Z. Phys. D 40, 36–39 (1997)

ZEITSCHRIFT
FÜR PHYSIK D

Small silicon oxide clusters: chains and rings

Lai-Sheng Wang[1,2], **S.R. Desai**[2], **H. Wu**[1], **J.B. Nichloas**[2]

[1] Department of Physics, Washington State University, Richland, WA 99352, USA
[2] EMSL, Pacific Northwest National Laboratory, MS K2-14, Richland, WA 99352, USA

Received: 4 July 1996

Abstract. We study several silicon oxide cluster series with different Si:O stoichiometries using photoelectron spectroscopy (PES) of size-selected anions: $(SiO)_n^-$ ($n = 3$–5), $(SiO_2)_n^-$ ($n = 1$–4), and $Si(SiO_2)_n^-$ ($n = 2,3$). The $(SiO)_n$ clusters are shown to be closed-shell molecules and the HOMO-LUMO gaps are observed from the PES spectra to decrease for larger n. These clusters are shown to have ring sturctures. Si_3O_4 is known to have a D_{2d} structure with two perpendicular Si_2O_2 rhombuses.The PES spectrum of $Si_4O_6^-$ is very similar to that of $Si_3O_4^-$. It is concluded that Si_4O_6 has a similar structure with a chain of three Si_2O_2 rhombuses. The $(SiO_2)_n$ clusters all exhibit high electron affinities and only one band is observed at 4.66 eV photon energy. These clusters are shown to have similar chain structures containing Si_2O_2 rhombuses, but the two terminal Si atoms are bonded to an extra O atom each. The possibility of using these clusters to provide structural models for oxygen-deficient defects in bulk silicon oxides is also discussed.

PACS: 36.40.-c; 33.80.Eh; 31.15.Ar

---

1 Introduction

Silicon oxide is an important material in many technological areas [1]. Obtaining a molecular level description of the various silicon oxide polymorphs would greatly aid their applications to new areas. Clusters of silicon oxide provide useful and simple models to help our understanding of the structure and bonding in the bulk materials. The small size of the clusters allows accurate theoretical calculations to be performed, which help verify experimental interpretation. Surprisingly, very few experimental investigations have been done [2–8], and only a handful of theoretical studies have been performed [9–15]. Pure silicon oxides come in two stoichiometries, SiO_2 (principally as quartz) and SiO. However, there are many structural motifs in the bulk materials, such as SiO_4 tetrahedra and $(SiO)_n$ rings [16]. It would be of considerable interest to see if the bulk structural motifs can be identified in the small clusters.

We are engaged in a major effort to study the structure and bonding of silicon oxide clusters, both experimentally and theoretically [17–20]. Experimentally, we use photoelectron spectroscopy (PES) of size-selected anions, which yields unique electronic and bonding information about the neutral clusters. Theoretical calculations are then performed, which give detailed structural and bonding information about the clusters. In the current work, we focus on clusters that have stoichiometries similar to those found in the bulk oxides.

Through a combined experimental and theoretical study, we have found previously that the unsaturated silicon oxide cluster, Si_3O_4, has a D_{2h} structure with two Si_2O_2 rhombuses sharing one Si atom [17]. The central Si atom possesses a distorted tetrahedral bonding geometry while the two terminal Si atoms are coordinated only to two O atoms, each with a lone pair electron. Very recently, we have reported an experimental PES study of SiO_2,Si_2O_3, and Si_2O_4 and their Ge analogs [19]. SiO_2 is similar to CO_2 with a symmetric linear structure while Si_2O_4 has a D_{2h} structure with a Si_2O_2 rhombus and two Si=O double bonds. In the present paper, we extend the previous works to larger silicon oxide clusters. We find that Si_4O_6 is similar to Si_3O_4 with one more Si_2O_2 rhombus. It essentially has a chain type of structure containing three perpendicular Si_2O_2 rhombuses. For the $(SiO_2)_n$ series, we show that for up to $n = 4$ the clusters take on similar chain type of structure. In addition, we report results for the $(SiO)_n$ series of clusters, which have ring type of structures for $n = 2$–4. Therefore, we begin to understand systematically the hierarchy of the structure and bonding of the small silicon oxide clusters. We will also comment on the possibility of Si_3O_4 as a structural model for O-deficient defect sites in bulk silicon oxides.

