphous SiO$_2$, which is abundant in nature, has also been investigated and used in various technological applications. These silica bulk phases have been studied by several experimental [5, 6] and theoretical [7, 8, 9, 10, 11, 12, 13] methods. Silica is a very good electrical insulator. Macroscopic silica wires are used as waveguides in the visible and near-infrared spectral ranges. Silica films are often applied in optics, and are used as electric and thermal insulators in electrical devices [14]. SiO$_2$ substrates are important in microelectronics, optics and chemical applications. Therefore silica surfaces have been also investigated [15].

Much less study has been devoted to silica nanostructures. Various cylindrical nanostructures of silica recently have been synthesized: nanowires, nanotubes, nanoflowers, bundles, and brush-like arrays [16, 17, 18, 19]. Their structural, mechanical, optical, and catalytic properties have been examined. Silica nanowires, with diameters ranging from ten to several hundred nanometers, have been produced using various experimental techniques. They have been proposed for use as high-intensity light sources, near-field optical microscopy probes, and interconnections in integrated optical devices.

The properties of infinite silica chains have not been theoretically investigated. However, several theoretical studies of silica clusters have been carried out using Gaussian [20, 21, 22, 23, 24, 25, 26], GAMESS [27], SIESTA [28] and DMOL [21] packages, as well as several other density functional theory (DFT) programs [29, 30, 31, 32]. Nanotubes of SiO$_x$, $x = 1, 2$, have recently been studied using the VASP DFT program [33]. All these computational studies of silica nanostructures, have shown that their properties are often different in relation to the bulk. Therefore, it is also important to study infinite silica nanochains where periodic boundary conditions are used along the axis. These one-dimensional structures of silica are interesting from the theoretical point of view, as well as models of very long real nanowires. They provide additional systems for investigating the structure and bonding in silica materials, and offer possibilities of designing new nanostructures. It is possible to prepare such thin silica wires on the substrates. The one that is the most interesting for applications is the assembly of silica chains on silicon surfaces and nanowires.

In this work, the structure, energetics and electronic properties of thin silica
nanowires were investigated using a computational method. Infinite linear and zigzag chains, as well as a nanowire composed of periodically repeated Si$_4$O$_8$ structural units, were constructed and optimized using a plane wave pseudopotential approach to the density functional theory. The rest of the paper is organized as follows. Section 2 presents the method. In section 3 the results and discussion are given. Conclusions are outlined in section 4.

2. Computational Method

*Ab initio* DFT calculations [34, 35] within the plane-wave pseudopotential method were performed to study silica chains. The pseudopotential approach has been very successful in describing the structural and electronic properties of various materials [36]. The ABINIT code was used [37]. The same method has already been applied to calculate various properties of bulk silica [9, 10, 11, 12, 13] and the (0001) α-quartz surface [15]. In this calculation the generalized gradient approximation and the exchange-correlation functional of Perdew, Burke, and Ernzerhof were applied [38]. The pseudopotentials of Troullier and Martins [39] generated by the Fritz Haber Institute code [40] were used; these pseudopotentials were taken from the ABINIT web page [37]. They were tested by doing calculations for the bulk α-quartz, and these results were compared with experiments [41]. It was found that the computationally optimized structural parameters of quartz were very close to the experimental ones; the differences are below 0.1%. Several properties of silica nanowires were also calculated using the local density approximation (LDA) with the Teter extended norm-conserving pseudopotentials taken from the ABINIT web page [42, 37]. The results obtained using the Teter pseudopotentials were compared with experiments for bulk quartz structure, and differences of 0.1% have been obtained. Only minor quantitative differences were found between the LDA and GGA results for silica nanowires. The calculations were performed with a kinetic-energy cutoff of 35 Hartree. The wires were positioned in a supercell of side 30 a.u. along the x and y directions. The axis of the wires was taken along the z direction, and the periodic boundary conditions were applied. The Monkhorst-Pack method with 15 k-points sampling along the z direction was used in the integration of the Brillouin zone [43]. Structural relaxation for silica nanowires was carried out by performing a series of self-consistent calculations and computing the forces on atoms. The geometry optimizations were performed using the Broyden method of minimization until the forces were less than $2.6 \times 10^{-4}$ eV/Å. All atoms were allowed to relax without any imposed constraint.

