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Fluorine incorporation in silica glass by MCVD process – a critical study

M. C. PAUL, R. SEN, T. BANDYOPADHYAY*
Communication Fibre Laboratory, Central Glass & Ceramic Research Institute, Calcutta 700 032, India

The chemistry of fluorine incorporation in silica glass preparatory to preform fabrication by MCVD process was critically analysed on the basis of the thermodynamic properties of the constituent reagents. The theoretical findings were compared with the experimental results, pointing out the anomalies observed by different workers. The addition of phosphorus is found to have an insignificant role in modifying the fluorine incorporation level. The accepted model of dependence of fluorine content in the glass on the partial pressure of SiF_4 to the power of 0.25 finds poor agreement with the experimental data at low fluorine dopant concentration.

1. Introduction

Fluorine incorporation in silica glass has been extensively studied for more than a decade [1–9] to produce optical fibres of improved designs with better characteristics of loss and dispersion. Several fluorine-containing chemicals such as SF_6, SiF_4, CF_4, CCl_2F_2 etc. were used [3] for this purpose to establish a precise relation between the refractive index changes with fluorine concentration and to find out the mechanism of fluorine incorporation in silica glass. It was observed that regardless of the nature of source chemicals the main fluorinating species was SiF_4 and its concentration in the gas phase was directly proportional to the fluorine content in glass [10–13]. Beginning with this basic premise fluorine doping experiments were carried out by the MCVD process using CCl_2F_2 as source reagent. While comparing the results of these experiments with the thermodynamic equilibrium reaction products certain anomalies were observed. The present study includes critical analyses of the thermodynamic equilibrium conditions of the gas phase reactions pointing out the anomalies observed in the results of the theoretical findings with the experimental results.

2. Background information

On a study of the relative formation of the various halogen species using CCl_2F_2 as the fluorine source, Walker *et al.* [4, 13] reported that, besides SiF_4 which is the most abundant component, SiF_3Cl formation exceeds that of SiF_2Cl_2 and $SiFCl_3$, of which $SiFCl_3$ is the minimum. However, the SiF_3Cl concentration becomes comparable to that of SiF_4 at low oxygen or high chlorine levels. As the fluorine incorporation in the glass is a function of the input gas concentrations and the temperature at which the particulate layer consolidates, the presence of phosphorus, which helps to lower the consolidation temperature during deposition, has been suggested to play a significant role. The refractive index depression relative to silica is proportional to the partial pressure of SiF_4 to the $\frac{1}{4}$ power except at high fluorine dopant level where it corresponds to the power $\frac{1}{2}$ of SiF_4 partial pressure.

Kirchhof *et al.* [10] observed that the addition of a small amount of P_2O_5 has no influence on the fluorine incorporation for a constant molar ratio of the fluorine containing species with $SiCl_4$, although the deposition temperature is lowered considerably due to the presence of P_2O_5. The result is not in agreement with that reported by Walker *et al.* [4]. Kirchhof *et al.* further found that the fluorine incorporated in the glass is practically independent of the deposition temperature between 1650 and 1900 °C up to a total flow rate of 1600 s.c.c.m. except for a small deviation at higher $C_2F_3Cl_3$ to $SiCl_4$ molar ratio. This behaviour was suggested to be analogous to that of other fluorine sources, including CCl_2F_2.

The observation by Marshall *et al.* [14] assumes special importance as they mentioned that at low $CCl_2F_2/SiCl_4$ ratio (up to about 0.50) little or no SiF_4 was detected, but fluorine incorporation took place with the direct oxidation of $SiCl_3F$ formed by the reaction between $SiCl_4$ and the fluorinating agents. They studied the formation of chlorofluorosilanes both with and without oxygen at different $CCl_2F_2/SiCl_4$ ratios and even at lower temperatures (up to 1100 °C) and proposed the above model. It was not totally accepted by Kirchhof *et al.* [10] as no conversion of solid bonded fluorine to the gas phase

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* Author to whom correspondence to be addressed.

was considered in the equilibrium reactions which they observed to be the controlling step for determining the final fluorine concentration in the glass.

