# X-RAY PHOTOELECTRON SPECTROSCOPY OF SILOXENE: A MODEL COMPOUND REPRESENTING INTERMEDIATE OXIDATION STATES OF SILICON AND INTERFACE DEFECT SITES

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## ABSTRACT

Siloxene is a stable Si(+1) compound with a molecular formula of $H_6Si_6O_3$, which has been prepared in 50% purity. An O1s-Si2p separation of 432.9 eV was found for Si(+1) in this system. The impurities represent a distribution of silicon oxidation states from -1 to +4. Controlled oxidation of this system generates high concentrations of Si(+2) and Si(+3). Electron irradiation converted Si(+3) to Si(+4) similar to thermal $SiO_2$, which provided a convenient reference for approximate comparison of the lower oxidation states with each other, with crystalline Si(0), and with the interface of a thin, thermal $SiO_2$ layer on a crystalline silicon substrate.

## INTRODUCTION

Recent investigations by x-ray photoelectron spectroscopy (XPS) on silicon/oxide interfaces have shown consistent evidence of silicon oxidation states intermediate between zero and +4.[1-3] In particular, the Si(+1) state has been difficult to characterize because of its close proximity to the silicon element signal, which is usually much more intense. Siloxene is an unusual silicon oxide in which all the silicon is found in the Si(+1) state. It has been prepared in reasonably pure form to help characterize the Si(+1) state and aid our understanding of silicon interfaces. Siloxene was first studied in pure form by Kautsky and Hengge.[4] It is a planar molecule composed of six-membered Si rings and has a molecular formula of $H_6Si_6O_3$, or $H_2Si_2O$ (see Fig. 1). The rings, which resemble the Si(111) crystal face, are interconnected by oxygen bridges, thus forming a two-dimensional polymer. Siloxene shows EPR activity attributed to a silicon dangling bond defect.[5]

## EXPERIMENTAL

Siloxene was prepared by hydrolysis of $CaSi_2$ in alcoholic HCl.[4] The product, a powder, was mounted for XPS by two methods. An optically flat, gold-plated silicon wafer was covered with a thin hydrocarbon polymer film by solution evaporation. This film was found to be reasonably conductive in the photon beam. The powder was evenly distributed over this film and run at 250 K. Another sample of powder was pressed into a graphite pellet and run at room temperature. Spectra were obtained on a modified Hewlett-Packard 5950A spectrometer using monochromatic

Al x-rays. Stoichiometries were determined by correcting integrated intensities for relative cross-section[6] and escape depth.[7]

## RESOLUTION ENHANCEMENT/DECONVOLUTION

A powerful method of spectral reconstruction has been under development at JPL for several years; it has been described elsewhere.[2,3,8] Application to experimental data requires spectra with reasonable signal-to-noise ratio, knowledge of a broadening function, and the ability to accurately reconstruct the unbroadened signal. Selection of the broadening function depends on mathematical criteria relatively free of user prejudice. Reconstruction involves Fourier division and linear prediction based on a maximum-entropy criterion. Test cases based on trial data generated by computer from known functions have shown the power (Fig. 7, Ref. 3) and the limitations of the method. Major peaks can be reconstructed within ± 0.2 eV and ± 10% in intensity. Moderate peaks are within ± 0.3 eV and ± 30% in intensity. Minor features may be subject to averaging.

Given siloxene's reactivity and the absence of a crystal structure, it could not be assumed that the main Si2p peak was due to $H_2Si_2O$. To confirm the assignment of the main peak, deconvolution will be used to separate components due to differential charging and higher oxide impurities from the intensity of the main peak and calculate a mass balance between silicon and oxygen. It will not be necessary to make unique and positive identification of the higher oxides; these determinations will be made in subsequent oxidation experiments without deconvolution. It will be sufficient to estimate intensities and oxygen stoichiometries (i.e., oxidation states) from approximate positions.

