

Si₃O_y (y = 1–6) Clusters: Models for Oxidation of Silicon Surfaces and Defect Sites in Bulk Oxide Materials

Lai-Sheng Wang,^{1,2} John B. Nicholas,² Michel Dupuis,² Hongbin Wu,¹ and Steven D. Colson²

¹Department of Physics, Washington State University, Richland, Washington 99352

²Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington 99352

(Received 6 December 1996)

We studied the structure and bonding of a series of silicon oxide clusters, Si₃O_y (y = 1–6), using anion photoelectron spectroscopy and *ab initio* calculations. For y = 1–3 the clusters represent the sequential oxidation of Si₃, and provide structural models for the oxidation of silicon surfaces. For y = 4–6, the clusters contain a central Si in a tetrahedral bonding environment, suggesting the onset of the bulklike structure. Evidence is presented that suggests the Si₃O₄ cluster (D_{2d}) may provide a structural model for oxygen-deficient defect sites in bulk SiO₂ materials. [S0031-9007(97)03307-3]

PACS numbers: 68.35.-p, 31.15.Ar, 36.40.Mr

Silicon and silicon oxides are technologically important materials. A large body of research has focused on understanding the oxidation of silicon surfaces and the structure of the Si/SiO₂ interface [1–5]. However, a precise atomic-level description of the oxidation processes and the Si/SiO₂ interface is still lacking. Equally important are the structures of the defects in SiO₂ that strongly influence the physical and chemical properties of the bulk material. The atomic-level structure of many defects, and particularly, the oxygen-deficient defects, are not well known [6–8]. Using a combined experimental and theoretical approach, we are systematically studying the structure and bonding of small silicon oxide clusters with Si_xO_y stoichiometry [9]. Our aim is to discover clusters with the stoichiometry and geometry needed to correctly model the defect sites. Experimentally, we synthesize negatively charged clusters (Si_xO_y[−]) with a laser vaporization cluster beam technique. We perform photoelectron spectroscopy (PES) experiments to obtain information about the electronic structure of size-selected clusters. *Ab initio* molecular orbital (MO) calculations are then carried out and compared to the experiments to obtain atomic structure and chemical bonding information about both the neutral and negative clusters.

In this Letter, we report studies on a series of Si₃O_y[−] (y = 1–6) clusters. For y = 1–3, the clusters represent the sequential oxidation of Si₃, for which each additional O atom bridge bonds to two Si, giving cyclic structures. At Si₃O₄, the cluster begins to adopt a three-dimensional structure in which a central Si atom is tetrahedrally bonded by the four O. For y = 5 and 6, the extra O atoms are added to the two-coordinated terminal Si of the Si₃O₄ cluster through Si=O double bonds. On the basis of the bonding environment, this sequence of clusters (y = 1–6) is similar to models proposed for the initial oxidation of silicon surfaces. We also find structural and spectroscopic evidence that the Si₃O₄ cluster may provide a reasonable molecular model for the diamagnetic oxygen-deficient defect sites in bulk silicon oxides.

The PES experiments are performed on an apparatus that couples a laser vaporization cluster source and a magnetic-bottle-type time-of-flight (TOF) PES analyzer. The details of the apparatus have been published previously [10]. Briefly, the Si₃O_y[−] clusters are produced by vaporizing a pure silicon target with a helium carrier gas that contains 0.1% O₂. Individual Si₃O_y[−] clusters, formed through plasma reactions between Si and O, are size selected by a TOF mass spectrometer and detached by a laser beam from a Q-switched Nd:YAG laser at 355 nm (3.49 eV) or 266 nm (4.66 eV). Figure 1 shows the PES spectra of Si₃O_y[−] (y = 1–6) at 266 nm. The 355 nm spectra are better resolved, but do not reveal the high BE features. In particular, the binding energy (BE) of the Si₃O₆[−] cluster is too high to be studied at 355 nm. Even at 266 nm, the Si₃O₆[−] spectrum appears to display only an onset. While