Summarizing the observations of the earlier workers it appears that (1) the formation of the relative amount of the different chlorofluorosilanes under various conditions particularly at low $CCl_2F_2/SiCl_4$ ratio, (2) the mechanism of fluorine incorporation at low CCl_2F_2 levels and (3) the effect of temperature or the addition of a small amount of P_2O_5 on the amount of fluorine incorporated into glass need further study to have a better understanding of the chemistry of fluorine incorporation.

3. Experimental procedure

Preforms were fabricated by the usual MCVD process [15] to deposit SiO_2–F layers of various compositions, using CCl_2F_2 as the fluorine source. The fluorine concentration in the glass was varied by changing the relative amount of CCl_2F_2 and $SiCl_4$ at the input end. A small amount of $POCl_3$ was added to facilitate the sintering of the deposited soot layers. The temperature used for the deposition was 1850 °C.

The preforms were characterized by a preform analyser to determine the refractive index profile and the thickness of the various layers. The fluorine concentration was determined from the refractive index depression relative to silica.

4. Theoretical

Since thermodynamic equilibria control the reactions for the formation of various halogen species during the reaction of CCl_2F_2 with $SiCl_4$ in presence of O_2 above 1500 °C [12, 13], the concentration of SiF_4 and other chlorofluorosilanes were determined from the equilibria of the following simultaneous reactions

$$K = [Cl_2]^2[SiCl_4]^{-1}[O_2]^{-1}$$

$$K = [SiF_4][Cl_2]^2[CO_2]^2[CCl_2F_2]^{-2}[O_2]^{-1}$$

$$K = [SiF_3Cl][O_2]^{0.25}[SiF_4]^{-0.75}[Cl_2]^{-0.5}$$

$$K = [SiFCl_3][O_2]^{0.75}[SiF_4]^{-0.25}[Cl_2]^{-1.5}$$

$$K = [Cl][Cl_2]^{-0.5}$$

The equilibrium constant values were evaluated from the free energy of formation of the different halogen species. The formation of SiF_2Cl_2 could not be considered as its free energy of formation was not available from the JANAF table [16]. This is not likely to introduce much error because its concentration was found to be much lower than that of SiF_3Cl [13].

The concentrations of SiF_4, SiF_3Cl and $SiFCl_3$ were calculated with variation in the proportion of CCl_2F_2 and $SiCl_4$ at temperatures of 1500, 1800, 2100 and 2300 K to find out the relative changes in their concentrations with respect to temperature at different CCl_2F_2 levels. The values obtained at 1500 K may deviate a little from the correct value as the reactions are not guided solely by thermodynamic equilibria [13] at this temperature. The effect of O_2 partial pressure was studied at 2100 K by repeating the calculations with change in the proportion of O_2 with respect to $SiCl_4$.

From the experimental data, a relation could be developed between the mol % of fluorine incorporated in the glass and the partial pressure of SiF_4 at equilibrium or the partial pressure of CCl_2F_2 in the input mixture of gases. The changes in the amount of silica deposited with variation in $SiCl_4$, CCl_2F_2 and O_2 ratios were evaluated and compared with the experimentally obtained values.

Computations were also carried out by taking a K value of 0.68 (proposed by Walker *et al.* [13] instead of 0.025 evaluated from JANAF table [16]) for the formation of SiF_3Cl at 2100 K. This was done to examine the extent of variation in the relative proportions of the various halogen species due to the difference in the equilibrium constant values of SiF_3Cl and to study their influence on the guiding mechanism for fluorine incorporation.

