

HIGH TEMPERATURE REACTION OF SiCl_4 AND O_2 IN QUARTZ TUBES

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ABSTRACT

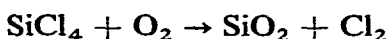
The reaction between SiCl_4 and O_2 at 1 atm between 25 and 1200°C has been followed by mass spectrometry. Below 600°C no reaction with O_2 is noted. Above 600°C the reaction proceeds in two steps. Between 800 and 1000°C the $^{28}\text{Si}/^{32}\text{O}_2$ peak height ratio is constant with no evolution of Cl_2 . It is suggested that silicon oxychlorides are being formed in this temperature regime. Above 1000°C the reaction between SiCl_4 and O_2 intensifies with concomitant production of Cl_2 . It is suggested that above 1000°C the reaction $\text{SiCl}_4 + \text{O}_2 \rightarrow \text{SiO}_2 + \text{Cl}_2$ becomes important.

At low temperatures (<800°C) adsorbed H_2O and OH groups from the surface of the fused silica tube react with SiCl_4 to form HCl. The importance of this reaction decreases with increasing temperature. The increased production of HCl above 1000°C is ascribed to H_2O and H_2 diffusing from the tube.

INTRODUCTION

Optical communication using low-loss glass fibers to transmit digital light signals shows promise of becoming an important technology during the coming decade. One proven method of producing such fibers is that of Modified Chemical Vapor Deposition (MCVD)¹. In this technique silicon tetrachloride and appropriate dopant chlorides are reacted at high temperature to produce an extremely pure fused silica. Understanding this reaction is important to optimize the process.

The reaction between SiCl_4 and oxygen as described by inorganic textbooks appears simple



This reaction has been confirmed at temperatures above 1160°C in recent studies by French and Pace². However, some complexity is indicated by the reports of Schumb and Holloway^{3, 4} who found a series of silicon oxychlorides having the general form $\text{Si}_n\text{O}_{n-1}\text{Cl}_{2n+2}$ ($n > 1$). Although these were formed by heating Si, Cl_2 and O_2 together at "dull red heat", the possibility of forming them by reactions between SiCl_4 and O_2 cannot be ignored.

The objective of the present investigation is to qualitatively ascertain the

reaction products which occur in the MCVD process rather than determine the detailed kinetics of the reaction.

EXPERIMENTAL PROCEDURES

Mass spectrometry was chosen to monitor the MCVD techniques. Ban⁵ has shown the poser of such a technique in studying open tube reactions. Unfortunately, the reaction system herein produces copious quantities of solid which cannot be filtered before entrance to the capillary inlet to the mass spectrometer, nor can it be vaporized out of the capillary as Ban does in his studies. As a result the capillary leak was located further downstream and the opportunity to measure reactive intermediates sacrificed.

The experimental apparatus employed is indicated in Fig. 1. Oxygen (Matheson, 11 ppm H₂O) was bubbled through SiCl₄ (Texas Instruments, epitaxial grade (<0.5% SiHCl₃)) at room temperature and mixed with Ar (Matheson, 5.3 ppm H₂O) before flowing into a 23 mm × 25 mm fused quartz tube (Amersil TO8 grade). The gases were heated using a tube furnace (30 cm long) in conjunction with a West Model JC controller. The effluent was discharged partly out the open end of the silica tube and partly into a sampling tube. This permitted introduction of reaction products into a PAI model 2100 quadrupole mass spectrometer through a controlled leak (Gilmont micrometric needle valve). Pressures within the sampling chamber of the mass spectrometer were maintained at less than 10⁻⁵ torr as measured by an uncalibrated ionization gauge.

