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A Kinetic and Equilibrium Analysis of Silicon Carbide Chemical Vapor Deposition on Monofilaments

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A KINETIC AND EQUILIBRIUM ANALYSIS OF SiC CVD ON MONOFILAMENTS

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SUMMARY

Chemical kinetics of atmospheric pressure silicon carbide CVD from dilute silane and propane source gases in hydrogen is numerically analyzed in a cylindrical upflow reactor designed for CVD on monofilaments. The chemical composition of the SiC deposit is assessed both from the calculated total fluxes of carbon and silicon and from chemical equilibrium considerations for the prevailing temperatures and species concentrations at and along the filament surface. The effects of gas and surface chemistry on the evolution of major gas phase species are considered in the analysis.

INTRODUCTION

High temperature properties of SiC make it a very attractive fiber and/or coating material for the aerospace industry. Combined with the versatility of the CVD technique for fabricating materials, developing models for SiC CVD is receiving increased attention to optimize and scale-up the process.

Earlier predictions of SiC deposit chemical composition based on thermochemical equilibrium approaches proved to be quite inadequate when compared to experimental measurements (refs. 1 and 2), suggesting the importance of chemical kinetic constraints. Indeed, it has been demonstrated that the reactive sticking coefficients of gas phase species such as CH_4 , C_2H_2 , C_2H_4 , SiH_4 , SiH_2 , and Si_2H_6 , expected to be present in SiC deposition, can span five orders of magnitude (refs. 3 to 5). However, more recent models proposed so far, including detailed gas and surface chemistry, predict only SiC deposition rates, not deposit composition, as a function of reactor parameters (refs. 6 to 8), i.e., the deposit is prescribed to have a silicon to carbon atom ratio of unity such that any nonstoichiometric SiC deposition is disallowed. Hence, these models provide only limited guidance for controlling the silicon to carbon atom ratio in the deposit.

Recent experiments of Komiyama and coworkers (refs. 9 and 10) propose the possibility of the importance of organosilicon species for SiC CVD. They provide a plausible explanation of the composition change of SiC_x ($x = 1 - 2$) due to the presence of organosilicon species in the system (ref. 11). Indeed, the most recent and detailed equilibrium analyses suggest that the role of organosilicon compounds may be quite significant for SiC CVD (refs. 12 and 13). However, due to the lack of kinetic information to incorporate such organosilicon species into our model, this study is limited to a reduced mechanism (ref. 7).

Based on the calculated concentration profiles of individual Si and C species within the reactor the model predicts the surface fluxes of each species along the fiber surface. Deposit composition is inferred from the total elemental fluxes of Si and C. The resulting concentrations of each species along the fiber surface is also determined. Using these concentrations and the fiber surface temperatures, another approach is taken to calculate the composition of the deposit that would prevail if there were local thermochemical equilibrium at the fiber surface, i.e., no surface chemical kinetic barriers. Specific problems associated with CVD on thin fibrous substrates are extensively discussed in our earlier publications (refs. 14 and 15) and will not be elaborated on in this paper.

MODELING APPROACH

A finite-volume based computational code FLUENT 3.03 is adopted for the simultaneous treatment of gas phase transport processes and finite rate chemical kinetics (ref. 16). The CVD capabilities of this version of FLUENT such as the temperature dependent thermophysical and transport properties, Soret diffusion, and gas and surface chemical reactions are fully exploited. The model is applied to an experimental reactor which is a vertically oriented cylindrical tube as is schematically shown in figure 1. The details of the numerical simulation and experimental setup are described in references 14 and 15.

The model uses the experimentally measured fiber and reactor wall temperature profiles given in table I for the two fiber temperatures considered, namely, "1150 °C" and "1450 °C". The dilute source gas precursors are SiH₄ and C₃H₈ in a H₂ carrier gas. Throughout this analysis the total gas flowrate and inlet SiH₄ mole fraction are fixed at 1 slm and 0.3 percent, respectively. The inlet C₃H₈ mole fraction is either the lower value of 0.3 percent for the "1150 °C" case (hereafter referred to as the L/L case) or the higher value of 0.9 percent for the "1450 °C" case (hereafter referred to as the H/H case).