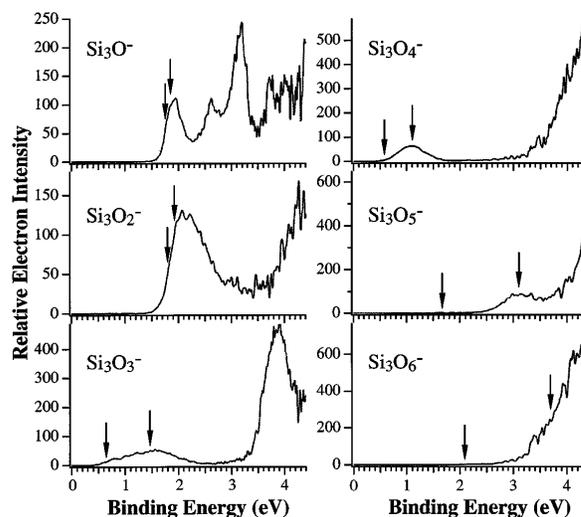


FIG. 1. Photoelectron spectra of Si₃O_y[−] (y = 1–6) at 266 nm (4.66 eV). The arrows indicate the theoretical adiabatic and vertical electron affinities of the neutral clusters. Notice the large difference between the adiabatic and vertical transitions in Si₃O₅[−] and Si₃O₆[−] as a result of the large geometry changes between the anion and the neutral.

Si_3O_5^- and Si_3O_6^- exhibit high abundance in the mass spectra, their photoelectron signals are quite weak.

The PES spectra shown in Fig. 1 represent transitions from the ground state of the anions to the ground and excited states of the neutral clusters, governed by the Franck-Condon principle. The lowest BE feature in each spectrum is the transition to the ground state and yields the electron affinity (EA) of the neutral clusters. When vibrational structure is resolved, the EA can be obtained quite accurately. To enhance the PES resolution, all spectra are also taken at lower photon energies where possible. We have previously shown a vibrationally resolved spectrum for Si_3O_4^- at 532 nm (2.32 eV) [9]. The 355 nm spectra of both Si_3O^- and Si_3O_2^- are partially vibrationally resolved. The vertical EA (VEA) is measured from the peak maxima in each spectra. The adiabatic EA (AEA) can be estimated only from the onset of each spectra, which frequently yields only the upper limits of the true AEA, depending on the geometry changes between the anion and the neutral. We list the VEA and AEA for all the clusters in Table I. All the Si_3O_y^- spectra for $y \geq 2$ show rather broad Franck-Condon envelopes, suggesting significant geometry changes upon detachment of the extra electron. The higher BE features in each spectra shown in Fig. 1 represent the excited states of the neutral clusters. While several excited states are observed for Si_3O , only one higher BE feature is observed for Si_3O_y^- ($y = 2-5$). The large energy gap observed in the spectra of Si_3O_3^- and Si_3O_4^- suggests that the neutral clusters are closed shell. The gap represents the energy separation between the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO).

In the theoretical part of this work, we used *ab initio* MO techniques to obtain the minimum energy geometry of each of the clusters (both neutral and anion). Optimizations are performed using the modern gradient techniques of the computer program GAUSSIAN94 [11]. Initial opti-

TABLE I. Comparison of experimental and calculated AEA and VEA (eV) for the Si_3O_y ($y = 1-6$) clusters. Theoretical predictions at the MP2/6-311 + $g(2df, 2pd)$ //MP2/6-311 + G^* level.

	AEA		VEA	
	Experiment	Theory	Experiment	Theory
Si_3O	1.76 (0.08) ^a	1.74	1.96 (0.06)	1.84
Si_3O_2	1.81 (0.09) ^a	1.80	2.03 (0.06)	1.91
Si_3O_3	0.6 (0.1) ^b	0.63	1.5 (0.1)	1.44
Si_3O_4	0.46 (0.07) ^a	0.57	1.055 (0.050)	1.10
Si_3O_5	<2.5 ^c	1.56	3.1 (0.1)	3.09
Si_3O_6	<3.1 ^c	2.09	>3.5 ^d	3.68

^aDerived from 355 nm spectra which are partially vibrationally resolved.