2 Experimental

The $Si_xO_y^-$ cluster anions are formed by laser vaporizing a pure silicon target into a helium atmosphere containing 0.1 % O_2. The cluster beam-photoelectron spectroscopic apparatus has been described in detail before [17–19, 21]. Briefly, we use a magnetic bottle time-of-flight photoelectron analyzer, which has nearly 100 % collecting efficiency. A Q-switched

Nd:YAG laser (20 mJ output of the second harmonic) is used as the vaporization laser. The plasma reactions between the laser vaporized silicon atoms and the O_2 seeded in the carrier gas produce a series of $Si_xO_y^-$ clusters. The negative clusters are extracted perpendicularly from the beam and subjected to a time-of-flight mass analysis. The desired $Si_xO_y^-$ species are mass selected and subsequently decelerated before interacting with the detachment laser from the fourth harmonic output (266 nm, 4.66 eV) of another Q-switched Nd:YAG laser. The spectra are taken at 20 Hz with the vaporization laser off at alternating shots for background subtraction. The electron energies are calibrated with the known spectrum of the Cu^- anion and are subtracted from the photon energy to obtain the PES binding energy (BE) spectra presented.

3 Results and discussion

3.1 $Si(SiO_2)_n$ ($n = 2, 3$)

The spectra of $Si(SiO_2)_n^-$ ($n = 2, 3$) at 4.66 eV are shown in Fig. 1. Each has a feature at low BE followed by a large energy gap and more features at high BE. The two spectra are quite similar except for the size of the energy gap (~2.8 eV for $Si_3O_4^-$ and ~2.1 eV for $Si_4O_6^-$).

We have reported a vibrationally resolved spectrum for the first feature of $Si_3O_4^-$ at 2.33 eV photon energy where the energy gap was not observed [17]. Ab initio calculations have also been performed for this cluster [17]. The optimized geometries for both the neutral and the anion are shown in Fig. 2 (left). The two terminal Si atoms, coordinated to only two O atoms, each have a lone pair electron (Fig. 2, right) and an empty $3p$ orbital perpendicular to the plane of the respective Si_2O_2 rhombus. The highest occupied molecular orbital (HOMO) of Si_3O_4 consists of the $3s$ lone pairs while the lowest unoccupied MO (LUMO) is mainly of the $3p$ character. In the anion, the extra electron enters the LUMO and is localized on one of the terminal Si atoms (Fig. 2, right). This makes the two Si_2O_2 rhombuses inequivalent and distorts the anion to a C_{2v} symmetry. The lower BE feature in the PES spectrum represents the ground state of the neutral Si_3O_4 created by removing the extra electron. The second higher BE feature is from the removal of a $3s$ electron, corresponding to a triplet excited state of the neutral Si_3O_4. Therefore, the measured energy gap of 2.8 eV is essentially the triplet state excitation energy.

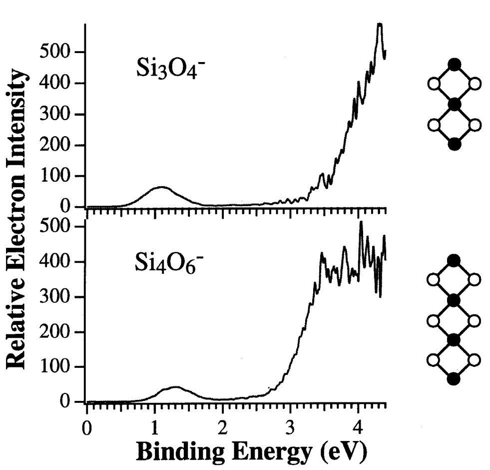

Fig. 1. Photoelectron spectra of $Si(SiO_2)_n^-$ ($n = 2,3$) at 4.66 eV photon energy. The structures of the neutral clusters are shown schematically

