# **Direct Mass Spectrometric Identification of Silicon Oxychloride Compounds**

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#### ABSTRACT

Silicon oxychloride compounds formed during the high temperature reaction of Si and SiC with Cl<sub>2</sub>/O<sub>2</sub> mixtures at 930° and 950°C have been directly observed with an atmospheric pressure mass spectrometer sampling system. Molecules with the formulas Si<sub>2</sub>OCl<sub>6</sub> and Si<sub>3</sub>OCl<sub>8</sub> have been identified. These compounds are very likely formed by a gas phase reaction between the oxygen gas in the system and silicon tetrachloride which is produced by chlorination of the silicon-based material.

The reactions of silicon containing materials with mixed oxygen-chlorine environments are important in a number of areas. There is currently interest in using Sibased materials, such as SiC and Si<sub>3</sub>N<sub>4</sub>, for high temperature structural applications. In certain applications (1), these materials may be subject to mixed chlorine-oxygen attack. The semiconductor industry uses HCl(g) or Cl<sub>2</sub>(g) to limit the impurity content of SiO<sub>2</sub> growing on Si. Thermodynamic calculations for silicon containing materials in a mixed oxygen-chlorine environment predict SiO<sub>2</sub> as the stable phase; however, in regions of low oxygen potential, volatile silicon chlorides such as SiCl<sub>4</sub> and SiCl<sub>3</sub> may form (2). The formation of silicon oxychlorides has been suggested as well (3-12). The purpose of this paper is to report some experiments which clearly show the existence of these species in the vapor form.

The previous work in this area centers on the incorporation of chlorine into the growing oxide on high purity silicon. Secondary ion mass spectrometry (SIMS) studies have shown that the chlorine tends to segregate at the Si/SiO<sub>2</sub> interface (3-7). Monkowski and co-workers (7-9), have suggested that the chlorine actually reacts with the growing oxide to produce a silicon oxychloride phase. They suggest that the entrapment of this gaseous phase at the interface is responsible for the bubbling of the oxide films which is often observed.

The composition of such compounds in this system is somewhat disputed. Tsai (6) suggests the existence of  $\mathrm{Si}_2\mathrm{O}_3\mathrm{Cl}_2$  based upon electron diffraction patterns which show an amorphous phase with lower silicon and oxygen concentrations than those detected for normal SiO<sub>2</sub> gases. Hirabayashi and Iwamura (10) analyzed gases produced during the reaction of Si with mixed hydrogen chloride/ oxygen gases using infrared spectroscopy. They observed a broad-band absorption at approximately 9 µm which they attributed to the molecule Si<sub>2</sub>OCl<sub>6</sub>.

Some silicon oxychloride compounds have been isolated. The existence of a homologous series of compounds with the formula  $\mathrm{Si}_n \mathrm{O}_{n-1} \mathrm{Cl}_{2n+2}$  was first reported by Schumb and Holloway (11) in 1941. By fractional distillation of the condensed products formed during heating of Si in oxygen/chlorine mixtures, they isolated the first six members of this series. Schumb and Stevens (12), also produced silicon oxychloride compounds by the partial hydrolysis of silicon tetrachloride dissolved in anhydrous ether.

This paper presents direct mass spectrometric evidence for the existence of these compounds in the high-temperature reaction of Si and SiC with mixed oxygen/chlorine gases. The mechanism of formation of these species is also discussed.

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#### Experimental

High purity (99.99%) single-crystal silicon<sup>2</sup> and various types of commercially available silicon carbide ceramics were analyzed in a variety of mixed oxygen/chlorine gases. The silicon material contained ppm impurities of phosphorous, calcium, and iron. The SiC materials were formed by a number of processing methods using different densification aids. For the purpose of this paper only the behavior of a hot-pressed material<sup>3</sup> containing 1.5 weight percent (w/o)  $Al_2O_3$  aid will be discussed.

The volatile products formed by reaction of these materials with flowing 1% Cl<sub>2</sub>/Ar or 1% Cl<sub>2</sub>/1% O<sub>2</sub>/Ar gas streams

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Fig. 1. Mass spectrometer sampling system

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Table I. Mass spectrometer data for Si + 1% Cl<sub>2</sub>/Ar and 1% Cl<sub>2</sub>/1%  $O_2/Ar$ .  $T = 930^{\circ}C$ . Peak intensities summed over principal isotopes.