Infinite Si-O chains were investigated. Two, four, and six atoms in a unit cell of a chain were studied to explore a possible dimerization and the existence of a zigzag structure. In previous studies of silica clusters it has been found that in stable structures there often exists a unit of two Si$_2$O$_2$ rhombuses sharing one silicon atom. This unit contains a tetrahedrally bonded Si atom and therefore shows the structural feature most often present in the bulk of SiO$_2$. Two adjacent rhombohedral rings in clusters are
perpendicular to each other. It was calculated in this work that an optimized infinite silica wire forms if a Si$_4$O$_8$ unit is repeated periodically along a direction where the silicon atoms are positioned. The Si$_4$O$_8$ unit contains three whole Si$_2$O$_2$ rhombuses. Infinite tubular nanostructures of silica, similar to the finite MgO nanotubes studied recently [44], are not stable because their oxygen atoms are in the 4-fold coordinated configurations. However, calculations on silica clusters have shown that the oxygen atom prefers a lower coordination. In experimental studies of silica nanowires, much bigger structures having diameters 15 – 100 nm and lengths up to tens of millimeters have been prepared [16] [17] [18] [19]. It has been shown that these silica nanostructures synthesized in the laboratories are amorphous. DFT-based studies of such already fabricated silica nanowires are not feasible within current computational power.

3. Results and discussion

The optimized distances and the binding energies of all nanowires are presented in table 1. The optimized geometries of silica chains are shown in figure 1. No dimerization was found for the linear chain. The zigzag chain is also stable and its energy is above that of the linear chain. Nonlinearity of the O-Si-O bonds is less favorable in a situation
Table 1. The geometry and the binding energy of optimized structures. In this table, \(a\) is the Si-O distance, while \(l\) is the Si-Si distance. The length unit is nm. Energies \(E\) are given in eV/atom.

| Structure        | Linear chain | Zigzag chain | Si\(_4\)O\(_8\) nanowire |
|------------------|--------------|--------------|--------------------------|
| \(a\)            | 0.175        | 0.170        | 0.167                    |
| \(l\)            | 0.35         | 0.291        | 0.234; 0.235             |
| \(E\)            | -6.40        | -5.51        | -7.38                    |

where there is no additional oxygen atoms, as in the case of the bulk tetrahedral SiO\(_4\) bonding. The optimized structure of the Si\(_4\)O\(_8\) unit is shown in figure 2(a). It is well known that the Si-O distance in the bulk silica is most often about 0.16 nm. It was calculated here that a larger Si-O distance of 0.175 nm exists in a linear chain, 0.170 nm in zigzag one, and 0.167 nm in a Si\(_4\)O\(_8\) nanowire. In the zigzag chain the angles are \(\alpha = 118^{\circ}\). The width of the nanowire shown in figure 2(a) is up to about 0.24 nm. In the Si\(_4\)O\(_8\) wire the oxygen atoms are bonded to two silicon atoms and the silicon atoms are bonded to four oxygen atoms. Such SiO\(_4\) tetrahedra are typical for bulk materials involving silicon and oxygen. In the rhombuses of the Si\(_4\)O\(_8\) wire the Si-O-Si angles are \(\delta = 89.4^{\circ}\) and \(\gamma = 89.5^{\circ}\), while the O-Si-O ones are \(\beta = 90.4^{\circ}\) and \(\alpha = 90.6^{\circ}\). The O-Si-O angle is \(\epsilon = 119.7^{\circ}\) when the oxygen atoms are in adjacent rhombuses. Thus, the coordination of the silicon atoms is distorted from an ideal tetrahedral geometry.