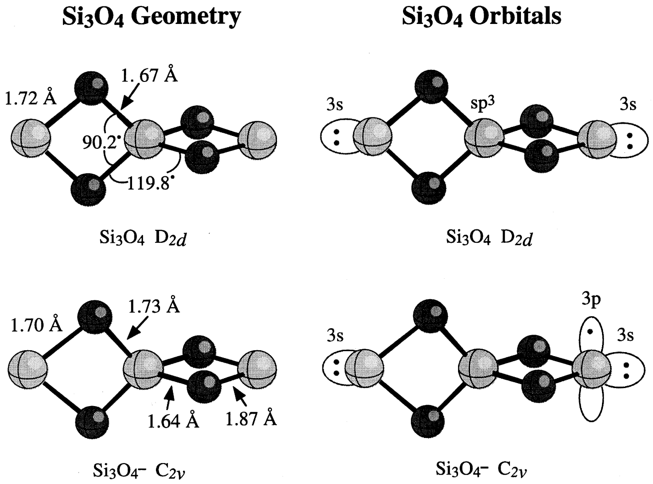

Fig. 2. MP2/6-311+G* optimized structures of Si_3O_4 and $Si_3O_4^-$ and their valence orbital occupancy. Details of the calculations can be found in [17]

The $Si_4O_6^-$ PES spectrum is very similar to that of $Si_3O_4^-$, suggesting that they have similar electronic and geometrical structure. The most reasonable structure for this cluster is the one shown schematically in Fig. 1 alongside the spectrum. This structure is an extension of the D_{2d} structure of Si_3O_4 by an extra Si_2O_2 rhombus, where the central rhombus is perpendicular to the two end-rhombuses, leaving the two middle Si atoms with a distorted tetrahedral coordination. The two terminal Si atoms are similar to that in Si_3O_4, giving rise to the similar PES spectrum. Preliminary calculations support this chain structure for Si_4O_6 [20].

3.2 $(SiO_2)_n$ ($n = 1–4$)

Figure 3 displays the spectra of $(SiO_2)_n^-$ for $n = 1–4$. For both SiO_2^- and $Si_2O_4^-$, one broad band is observed and they both have rather high electron affinities (EAs). Only an onset is observed for the spectra of $Si_3O_6^-$ and $Si_4O_8^-$. Following the trend of the EA in the $(SiO_2)_n$ series, we suspect that the onset of $Si_4O_8^-$ only represents a lower limit.

The structure and bonding of SiO_2 and Si_2O_4 have been studied both theoretically and experimentally [5, 12, 19]. SiO_2 has a $D_{\infty h}$ linear structure, similar to CO_2 while Si_2O_4 has a D_{2h} structure with a Si_2O_2 rhombus and two terminal $Si=O$ bonds, as shown schematically in Fig. 3. Our calculations indicate that the SiO_2^- anion has a bent structure with a 140 degree bond angle [20]. This explains the broad nature of the SiO_2^- spectrum. For the Si_2O_4 cluster, the Si atoms are in approximate sp^2 hybridization. Our calculations suggest that in the anion the extra electron tends to localize on one Si atom and changes its hybridization from sp^2 to sp^3, distorting the terminal O atom to be out of the molecular plane. The large geometry change between the anion and the neutral is consistent with the broad spectrum observed for $Si_2O_4^-$.

