JOURNAL OF MATERIALS SCIENCE 13 (1978) 1761–1768

Investigation of the reactions of $SiCl_4$ and O_2 at elevated temperatures by infra-red spectroscopy

D. L. WOOD, J. B. MACCHESNEY, J. P. LUONGO
Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974, USA

The modified chemical vapour deposition (MCVD) process for making fibre optic preforms uses direct oxidation of $SiCl_4$, together with dopant chlorides to produce core glass. This reaction has been studied by direct infra-red absorption spectrophotometry of the flowing gas system. The spectrum of the $SiCl_4$ reactant is recognizable, its decrease with increasing temperature was measured, and the absorption spectra of SiO_2 and of silicon oxychloride reaction products were recognized in the flowing gas stream. The oxychlorides began to appear in the spectra at 900° C and increased with temperature to 1110° C. Their concentration decreased drastically between 1110° C and 1160° C above which only the spectrum of SiO_2 was observed. The identities of the oxychloride molecular species produced are uncertain, but small amounts of Si_2OCl_6 and the cyclic $Si_4O_4Cl_8$ were present together with several unidentified higher molecular weight compounds. The particulate matter formed in the MCVD process shows infra-red spectra varying with conditions of formation. At temperatures below 1160° C the particulate matter shows absorption bands attributable to silicon oxychlorides. At higher temperatures, the particulate matter is free of oxychloride bands and shows only the proper SiO_2 spectrum. If moisture is present, these spectra are modified.

1. Introduction

The modified chemical vapour deposition (MCVD) process for making optical fibres for communication purposes operates by direct oxidation of $SiCl_4$ to SiO_2. This oxide, suitably doped, then forms the core of the fibre after drawing [1]. It is important therefore, to understand the chemical reactions and the factors affecting the conversion of $SiCl_4$ to SiO_2 in order to optimize the production procedures for fibres. We report here the results of a study of these reactions by means of infra-red absorption spectrophotometry.

It has been known for a long time that $SiCl_4$ reacts with O_2 at elevated temperatures [2, 3], and that the reaction products can be either SiO_2 or any of a long series of silicon oxychlorides. In our infra-red study we have sought to eliminate hydrogen from starting materials and reaction vessels in order to study hydrogen-free reactions, and we avoided sampling problems by investigating the gas stream compositions directly by optical absorption spectroscopy of the entire flowing gas column of the MCVD process. We studied the wavelength region where molecular vibrations are most characteristic, namely from $400\,cm^{-1}$ to about $2000\,cm^{-1}$ in frequency or 5 to 25 μm in wavelength.

2. Apparatus

In the manufacturing process O_2 and $SiCl_4$ are admitted in gaseous form to a fused silica tube mounted in a glass-working lathe and heated with an oxy-hydrogen flame [1]. As the reaction proceeds, a deposit builds up on the inside of the silica tube and is fused to the walls as the torch passes over it. Suitable dopants are introduced in the gas stream and are incorporated in the vitreous silica deposit inside the tube. Fibres are drawn

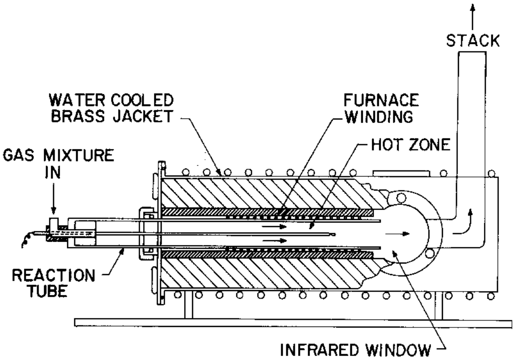

Figure 1 Apparatus for studying MCVD reaction between $SiCl_4$ and O_2 by infra-red absorption spectrophotometry. Gas mixture enters central reaction tube at left, passes through hot zone produced by Pt–20% Rh furnace winding, passes through infra-red beam entering KBr windows, and exits through stack. Brass jacket is water cooled, and entire assembly fits into sample space of Model 21 Perkin–Elmer double beam spectrophotometer. The furnace was manufactured by Lamont Sci. Co., State College, PA.

from preforms after collapsing the tube and its inner coating into a cylindrical rod.