The formation of different chlorofluorosilanes was also investigated in presence of very low quantity of oxygen close to the stoichiometric limit, as well as in absence of oxygen which was earlier studied by Marshall *et al.* [14]. The following equilibria were considered in oxygen deficient condition

$$K = [SiF_4][Cl_2]^4[SiCl_4]^{-1}[CCl_2F_2]^{-2}$$

$$K = [SiF_3Cl][Cl_2]^3[SiCl_4]^{-1}[CCl_2F_2]^{-1.5}$$

$$K = [SiFCl_3][Cl_2][SiCl_4]^{-1}[CCl_2F_2]^{-0.5}$$

$$K = [Cl][Cl_2]^{-0.5}$$

The relative concentrations of various halogen species under the different conditions considered above were analysed and fitted with the experimental data to have an in-depth study of the probable mechanism of fluorine incorporation into the glass.

5. Results and discussion

The amount of SiF_3Cl and $SiFCl_3$ expected to be formed with respect to SiF_4 at equilibrium in presence of excess oxygen at different temperatures are presented in Figs 1 and 2, respectively. With variation in the ratio of $CCl_2F_2/SiCl_4$ up to about 1.8, SiF_4 will be the major product, while the formation of $SiFCl_3$ remains the lowest. This result agrees well with the earlier observation by Walker *et al.* [13]. The ratio of SiF_4/SiF_3Cl and $SiF_4/SiFCl_3$ are found to decrease with increase in temperature, except in the case of the latter where a reversal in the values is noted between 2100 and 2300 K when the $CCl_2F_2/SiCl_4$ ratio exceeds 0.30. The values at 1500 K in both cases are found to differ much from those at other temperatures. Thus at a typical $CCl_2F_2/SiCl_4/O_2$ ratio of 1:1:25 the magnitude of SiF_4/SiF_3Cl shows a variation of more than eight times for a change in temperature from 1500 to 2300 K indicating a considerable variation in their relative proportion with respect to temperature. The variation of $SiF_4/SiFCl_3$ with temperature and/or with $CCl_2F_2/SiCl_4$ are found to be much more

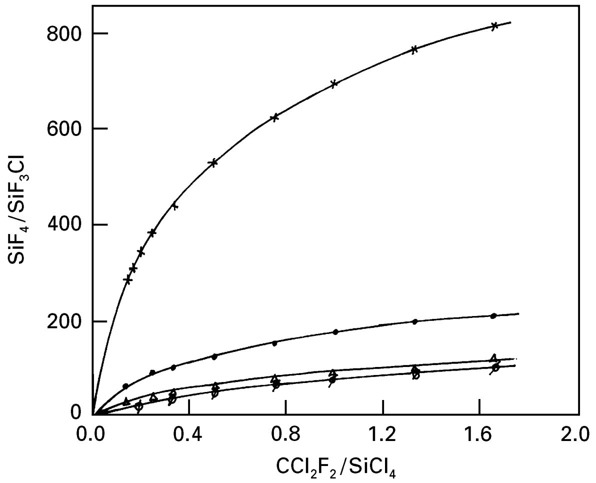

Figure 1 Formation of SiF_4 relative to SiF_3Cl as a function of $CCl_2F_2/SiCl_4$ at different temperatures for initial partial pressure of O_2 of 0.0768 MPa. (X) 1500 K; (●) 1800K; (△) 2100 K; (∅) 2300 K.

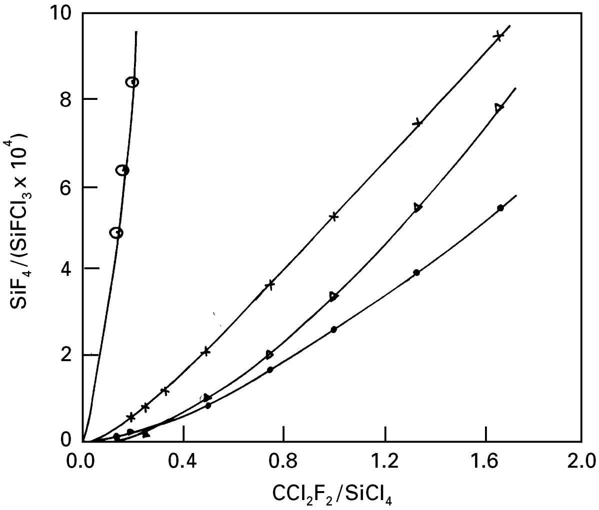

Figure 2 Formation of SiF_4 relative to $SiFCl_3$ as a function of $CCl_2F_2/SiCl_4$ at different temperatures for initial partial pressure of O_2 of 0.0768 MPa. (○) 1500K; (X) 1800 K; (△) 2300 K; (●) 2100 K.