Figure 1 also presents the bonding wells for the chains. The minima are rather pronounced and show a substantial stability of these nanowires. By contrast, it was not possible to obtain a similar figure for the Si\(_4\)O\(_8\) wire. Even very small perturbations (\(\sim 1\%\)) of the length along the wire axis destabilize the Si\(_4\)O\(_8\) wire. A small difference between the angle within one rhombus exists (\(\beta = 90.4^{\circ}\) vs \(\alpha = 90.6^{\circ}\)). It was not possible to stabilize such a three-dimensional thin wire using a smaller Si\(_2\)O\(_2\) cell. The Si\(_4\)O\(_8\) nanowire is at the border of instability. However, it was also found that the calculation where the LDA approximation to the DFT theory with the Teter extended norm-conserving pseudopotentials [42] was used produces a similar optimized Si\(_4\)O\(_8\) infinite wire. For example, in this LDA approximation the Si-Si distance is \(l = 0.232\) nm, whereas the Si-O distances are \(a = 0.164; 0.165\) nm. It should be possible to assemble silica chains on the surfaces, using various nanotubes and nanowires, or long channels in porous materials. The role of the substrate is to increase the stability of very thin silica nanowires.

The band structure of silica chains is shown in figure 3. The plot of the electronic structure of a linear chain (presented in figure 3(a)) shows that one band crosses the Fermi level; therefore this system is metallic. The electronic structure of a zigzag chain is shown in figure 3(b). This wire is an insulator. The band plot in figure 2(b) shows that the Si\(_4\)O\(_8\) nanowire is also an insulator. When the number of neighbours in Si-O nanowires increases, electronic behavior goes from metallic to insulating, as in the bulk. At the Gamma point, the difference between the valence and conduction band is 5.646.
Figure 2. (a) The three-dimensional structural Si$_4$O$_8$ unit which repeats periodically along the wire axis and forms an optimized but almost unstable infinite nanowire (angles and lengths are given in the text). Light and dark balls are used to represent the O and Si atoms respectively. The middle rhombohedral ring is in the plane perpendicular to two edge rhombuses. (b) Electronic structure of the structure shown in (a). The Fermi level is denoted by the dashed line.

eV for the Si$_4$O$_8$ nanowire, and 2.514 eV for the zigzag chain. Tetrahedral SiO$_4$ clusters exist in the Si$_4$O$_8$ nanowire. This structure is similar to the fragments of the cristobalite bulk lattice. The three-dimensional Si$_4$O$_8$ wire behaves as an insulator, and a similar electronic behavior and a band gap value exist in the cristobalite crystal [8]. Table 1 shows that the Si-O and Si-Si distances are smaller in the zigzag chain than in the linear one. This compression of bonds as a result of the rearrangement of atoms into the zigzag chain removes a crossing band from the Fermi level, and an insulating behavior arises in this structure. The Si-O distance in the linear chain is larger than in the majority of silica bulk phases, as well as in the zigzag and Si$_4$O$_8$ wires. That decreases the extent of π bonding between silicon and oxygen atoms in the linear wire. The weak metallic behavior arises in the linear silica chain as a consequence of this weaker bonding and a small coordination.

Atomic charges were calculated using the Hirshfeld partitioning of the electron density [47, 48, 49]. The Hirshfeld method (or “stockholder” partitioning) uses the charge density distribution to determine atomic charges in the molecule or nanostructure. First, the reference state of the promolecule density is defined as $\rho^{\text{pro}}(\vec{r}) = \Sigma_A \rho_A(\vec{r})$, where $\rho_A(\vec{r})$ is the electron density of the isolated atom A placed at
its position in the molecule. The atomic charge is

\[ q_A = -\int \delta \rho_A(\vec{r}) d\vec{r}, \]  

(1)

where \( \delta \rho_A(\vec{r}) \) is the atomic deformation density given by

\[ \delta \rho_A(\vec{r}) = w_A(\vec{r}) \Delta \rho(\vec{r}). \]  

(2)

In equation (2), \( w_A(\vec{r}) \) is the relative contribution ("share") of the atom A in the promolecule, whereas \( \Delta \rho(\vec{r}) \) is the molecular deformation density. The sharing factor is a weight that determines a relative contribution of the atom \( x \) to the promolecule density in the point \( r \). It is defined as

\[ w_A(\vec{r}) = \frac{\rho_A(\vec{r})}{\rho_{\text{pro}}(\vec{r})}. \]  