It is not possible, however, to study directly the gas stream in the actual silica tube used to make the preform because of the opacity of the silica in the infra-red spectral region of interest. We constructed, therefore, the tube furnace system shown in Fig. 1 to approximate closely the actual fibre preform process, but yet allow infra-red measurements to be made. This furnace controls the temperature of a silica tube similar to that used in the preform production process, but heated electrically by windings of Pt–Rh alloy wire, and arranged with infra-red transmitting windows at the end of the silica tube so that a transverse infra-red radiation beam could pass through the gas stream as it emerged from the flow reaction zone. The effluent escaped through a stack, and the gas stream temperature was measured with a thermocouple on the axis of the reaction tube at the point of maximum temperature. The assembly was heavily insulated and contained within a water-cooled brass outer jacket, which fitted into the sample space of a Perkin–Elmer Model 21 double beam infra-red spectrophotometer. The entire spectrum of the gas stream could be scanned in about 5 minutes through the KBr windows of the furnace. Silicon tetrachloride vapour was produced by bubbling the oxygen carrier gas through liquid $SiCl_4$, and the composition of the gas stream was controlled by needle valves and flow-meters connected with Teflon tubing. The flow-meters were calibrated by measuring volume versus time in a calibrated chamber having a mercury seal. A separate supply of oxygen was blown over the infra-red windows inside the furnace assembly to reduce condensation of SiO_2 soot and oxychloride reaction products on the windows.

3. Experiments and results

With the furnace shown in Fig. 1 at room temperature the flow rates for O_2 and $SiCl_4$ were adjusted to about $220\,cm^3\,min^{-1}$ and $18\,cm^3\,min^{-1}$ respectively so that the absorption band of $SiCl_4$ at $615\,cm^{-1}$ was nearly saturated for the optical path length through the gas stream. The temperature was then raised and spectra were recorded at each temperature. (During the time required to establish each new temperature equilibrium the $SiCl_4$ was turned off in order to minimize the deposit of reaction products on the KBr windows.) The first effect of this elevation of temperature was the expansion of the gas stream in the reaction tube causing a reduction in the number of $SiCl_4$ molecules in the fixed optical path length of the infra-red radiation. The reduction of intensity with increasing temperature for the $615\,cm^{-1}$ fundamental band and

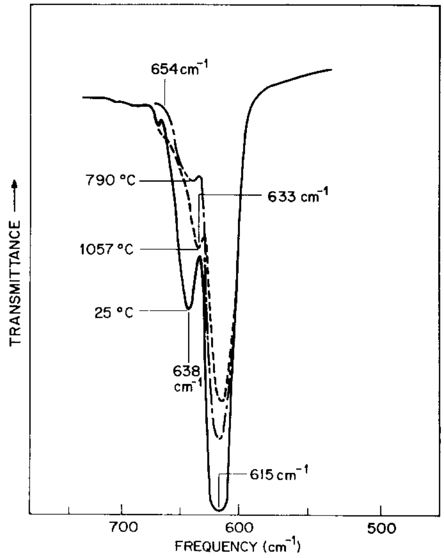

Figure 2 Detail of infra-red absorption spectrum of gas stream in the reaction apparatus of Fig. 1. The $615\,cm^{-1}$ band is due to $SiCl_4$ as is the shoulder at $638\,cm^{-1}$. The bands at 633 cm and $654\,cm^{-1}$ are due to silicon oxychloride reaction products.