Reaction of SiCl₄ and O₂ was studied as a function of temperature. Ar was

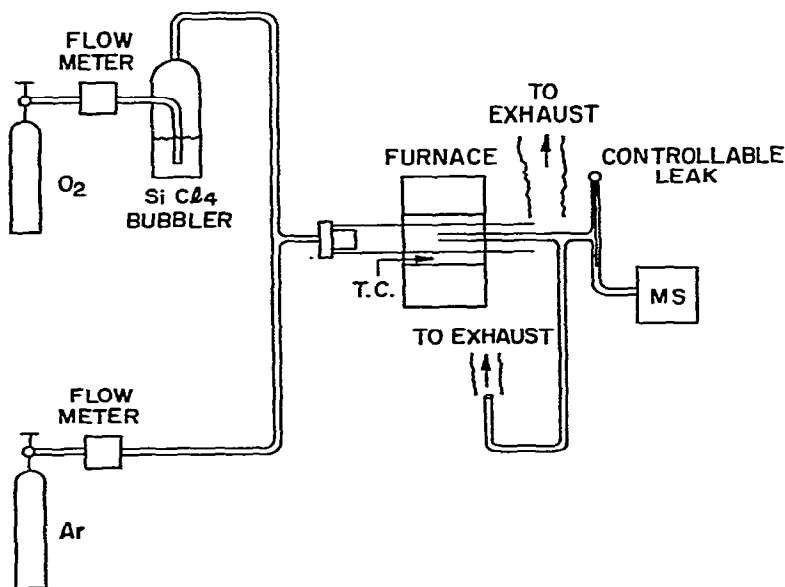


Fig. 1. Block diagram of reaction system. All tubing and plugs are Teflon except Tygon is used to exhaust.

added to the gas flow to serve as an internal standard. Flows of 640 cc(STP)/min of O_2 , 90 cc(STP)/min of $SiCl_4$ and 34 cc(STP)/min of Ar were maintained with O_2 in excess as in the MCVD reaction. The gas flow and temperature were allowed to equilibrate for 30 min after changes. This resulted in consistent analysis, although some changes were observed over longer periods particularly at low temperatures. At all temperatures, changes in peak heights between 5 and 30 min were negligible.

There are several areas of concern regarding the measurements. Sampling procedures involving measurements at low pressures of reactions occurring at 1 atm are difficult. To eliminate convection of air into the reaction tube it was necessary to have the inlet tube to the controlled leak extend into the furnace area. This led to a stagnant volume in the inlet tube which was large compared to the amount leaked into the mass spectrometer. The effect of this volume was minimized by using a small diameter outlet tube connected to a hood.

Another difficulty was the slow drift in sensitivity of the mass spectrometer which occurred with time. This was due to the gradual buildup of an insulating film in the analyzer assembly. The filament was the most vulnerable to this attack. In order to compensate for this degradation of performance argon was used as an internal, nonreacting standard. The experimental data which are discussed in the next section have been normalized with respect to the argon standard.

In addition to mass spectrometric analysis of the gas phase reaction, the character of the surface of the TO8 silica tube was also investigated using evolved gas analysis (EGA). Techniques and details of this analysis have been previously described⁶. Essentially these measurements involved heating in vacuum powdered TO8 glass or the silica powder derived from these experiments. The sample was contained in a small platinum crucible held immediately below a mass spectrometer head. In the case of the TO8 glass, masses 2 and 18 were repetitively scanned. Powder from the reaction was also analyzed using wet chemical techniques.

RESULTS AND DISCUSSION

The HCl/Cl (Mass 36/Mass 35) ratio

Typical behavior of the HCl/Cl ratio is indicated in Fig. 2. It should be emphasized that "typical" refers primarily to the changes in the ratio as a function of temperature rather than changes in the values themselves. The value of the ratio, for instance, could initially be above 1, depending on the glass tube used. The most obvious source of the hydrogen was H_2O absorbed on the reaction tube. Contamination from atmospheric H_2O adsorbed on Teflon tubing or other surfaces when a system is opened has been reported by French et al.⁷. This no doubt occurs in the present work but other sources are more important. As might be expected, the initial reaction of $SiCl_4$ with H_2O was pronounced at room temperature. That the reaction persisted at temperatures up to 800°C is evidenced by the continued, though decreasing, presence of HCl in the effluent gas. This continued formation of HCl is a result of gradual warming by conduction, etc., of the unheated section of the silica

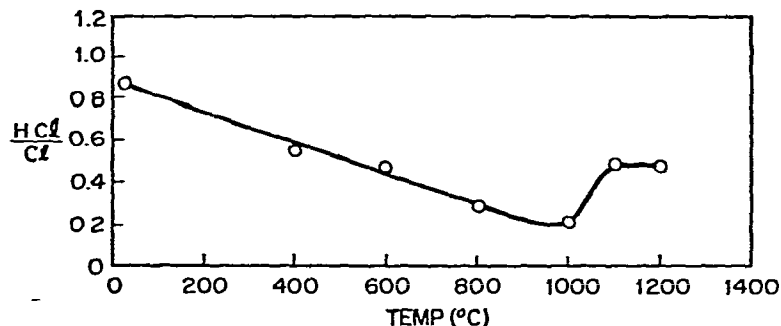


Fig. 2. Peak height ratio of HCl/Cl (Mass 36/Mass 35) as a function of temperature.

