A Photoelectron Spectroscopic Study of Small Silicon Oxide Clusters: 
SiO₂, Si₂O₃, and Si₂O₄

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We present an anion photoelectron spectroscopic study of SiO₂, Si₂O₃, and Si₂O₄. We obtained the photoelectron spectra of these small silicon oxide anion clusters at 4.66 eV photon energy. All the spectra show broad photodetachment features, suggesting that there is considerable geometry change between the anion and the neutral. The vertical detachment energies are determined to be 2.76 (0.10), 2.75 (0.10), and 3.63 (0.1) eV for SiO₂⁻, Si₂O₃⁻, and Si₂O₄⁻, respectively. The spectrum of Si₂O₃⁻ shows a weak feature at lower binding energy, suggesting existence of another isomer. The spectra of GeO₂⁻ and Ge₂O₃⁻ are also obtained and are compared to the silicon analogs. They are similar to the silicon oxide species, but both have higher detachment energies, 2.93 (0.07) eV for GeO₂⁻ and 3.01 (0.07) eV for Ge₂O₃⁻. The Ge₂O₃⁻ spectrum is consistent with only one isomer. The structure and bonding of these small oxide clusters are discussed.

1. Introduction

Silicon oxide is the most abundant substance on earth and is important in many technological areas. An understanding of the structure, bonding, surfaces, and defects in silicon oxide could aid development in diverse applications such as catalysis, amorphous materials, environmental sciences, and electronic device physics. Small molecules containing Si, O, and H have been used to model properties of bulk silicon oxide. 1, 2 It was found that the SiOSi bond angles and bond lengths obtained for the small molecules compare favorably with that in the bulk and yield reasonable bulk properties when used in bulk calculations. However, to model the wide range of structural properties and defects in the bulk and on surfaces, a wider range of structural models may be required. Clusters of the type SiₓOᵧ, where x and y can be continuously varied, fulfill these roles, and they now can be synthesized experimentally with cluster beam techniques. 3 We use photoelectron spectroscopy (PES) of size-selected SiOₓ⁻ anions to obtain electronic and spectroscopic information of these clusters. The PES experiments yield unique structure and bonding information about the neutral clusters and allow systematic studies of a wide range of cluster sizes.

In this paper, we present a study of SiO₂, Si₂O₃, and Si₂O₄ and the germanium analogs. Although SiO₂ is known to be linear in the gas phase, 4, 5 there are few studies of their electronic structure. 6 There is no previous study on the Si₂O₃ species. Si₂O₄ can be viewed as a dimer of SiO₂ and has been studied in a low-temperature matrix experiment 7 and in a theoretical calculation. 8 It has a D₅h structure and has been named 2,4-dioxocyclosiloxane. In a recent calculation, both Si₂O₃⁻ and Si₂O₄⁻ have been studied in an effort to search stable doubly charged anions. 9

We obtained the photoelectron electron spectra of SiO₂⁻, Si₂O₃⁻, and Si₂O₄⁻ as well as GeO₂⁻ and Ge₂O₃⁻ at 4.66 eV photon energy. The spectrum of Si₂O₃⁻ shows one broad feature at higher binding energy and a weak broad feature at lower binding energy and is concluded to be due to two isomers. Only one broad feature is observed in all the other spectra. The germanium analogs both have higher binding energies and show slightly narrow bandwidths. The spectrum of GeO₂⁻ is similar to that of SiO₂⁻, while the spectrum of Ge₂O₃⁻ is similar to the higher binding energy feature of the Si₂O₃⁻ spectrum. Significant geometry change from the anion to the neutral in all the clusters is inferred from the broad spectra.

In the following, the experimental apparatus and procedure are presented. In section 3, we report the results and discuss the structure and bonding of these clusters based on the experimental observations. In addition, the structures of all the SiₓOᵧ (x = 1–4) clusters are compared, which can be viewed as a sequential oxidation of a Si₂ dimer. Finally, a brief summary is presented in section 4.