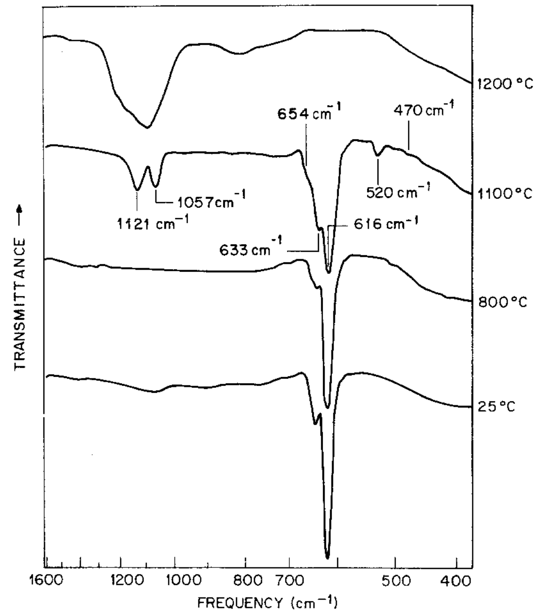

Figure 3 Infra-red spectra of reactions in flowing gas stream at various temperatures. Bands marked in the curve for 1100° C are characteristic of silicon oxychlorides, although the 616 cm^{-1} band is overlapped by that of the $SiCl_4$ starting reactant. The top curve for 1200° C is characteristic of solid SiO_2.

for the 638 cm^{-1} combination band of $SiCl_4$ is shown in Fig. 2. Accompanying this was the appearance of the 633 cm^{-1} band which increased with increasing temperature. This band is also shown in Fig. 2. As we shall discuss in more detail later, the 633 cm^{-1} band is attributed to the appearance of oxychlorides as reaction products in the gas stream. A more inclusive view of the spectrum is shown in Fig. 3 where in addition to the decrease in $SiCl_4$ absorption one can see the appearance of two bands at 1057 cm^{-1} and 1121 cm^{-1} as well as that at 633 cm^{-1} and the shoulder at 654 cm^{-1}. Small bands at 520 cm^{-1} and 470 cm^{-1} are also observed. At temperatures above 1160° C, the absorption due to Si–Cl vibrations in the region from 470 cm^{-1} to 660 cm^{-1} is lost entirely and now only the Si–O vibrations near 1150 cm^{-1} characteristic of SiO_2 remain. This transition coincides with the appearance of visible particulate material in the gas stream, and represents complete conversion from $SiCl_4 + O_2$ to SiO_2 soot.

The temperature dependence of absorption for the 615 cm^{-1} band of $SiCl_4$ is shown in Fig. 4 where three curves are plotted. In A, the points represent the reduction in absorption expected from thermal expansion alone, while those of curve B represent the observed absorptions. The deviation of B from A starting at 900° C represents the onset of the reaction between $SiCl_4$ and O_2 with the reduction in concentration of the former over and above that for thermal expansion. Essentially all (>98%) of the $SiCl_4$ is gone at 1160° C. Curve C in Fig. 4 shows the intensity of the absorption band at 633 cm^{-1} which we attribute to oxychloride reaction products in the gas stream. Its value below 900° C is not reliable because of the overlap with the strong bands of $SiCl_4$ on either side (see Fig. 3), but its increase to a peak value around 1110° C is unmistakable, and its reduction to zero intensity at 1160° C is also without question.

It is clear, therefore, that in the absence of hydrogen, oxychlorides are formed from $SiCl_4$ and O_2 from about 900 to 1160° C, and then at higher temperatures the reaction goes directly to SiO_2. This is consistent with results in the literature [2–6] although the published work involves somewhat different preparative conditions.

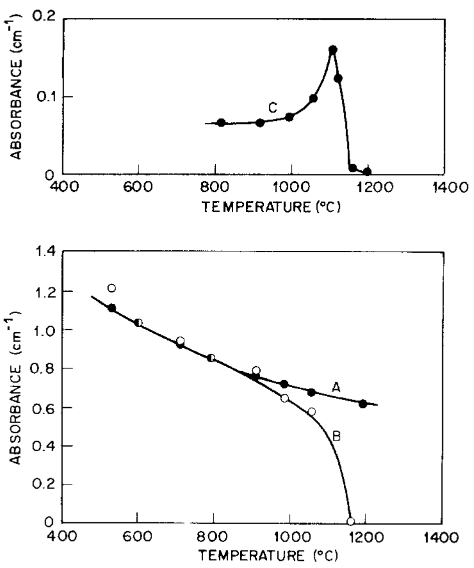

Figure 4 Absorption intensity of gas flow reaction at various temperatures. Curve A represents that expected for the 615 cm^{-1} band of $SiCl_4$ on the basis of thermal expansion alone. Curve B is the actually observed intensity versus temperature. Note that departure from the thermal expansion curve at 900° C denotes the onset of a reaction between $SiCl_4$ and O_2, and that at 1160° C no more $SiCl_4$ reactant remains in the gas stream. Curve C represents the absorption intensity versus temperature for the 633 cm^{-1} band of silicon oxychloride reaction products produced in the gas stream.