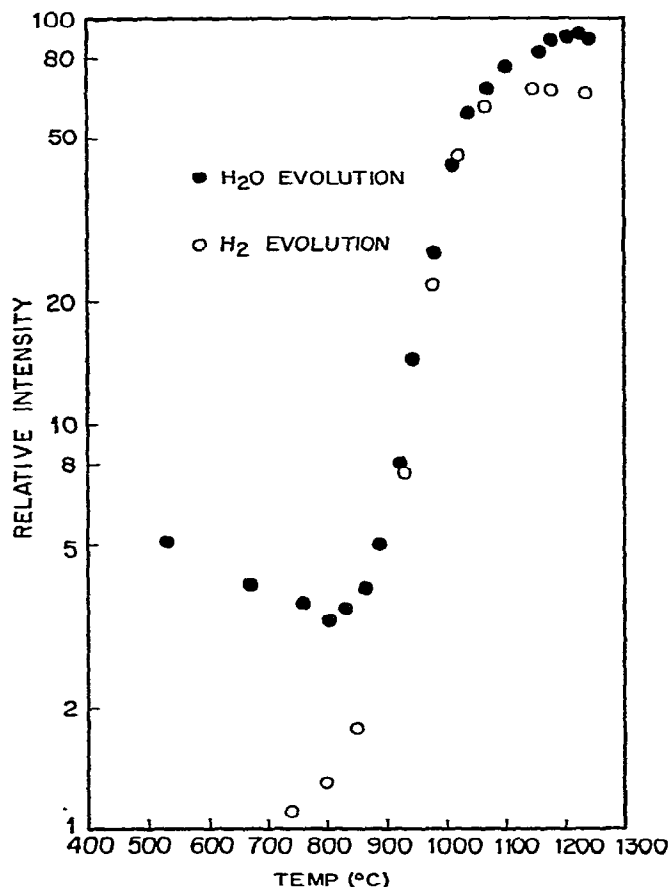


Fig. 3. H₂O (Mass 18) and H₂ (Mass 2) evolution from crushed Amersil TO8 silica glass.

tube with consequent activation of more strongly held absorbed H₂O or OH. Studies of reactions of SiCl₄ with OH groups absorbed on fused SiO₂⁸⁻¹⁰ indicate that some absorbed OH remains at temperatures as high as 800°C and that this OH can still react with SiCl₄.

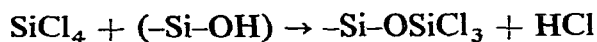
The rise again in the HCl/Cl ratio above 1000°C was initially puzzling. However, EGA of powdered TO8 glass explained these results; above 1000°C there is significant evolution of both H₂O and H₂, as shown in Fig. 3. These species must

come from the bulk of the fused quartz tube. Although one can imagine the H_2 flux as resulting from molecular H_2 dissolved during preparation of the fused quartz, studies by Bell et al.¹¹ and Lee and Fry^{12, 13} indicate that the main contributor for the H_2 impurity is decomposition of OH groups in the fused silica, resulting in a slight oxygen excess in the SiO_2 lattice. The presence of OH in TO8 is not surprising since it is made by dropping powdered quartz through the flame of an oxy-hydrogen torch¹³. The OH content is reported to be 120–180 ppm¹⁴.

The argument that hydrogen-containing species are evolved by heating at temperatures in excess of 1000°C is buttressed by O'Connor's recent work¹⁵. O'Connor showed that extensive heating of Vycor and TO8 tubes at temperatures of 1500°C and above prior to deposition of the core material ultimately results in a fiber showing no characteristic OH absorption at 0.95 μm (the second overtone of the fundamental OH peak at 2.7 μm). Fibers made without such pretreatment typically show absorption peaks at this wavelength equivalent to an OH concentration in the core of several ppm. Since fabrication conditions, except for pretreatment, were identical, it is supposed that such OH contamination occurs as the result of diffusion of OH to the core as this material is deposited at high temperatures. Finally, recent work of Ainslie et al.¹⁶ concludes that in fiber manufacture OH diffuses into the core deposit from the supporting silica tube in response to the length of time the preform is held at the fiber drawing temperature.