2. Experimental Section

We generate the SiₓOᵧ⁻ anions by laser vaporizing a pure silicon target into a helium atmosphere containing 0.05% O₂. The cluster beam photoelectron spectroscopic apparatus has been described in detail before. 10, 11 Briefly, we employ a magnetic bottle time-of-flight (MTOF) photoelectron analyzer, which has nearly 100% collecting efficiency. 12, 13 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 O₂ seeded in the carrier gas produce a series of SiₓOᵧ⁻ clusters. The helium carrier gas and the oxide clusters undergo a supersonic expansion and form a cold molecular beam collimated by a skimmer. The negative clusters are extracted perpendicularly from the beam with a 1 kV high-voltage pulse and subjected to a time-of-flight mass analyzer. The desired SiₓOᵧ⁻ species are mass selected and subsequently decelerated before interacting with the detachment laser. For the germanium oxide clusters, the silicon target is replaced with a germanium one. The fourth harmonic output (266 nm) of another Q-switched Nd:YAG laser is used for photodetachment. The electron energies are calibrated with the...
known spectrum of the Cu\(^-\) anion and are subtracted from the photon energies to obtain the PES binding energy spectra presented. The spectra are taken at 20 Hz with the vaporization laser off at alternating shots for background subtraction. All the spectra are smoothed with a 10 meV window.

### 3. Results and Discussion

Figure 1 shows the PES spectra of SiO\(_2^-\), Si\(_2\)O\(_3^-\), and Si\(_2\)O\(_4^-\) at 4.66 eV photon energy. The spectra of GeO\(_2^-\) and Ge\(_2\)O\(_3^-\) are displayed in Figure 2. Only one broad band is observed for all the spectra except for that of Si\(_2\)O\(_3^-\) which appears as two broad features, one at higher binding energy (labeled “B”) and one weak feature at lower binding energy (labeled “A”). The spectra of the two germanium oxide species appear narrower. All of these species show quite low detachment cross sections, probably caused by the broad nature of the detachment transitions. Substantial low-energy electron noise (at high binding energies) was present due to the scattered photons. The noise was more severe in the germanium cases due to their lower binding energies. There were similar peak profiles obtained.

These spectra represent photodetachment transitions from the ground state of the anion to the neutral states. The vertical detachment energies (VDE) are obtained from the peak maxima. However, the adiabatic detachment energies (ADE) are more difficult to determine due to the lack of vibrational resolution. The broad nature of these spectra, suggesting large geometry changes from the anion to the neutral, also implies that there should be little Franck–Condon factor for the 0–0 transition. An estimate of the upper bound of the ADE is obtained by drawing a straight line at the leading edge of the spectra and taking the intersect with the binding energy axis. The so-obtained ADE and VDE are listed in Table 1. The two germanium oxide species show similar VDEs, which are higher than the silicon analogs. The VDE of SiO\(_2^-\) is also quite similar to that of feature “B” of Si\(_2\)O\(_3^-\). There is a significant increase of VDE from SiO\(_2^-\) to Si\(_2\)O\(_4^-\).

#### 3.1. SiO\(_2^-\) and GeO\(_2^-\)\(^-\)

The structure of the SiO\(_2\) molecule is well-known, and its electronic structure has also been studied.\(^4\)–\(^6\) The valence electronic structures of both SiO\(_2\) and GeO\(_2\) should be similar to CO\(_2\), which has a linear symmetric structure. It is also well-known that CO\(_2\) does not have a positive electron affinity and that CO\(_2^-\) anion is bent.\(^1\)\(^4\) Indeed, the photoelectron spectrum of CO\(_2^-\) shows a rather broad peak with a VDE of 1.4 eV, reflecting the large equilibrium geometry difference between the anion and the neutral.\(^1\)\(^4\) The broad Franck–Condon envelope is along the bending mode. Analogously, the SiO\(_2^-\) and GeO\(_2^-\) are expected to be bent as well. Indeed, the broad spectra of SiO\(_2^-\) and GeO\(_2^-\) agree with this analogy. However, both SiO\(_2\) and GeO\(_2\) appear to have positive electron affinities, and their anions show rather high ADEs and VDEs. Another interesting observation is that the width of the observed broad peak decreases from CO\(_2^-\) to GeO\(_2^-\), suggesting that the bending angle is probably decreasing from CO\(_2^-\) to GeO\(_2^-\) i.e., the anion is closer to the linear structure for the heavier anions. This is consistent with the observation that the heavier molecules should have positive electron affinities.