^bEstimate due to lack of sharp threshold onset.

^cUpper limit due to long tail extending to lower binding energies, indication of large geometry change from anion to neutral.

^dEstimate due to large tail in the high binding energy.

mizations were done at the Hartree-Fock level using the 6-31 + G^* basis set [12]. The frequencies calculated at this level of theory are all positive, indicating that the optimized structures represent minima on the potential energy surface. To obtain more accurate geometries and energetics we then optimize the clusters using second order Møller-Plesset perturbation theory (MP2) [13] with the 6-31 + G^* and 6-311 + G^* basis sets [14]. Finally, we calculate the MP2/6-311 + $G(2df, 2pd)$ [15] energies at the MP2/6-311 + G^* geometries. Core electrons are frozen in the MP2 calculations. The accuracy imparted by the electron correlation and the large basis sets is sufficient to determine the preferred geometry and gives good agreement with experimentally determined properties. We report the optimized geometries from only the MP2/6-311 + G^* calculations, while VEA and AEA values are given at the MP2/6-311 + $g(2df, 2pd)$ //MP2/6-311 + G^* level. The difference in total energy between the anion and neutral represents the AEA. The energy difference between the anion and the neutral at the anion geometry gives the VEA. The calculated VEA and AEA are given in Table I and indicated by the arrows in Fig. 1. The optimized geometry of the neutral clusters is shown in Fig. 2.

The Si_3O cluster [C_{2v} , 1A_1 , Fig. 2(a)], in which O bridge bonds to two Si, has been studied before [16,17]. The

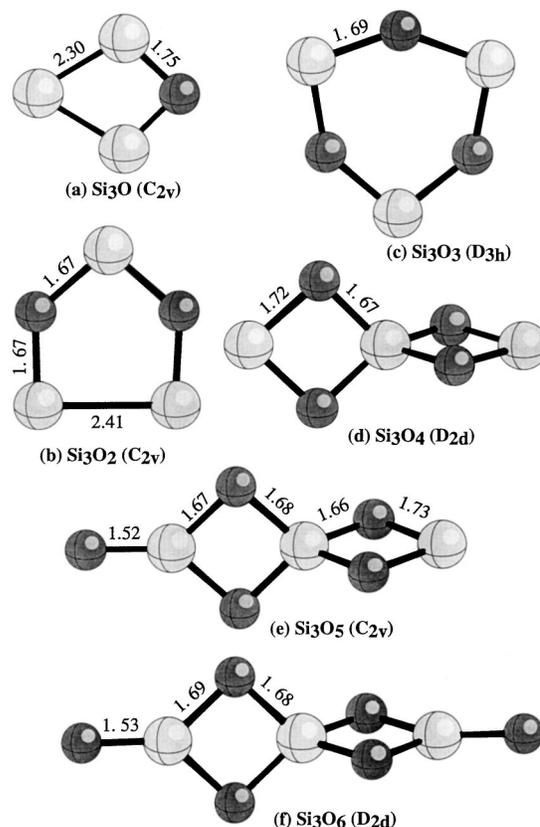


FIG. 2. MP2/6-311 + G^* optimized structures of the Si_3O_y ($y = 1-6$) clusters. All bond lengths are in Å. Note that for $y = 1-4$, all the O atoms are bridge bonded to two Si.

previous theoretical investigation predicts an AEA value of 1.7 ± 0.2 eV [17], in excellent agreement with our calculation. The theoretically predicted geometry change between Si_3O and Si_3O^- (C_{2v} , 2B_2) is small, resulting in a relatively small difference between the AEA and VEA, consistent with our experimental observation.

In Si_3O_2 [C_{2v} , Fig. 2(b)], each O bridges two Si, resulting in a pentagonal ring. We find that the ground state of Si_3O_2 is a 3B_1 state, with a 1A_1 state only 0.25 eV higher. The arrows in Fig. 1 indicate the AEA and VEA values for the triplet state. However, transitions to the singlet state are also present in the spectrum, giving rise to the rather broad peak in the Si_3O_2^- spectrum. The singlet features are seen more clearly in the 355 nm spectrum. An extensive theoretical treatment of the Si_3O_2 system has been completed and will be published elsewhere [18].