4. Interpretation of infra-red spectra

It would be of interest to know which particular silicon oxychlorides are prominent in the flow reaction and which give rise to the infra-red spectra of Figs. 2 and 3. It is known that there are many molecular species formed in the reaction of $SiCl_4$ and O_2, but very little has been published on the infra-red spectra of these compounds. Schumb and Lefever [7] show spectra of liquid films in the $1100\,cm^{-1}$ region but their sample thicknesses are too great to resolve much detail. Chambers and Wilkins [8] have measured spectra of solutions in carbon tetrachloride for several chlorosiloxanes, but only for the $1110\,cm^{-1}$ band attributable to Si–O vibrations. When we compared the solution spectrum with the gas spectrum for Si_2OCl_6 we found quite drastic differences which probably cannot be attributed to solvation effects. Because of the presence of trace amounts of H_2O in reagent grade CCl_4, it is likely that the differences are due to molecular rearrangements of the hexachlorodisiloxane molecule because of the moisture present, resulting in an array of several end products whose summed spectra are different from that of the gas. We did not pursue the use of CCl_4 solutions to identify siloxanes further. A Russian paper on the infra-red spectrum of hexachlorodisiloxane [9] has been questioned [10, 11] on the basis of incomplete separation from other compounds.

It therefore appears that reliable infra-red spectra have really only been published for three compounds: The starting species $SiCl_4$ [12–18], one oxychloride, Si_2OCl_6 (hexachlorodisiloxane [11]), and the dimer Si_2Cl_6 (hexachlorodisilane [19, 20]). The dearth of information on the higher siloxanes in which we are interested comes from the fact that there are many compounds which form under very similar reaction conditions, that these compounds are very reactive toward atmospheric moisture, and that they are difficult to separate, purify and identify. We did, however, explore this difficult subject with a set of experiments which we describe next.

A separate reaction system was set up with a gas flow tube and furnace similar to that of Fig. 1 but without the infra-red windows. The effluent reaction products from the heated reaction zone were caught in a trap held at room temperature, and the excess oxygen carrier gas was vented to an exhaust system. Over a period of several hours, it was possible to collect several cubic centimetres of liquid condensate. This was then distilled at atmospheric pressure in a glass apparatus. As each fraction was collected its vapour phase spectrum was run in a Perkin–Elmer Model 421 spectrometer over the region from $1400\,cm^{-1}$ to $350\,cm^{-1}$ by introducing a few drops of the fraction into the bottom of a demountable 10 cm gas cell having KBr windows and which had been purged with dry N_2 before filling. Our separation was by no means complete, but Fig. 5 shows spectra of those fractions which exhibited the presence of new species. When the distillation exceeded the maximum temperature for which the still was designed, we collected a viscous residue from the still pot.

To identify the fractions whose spectra are shown in Fig. 5 we first made a direct comparison with the spectra of three commercially available compounds, $SiCl_4$, Si_2Cl_6, and Si_2OCl_6 which are shown in Fig. 6. The top curve in Fig. 6 is for the $SiCl_4$ starting compound in the MCVD process, and it shows the two absorption peaks at