#### 3.2. Si\(_2\)O\(_3^-\)\(^-\)

Si\(_2\)O\(_3\) can be viewed as the dimer of SiO\(_2\), and the dimerization energy has been estimated to be about 4.7 eV.\(^7\)\(^,\)\(^8\) However, the main vapor species of silica is the SiO diatomic.\(^1\)\(^5\) The Si\(_2\)O\(_4\) molecule was first observed and studied in a matrix infrared experiment where it was formed by reacting Si\(_2\)O\(_2\) with O\(_2\).\(^7\) Its ground state structure is concluded to be a symmetric D\(_{2h}\) molecule with two terminal O atoms and two bridging O atoms (2,4-dioxycyclodisiloxane).

If we assume that the Si\(_2\)O\(_4^-\) observed in our experiment corresponds to the D\(_{2h}\) neutral molecule, then the broad photoelectron spectrum shown in Figure 1 strongly suggests that there is a considerable geometrical change in the anion. Interestingly, a recent calculation on doubly charged Si\(_2\)O\(_4^2^-\) anion found that the two extra electrons enter an antibonding orbital and distorted the anion to a C\(_1\) structure, in which one terminal O atom is bent out of the molecular plane.\(^9\) It is expected that the singly charged anion should exhibit a similar

### Table 1: Adiabatic and Vertical Detachment Energies (eV) of SiO\(_2^-\), Si\(_2\)O\(_3^-\), Si\(_2\)O\(_4^-\), GeO\(_2^-\), and Ge\(_2\)O\(_3^-\)

<table>
<thead>
<tr>
<th>Species</th>
<th>ADE</th>
<th>BDE</th>
<th>VDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2^-)</td>
<td>2.1</td>
<td>1.9</td>
<td>2.6</td>
</tr>
<tr>
<td>Si(_2)O(_3^-)</td>
<td>0.9</td>
<td>1.4</td>
<td>2.50</td>
</tr>
<tr>
<td>Si(_2)O(_4^-)</td>
<td>2.75</td>
<td>3.63</td>
<td>2.93</td>
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<tr>
<td>GeO(_2^-)</td>
<td>2.50</td>
<td>3.01</td>
<td>2.43</td>
</tr>
<tr>
<td>Ge(_2)O(_3^-)</td>
<td>2.43</td>
<td>3.01</td>
<td>2.43</td>
</tr>
</tbody>
</table>

a Estimate of the upper bound of ADE.

Less noise problem was present for the spectra of the silicon oxide clusters. Nonetheless, the tail at the higher binding energy side for the SiO\(_2^-\) and Si\(_2\)O\(_3^-\) spectra is still partly caused by the imperfect background subtraction.

The spectra of the two germanium oxide species appear two broad features, one at higher binding energy (labeled “B”) and one at lower binding energy (labeled “A”). The spectra are smoothed with a 10 meV window.
distortion, as evidenced by our observed broad photoelectron spectrum. A low-frequency bending mode should be excited in the photoelectron spectrum, making it difficult to resolve vibrational structures. Indeed, more recent calculations obtain similar conclusions.16

It is interesting to compare Si2O4 with (CO2)2, whose anion has been studied both theoretically and experimentally.17,18 While the SiO2 and CO2 molecules are similar, their dimers are very different, reflecting the well-known difference between the carbon and silicon chemistries. The ground state of the CO2 dimer is a weakly bonded van der Waals species with a D2h structure,17 although it also has a rather high VDE of 2.79 eV. On the other hand, the Si2O4 molecule is a strongly covalent bonded molecule. The solids of the two molecules display exactly the same difference.