(3)

The molecular deformation density (used in equation (2)) is

\[ \Delta(\vec{r}) = \rho(\vec{r}) - \rho_{\text{pro}}(\vec{r}), \]  

(4)

where \( \rho(\vec{r}) \) is the molecular electron density. The Hirshfeld partitioning is almost insensitive to the basis set and minimizes missing information [47, 48, 49]. The Hirshfeld charges are presented in table 2. The calculations show that for all silica wires the charge transfer occurs from Si to O atoms. This indicates ionic bonding. All oxygen atoms get similar amounts of the electron density, regardless of the structure.
Table 2. The Hirshfeld atomic charges. The calculated average charge transfers $\delta Q$ are shown.

| Structure     | Linear chain | Zigzag chain | $\text{Si}_4\text{O}_8$ nanowire |
|---------------|--------------|--------------|----------------------------------|
| $\delta Q(\text{Si})$ | 0.212        | 0.275        | 0.446                            |
| $\delta Q(\text{O})$  | -0.212       | -0.275       | -0.225                           |

Figure 4. Charge density contour plots drawn using 0.4 $e/\alpha_0^3$ isovales. The dark spheres are O, whereas the light ones are Si atoms. Side views of unit cells for: (a) linear chain, (b) zigzag chain. (c) A top view of the cell for the $\text{Si}_4\text{O}_8$ nanowire: isolines around two top oxygen atoms are shown and the central ball represents the strand of Si atoms.

The character of the bonding was also analysed using the electronic charge density. In figure 4 the charge density isosurface plots are presented. This visualization was performed by the XCrySDen package [50]. The well-defined spherical charges are located and accumulated on the oxygen atoms. Similar charge density plots that show a predominantly ionic bonding have been, for example, obtained for bulk $\alpha$-quartz [7].

4. Conclusions

Three configurations of infinite silica nanowires were optimized and studied using $ab\ initialo$ DFT calculations in the pseudopotential approximation. The structural properties of these wires were investigated. It was found that a linear chain is energetically more favorable than a zigzag wire. The calculations of the bonding wells showed that both chains are stable, whereas the infinite $\text{Si}_4\text{O}_8$ wire is at the border of instability. The
Hirshfeld charges were calculated and the results show that a similar transfer of a charge to oxygen atoms exists for all wires. It was found that the zigzag chain and the Si₄O₈ wire are insulators, while a single state crosses the Fermi level in the band plot of the linear chain. The existence of a metallic state offers the possibility to use simple long silica chains in conducting nanodevices without doping. It is possible to deposit and assemble these chains on various surfaces, nanotubes, or inside the long and wide pores of suitable bulk materials.