	<b>Probable</b> ion	$I/I(Cl_2^+)$		
Principal m/e		Si + 1% Cl <sub>2</sub> /Ar	Si + 1% Cl <sub>2</sub> /1% O <sub>2</sub> /Ar	
63	SiC1 <sup>+</sup>	$5.1 \times 10^{-2}$		
98	SiCl <sub>2</sub> +	$8.7 imes10^{-3}$		
133	SiCl <sub>3</sub> <sup>+</sup>	$4.3 imes10^{-2}$	$2.8 imes10^{-4}$	
170	SiCl <sup>4+</sup>	$1.3  imes 10^{-2}$		
151	SiOCl <sub>a</sub> <sup>+</sup>	$8.2 \times 10^{-5}$		
249	Si <sub>2</sub> OCl <sub>5</sub> <sup>+</sup>	$1.3 \times 10^{-3}$		
284	Si <sub>2</sub> OCle <sup>+</sup>	$8.5 \times 10^{-5}$		
312	Si <sub>3</sub> OCl <sub>6</sub> <sup>+</sup>	$3.7  imes 10^{-5}$		

were identified with the mass spectrometer sampling system shown in Fig. 1. The system consists of a small quartz tube furnace and a high pressure sampling mass spectrometer. This mass spectrometer system has been discussed in detail elsewhere (13, 14) and will only be briefly described here. As shown in Fig. 1, the specimen is held in close proximity to a thermocouple and to a 0.022 cm orifice located at the tip of a platinum/rhodium sampling cone. Volatile reaction products produced by the specimen-gas interaction enter the sampling cone. The gas stream undergoes free-jet expansion and proceeds as a molecular beam through the differentially pumped vacuum system. The molecular beam produced is modulated by a chopper which separates the source and background signals. This sampling configuration allows the volatile species generated during a 1 atm chemical process to be directly analyzed by a quadrupole mass filter which operates under high vacuum (10<sup>-8</sup> atm). The chemical and dynamic integrity of the reaction products formed in the furnace are preserved until they reach the actual mass filter.

Experiments were initiated by holding the sample in the cold end of the furnace until the furnace temperature had stabilized and a stable reactant gas signal was obtained in the mass spectrometer trace. After system stabilization (~15 min) occurred, the sample was rapidly raised into the hot-zone of the furnace and the volatile products generated were analyzed by the mass spectrometer system. The peaks obtained in the mass spectrum were identified from their mass-to-charge ratios and also from their "isotopic fingerprint." This fingerprint is quite characteristic for chlorine containing compounds due to the isotopic distribution of elemental chlorine, approximately 75% at mass 35 and 25% at mass 37. Vapor species containing chlorine tend to form a cluster of peaks spaced by two mass units.

#### Results

Initial experiments were performed with pure silicon in 1% Cl<sub>2</sub>/Ar and 1% Cl<sub>2</sub>/1% O<sub>2</sub>/Ar at 930°C. The mass spec-

trometer data for these experiments are given in Table I. Consider first the 1% Cl<sub>2</sub>/Ar experiments. Comparison of the fragmentation pattern to a known pattern for SiCl<sub>4</sub>(v) and examination of appearance potentials leads to the conclusion that the major vapor species from this system are primarily SiCl<sub>4</sub>(v) and smaller amounts of SiCl<sub>3</sub>(v) (2). As shown in Table I, there were a number of peaks at mass-tocharge ratios above that for SiCl<sub>4</sub>(v). These were identified both from their mass-to-charge ratio (assuming singly charged ions) and by comparing their isotopic ratios to those calculated from a computer program (15).

The first member of the homologous series of silicon oxychloride compounds (Si<sub>2</sub>OCl<sub>6</sub>) and the fragments of this molecule were used for the initial identification procedure. This analysis showed that the group of peaks at m/e= 284 correspond to the Si<sub>2</sub>OCl<sub>6</sub><sup>+</sup> ion while the peaks in the 249 range correspond to Si<sub>2</sub>OCl<sub>5</sub><sup>+</sup> fragmented from the Si<sub>2</sub>OCl<sub>6</sub> parent molecule. In addition the peaks in the 151 range are attributed to SiOCl<sub>3</sub><sup>+</sup> fragmented from Si<sub>2</sub>OCl<sub>6</sub>. Table II shows that the measured isotopic distributions from each of these three ions are in good agreement with the calculated isotopic distributions, verifying their identity.