3.3. Si2O3− and Ge2O3−. These two species are expected to show similar properties. However, their photoelectron spectra are quite different. The Si2O3− spectrum shows two broad features: one strong feature at higher binding energy ("B" in Figure 1) and one weak feature at lower binding energy ("A" in Figure 1). The Ge2O3− spectrum displays only one broad feature with a rather high binding energy. It should be noted that the feature "B" of Si2O3− is rather similar compared to that of SiO2−. The same similarity is also observed between the spectra of Ge2O3− and GeO2−. This suggests that the feature "A" in the Si2O3− spectrum is most likely due to a different isomer.

The Si2O3 species can be viewed to be formed by removing an O atom from the Si2O4 molecule. There are two ways to do this, either removing a terminal O or a bridging O atom, giving two different Si2O3 structures. In reality, the Si2O3 species are probably the intermediate to form Si2O4 in the laser vaporization source. As a matter of fact, the Si2O3 molecule formed from the reaction between Si2O2 and O2 in the previous matrix experiment is most likely through such Si2O3 intermediates.7

The isotope substitution experiment using Si2O2 and isotopically labeled Si2O2 yields two isomers: 18O−SiO(OSi18O) and 18O−SiO−(18O)Si18O, where the two O atoms in the parentheses indicate the bridging O atoms (Figure 3). The intermediates in the formation of these two Si2O3 isomers are consistent with the two Si2O3 isomers proposed above.

While our experiment cannot distinguish the two isomers, recent calculations predict Si2O3 has a cyclic Si2O2 with a third terminal O atom (Figure 3),16 i.e., the structure formed by removing a terminal O atom from Si2O4. We attribute the major feature “B” in our spectrum to this isomer. The low intensity of feature “A” indicates the low abundance of this isomer, implying this isomer probably is less stable. The analogous Ge2O3 isomer is negligible, judging from the single feature observed in the Ge2O3− spectrum. Therefore, we conclude that the dominating isomer for both Si2O3− and Ge2O3− is the one with a cyclic M2O2 unit plus a terminal O atom (Figure 3). The broad nature of the M2O2− spectra suggests again that there is significant geometry change between the anion and the neutral species.

3.4. From SiO to Si2O4. Although we are not able to study the smaller clusters, SiO and Si2O2 due to difficulty to produce the anions in our source, it is still interesting to discuss the structural evolution of this series of clusters as the O content is increased. SiO has been studied and its structure is known to be C2v with a bridging O atom.19−21 Si2O2 has also been extensively studied and is known to be a cyclic D2h molecule.22−27 We previously reported that Ge2O2 has a similar structure.28

The structures of these molecules are shown schematically in Figure 3, where only the major isomer for Si2O3 is included. This series can be viewed as a sequential oxidation of the Si2 dimer. The oxidation state of the Si atoms are increased from +1 in SiO to +4 in Si2O4. Similar variation of Si atom oxidation states are known to exist in the important bulk Si/SiO2 interface.29 Therefore, this series of clusters may be viewed as the smallest models for the oxidation of a Si surface. Large clusters of the kind, Si2Ox, will undoubtedly provide better models and are being actively pursued.

4. Conclusions

We report the photoelectron spectra of small silicon oxide clusters involving one and two silicon atoms and the germanium analogs. Broad spectra are observed and suggest that there is considerable geometry change from the anion to the neutral. The SiO2− and GeO2− spectra indicate that their neutral molecules should possess positive electron affinities, in contrast to CO2. The spectral width suggests that the bending of the anions decreases from CO2− to GeO2−. The SiO2− spectrum shows a considerably lower VDE, compared to that of SiO3−. Two isomers are observed for Si2O3−, which can be viewed by removing a terminal or bridging O atom from the D2h Si2O4, with the former dominating. These small clusters plus the previously known Si2O and Si2O2 species form a series of oxide clusters which can be viewed as a sequential oxidation of a Si2 dimer and provide the smallest cluster models for the oxidation of a silicon surface.

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References and Notes

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