The kinetic model employed in this study assumes that Si and C deposition proceed independently from one another with no interaction (i.e., no organosilicon compounds). The gas phase and surface reactions are given below.

Gas phase		Surface	
(G1)	SiH ₄ ⇌ SiH ₂ + H ₂	(S1)	SiH ₄ → Si(s) + 2H ₂
(G2)	Si ₂ H ₆ ⇌ SiH ₂ + SiH ₄	(S2)	Si ₂ H ₆ → 2Si(s) + 3H ₂
(G3)	C ₃ H ₈ ⇌ CH ₃ + C ₂ H ₅	(S3)	SiH ₂ → Si(s) + H ₂
(G4)	C ₂ H ₅ ⇌ C ₂ H ₄ + H	(S4)	C ₃ H ₈ → 3C(s) + 4H ₂
(G5)	C ₂ H ₄ ⇌ C ₂ H ₂ + H ₂	(S5)	C ₂ H ₅ → 2C(s) + 2.5H ₂
(G6)	CH ₃ + H ₂ ⇌ CH ₄ + H	(S6)	C ₂ H ₄ → 2C(s) + 2H ₂
		(S7)	C ₂ H ₂ → 2C(s) + H ₂
		(S8)	CH ₄ → C(s) + 2H ₂
		(S9)	CH ₃ → C(s) + 1.5H ₂

Note that the gas phase reactions given above are considered reversible reactions, i.e., the actual number of gas phase reactions included in the model is in fact 12. The NIST Chemical Kinetics Data Base (ref. 17) is utilized for selecting the proper reaction rates. For reversible reactions (G1) and (G2) the rate expressions are taken from reference 18. The data of Warnatz (ref. 19) is used for reversible reactions (G3), (G4), and (G6). The kinetics for the reversible reaction (G5) are obtained from reference 20. Note also that all surface reactions are considered to be irreversible. Reaction rates for (S1), (S2), and (S3) are the same as in reference 18, for (S4), (S6), and (S8) are taken from the measurements of reference 5, and for (S5), (S7), and (S9) are the same as the estimated values of reference 7. Nine different species are considered in the transport/kinetic calculations.

For thermochemical equilibrium calculations the NASA CEC computer program based on free-energy minimization (ref. 21) is used. Equilibrium gas phase compositions are calculated for cases where (1) condensed phases are not allowed, corresponding to a situation where the surface is far from equilibrium and deposition reactions are much slower than gas phase reactions and (2) condensed phases are allowed to be in equilibrium with the gas phase, which enables the prediction of deposit composition under conditions locally prevailing at the surface.

RESULTS AND DISCUSSION

Before any kinetic considerations, the NASA CEC program is used for evaluating the major chemical species which are likely to be present in the system at equilibrium at the inlet conditions. Two subcases are analyzed for each of the L/L and H/H cases: (1) it is assumed that the surface kinetic barriers are too high for solid phases to form and (2) the surface reactions are also assumed to be fast enough for equilibrium to be established at the gas/solid interface. Table II lists the mole fractions of the first seven C and Si species expected to be present in the gas phase for each case.

It is interesting to note that the condensed phases are C-rich in both L/L and H/H cases, with SiC constituting 58 percent of the deposit for the L/L case and only 18 percent of the deposit for the H/H case. The remainder in each case is graphitic C. For the L/L case, CH_4 seems to dominate over other carbon species such as C_2H_2 , C_2H_4 , and CH_3 , whereas SiH_4 is the most abundant among the silicon species. However, Si_2C and Si_3 appear to be as important as SiH_4 and SiH_2 when solid phases are not allowed, indicating the propensity of the system to form organosilicon compounds and for gas phase nucleation. SiH_x 's are favored when interface equilibrium is allowed. For the H/H case, C_2H_2 becomes significant compared to CH_4 , SiH_2 becomes more stable than SiH_4 , and, when solid phases are not allowed, the system favors to form the organosilicon Si_2C with little indication of the tendency for gas phase nucleation.