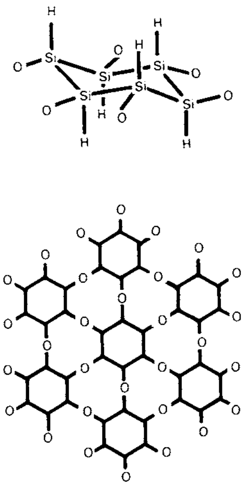

Fig. 1. Siloxene structure proposed by Kautsky and Hengge based on optical spectra, composition, substitutional chemistry, and crystallite morphology. No crystals large enough for x-ray diffraction have been obtained.

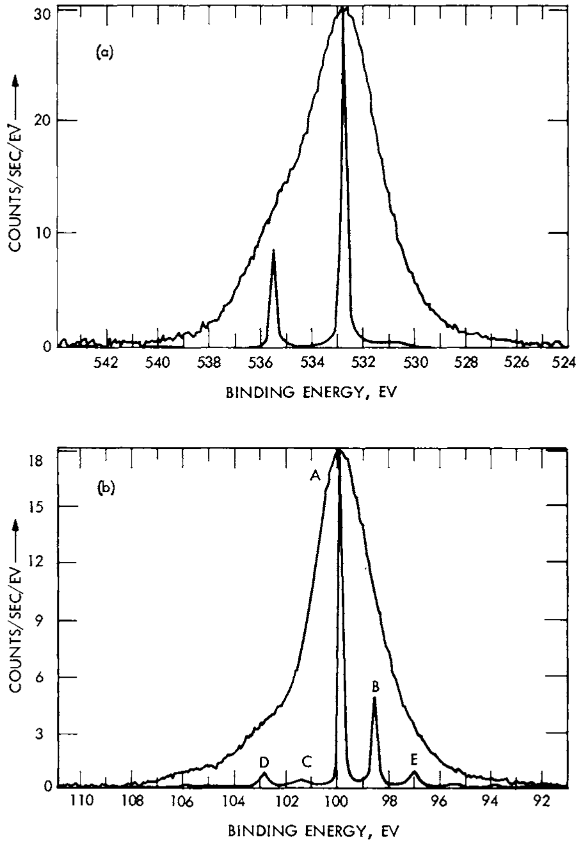

Fig. 2. Siloxene XPS spectra: (a) O1s, (b) Si2p.

## RESULTS AND DISCUSSION

O1s and Si2p raw data with background removed are shown in Fig. 2 for siloxene mounted on the hydrocarbon film. The results are a combination of chemistry and charge broadening. The integrated raw data show an overall stoichiometry of $Si_{1.4}O$ (cf. $Si_2O$ theo.). This ratio, plus the high binding energy (HBE) shoulders on O1s and Si2p, indicate the presence of oxidized impurities.

Deconvolutions are also plotted in Fig. 2. For clarity, they have been scaled to match the height of the raw data. The O1s data show a moderate peak at 536 eV and a main peak. The Si2p data show a main peak, A, a moderate contribution, B, and three minor signals: C, D, and E. Still lower intensity projects out toward 106 eV.

The Si/O stoichiometry of the 106 eV and 536 eV signals is reasonably close to $SiO_2$. The O1s-Si2p separation is also similar to that observed for amorphous $SiO_2$. These HBE signals probably represent $SiO_2$ impurities translated toward HBE by differential charging.

The main Si2p peak in Fig. 2b may be attributed to Si(+1) as $H_2Si_2O$, as shown by the mass balance below. Peak B, found at 1.3 eV toward low binding energy (LBE), can be attributed to a 23% impurity of Si(0) which, unlike crystalline Si(0), is in the form of a dihydride. This assignment is consistent with combining the 0.3 eV group shift observed for H on Si[9] with a 1 eV shift corresponding to the formation of a single Si-O bond.[2,3,5] Peak E may correspond to a $CaSi_2$ impurity.

The higher oxides indicated by the Si2p shoulder at 103 eV correspond to peaks C and D. Peak D is best interpreted as representing the combined intensity of both Si(+3) and Si(+4), having a position near the average between these two states.