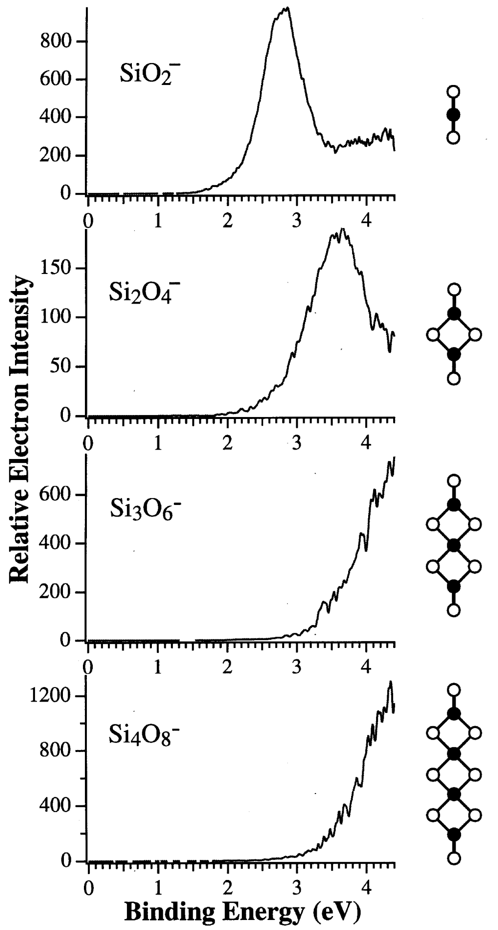

Fig. 3. Photoelectron spectra of $(SiO_2)_n^-$ ($n = 1$–4) at 4.66 eV photon energy. The structures of the neutral clusters are shown schematically

For Si_3O_6, our calculations suggest that it has a D_{2d} structure similar to that of Si_3O_4, except that the two terminal Si atoms are now double-bonded to a third O atom [20], as shown in Fig. 3. A recent calculation by Harkless et al. arrived at a similar conclusion [9]. In the $Si_3O_6^-$ anion, the extra electron localizes on one terminal Si atom and causes the terminal O atom to bend out of the Si_2O_2 rhombus plane. Thus, a fairly broad PES spectrum is expected for $Si_3O_6^-$, in agreement with the observation of the broad onset of the $Si_3O_6^-$ shown in Fig. 3.

There is only one previous work on the Si_4O_8 cluster by Harkless et al. [9]. They found five isomers including the chain structure shown in Fig. 3. This structure is similar to that of Si_4O_6 by attaching an O atom to each of the two terminal Si atoms. Our preliminary calculations also suggest a similar chain structure [20]. Although our PES spectrum does not provide definitive spectroscopic evidence to distinguish the different isomers, the chain isomer is a reasonable candidate based on the structures of the smaller clusters. It is clear that as the cluster size increases there will be more isomers that need to be considered and more experimental data will be required to compare with the calculations to firmly establish the cluster structure.

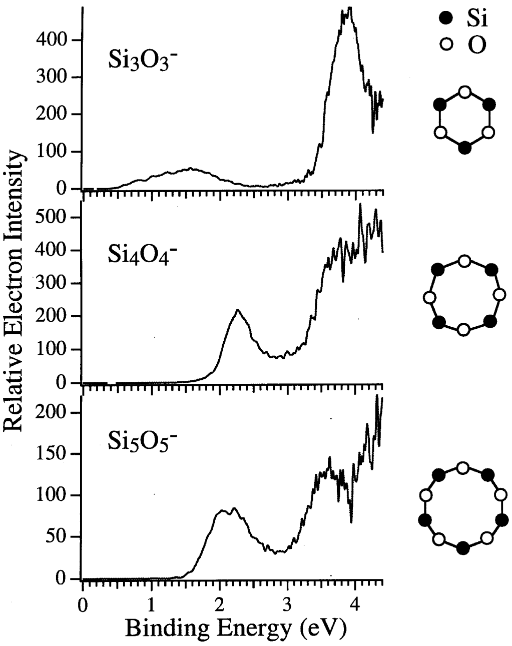

Fig. 4. Photoelectron spectra of $(SiO)_n^-$ ($n = 3$–5) at 4.66 eV photon energy. The structurs of the neutral clusters are shown schematically

3.3 $(SiO)_n$ ($n = 3$–5)

The spectra of $(SiO)_n^-$ ($n = 3$–5) are shown in Fig. 4. Each spectrum has a broad feature at lower BE followed by an energy gap and a higher BE feature. The spectra suggest that all of these clusters in the neutral forms are closed-shell and the gaps are measures of their HOMO-LUMO energy separations. The broad features indicate that there is a large geometry change between the anions and the neutrals.