In Si_3O_3 [${}^1A'$, Fig. 2(c)] the third O again bridges two Si, resulting in a cyclic D_{3h} structure, known from previous matrix infrared absorption work [19]. In Si_3O_3^- (${}^2A'$, C_s), one O bends out of the plane. This large geometry change leads to the very broad ground state feature in the PES spectrum (Fig. 1). No vibrational structures can be resolved for the spectrum of Si_3O_3^- , even when a low detachment photon (532 nm) is used, possibly due to excitation of several vibrational modes [20].

The Si_3O_4 cluster [1A_1 , D_{3d} , Fig. 2(d)] has two Si_2O_2 rhombuses sharing a central Si [9]. In the Si_3O_4^- anion (2B_2 , C_{2v}), the two Si_2O_2 rhombuses are inequivalent due to the localization of the extra electron on one of the terminal Si atoms. Si_3O_4 has a real three-dimensional structure, compared to the smaller Si_3O_y clusters which are all planar. The central Si atom in Si_3O_4 is tetrahedrally bonded, albeit slightly distorted from the ideal tetrahedral geometry.

In Si_3O_5 (1A_1 , C_{2v}) and Si_3O_6 (1A_1 , D_{2d}), the extra O atoms are subsequently bonded to the terminal Si atoms in Si_3O_4 , forming essentially Si=O double bonds [Figs. 2(e) and 2(f)]. For both Si_3O_5^- (${}^2A'$, C_s) and Si_3O_6^- (${}^2A'$, C_s), the extra electron mainly localizes on the terminal Si atom that is bonded to three O, changing the hybridization of the Si atom from sp^2 to sp^3 . This makes the terminal O atom bend out of the plane of the Si_2O_2 rhombus relative to the neutral. This geometry change in both Si_3O_5^- and Si_3O_6^- is so severe that there is little Franck-Condon factor (FCF) for the adiabatic detachment transition, as indicated in Fig. 1. This also explains the unusually weak detachment signals observed for Si_3O_5^- and Si_3O_6^- due to the poor FCFs.

Overall, the agreement between the theoretical and experimental EAs is excellent. The variation of the EAs with the number of O atoms in the clusters is found to be highly irregular. It is interesting to compare this observation to that of metal oxide clusters for which the detachment energies always increase with the number of O atoms for a given number of metal atoms in the cluster [21], as a result of the ionic nature of the metal-oxygen bonding. The

irregularity of the EAs in the Si_3O_y^- series reflects their characteristic electronic structure and the nature of their covalent chemical bonding. Si_3O_3^- and Si_3O_4^- have low EA values because the extra electron resides in Si 3*p*-type orbitals. In Si_3O_5^- and Si_3O_6^- , the extra electron localizes in an orbital on Si with substantial 3*s* character (an *sp* hybrid), resulting in the observed high EAs.

The clusters presented here are relevant to a variety of properties of the extended materials, including the possible mechanisms for the initial oxidation of bulk Si surfaces, the atomic structures of the Si/SiO₂ interface, and defect structures in bulk SiO₂ materials. Figure 3(a) shows simplified structural models proposed for the evolution of the initial oxidation of a Si(100) surface by atomic oxygen [2]. The key structural feature is that each O atom is bridge bonded to two Si, eventually leading to the tetrahedrally bonded SiO₄ units and the amorphous silicon dioxide surface layer [2]. On an atomic level, the bonding in the Si_3O_y series is consistent with this oxidation model of the bulk Si surfaces by O atoms: from Si_3O to Si_3O_3 , each O bridges two Si atoms, resulting in the sequential oxidation of Si_3 . The Si_3O_4 cluster, with a tetrahedrally bonded Si, represents the onset of formation of bulk SiO₂ in a microscopic scale. The SiO₄ unit is a key structural feature of bulk silicon oxide. The Si_3O_4 is probably the smallest cluster to realize such a bulk feature. However, the two terminal Si atoms are only bonded to two O atoms in Si_3O_4 . We will show below that this particular structural feature may provide the model for the oxygen-deficient defect sites commonly found in bulk silicon oxide materials.