The transport/kinetic analysis can shed some light on how far our specific system is from equilibrium both in the gas phase and at the interface and its consequences on the chemical composition of the deposit. Figures 2(a) and (b) show the mole fractions of the species considered at and along the gas/fiber interface for the L/L case. SiH_4 and C_3H_8 dominate the gas composition with practically no depletion during the ~ 1 -sec residence time of the gases in the reactor. However, deposition fluxes are related to the product of concentration and reactive (surface) sticking coefficient of the molecule. Hence, the differences in the surface reactivities of the species lead to a different ranking of the contributions of species on deposition rates as shown in figures 2(c) and (d), i.e., SiH_2 becomes more important than SiH_4 for silicon deposition, and CH_3 and C_2H_4 deliver more carbon to the surface than C_3H_8 . Indeed, the deposition rate profiles will follow the combined surface flux profiles of the most significant contributors. Figure 2(e) shows the ratio of the total elemental silicon flux to the total elemental carbon flux along the fiber surface and is an indication of the deposit chemical composition. Contrary to the equilibrium analysis, the transport/kinetic analysis indicate a highly silicon-rich deposit.

A third approach is taken to determine the composition of the deposit along the fiber surface. It assumes that the interface reaches equilibrium for the local temperature and element compositions calculated at the fiber surface by the transport/kinetic model. This surface equilibrium approach is not incorporated into the transport/kinetic analysis consistently, because the downstream elemental compositions at the interface are obtained by using surface kinetics, rather than by using the upstream surface equilibrium conditions. Yet, it provides a quick guidance for showing the propensity of the interface at equilibrium to favor a particular deposit composition. Figure 2(f), obtained by this approach, displays that the deposit is pure stoichiometric SiC along the fiber.

Figures 3(a) to (f) refer to the H/H case. The major differences from the L/L case (figs. 2(a) to (f)) are noted as follows: There is substantial silane depletion due to higher SiH_4 dissociation (fig. 3(a)), and, therefore, Si deposition rates (fig. 3(c)). C_2H_4 and CH_4 mole fractions are now even larger than C_3H_8 , indicating a faster approach towards equilibrium at higher temperatures (fig. 3(b)). Carbon deposition is dominated by CH_3 and C_2H_4 , and C_3H_8 has the smallest surface flux (fig. 3(d)). From the transport/kinetic analysis the deposit is expected to be more stoichiometric because elemental Si and C surface fluxes are more comparable (fig. 3(e)). However, the post transport/kinetic analysis surface equilibrium calculations result in a substantially C-rich deposit (fig. 3(f)).

SUMMARY AND CONCLUSIONS

Different approaches are taken to assess the feasibility of predicting the deposit composition on mono filaments in a reactor built for SiC CVD using silane and propane precursors. One approach assumed thermochemical equilibrium in the gas phase at inlet gas composition and fiber temperature while the gas/solid interface is either assumed to be at equilibrium or is not allowed to form a condensed phase. Another parallel approach incorporated the gas phase and surface chemical kinetics into a transport model. Based on the evolution of the chemical species in the transport/kinetic analysis, the gas phase is found to be far from equilibrium under practical operating conditions even at higher temperatures. On the other hand, the equilibrium analysis indicated that the transport/kinetic analysis needs to consider organosilicon species and allow for mechanisms for the formation of embryonic nuclei leading to gas phase nucleation. Yet a third approach based on equilibrium is used in series with the transport/kinetic model. This method used the elemental compositions along the interface calculated by the transport/kinetic model for the subsequent equilibrium predictions of the deposit composition.