The peaks observed at 312 are 28 mass units above the  $Si_2OCl_6$  peaks. Elemental silicon has a molecular weight of 28, indicating that this ion is  $Si_2OCl_6^+$  with an extra silicon atom— $Si_3OCl_6^+$ . The identification of this ion has not been previously reported in the literature. In light of this fact, numerous combinations of silicon, oxygen, and chlorine were considered in the computer predictions. The possibility of clustering of the silicon chloride compounds was also considered. Clustering of molecules is often an artifact associated with free jet expansion sampling due to the cooling of the gas stream as it passes through the sampling orifice (13). Comparison of all of the group at 312 showed the closest fit for a formula of  $Si_3OCl_6^+$ .

Table I also contains the results for Si +  $1\% \text{ Cl}_2/1\% \text{ O}_2/\text{Ar}$  at 930°C. In this case, the amount of volatile species is dramatically reduced. Apparently this quantity of oxygen is enough to cause the formation of a dense, protective SiO<sub>2</sub> layer which is not easily attacked or penetrated by Cl<sub>2</sub> (2).

Figures 2a and b show the mass spectrometer results for SiC + 1% Cl<sub>2</sub>/1% O<sub>2</sub>/Ar at 950°C graphically. These are very similar to the results obtained for Si + 1% Cl<sub>2</sub>/Ar at 930°C. The clusters of peaks at the higher mass numbers were identified both by their mass-to-charge ratio and their isotopic abundances as shown in Table II. Note that in this case Si<sub>3</sub>OCl<sub>7</sub><sup>+</sup> was also observed. Carbon chlorides were not observed—they would not be stable at these temperatures. The carbon presumably comes off as CO(g) and CO<sub>2</sub>(g); however, these peaks were masked by the background gases. The role of carbon is discussed in more de-

Table II. Comparison of observed and calculated isotopic abundance
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Species		 I/I <sub>max</sub>			
		Observed			
	m/e	${{ m Si}}$ + 2% Cl <sub>2</sub> T = 930°C	$\frac{\text{SiC} + 1\% \text{ Cl}_2/1\% \text{ O}_2}{T = 950^{\circ}\text{C}}$	Calculated	
Si <sub>3</sub> OCl <sub>7</sub>	345		35	41	
	340		00 100	95	
	351		65	100	
	353		25	21	
Si-OCL	312	100	100	100	
5130016	314	03	65	97	
	316	40	20	42	
Si <sub>2</sub> OCl <sub>6</sub>	282	45	56	50	
	284	100	100	100	
	286	68	81	85	
	288	50	44	30	
	290	-	_	11	
Si <sub>2</sub> OCl <sub>5</sub>	247	64	58	59	
	249	100	100	100	
	251	64	64	69	
	253	19	26	25	
SiOCl <sub>3</sub>	151	100	100	100	
	153	53	38	35	
	155		_	4	

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Fig. 2. Typical mass spectrum for hot-pressed SiC reacted in 1%  $Cl_2/1\% O_2/Ar$  at 950°C for 30 min, (b) covers the high mass region in (a) and has an expanded intensity scale.

tail elsewhere (2).

#### Discussion

The observed ions suggest the existence of two distinct parent molecules:  $Si_2OCl_6$  and  $Si_3OCl_8$ . The structure of the  $Si_2OCl_6$  molecule has been previously described as linear (11) with an Si-O-Si backbone

$$\begin{array}{ccc} Cl & Cl \\ | & | \\ Cl - Si - O - Si - Cl \\ | & | \\ Cl & Cl \end{array}$$

The fragments observed in this analysis support this structure.  $Si_3OCl_8$  does not fit the homologous series of  $Si_nO_{n-1}Cl_{2n+2}$  compounds, but does satisfy the conditions of electroneutrality. The fragments observed in this analysis suggest a linear molecule with a molecular structure of

$$\begin{array}{c|ccccc} Cl & Cl & Cl \\ & & | & | \\ Cl & Si & -Si & -O & -Si & -Cl \\ & & | & | \\ Cl & Cl & Cl \end{array}$$

Note that the ion  $Si_3OCl_8^+$  is not observed in the mass spectra. The ease of fragmenting a Cl atom from this compound appears to produce  $Si_3OCl_7^+$  as the principal ion.