Si_3O_3 has been studied in a previous matrix infrared experiment [2], which suggested a planar D_{3h} ring structure. Our calculations found that indeed the Si_3O_3 cluster has a D_{3h} ring structure with a closed-shell ground state [20]. However, in the anion, one O atom is bent out of the molecular plane distorting the cluster to C_s symmetry. This large geometry change betweeen the anion and the neutral causes the broad PES spectrum observed for $Si_3O_3^-$.

The PES spectrum of $Si_4O_4^-$ is similar to that of $Si_3O_3^-$. However, Si_4O_4 exhibits a higher EA, a smaller HOMO-LUMO gap, and its first band is also narrower than that of $Si_3O_3^-$. There is no previous work on this cluster. A matrix IR experiment on Ge_4O_4 suggested that it has a C_{4v} ring structure [22]. Si_4O_4 is expected to have analogous properties as Ge_4O_4. As we have shown previously, the smaller cluster Ge_2O_2 possesses a similar rhombus structure as Si_2O_2 [18]. It is also known that both Ge_3O_3 and Si_3O_3 have similar D_{3h} structures [2, 22]. We have obtained the PES spectrum of $Ge_3O_3^-$ which is nearly identical to that of $Si_3O_3^-$. Therefore, we conclude that Si_4O_4 is likely to have a similar ring structure.

The spectrum of $Si_5O_5^-$ resembles that of $Si_4O_4^-$ except that it is shifted to lower BE. There is no previous work on the Si_5O_5 cluster. Based on the spectral similarity between $Si_5O_5^-$ and $Si_4O_4^-$, we propose Si_5O_5 to also have a ring structure. However, our preliminary calculations suggest that the Si_5O_5 ring is not planer. This might explain the spectral shift from $Si_4O_4^-$ to $Si_5O_5^-$. Clearly, there will be other isomers for the larger clusters that need to be considered before a definitive structure can be established.

3.4 O-deficient defects in bulk silicon oxides

Defects play important roles in determining the properties of the bulk silicon oxides. Oxygen-deficient defects have been the subject of considerable controversy in the literature and are still not well understood [23–26]. These defects contain centers that have singlet electronic states and characteristic optical absorption and luminescence [27, 28]. There are two structural proposals for this type of defect: one involves two-coordinated Si sites, $:Si(O)_2$, the other involves a direct Si–Si bond, $(O)_3Si–Si(O)_3$ [23–28]. In particular, these defects have a blue luminescence band at $\sim$2.7 eV, which has been determined to be due to a triplet-singlet transition [27, 28]. Many model calculations have been carried out to determine the structure of these defects [24–26]. However, no definitive answer has been reached.

The energy gap observed in Si_3O_4 is very close to the energy of the luminescence for the O-deficient defects. Interestingly, the excitation in Si_3O_4 involves a singlet-triplet excitation on a two-coordinated Si atom. We think that this lends strong support to the two-coordinated Si centers as the structural model for the O-deficient defect sites [23]. Further studies will be required to obtain the higher excited states of the Si_3O_4 clusters and to see if they agree with the other optical characteristics of the O-deficient defects [27, 28]. In any case, it appears promising that studies of the Si_xO_y clusters will provide useful models for the bulk defect sites.

Conclusion

We have shown that small silicon oxide clusters have chain or ring types of structures depending on the Si:O compositions. It is expected that as the cluster size increases other three dimensional structures may occur and there will also be more structural isomers. It would be interesting to determine when this structural diversification takes place. A complete understanding of the structural hierarchy of the small silicon oxide clusters will not only provide good models to test theories but also help understand the bulk properties of the many materials based on silicon oxides. This understanding may also aid the design of new materials with novel structural building blocks.