prominent compared to those of SiF_4/SiF_3Cl, because the amount of $SiFCl_3$ is always much lower than that of SiF_3Cl. It therefore appears that lower temperature is preferable for deposition of F-doped layer as the formation of other chlorofluorosilanes decreases relative to that of SiF_4 with simultaneous decrease in temperature.

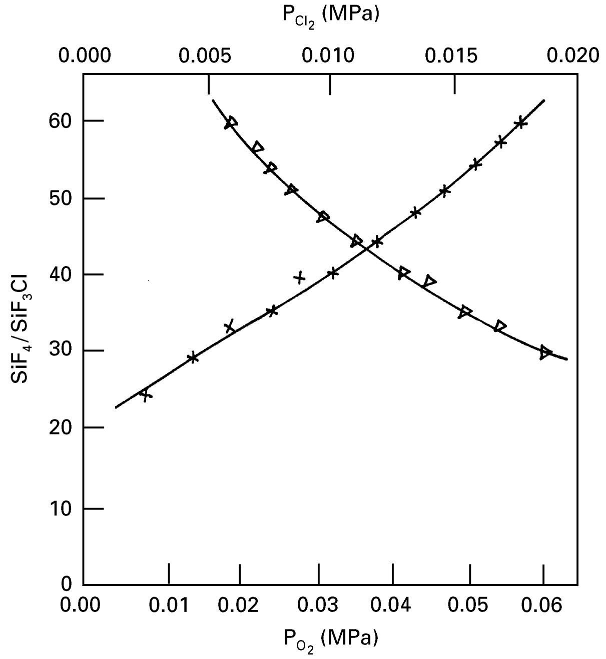

Figure 3 Variation of SiF_4/SiF_3Cl against the change of partial pressures of O_2 (X) and/or Cl_2 (▽) at 2100 K for initial partial pressures of $SiCl_4$ and CCl_2F_2 of 0.0225 MPa and 0.0225 MPa, respectively.

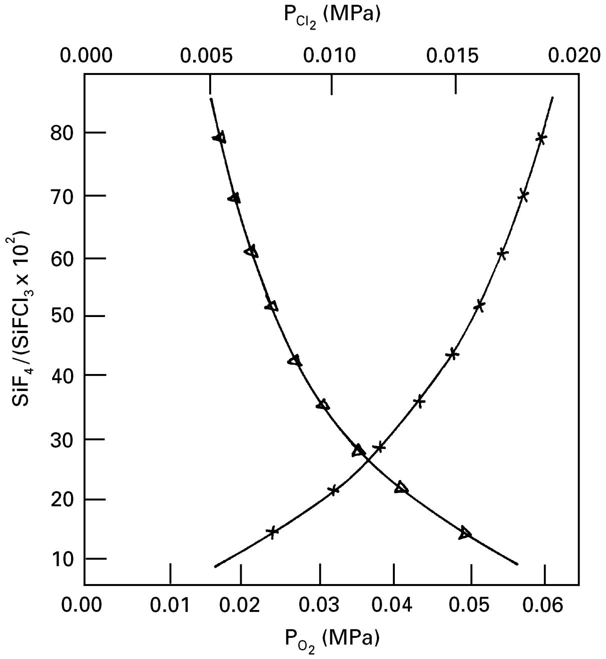

Figure 4 Variation of $SiF_4/SiFCl_3$ against the change of partial pressures of O_2 (X) and/or Cl_2 (▽) at 2100 K for initial partial pressures of $SiCl_4$ and CCl_2F_2 of 0.0225 MPa and 0.0225 MPa, respectively.