Peak C shows many characteristics of Si(+2). Its 1.5 eV separation from the $H_2Si_2O$ Si(+1) peak is consistent with previous work[2,3] and consistent with combining the shifts due to loss of an Si-H[9] bond and formation of an Si-O bond.[2,3,5] Its separation from crystalline Si(0) (Table I) agrees with data obtained on SiO films.[5] Its O1s-Si2p separation of 431.4 eV is similar to the value (431.0 eV) derived from SiO.[5] This striking correspondence with data from many sources prompts the entry of peak C as Si(+2) in Table I. However, given the limitations of the deconvolution algorithm, it has been appropriately marked with an approximation sign.

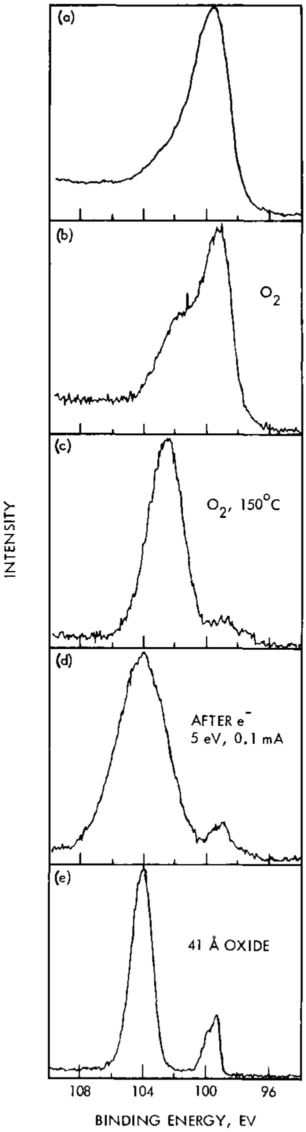

Fig. 3. Siloxene Si2p spectra (a) before and (b,c) after exposure to oxygen and (d) electrons; (e) 41 Å $SiO_2$ on Si for comparison.

It is conspicuous that Fig. 2 shows only two O1s peaks compared to a manifold of Si2p peaks. To a first approximation, the main O1s peak represents oxygen atoms in the same oxidation state, -2. The corresponding silicon oxidation states range from -1 to +4. In reality, the O1s signals do not coincide; Table I implies a shift of 0.9 eV between O1s from $H_2Si_2O$ and $SiO_2$. The corresponding Si2p shift is four times greater. Further, there is four times more oxygen per silicon atom in $SiO_2$ than $Si_2O$. Thus, in the Si2p spectrum, an $SiO_2$ peak may be small compared to the main

$Si_2O$ peak, but the corresponding O1s peaks will be nearly comparable in intensity. Therefore, in Fig. 2, the main O1s peak represents closely spaced peaks of comparable height whereas the Si2p spectrum is composed of a main peak with widely space secondaries.

Since discrete O1s signals could not be resolved for the separate oxides, one cannot calculate stoichiometries directly. One can, however, obtain a mass balance between the main O1s signal and Si2p peaks A, C, and D. Indeed, if one estimates the amount of O1s intensity expected from Si2p peak A based on $H_2Si_2O$, and adds similarly calculated estimates for peaks C and D based on average stoichiometries for Si(+2) and Si(+3, +4), the sum is equal within 3% to the observed intensity of the main O1s peak.

Thus, the O1s and Si2p spectra in Fig. 2 are consistent with an assignment of Si2p peak A as Si(+1) in the form of $H_2Si_2O$, as expected. The product is 50% $H_2Si_2O$ with 15% higher oxide impurities—apparently as Si(+2) and Si(+3, +4). An O1s-Si2p separation of 432.9 eV is observed for Si(+1) as $H_2Si_2O$.

It is significant that the mass balance shows close consistency between O1s and Si2p. The lineshapes and parameters were selected independently; the agreement between the two spectra was not built into the deconvolution. In general, it is essential to compare two different core levels from the same sample to reach reliable conclusions.