Extensive research has been directed at achieving an atomic-level description of the Si/SiO₂ interface [3], which plays a vital role in the functioning of electronic devices. It is well known that at the interface there are Si atoms with different oxidation states, depending on how

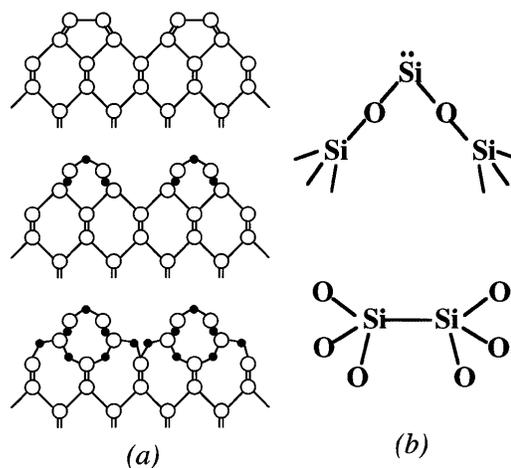


FIG. 3. (a) Simplified structural models for oxidation of a clean Si(100)-(2 × 1) surface (top) by oxygen atoms with increasing coverage (from Ref. [2]). (b) Two atomic structure models proposed for the diamagnetic oxygen-deficient defects in bulk SiO₂.

many O atoms each Si atom is bonded to. Distinct binding energy shifts have been observed for Si(I), Si(II), and Si(III) in x-ray PES of model Si/SiO₂ interfaces [3]. All of these partial oxidation states of Si can be identified from the set of Si₃O_y clusters presented here (Fig. 2). Therefore, this series of clusters may be considered as simple structural models for the Si/SiO₂ interface in terms of the range of the partial oxidation states.

Finally, the atomic structures of diamagnetic oxygen-deficient defects are still a subject of controversy [6–8]. There are two basic structural models for these defects: one is the so-called two-coordinated Si [Si(II)] and the other involves a Si—Si bond [Si(III)], as shown in Fig. 3(b). Both models give singlet ground states, but there is no direct experimental method able to differentiate between the two. An interesting characteristic of these defects is a blue luminescence band (~2.75 eV), known to be due to a singlet-triplet transition [7]. The energy gap observed in our Si₃O₄⁻ PES spectrum is in almost the same energy range (Fig. 1). As discussed above, this big HOMO-LUMO gap suggests that Si₃O₄ has a singlet ground state, as predicted by the theoretical calculations. The first excited state feature is then the triplet, and the energy gap represents the singlet-triplet excitation of Si₃O₄. If the structure of the Si₃O₄ cluster is similar to that of the defect, the cluster may be expected to have a similar singlet-triplet excitation energy since the excitation in the bulk tends to be localized [22]. The fact that Si₃O₄ possesses the right optical excitation suggests that it may provide a good candidate as a molecular model for the defect site and that the two-coordinated Si model is the correct structure for the oxygen-deficient defect in bulk silicon oxide [8]. Recent theoretical work by others [23] on the optical excitation spectrum of the two-coordinated Si atoms supports our observation.

In conclusion, we have presented a theoretical and experimental study of a series of Si₃O_y clusters. The results suggest that these clusters provide structural models for the oxidation of silicon surfaces and Si/SiO₂ interfaces. We also present evidence that Si₃O₄ may provide a structural model for the oxygen-deficient defect in bulk silicon oxide materials, suggesting that the two-coordinated Si(II) model is the correct structure for this type of defect. This work shows that the understanding of small clusters can provide real insight into bulk phenomena at the molecular level.

We thank Dr. J. Fan and Dr. S. R. Desai for experimental assistance and Dr. D. A. Dixon and Dr. L. R. Corrales for helpful discussions. This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Science Division. Computer resources were provided by the Scientific Computing Staff, Office of Energy Research, at the National Energy Research Supercomputer Center, Berkeley, CA. Pacific Northwest

National Laboratory is operated by Battelle for the DOE under Contract No. DE-AC06-76RLO 1830.