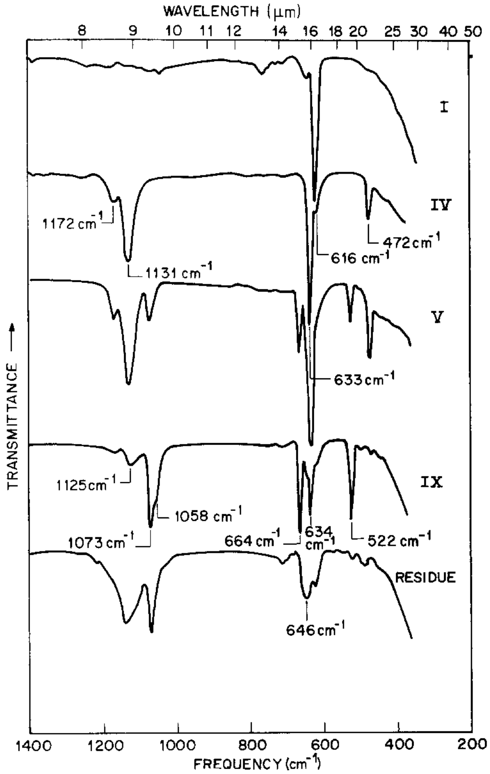

Figure 5 Infra-red absorption spectra of certain distillation fractions from a batch of silicon oxychlorides made by the MCVD process between 900 and 985° C. Fraction I is $SiCl_4$, and fraction IV is Si_2OCl_6 on the basis of spectra of known model compounds.

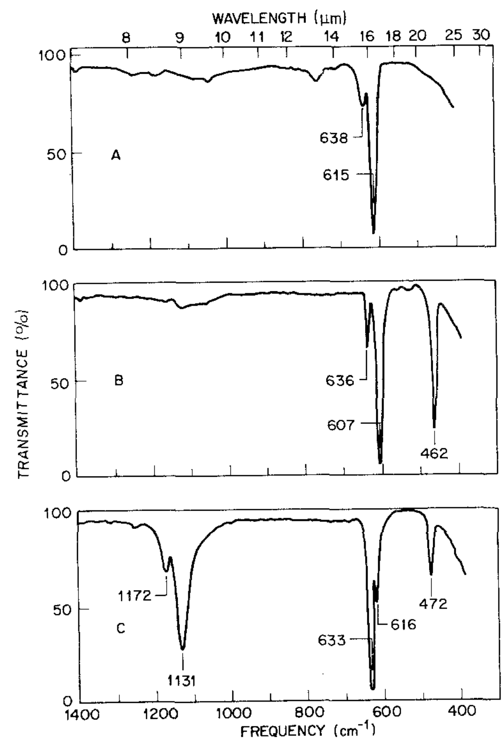

Figure 6 Infra-red absorption spectra of three known silicon chloride compounds. Curve A, the $SiCl_4$ starting material for the MCVD process. Curve B, commercial Si_2Cl_6, hexachlorodisilane. Curve C, commercial Si_2OCl_6, hexachlorodisiloxane.

615 cm^{-1} and 638 cm^{-1} which have been discussed before. The middle curve, for Si_2Cl_6 shows an additional absorption at 462 cm^{-1} and a shift in the two bands at 607 cm^{-1} and 636 cm^{-1} relative to the two corresponding bands for $SiCl_4$. In the curve of Fig. 6 for Si_2OCl_6, there are still two more absorption peaks at 1131 cm^{-1} and 1172 cm^{-1} arising from the Si–O linkage and the shift in frequency for the other Si–Cl bands which is usually expected for the different molecular structure. We conclude that fraction I in Fig. 5 is $SiCl_4$, and fraction IV is Si_2OCl_6 since the spectra match very well. No match was found for the bands of Si_2Cl_6 in any fraction, and we conclude that it was not formed, nor does it contribute to the spectrum of the flow reaction effluents.

The results of this comparison leave fractions V through IX and the still pot residue without matching spectra for an identified, pure compound. There is no question that all these are siloxanes, since the Si–O group vibrations between 1000 cm^{-1} and 1200 cm^{-1} are present as well as the Si–Cl vibrations between 400 cm^{-1} and 700 cm^{-1}. On the basis of spectra–structure correlations and the literature, the probable structure of the other reaction products can be determined as follows: In fraction V of Fig. 5 the new absorptions not observed in Si_2OCl_6 occur 522, 664 and 1073 cm^{-1}. The 522 cm^{-1} band must arise from the $SiCl_2$ group because it is in the expected frequency range for Si–Cl vibrations and it is absent in the three pure compound spectra of Fig. 6 where this group is absent. The 1073 cm^{-1} band whose intensity appears to be related to that of the 522 cm^{-1} band has been reported for cyclic siloxanes [22, 23] and it occurs near this low frequency in smaller rings such as the cyclic tetramer, $Si_4O_4Cl_8$. It is expected to fall at a higher frequency in linear siloxanes [22, 24]. The 664 cm^{-1} band is also related to the 522 and 1073 cm^{-1} bands in both fraction V and fraction IX in Fig. 5. A band is expected in this region due to $SiCl_2$ groups in cyclic siloxanes with higher frequencies up to 665 cm^{-1} for the smaller rings [23]. Since it was concluded [25, 27] that the most likely cyclic siloxane to form would be the tetramer, we tentatively conclude that this compound, $Si_4O_4Cl_8$, is present in fraction V and in higher concentration in fraction IX. The additional Si–O group vibration at 1058 cm^{-1} in fraction IX suggests that there are also other cyclic siloxanes present in that fraction. Broad bands of the still pot residue spectrum in the region near 646 and 1100 cm^{-1} suggest that there are many siloxane compounds present, but we were unable to separate or identify them further.