This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Science Division and is conducted at Pacific Northwest National Laboratory, operated for the U.S. Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

References

1. Helms, C.R., Deal, B.E. (eds.): The Physics and Chemistry of SiO_2 and the Si-SiO_2 Interface. New York: Plenum Press 1988
2. Anderson, J.S., Ogden, J.S.: J. Chem. Phys. **51**, 4189 (1969)
3. Tremblay, B., Roy, P., Manceron, L., Alikhani, E.M., Roy, D.: J. Chem. Phys. **104**, 2773 (1996)
4. Flank, A.M., Karnatak, R.C., Blancard, C., Esteva, J.M., Lagarde, P., Connerade, J.P.: Z.Phys. D **21**, 357 (1991)
5. Mehner, T., Gocke, H.J., Schunck, S., Schnockel, H.: Z. Anorg. Allg. Chem. **580**, 121 (1990)
6. Khanna, R.K., Stranz, D.D., Donn, B.: J. Chem. Phys. **74**, 2108 (1981)
7. Schnockel, H., Mehner, T., Plitt, H.S., Schunck, S.: J. Am. Chem. Soc. **111**, 4578 (1989)
8. Goldberg, N., Iraqi, M., Koch, W., Schwarz, H.: Chem. Phys. Lett. **225**, 404 (1994)
9. Harkless, J.A.W., Stillinger, D.K., Stillinger, F.H.: J. Phys. Chem. **100**, 1098 (1996)
10. Sommerfeld, T., Scheller, M.K., Cederbaum, L.S.: J. Chem. Phys. **103**, 1057 (1995)
11. Sommerfeld, T., Scheller, M.K., Cederbaum, L.S.: J. Chem. Phys. **104**, 1464 (1995)
12. Ystenes, M.: Spectrochim. Acta **50** A, 219 (1994)
13. Boldyrev, A.I., Simons, J.: J. Phys. Chem. **97**, 5875 (1993)
14. Snyder, L.C., Raghavachari, K.: J. Chem. Phys. **80**, 5076 (1984)
15. Bencivenni, L., Pelino, M., Ramondo, F.: J. Mol. Struct. **253**, 109 (1992)
16. Elliott, R.: J. Non-Cryst. Solids **182**, 1 (1995)
17. Fan, J., Nicholas, J.B., Price, J.M., Colson, S.D., Wang, L.S.: J. Am. Chem. Soc. **117**, 5417 (1995)
18. Nicholas, J.B., Fan, J., Wu, H., Colson, S.D., Wang, L.S.: J. Chem. Phys. **102**, 8277 (1995)
19. Wang, L.S., Wu, H., Desai, S.R., Fan, J., Colson, S.D.: J. Phys. Chem. **100**, 8697 (1996)
20. Nicholas, J.B.: (to be published)
21. Wang, L.S., Cheng, H.S., Fan, J.: J. Chem. Phys. **102**, 9480 (1995)
22. Ogden, J.S., Ricks, M.J.: J. Chem. Phys. **52**, 352 (1970)
23. Skuja, L.: Non-Cryst. Solids **149**, 77 (1992)
24. Dianov, E.M., Sokolov, V.O., Sulimov, V.B.: J. Non-Cryst. Solids **149**, 5 (1992)
25. Sulimov, V.B., Sokolov, V.O.: J. Non-Cryst. Solids **191**, 260 (1995)
26. Sokolov, V.O., Sulimov, V.B.: Phys. Status Solidi (b) **186**, 185 (1994)
27. Tohmon, R., Shimogaichi, Y., Mizuno, H., Ohki, Y., Nagasawa, K., Hama, Y.: Phys. Rev. Lett. **62**, 1388 (1989)
28. Nishikawa, H., Watanabe, E., Ito, D., Ohki, Y.: Phys. Rev. Lett. **72**, 2101 (1994)