To obtain high concentrations of the other sub-oxides and to obtain a suitable Si(+4) reference signal for comparing siloxene to a real silicon interface, the graphite sample was subjected to controlled oxidation. The initial sample is shown in Fig. 3a. Exposure to an atmosphere of $O_2$ produced a modest result. The unexpected stability against $O_2$ is shown in Fig. 3b, where a shoulder roughly in the Si(+2) region was formed. Exposure to $O_2$ at 150 C generated nearly complete oxidation and left a low-level signal which probably represents Si(0) at various levels of hydrogenation (Fig. 3c). The Si2p position is consistent with Si(+3) (see Table I); the O1s spectrum showed stoichiometry of $Si_2O_3$. It seems, therefore, that this method generates a signal which is probably a mixture of states, predominantly Si(+3), with an average atomic ratio of $Si_2O_3$.

It was found that this signal could be converted, at least in part, to Si(+4) as $SiO_2$. A 0.1 mA beam of 5 eV electrons deposited sufficient energy to drive the conversion. The resulting peak shifted toward HBE and showed an O1s-Si2p separation of 429.4 eV, in agreement with the separation of 429.5 eV observed for thermal $SiO_2$ on silicon.[3] Thus, it appears that it is possible to prepare an oxide on siloxene which is very similar to thermal $SiO_2$. On this assumption, the siloxene spectra of Figs. 2 and 3a-d were shifted to be consistent with this reference point, and compared to a 41 Å thermal oxide (Fig. 3e). Siloxene peak positions with respect to crystalline Si(0) were derived from this comparison. The results are summarized in Table I along with similar data from Si/$SiO_2$ interfaces[2,3] and SiO[5] films. Any such reference is, to some extent, arbitrary due to differential charging and relaxation effects, but the absence of abnormal shifts in O1s plus a secondary reference of C1s from adsorbed hydrocarbons both suggest that the comparison is accurate to within 0.5 eV and probably much better.

## CONCLUSIONS

It has been possible to prepare, with 50% purity, A Si(+1) compound which has structural relevance to the Si/$SiO_2$ interface. Preliminary results on controlled oxidation showed an unexpected resistance toward molecular oxygen at room temperature; only partial conversion to Si(+2) was achieved. Moderate temperatures converted the system to an average stoichiometry of $Si_2O_3$, i.e., Si(+3), in high concentration. This form of $Si_2O_3$ was found to be unstable with respect to conversion to Si(+4), $SiO_2$, under 5 eV electron irradiation. Signals attributable to Si in various stages of hydrogenation have also been derived. Stoichiometries, O1s-Si2p separations, and Si2p separations from crystalline Si(0) have been established. These are useful parameters for characterizing low-intensity signals of intermediate oxidation states at the Si/$SiO_2$ interface. Despite possible

TABLE I. Binding Energy Separations (eV).

| | O1s-Si2p Separation | Separation from silicon element peak | | |
|---|---|---|---|---|
| | | Siloxene | $Si/SiO_2$[3,7] | SiO[5] |
| Si(0) (dihydride) | | -0.7[b] | | |
| Si(+1) (hydride, $H_2Si_2O$)[c] | 432.9 | 0.5 | | |
| Si(+1) ($Si_2O$)[d] | | 0.8 | 0.6 | |
| Si(+2) | ~431.4 | ~2.1 | 1.7-2.2 | 2.2 |
| Si(+3) ($Si_2O_3$) | 430.0 | 3.4 | 2.9-3.3 | |
| Si(+4) ($SiO_2$) | 429.5 | 4.8 | 4.5 | 4.4 |

a) Approximate. From comparing oxidized siloxene to 41 Å $SiO_2$ film.
b) Minus sign means toward lower binding energy.
c) This is the hydrogenated form of Si(+1) found in siloxene.
d) An estimate of where $Si_2O$ might be found at a silicon interface. Corrects (c) by silicon group shift of 0.3 eV (Grey et al.).

differential charging [-0.2 - 0.4 eV for Si(+3) and Si(+4)], the results from the model systems show close to excellent agreement with ranges of results expected and observed at a real $Si/SiO_2$ interface. Thus, the question of intermediate oxidation states has been approached from complementary points of view: the silicon interface and a system of model compounds; similar results are reached in both cases. This agreement lends support to conclusions reached previously on the distribution of oxidation states at the $Si/SiO_2$ interface.[2,3]

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