Referring to Fig. 3 it is possible to comment on the composition of the gas flow reaction products by comparison with the spectra of Fig. 5. The absorption peaks at 615 and 638 cm^{-1} in Fig. 2 and in the room temperature curve of Fig. 3 are identical with those of fraction I, which is $SiCl_4$. The strongest of the absorption bands prevails at 616 cm^{-1} for the reaction at 1100° C as shown in Fig. 3, and this band is present in the flow reaction at all temperatures up to 1160° C. The shoulder at 633 cm^{-1} which is clearly defined above 950° C and which is a major absorption feature at 1100° C (Fig. 3), coincides with that of fraction IV, or Si_2OCl_6 in this region. However, the bands at 1130 and 1172 cm^{-1} and that at 472 cm^{-1} in hexachlorodisiloxane are stronger relative to the 633 cm^{-1} band in this compound than they are in the gas flow spectrum of Fig. 3,

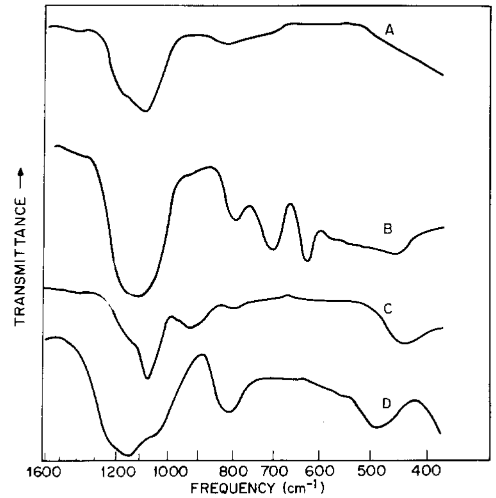

Figure 7 Spectra of non-gaseous reaction products from the MCVD gas flow process. Curve A is for solid SiO_2 particles in the reaction stream above 1160° C. Curve B is for a soot deposit on the windows of the furnace of Fig. 1 after reaction below 1160° C has been going on for some time. Oxychloride bands are present as well as those for SiO_2. Curve C is for a clear window deposit formed when moisture was present in the reaction chamber. Curve D is for a window deposit of SiO_2 soot from a high temperature gas flow reaction (above 1160° C).

and we conclude that only a small fraction of the oxychlorides formed in the gas stream reaction can be attributed to this molecule.

Again comparing the curves in Fig. 5 with those of Fig. 3 recorded for the 1100° C reaction, it is clear that some of the oxychlorides represented by fraction IX are present in the gas stream. For example, part of the intensity of the 522, the 664, and the 1073 cm^{-1} bands could be contributing to the absorptions in the 1100° C spectrum of Fig. 3, but only a small amount of the cyclic tetramer responsible for these three bands can be present in the gas flow reaction. In addition, there is little similarity between the details of the oxychloride bands in the 1100° C curve of Fig. 3 and those of the viscous still pot residue of Fig. 6. It is only possible to suggest that the 654 cm^{-1} absorption band of the gas flow reaction may arise from some of the same oxychlorides that are present in the residue, but their relative concentrations are not the same as in the residue.