The effect of oxygen partial pressure on the relative formation of SiF_4, SiF_3Cl and $SiFCl_3$ was studied at a CCl_2F_2:$SiCl_4$ ratio of 1:1, taking the temperature to be 2100 K. Increase in the quantity of additional oxygen helps the formation of SiF_4 but lowers the amount of other chorofluorosilanes by enhancing the dissociation of chlorine. As a result the proportion of SiF_4 to SiF_3Cl or $SiFCl_3$ increases with increase in partial pressure of oxygen (Figs 3 and 4). In this case also, the quantity of $SiFCl_3$ remains much lower than the other two and, therefore, the magnitude of $SiF_4/SiFCl_3$ greatly exceeds the ratio of SiF_4 to SiF_3Cl. The above figures also show the curves representing the variation in the proportions of SiF_4 with SiF_3Cl and $SiFCl_3$ with respect to the change in the partial pressure of chlorine, both of which reflect an opposite behaviour in comparison to that observed in case of oxygen due to the decrease in the amount of molecular chlorine with increase in oxygen partial pressure.

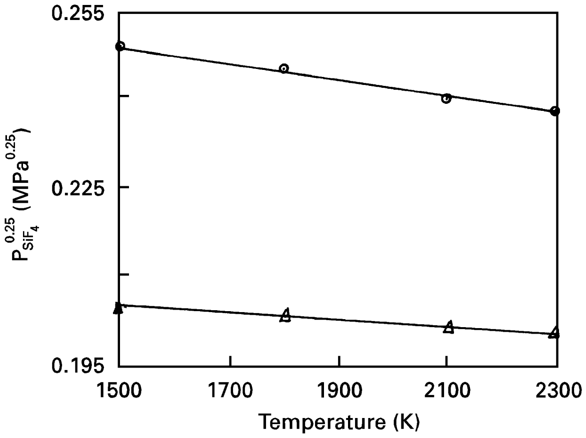

Figure 5 Variation of the partial pressure of SiF_4 to the power of one-fourth as a function of temperature for two different proportions of O_2. $SiCl_4$:CCl_2F_2:O_2; (○) 1:1:10, (△) 1:1:25.

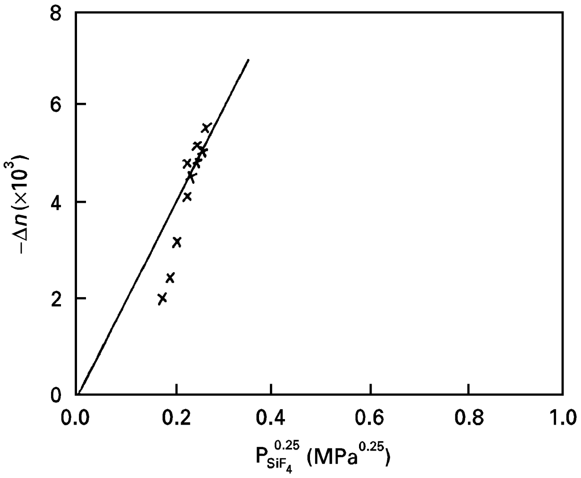

Figure 6 Refractive index depression as a function of the partial pressure of SiF_4 to the power of one-fourth at 2100 K, for initial partial pressures of $SiCl_4$ and O_2 of 0.0086 MPa and 0.0907 MPa, respectively.

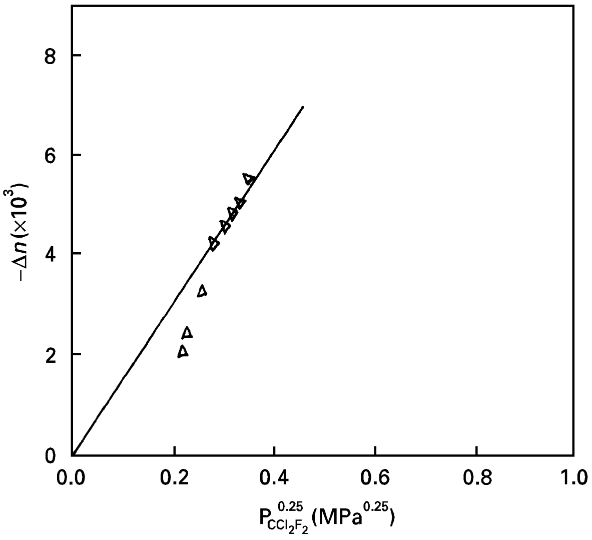

Figure 7 Refractive index depression as a function of the partial pressure of CCl_2F_2 to the power of one-fourth at 2100 K, for initial partial pressures of $SiCl_4$ and O_2 of 0.0086 MPa and 0.0907 MPa, respectively.