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References

[1] Agrait N, Levy Yeyati A and van Ruitenbeek J M 2003 Phys. Rep. 377 81
[2] Tongay S, Durgun E and Ciraci S 2004 Appl. Phys. Lett. 85 6179
[3] Service R F 2001 Science 294 2442
[4] Wyckoff R W G 1965 Crystal Structures (New York: Wiley)
[5] Nithianandam V J and Schnatterly S E 1988 Phys. Rev. B 38 5547
[6] Distefano T H and Eastman D E 1971 Solid State Commun. 9 2259
[7] Chelikowsky J R and Schlüter M 1977 Phys. Rev. B 15 420
[8] Xu Y N and Ching W Y 1991 Phys. Rev. B 44 11048
[9] Gonze X, Allan D C and Teter M P 1992 Phys. Rev. Lett. 68 3603
[10] Gonze X, Charlier J C, Allan D C and Teter M P 1994 Phys. Rev. B 50 R13035
[11] Lee C and Gonze X 1995 Phys. Rev. B 51 8610
[12] Detraux F and Gonze X 2001 Phys. Rev. B 63 15118
[13] Donadio D and Bernasconi M and Tassone F 2003 Phys. Rev. B 68 134202
[14] Miyata H, Suzuki T, Fukuoka A, Sawada T, Watanabe M, Noma T, Takada K, Mukaide T and Kuroda K 2004 Nature Materials 3 651
[15] Rignanese G M, DeVita A, Charlier J C, Gonze X and Car R 2000 Phys. Rev. B 61 13250
[16] Gole J L, Wang Z L, Dai Z R, Stout J and White M 2003 Colloid Polym. Sci. 281 673
[17] Yu D P, Hang Q L, Ding Y, Zhang H Z, Bai Z G, Wang J J, Zou Y H, Qian W, Xiong G C and Feng S Q 1998 Appl. Phys. Lett. 73 3076
[18] Zhang M, Ciocan E, Bando Y, Wada K, Cheng L L and Pirouz P 2002 Appl. Phys. Lett. 80 491
[19] Tong L, Gattass R R, Ashcom J B, He S, Lou J, Shen M, Maxwell I and Mazur E 2003 Nature (London) 426 816
[20] Wang L S, Nicholas J B, Dupuis M, Wu H and Colson S D 1997 Phys. Rev. Lett. 78 4450
[21] Nayak S K, Rao B K, Khanna S K and Jena P 1998 J. Chem. Phys. 109 1245
[22] Bromley S T, Zwijnenburg M A and Maschmeyer Th 2003 Phys. Rev. Lett. 90 035502
[23] Sun Q, Wang Q and Jena P 2004 Phys. Rev. Lett. 92 039601
[24] Bromley S T, Zwijnenburg M A, Flikkema E and Maschmeyer Th 2004 Phys. Rev. Lett. 92 039602
[25] Sun Q, Wang Q, Kawazoe Y and Jena P 2004 Nanotechnology 15 260
[26] Sun Q, Wang Q, Rao B K and Jena P 2004 Phys. Rev. Lett. 93 186803
[27] Lu W C, Wang C Z, Nguyen V, Schmidt M W, Gordon M S and Ho K M 2003 J. Phys. Chem. A 107 6936
[28] Zhao M W, Zhang R Q and Lee S T 2004 Phys. Rev. B 69 153403
[29] Chelikowsky J R 1998 Phys. Rev. B 57 3333
[30] Chu T S, Zhang R Q and Cheung H F 2001 J. Phys. Chem. B 105 1705
[31] Song J and Choi M 2002 Phys. Rev. B 65 R241302
[32] Bromley S T and Flikkema E 2005 Phys. Rev. Lett. 95 185505
[33] Singh K A, Kumar V and Kawazoe Y 2005 Phys. Rev. B 72 155422
[34] Hohenberg P and Kohn W 1964 Phys. Rev. 136 B864
[35] Kohn W and Sham L J 1965 Phys. Rev. 140 A1133
[36] Martin R M 2004 Electronic Structure (Cambridge: Cambridge University Press)
[37] Gonze X, Beuken J M, Caracas R, Detraux F, Fuchs M, Rignanese G M, Sindic L, Verstraete M, Zerah G, Jollet F, Torrent M, Roy A, Mikami M, Ghosez Ph, Raty J Y and Allan D C, 2002 Comput. Mat. Sci. 25 478, http://www.abinit.org
[38] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[39] Troullier N and Martins J L 1991 Phys. Rev. B 43 1993
[40] Fuchs M and Scheffler M 1999 Comput. Phys. Commun. 119 67
[41] Levien L, Prewitt C T and Weidner D, 1980 Am. Mineral. 65 920
[42] Teter M 1993 Phys. Rev. B 48 5031
[43] Monkhorst H J and Pack J D 1976 Phys. Rev. B 13 5188
[44] Bilalbegović G 2004 Phys. Rev. B 70 045407
[45] Sayle R and Milner-White E J 1995 Trends Biochem. Sci. 20 374
[46] Bernstein H J 2000 Trends Biochem. Sci. 25 453
[47] Hirshfeld F L 1977 Theor. Chim. Acta 44 129
[48] De Proft F, Van Alsenoy C, Peeters A, Langenaeker W and Geerlings P 2002 J. Comp. Chem. 23 1198
[49] Nalewajski R F and Parr R G 2000 Proc. Natl. Acad. Sci. USA 97 8879
[50] Kowalczyk J A 1999 J. Mol. Graphics Modelling 17 176, http://www.xcrysden.org