We conclude, therefore, on the basis of the infra-red spectra, that there are many different oxychlorides of silicon formed in the gas flow reaction at 1100° C, and that only small amounts of Si_2OCl_6 or of $Si_4O_4Cl_8$ are present. In addition, it can be deduced that reaction products of the MCVD process below 1160° C consist of siloxane compounds having fairly high molecular weights and probably not all linear.

5. Infra-red spectra of solid reaction products

One of the difficulties with the gas reaction vessel for infra-red spectroscopy (Fig. 1) was the precipitation of reaction products on the windows of the sample cell. We were able to overcome this particular problem by directing a stream of oxygen over the windows. But in experiments where deposits did occur, we were able to study several different forms of precipitate as they deposited on the cold KBr surfaces. Residues were of different forms: silica soot, clear liquid, solid film reaction products, or combinations thereof. Their infra-red spectra are shown in Fig. 7. Curve A does not actually represent a window deposit, but rather the high temperature (1200° C) gas reaction stream where $SiCl_4$ reacts directly with O_2 to produce $SiO_2 + Cl_2$. This curve represents the pure SiO_2 spectrum, and was similar to that observed for window deposits from reactions above 1160° C. The second curve (B in Fig. 7) represents the spectrum of a window deposit of SiO_2 from the reaction taking place below 1160° C, but above 900° C. The broad bands at 793, 698, and 620 cm^{-1} are not observed in SiO_2 itself, and are characteristic also of liquid oxychlorides which we studied both as window condensates and as liquid films from the distillation experiments. Curve C was obtained from a clear deposit on the furnace windows when the flow reaction between $SiCl_4$ and O_2 was conducted at 700° C but after the furnace had been open to room air for two weeks. We attribute this drastically different deposit spectrum to oxychloride compounds formed in the presence of moisture. After discovering this reaction, subsequent flow reaction experiments were conducted with greater care to eliminate moisture. For example, we always preheated the furnace to at least 600° C with a continuous purge of O_2 for a couple of hours before admitting $SiCl_4$. It is interesting to note also that we could obtain a spectrum very similar to Curve C in Fig. 7 from a thin film of liquid still pot residue (bottom curve in Fig. 5) after leaving it open to moist room air for several days. We wish to consider only the moisture-free reactions, and believe that the infra-red spectra assure us that our experiments were, indeed, free of the influence of H_2O.

It should be noted that there are several components in the Si–O absorption band around 1100 cm^{-1}, and these components vary in relative intensity according to how the Si–O molecular group occurs, and which compounds contribute to the absorption. We have already mentioned that the effect of moisture on the oxychloride formation and the significant differences near 1100 cm^{-1} between curve C and the others in Fig. 7 are important. But curves A and D are different in the 1100 cm^{-1} region also, and these were recorded for SiO_2 soot produced in the flowing gas system at high temperatures (above the region of oxychloride formations). Curve A, however, was recorded from the gas stream itself, while curve D was recorded from a window deposit of SiO_2 soot from a similar experiment. We are as yet unable to interpret the differences in soot spectra, especially in the 1100 cm^{-1} region, but clearly the curves of Fig. 7 show that the soot spectra reflect differences in the conditions under which the soot is formed. It is clear also from curve B that for SiO_2 soot formed under conditions where oxychlorides are present (below 1160° C and above about 800° C) there is considerable adsorption of oxychlorides onto the freshly formed soot particles, and this "low temperature soot" is quite different from the "high temperature soots" of curves A and D. It is possible to study the soot spectra by pressing dilute mixtures of solid powder with KBr powder into a relatively transparent pellet according to common infra-red spectroscopic procedures, and these investigations are being continued.

6. Summary and conclusions

Infra-red spectroscopy of the MCVD fibre optic preform process is practicable by molecular absorption of infra-red radiation passing through the flowing gas reaction zone in a separately constructed test apparatus. It was found that the absorption intensity of the $SiCl_4$ reactant decreased with increasing temperature. Below 900° C this could be accounted for by thermal expansion. Reaction with oxygen to form silicon oxychloride products occurred above 900° C and their concentration increased with temperature to a maximum at 1100° C. Further heating caused the oxychloride concentration in the gas stream to decrease until none was detected above 1160° C. At this temperature and above, the reaction of $SiCl_4$ with O_2 proceeded directly to SiO_2 without oxychloride formation. Small amounts of Si_2OCl_6 and $Si_4O_4Cl_8$ were identified among the reaction products, together with major amounts of unidentified higher molecular weight silicon oxychlorides. The infra-red spectra of particulate matter formed above 1160° C corresponded with that of solid SiO_2, but there were differences which depended on the conditions under which the material was formed. A correlation between these differences and the internal structure of the particles has not yet been made.