Fig. 5 represents the effect of temperature and oxygen partial pressure in a combined manner. The two curves show the variation of $(P_{SiF_4})^{0.25}$ with respect to temperature for $SiCl_4$:CCl_2F_2:O_2 ratios of 1:1:10 and 1:1:25, respectively. Since the partial pressure of SiF_4 is directly related to the amount of fluorine incorporation, the curves give an indication of the expected fluorine mol % in the glass. Considerable reduction in the value of $(P_{SiF_4})^{0.25}$ is observed due to a 2.5-fold increase in the proportion of additional oxygen so that an increase in fluorine incorporation at low oxygen partial pressure is clearly established. Though $(P_{SiF_4})^{0.25}$ is found to increase with lowering of temperature, the total change in its value between the temperatures from 1500 to 2300 K is found to be very small. The oxygen partial pressure is thus found to have greater influence on $(P_{SiF_4})^{0.25}$ in comparison to temperature. Furthermore, small variation in the magnitude of $(P_{SiF_4})^{0.25}$ with temperature signifies that addition of a small amount of $POCl_3$ in the input gas mixture to lower the deposition temperature, will not be helpful in increasing the fluorine incorporation level. The dependence of fluorine incorporation on consolidation temperature though cannot be totally ignored, seems to be insignificant. The result bears more similarity to that observed by Kirchhof *et al.* [10].

The experimental data of $-\Delta n$ versus $(P_{SiF_4})^{0.25}$ are represented in Fig. 6 where the SiF_4 partial pressure at equilibrium was calculated from the input $CCl_2F_2/SiCl_4$ ratio. It is observed that points above $CCl_2F_2/SiCl_4$ value of 0.50 fall on the straight line while those below it do not follow the linear relation. The deviation is more pronounced with lowering of the CCl_2F_2 level. A curve of $-\Delta n$ versus partial pressure of CCl_2F_2 in the input mixture (Fig. 7) shows an identical behaviour. It points out that below the $CCl_2F_2/SiCl_4$ level of 0.50 the fluorine incorporation in the glass will probably be controlled by a different mechanism compared to that at higher CCl_2F_2 level. From the curve of Fig. 6 the relation at higher CCl_2F_2 level is calculated to be $-\Delta n = 0.0199\ (P_{SiF_4})^{0.25}$ at 2100 K. A similar relation can be derived from the curve of Fig. 7 to study the dependence on CCl_2F_2 level in the input mixture and comes to $-\Delta n = 0.0153\ (P_{CCl_2F_2})^{0.25}$. Both the relations are useful to estimate the level of fluorine incorporation from the input gas composition.

The deviation observed at lower CCl_2F_2 level was reported by Marshall *et al.* [14] who predicted a mechanism through $SiFCl_3$ formation instead of that through the SiF_4 route, particularly below the $CCl_2F_2/SiCl_4$ ratio of 0.50. A similar deviation is observed from the results of Kirchhof *et al.* [10], also below the $C_2F_2Cl_3/SiCl_4$ level of 0.20 when the experimental data was compared with the theoretical results. However, the model proposed by Marshall *et al.* does not find much support as the formation of $SiFCl_3$ is found to be lower than SiF_3Cl and SiF_4