The Si/O₂ (Mass 28/Mass 32) ratio

Figure 4 shows the typical behavior of the Si/O₂ ratio after normalization as described previously. The Mass 28 peak was used as a diagnostic for the $SiCl_4$ molecule since the Mass 63 peak ($SiCl^+$) and the other fractions (98, 133 and 168) behaved similarly. The initial gradual rise in the silicon peak is linked to the accompanying decrease in the HCl/Cl ratio and suggests a reaction at low temperatures with surface OH⁷ which can be represented as



The extent of this reaction decreases with increasing temperatures as the surface OH

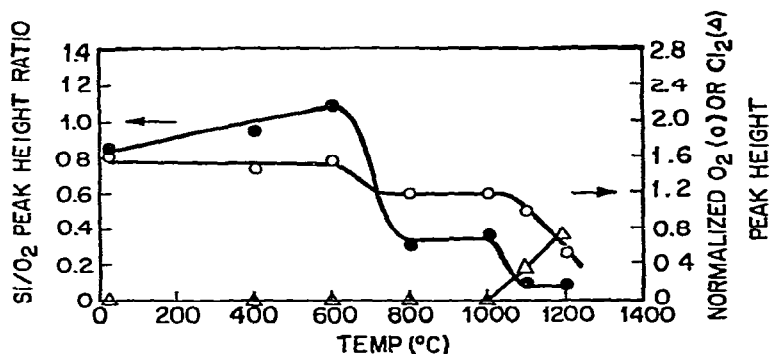


Fig. 4. Si/O₂ (Mass 28/Mass 32) peak height ratio, the normalized O₂ peak height and the normalized Cl₂ peak height as a function of temperature.

species are consumed. At higher temperatures, between 600 and 1000°C, the Si/O₂ ratio decreases strongly with a concomitant but less obvious decrease in the O₂ peak height. Reduction of the O₂ peak height is evidence that, at last, oxidation of SiCl₄ is occurring. However, since no Cl₂ is being evolved as shown in Fig. 4 complete oxidation by the reaction $\text{SiCl}_4 + \text{O}_2 \rightarrow \text{SiO}_2 + 2\text{Cl}_2$ does not occur. It seems quite reasonable that silicon oxychlorides as reported by Schumb and Lefever¹⁷ are being formed in this temperature range. Subsequent to this work an IR spectroscopic study by Wood et al.¹⁸ confirmed the production of oxychlorides at these temperatures.

Above 1000°C there is a further drop in the Si/O₂ ratio and a precipitous drop in the O₂ concentration. Accompanying this is the formation of a white, flocculent powder. Attempts to chemically characterize this solid could not distinguish the possibilities of a solid SiO₂ with capillary condensation of silicon oxychlorides and/or silicon tetrachloride or of solid silicon oxychlorides. The fact that the concentration of Cl₂ is rapidly rising between 1000 and 1200°C (of Fig. 4) is indicative that the formation of SiO₂ is becoming significant. If, after formation of the white powder in this high temperature region (i.e., $t > 1000^\circ\text{C}$), the flow of SiCl₄ is discontinued but the O₂ flow continued, Cl₂ persists, indicating that the kinetics for the formation of SiO₂ are still slow.

Further comments

Such reactions as $2\text{SiCl}_4 \rightarrow \text{Si}_2\text{Cl}_6 + \text{Cl}_2$ are always conceivable. However, no evidence for any higher molecular weight silicon chlorides was observed. Another possible reaction product is an oxychloride such as SiOCl₂. Nothing like this has been observed either, but the measurement technique is limited in this respect. Only stable compounds with a high vapor pressure can penetrate the Teflon-glass leak and pass into the mass spectrometer. A small SiO (Mass 44) peak was observed which increases somewhat above 1000°C. This could result from breakdown of an oxychloride but justification of such an inference would be quite tenuous on the basis of only these data.

SUMMARY

Based upon the data obtained from these investigations the following sequence of reactions is proposed.

At temperatures below 600°C SiCl₄ reacts with H₂, H₂O or OH from the surface of the tube, to produce HCl as a gaseous product.

At intermediate temperatures, 600–800°C, HCl production continues but at a decreasing rate. In addition, reaction between SiCl₄ and O₂ begins without formation of Cl₂.

Between 1000 and 1200°C particulates are formed which are a mixture of SiO₂ and silicon oxychlorides. The relative amount of SiO₂ increases with temperature as evidenced by the increasing Cl₂ peak.

Recognition of these reactions suggests thermal purging treatments of reaction

tubes before MCVD deposition to eliminate OH absorption from fibers ultimately produced from them. Further, this investigation suggests that 1200°C is the approximate lower temperature limit for the production of SiO₂ by the MCVD reaction.

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