Acknowledgements

We gratefully acknowledge the technical assistance of P. B. O'Connor and S. S. DeBala, and helpful discussions with W. R. Sinclair, J. E. Griffiths, and W. G. French.

References

1. J. B. MACCHESNEY, P. B. O'CONNOR and H. M. PRESBY, *Proc. IEEE* 62 (1974) 1280.
2. G. FRIEDEL and E. LADENBURG, *Compt. Rend.* 66 (1868) 539.
3. H. RHEINBOLDT and W. WISFELD, *Amer. Chem.* 517 (1935) 197.
4. W. R. SINCLAIR, J. B. MACCHESNEY, P. K. GALLAGHER and P. B. O'CONNOR, *Thermochim. Acta* (submitted for publication).
5. W. G. FRENCH and L. J. PACE, International Conference on Integrated Optics and Optical Communication, Tokyo, Japan (Institute of Electrical and Communications Engineers of Japan, Tokyo, 1977).
6. W. W. PULTZ, French Patent No. 2 006 440 assigned to Corning Glass Co. (1969).
7. W. C. SCHUMB and R. A. LEFEVER, *J. Amer. Chem. Soc.* 76 (1954) 2091.
8. D. W. S. CHAMBERS and C. J. WILKINS, *J. Chem. Soc.* (1960) 5088.
9. A. N. LAZAREV, M. G. VORONKOV and T. F. TENISHEVA, *Opt. i. Spektroskopia* 5 (1958) 365.
10. J. R. DURIG and K. L. HELLAMS, *Inorg. Chem.* 8 (1969) 944.
11. J. E. GRIFFITHS and D. F. STURMAN, *Spectrochim. Acta* 25A (1969) 1415.
12. R. R. HAUN and W. D. HARKINS, *J. Amer. Chem. Soc.* 54 (1932) 3917.
13. D. A. LONG, T. V. SPENCER, D. N. WATERS and L. A. WOOD, *Proc. Roy. Soc. (London)* A240 (1957) 499.
14. F. STITT and D.M. YOST, *J. Chem. Phys.* 5 (1937) 90.
15. M. KATAYAMA, T. SHIMANOUCHI, Y. MORINO and S. MIZUSHIA, *J. Chem. Phys.* 18 (1950) 506.
16. J. E. GRIFFITHS, *Spectrochim. Acta.* 25A (1969) 965.
17. F. HOEFLER, W. SAVODNY and E. HENGGE, *ibid.* 26A (1970) 819.

18. J. E. GRIFFITHS, *ibid.* **30A** (1974) 945.
19. Y. MORINO, *J. Chem. Phys.* **24** (1956) 164.
20. J. E. GRIFFITHS, *Spectrochim. Acta.* **30A** (1974) 169.
21. G. A. OZIN, *J. Chem. Soc.* **A19** (1969) 2952.
22. A. E. SMITH, "Analysis of Silicones" (J. Wiley & Sons, New York, 1974) p. 277.
23. L. J. BELLAMY "Infra-red Spectra of Complex Molecules" (J. Wiley & Sons, New York, 1958) p. 279.
24. C. W. YOUNG, P. C. SERVAIS, C. C. CURRIE and M. J. HUNTER, *J. Amer. Chem. Soc.* **70** (1948) 3758.
25. H. BAMFORD and C. F. H. TUPPER, "Comprehensive Chemical Kinetics", Vol. 6 (Elsevier, New York, 1949) 110.
26. F. A. COTTON and G. WILKINSON, "Advanced Inorganic Chemistry" (Interscience, New York, 1962) p. 356.
27. W. C. SCHUMB, *Chem. Rev.* **31** (1942) 587.

Received 9 November and accepted 16 December 1977.