It is important that silicon oxychlorides were observed in the case of Si + 2% Cl<sub>2</sub>/Ar and SiC + 1% Cl<sub>2</sub>/1% O<sub>2</sub>/Ar. In both these systems, a large quantity of SiCl<sub>4</sub>(v) is generated. It appears the amount of oxygen is secondary. In the 2% Cl<sub>2</sub>/Ar case, the amount of oxygen as impurity in the system (~100 ppm) is sufficient to form the silicon oxychloride species. In the SiC + 1% Cl<sub>2</sub>/1% O<sub>2</sub> case, a larger amount of oxygen forms these species. The above information suggests that the silicon oxychlorides might form by a gas phase reaction of SiCl<sub>4</sub>(v) and O<sub>2</sub>(g). In order to see if this is reasonable, a 50% O<sub>2</sub>/Ar gas stream was passed over a flask containing silicon tetrachloride liquid at room temperature. A wide variety of high mass silicon oxychloride compounds were observed from this reaction. The same species observed during the high temperature gas-solid reactions, including fragments of the molecule Si<sub>3</sub>OCl<sub>8</sub>, were all observed from this room temperature reaction. This result indicates that the silicon oxychlorides very likely form from the following reaction

$$4SiCl_4(g) + O_2(g) = 2Si_2OCl_6(g) + 2Cl_2(g)$$
 [1]

The existence of a gas phase reaction also raises further questions regarding the origin of the  $Si_3OCl_8$  molecule. These results indicate that  $Si_3OCl_8$  may be formed by reaction of  $Si_2OCl_6$  with silicon tetrachloride

$$Si_2OCl_6(g) + SiCl_4(g) = Si_3OCl_8(g) + Cl_2(g)$$
 [2]

or by an ion/molecule reaction between  $\rm Si_2OCl_5^+$  and  $\rm SiCl_3$  in the ionization chamber of the mass spectrometer

$$Si_2OCl_5^+(g) + SiCl_3(g) = Si_3OCl_8^+(g)$$
 [3]

It has been noted that pure Si did not yield these volatile oxychlorides when the reactant gases were  $1\% \text{ Cl}_2/1\% O_2/\text{Ar}$ . In this case a SiO<sub>2</sub> layer limits attack of the Si substrate and very little SiCl<sub>4</sub>(v) can form. However, at the Si/SiO<sub>2</sub> interface, the higher activity of Si would favor SiCl<sub>4</sub>(v) formation and, with sufficient O<sub>2</sub>, silicon oxychloride formation. This is consistent with other observations of silicon oxychlorides near the Si/SiO<sub>2</sub> interface (7-9).

Consider finally the difference between Si and SiC. When SiC reacts with  $1\% \text{ Cl}_2/1\% \text{ O}_2/\text{Ar}$  a much larger amount of SiCl<sub>4</sub>(v) forms than from Si. This suggests that the SiO<sub>2</sub> which forms on SiC is more easily penetrated by Cl<sub>2</sub> than the SiO<sub>2</sub> which forms on Si. This is very likely due to possible weak points in the scale (bubbles, pores, and microcracks) formed from the escape of CO(g) produced by the oxidation of SiC.

#### Conclusions

Silicon oxychloride compounds are formed during the high temperature reaction of Si with 1% Cl<sub>2</sub>/Ar at 930°C and SiC with 1% Cl<sub>2</sub>/1% O<sub>2</sub>/Ar at 950°C. Compounds of the formulas Si<sub>2</sub>OCl<sub>6</sub> and Si<sub>3</sub>OCl<sub>8</sub> have been directly identified by a mass spectrometer. It appears that the formation of large amounts of SiCl<sub>4</sub>(v) together with the oxygen present in the system are required to produce these compounds. It is likely that these silicon oxychlorides form by a gas-phase reaction of silicon tetrachloride and oxygen.

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## Luminescence Properties of the System $Gd_{1-x}Eu_x(IO_3)_3$

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#### ABSTRACT

The luminescence and energy transfer properties of the system  $Gd_{1-x}Eu_x(IO_3)_3$  ( $0.005 \le x \le 1$ ) have been investigated. In  $Eu(IO_3)_3$  diffusion limited energy migration occurs at T > 25 K. The diffusion constant has only a weak temperature dependence. The  $IO_3^-$  group does not luminesce. A comparison is made with related  $Eu^{3+}$  compounds.

During recent years the energy migration properties of inorganic lattices with a high concentration of  $Eu^{3+}$  ions have been investigated extensively. In our laboratory, the dimensionality of this energy migration has received particular attention (1-5). Analysis of the time development of the  $Eu^{3+}$  emission can yield information about the process by which energy migration takes place in the lattice under consideration. Some of these analyses are discussed in Ref. (6). An extensive discussion of the processes which can be responsible for excitation transfer among ions in solids has been given in Ref. (7) and (8).