- [1] *The Physics and Chemistry of SiO₂ and the Si-SiO₂ Interface*, edited by C. R. Helms and B. E. Deal (Plenum, New York, 1988).
- [2] T. Engel, Surf. Sci. Rep. **18**, 91 (1993).
- [3] M. M. B. Holl and F. R. McFeely, Phys. Rev. Lett. **71**, 2441 (1993); A. Pasquarello, M. S. Hybertsen, and R. Car, Phys. Rev. Lett. **74**, 1024 (1995); M. T. Sieger, D. A. Luh, T. Miller, and T. C. Chiang, Phys. Rev. Lett. **77**, 2758 (1996).
- [4] C. R. Helm and E. H. Poindexter, Rep. Prog. Phys. **57**, 791 (1994).
- [5] M. F. Jarrold, Science **252**, 1085 (1991).
- [6] E. P. O'Reilly and J. Robertson, Phys. Rev. B **27**, 3780 (1983); H. Imai *et al.*, Phys. Rev. B **38**, 12772 (1988); H. Hosono *et al.*, Phys. Rev. B **44**, 12043 (1991); H. Nishikawa *et al.*, Phys. Rev. B **45**, 586 (1992).
- [7] R. Tohmon *et al.*, Phys. Rev. Lett. **62**, 1388 (1989); H. Nishikawa *et al.*, Phys. Rev. Lett. **72**, 2101 (1994).
- [8] L. N. Skuja, A. N. Streletsy, and A. B. Pakovich, Solid State Commun. **50**, 1069 (1984); L. Skuja, J. Non-Cryst. Solids **149**, 77 (1992); V. B. Sulimov and V. O. Sokolov, J. Non-Cryst. Solids **191**, 260 (1995).
- [9] J. Fan *et al.*, J. Am. Chem. Soc. **117**, 5417 (1995); L. S. Wang *et al.*, J. Phys. Chem. **100**, 8697 (1996); L. S. Wang *et al.*, Z. Phys. D (to be published).
- [10] L. S. Wang, H. S. Cheng, and J. Fan, J. Chem. Phys. **102**, 9480 (1995); H. Wu, S. R. Desai, and L. S. Wang, J. Chem. Phys. **103**, 4363 (1995); H. Wu, S. R. Desai, and L. S. Wang, Phys. Rev. Lett. **76**, 212 (1996).
- [11] M. J. Frisch *et al.*, GAUSSIAN 94 (Gaussian, Inc., Pittsburgh, PA, 1994).
- [12] R. Ditchfield, W. J. Hehre, and J. A. Pople, J. Chem. Phys. **54**, 724 (1971).
- [13] C. Moller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).
- [14] R. Krishnan *et al.*, J. Chem. Phys. **72**, 650 (1980).
- [15] M. J. Frisch, J. A. Pople, and J. S. Binkley, J. Chem. Phys. **80**, 3265 (1984).
- [16] A. I. Boldyrev and J. Simons, J. Phys. Chem. **97**, 5875 (1993).
- [17] A. I. Boldyrev *et al.*, J. Phys. Chem. **98**, 1427 (1994).
- [18] M. Dupuis and J. B. Nicholas (to be published).
- [19] J. S. Anderson and J. S. Ogden, J. Chem. Phys. **51**, 4189 (1969).
- [20] The distortion in the Si₃O₃⁻ anion is probably caused by the Jahn-Teller effect, resulting in the broad and complicated spectral features.
- [21] L. S. Wang *et al.*, Phys. Rev. B **53**, 8028 (1996); L. S. Wang, H. Wu and S. R. Desai, Phys. Rev. Lett. **76**, 4853 (1996); H. Wu, S. R. Desai, and L. S. Wang, J. Am. Chem. Soc. **118**, 5296 (1996); S. R. Desai *et al.*, J. Chem. Phys. **106**, 1309 (1997).
- [22] Our calculated singlet-triplet excitation energy for the Si₃O₄ cluster is 3.1 eV.
- [23] K. Raghavachari (private communication).