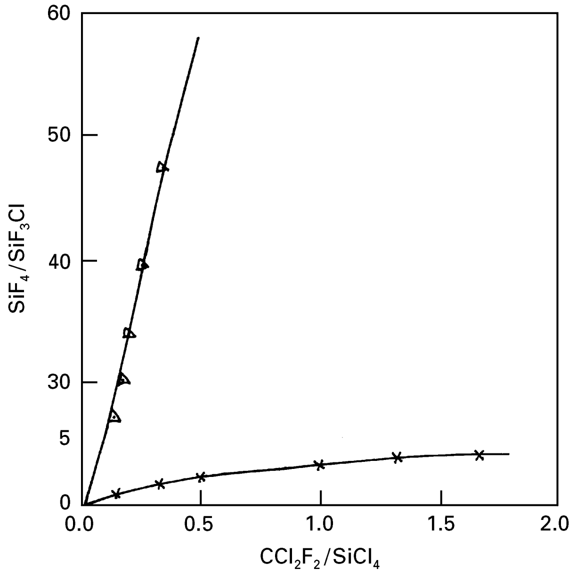

Figure 8 Formation of SiF_4 relative to SiF_3Cl as a function of $CCl_2F_2/SiCl_4$ at 2100 K for two different values of K_{SiF_3Cl} for initial partial pressure of O_2 of 0.0768 MPa. K_{SiF_3Cl}: (X) 0.68 and (△) 0.025.

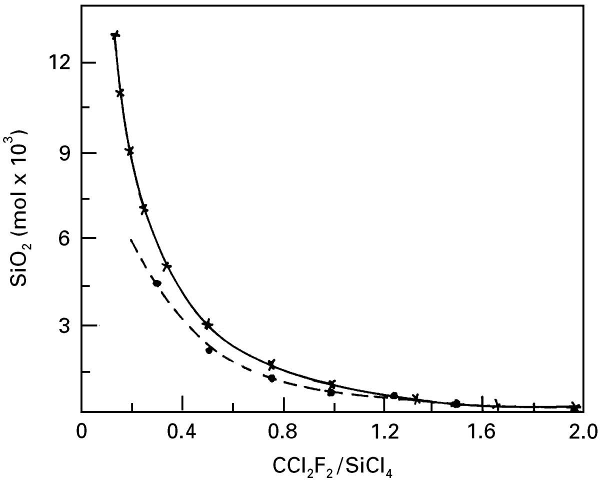

Figure 9 Comparison of the theoretically deduced data (X) against the experimental values (●) for the formation of SiO_2 with different molar ratios of CCl_2F_2 and $SiCl_4$ at 2100 K, (initial partial pressure of O_2 of 0.0768 MPa).

irrespective of temperature from the present calculations. Even by considering an equilibrium constant value of 0.47 at 2000 K and 0.68 at 2100 K for SiF_3Cl formation [4, 13] at various $CCl_2F_2/SiCl_4$ ratios and oxygen levels, $SiFCl_3$ is never found to be the major product. The amount of $SiFCl_3$ is only found to exceed that of SiF_4 in no oxygen atmosphere below a particular $CCl_2F_2/SiCl_4$ ratio, which varies from 0.33 to 0.55 for a change of temperature from 1800 to 2100 K. Here the amount of SiF_3Cl always remains the lowest. This is, however, only of theoretical interest as SiO_2 deposition is not possible in absence of oxygen and therefore is not of much importance for MCVD process chemistry.

An incorporation mechanism with $-\Delta n$ dependent on partial pressure of SiF_4 to the power of 0.5 is not expected at this dopant concentration. As such this mechanism will only be possible at high fluorine dopant levels [13]. Because the formation of SiF_2Cl_2 could not be considered due to the non-availability of free energy of formation data, which seems to be important at low fluorine levels [13], it is difficult to explain the deviation from linearity at low dopant concentration. The decrease in the SiF_4 to SiF_3Cl ratio at low CCl_2F_2 level may be a determining factor to affect the SiF_4 mechanism guiding the fluorine incorporation in which SiF_4 is taken to be the major dominant species. The relative change in the proportion of SiF_4 to SiF_3Cl is more prominent when K_{SiF_3Cl} is taken to be 0.025 as compared to the value of 0.68 (worked out by Walker *et al.*), as shown in Fig. 8.