A commonly encountered phenomenon in lattices which contain luminescent ions is the quenching of the luminescence when the concentration of these ions is increased. This may be due to cross relaxation, or to energy migration to quenching centers where the excitation energy is lost nonradiatively. The latter process occurs often in  $Eu^{3+}$  compounds (6). These quenching sites, or killers, may be impurities or defects, which are inevitably present in the lattice. The rare earth system under consideration in this paper,  $Gd_{1-x}Eu_x(IO_3)_3$ , appears to show unusually weak concentration quenching. The aim of our investigations was to look into this feature.

The crystal structure of  $Gd(IO_3)_3$  has been described in Ref. (9). The lattice is monoclinic with only one crystallographic site with eightfold coordination and site symmetry  $C_1$  for the rare earth ions. The shortest Gd-Gd distance is 5.9Å. In the pyramidal  $IO_3^-$  group the iodine ion has a formal oxidation state of +5, which makes it a  $5\text{s}^2$  ion. It has three oxygen neighbors at a distance of about  $1.8\text{\AA}$ ; there are three further neighbors at distances varying from 2.74 to  $3.19\text{\AA}$ . Since  $\text{s}^2$  ions are known to luminesce, we looked also for iodate luminescence. As far as we are aware, the optical properties of the iodate group have not yet been investigated.

#### Experimental

All measurements described in this paper were performed on powder samples. The samples were prepared according to Ref. (10). They were checked by x-ray powder diffraction. TGA measurements indicate that  $Eu(IO_3)_3$  is stable to 550°C. The compound  $Tb(IO_3)_3$  shows a similar behavior. Both compounds turn slightly pink upon heating in air.

Diffuse reflectance spectra were recorded using a Perkin-Elmer Lambda 7 UV-VIS spectrophotometer. General spectroscopic measurements at room temperature

and liquid helium temperature (LHeT) were performed using a Perkin-Elmer MPF44B spectrofluorometer, equipped with a liquid helium flow cryostat. For the recording of high resolution excitation and emission spectra a setup was used consisting of a Molectron DL 200 dye laser pumped by a Molectron UV-14 N<sub>2</sub> laser, in combination with a Spex 1704-X monochromator. The laser generated a pulse with a peak power of 30 kW and a width of 10 ns. The repetition rate of the laser was kept constant through all measurements at about 30 Hz. The linewidth of the laser was 4 cm<sup>-1</sup> at 530 nm. The detection device used was an RCA-C31034 fast photomultiplier tube, which was kept in a cooled housing at about  $-20^{\circ}$ C. Decay time measurements were executed by processing the PM signal with an ORTEC photon-counting system, consisting of a Model 9301 fast preamplifier, a Model 574 fast timing amplifier, a Model 436 100 MHz discriminator, and a Model 7100 multichannel analyzer. During the recording of the high resolution spectra and the decay curves, the temperature of the sample could be varied between 1.7 K and room temperature by using a Thor cryogenics liquid helium bath cryostat equipped with a Model 3020-II temperature controller.

#### **Results and Assignments**

Spectral properties.—All samples show a strong red luminescence upon ultraviolet excitation at room temperature and below. In the concentration series  $Gd_{1-x}Eu_x(IO_3)_3$  (x = 0.005, 0.01, 0.05, 0.1, and 1) and the sample with x = 1 shows the most intense luminescence. From x = 0.005 to x = 0.1, the luminescence of the samples increases approximately linearly with x.

The excitation spectrum of the  $Eu^{3+}$  emission of  $Gd_{1-x}Eu_x(IO_3)_3$  consists of a weak broad band with a maximum at about 280 nm and sharp lines in the region of 300-600 nm. The broad band is due to the charge-transfer transition between the  $Eu^{3+}$  and  $O^{2-}$  ions. The sharp lines correspond to electronic transitions within the  $4f^6$  configuration of the  $Eu^{3+}$  ion.

The diffuse reflectance spectrum of  $\text{Eu}(\text{IO}_3)_3$  shows two broad bands in addition to the sharp lines corresponding to the 4f<sup>6</sup> transitions of the Eu<sup>3+</sup> ion. The intensity of the broad bands does not depend on the europium concentration. There is a weak band with a maximum at about 480 nm, which is probably due to a center with a different valency. A similar observation has been made for Eu<sub>3</sub>ReO<sub>8</sub> (11). There furthermore is a strong and broad band with a maximum at about 250 nm, which must be ascribed to ab-

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