The amount of deposition of SiO_2 at various CCl_2F_2 and $SiCl_4$ concentrations has been experimentally determined from the deposition thickness of the different layers (Fig. 9) for comparison with the theoretically calculated values. The close agreement between the two curves underscores the validity of the model based on complete thermodynamic equilibrium, except at low CCl_2F_2 concentration where a gradual shifting of the experimental curve from the theoretical one is apparent. Because a closely similar configuration is observed in Fig. 6, the idea of a different fluorine incorporation mechanism at low fluorine dopant concentration cannot be ruled out.

6. Conclusions

The study of the relative formation of the various fluorine species such as SiF_4, SiF_3Cl and $SiFCl_3$ at different CCl_2F_2, $SiCl_4$ and O_2 ratios and temperatures on the basis of a complete thermodynamic equilibrium suggests that SiF_4 is always the major product, and therefore the fluorine incorporation in the silica via the SiF_4 route is the most likely mechanism during the deposition by MCVD process. The concentration of fluorine in the glass is related to the SiF_4 partial pressure to the $\frac{1}{4}$ power above $CCl_2F_2/SiCl_4$ ratio of 0.50. The deviation from this relation at low CCl_2F_2 level probably indicates a different fluorine incorporation mechanism at low dopant concentration. The partial pressure of oxygen is found to have a greater influence than temperature on the fluorine incorporation level so that a better control over the process can be achieved by adjusting the additional oxygen amount. The temperature dependence of the process is found to be insignificant over the temperature range of 1500 to 2300 K. Thus, the addition of a small amount of $POCl_3$ in the input gas mixture to lower the sintering temperature of the deposited soot layer has very little influence in enhancing the fluorine incorporation level. Because fluorine incorporation mechanism is always guided by SiF_4 formation, irrespective of the source of fluorine, the above results bear significance for all the common dopants used for fluorine incorporation by MCVD process.

Appendix

Values of K_p calculated at different temperatures (data obtained from the JANAF table)

Reaction	K_p at 1500 K	K_p at 1800 K	K_p at 2100 K	K_p at 2300 K
$SiCl_4 + O_2 \xrightarrow{K_{p_1}} SiO_2(s) + 2Cl_2$	2.3267×10^6	8.6665×10^4	8.3892×10^3	2.5010×10^3
$SiO_2 + 2CCl_2F_2 + O_2 \xrightarrow{K_{p_2}} SiF_4 + 2Cl_2 + 2CO_2$	8.9640×10^{32}	6.6817×10^{29}	3.6574×10^{27}	2.3542×10^{26}
$3SiF_4 + SiO_2 + 2Cl_2 \xrightarrow{K_{p_3}} 4SiF_3Cl + O_2$	6.7289×10^{-12}	4.172×10^{-9}	4.064×10^{-7}	4.403×10^{-6}
$SiF_4 + 3SiO_2 + 6Cl_2 \xrightarrow{K_{p_4}} 4SiFCl_3 + 3O_2$	1.3078×10^{-23}	5.394×10^{-18}	5.306×10^{-14}	6.28×10^{-12}
$Cl_2 \xrightarrow{K_{p_8}} 2Cl$	3.535×10^{-3}	0.1022139	1.146	4.06978
$SiCl_4 + 2CCl_2F_2 \xrightarrow{K_{p_5}} SiF_4 + 4Cl_2 + 2C$	2.0955×10^{11}	2.6694×10^{11}	3.0523×10^{11}	3.2308×10^{11}
$2SiCl_4 + 3CCl_2F_2 \xrightarrow{K_{p_6}} 2SiF_3Cl + 6Cl_2 + 3C$	3.7949×10^{14}	2.6226×10^{15}	9.8472×10^{15}	1.9270×10^{16}
$2SiCl_4 + CCl_2F_2 \xrightarrow{K_{p_7}} 2SiFCl_3 + 2Cl_2 + C$	5.8714×10^3	3.0616×10^4	9.7795×10^4	1.7816×10^5

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