The endeavor to predict the chemical composition of deposits grown by CVD is not a trivial task. The attempted predictions of Si/C compositions from different approaches in this study, varying from silicon-rich to stoichiometric to carbon-rich, indicate the need for more sophisticated surface reaction models which are consistent with the thermochemical equilibrium extremes, and consideration of more sophisticated gas phase chemical mechanisms and species as hinted by the gas phase equilibrium analyses, which are both thus far neglected.

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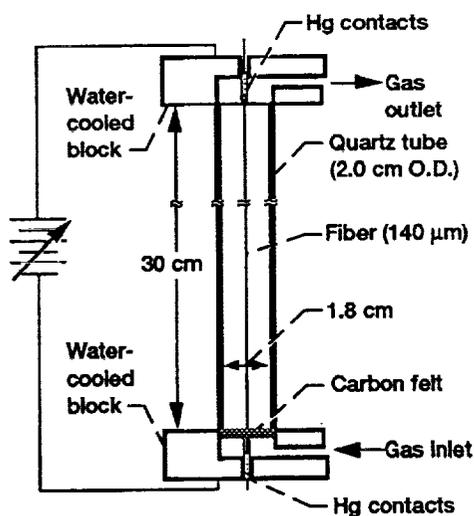


Figure 1.—Schematic of experimental reactor.

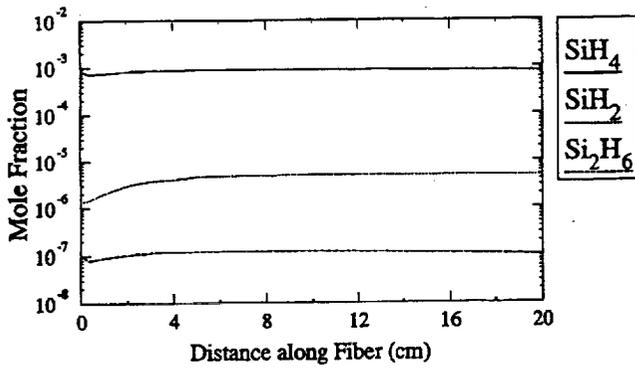
TABLE I.—EXPERIMENTALLY MEASURED
FIBER AND WALL TEMPERATURES

Distance along fiber, cm	"1150 °C case"		"1450 °C case"	
	Fiber temperature, °C	Wall temperature, °C	Fiber temperature, °C	Wall temperature, °C
1	1096	179	1421	246
2	1118	222	1434	294
3	1129	254	1442	328
4	1133	259	1448	328
5	1142	281	1450	354
10	1147	304	1452	379
15	1149	300	1449	378
20	1152	297	1447	374

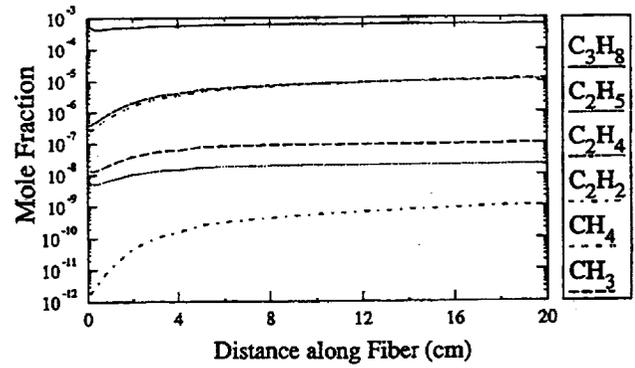
TABLE II.—EQUILIBRIUM MOLE FRACTIONS OF GAS PHASE SPECIES AND SOLID PHASES
FOR THE L/L AND H/H CASES

L/L.a		L/L.b*		H/H.a		H/H.b*	
Specimen name	Mole fraction						
CH ₄	3.84-03	CH ₄	8.47-03	CH ₄	9.83-04	CH ₄	8.71-03
C ₂ H ₂	3.97-06	C ₂ H ₂	1.96-05	C ₂ H ₂	1.01-04	C ₂ H ₂	8.20-03
C ₂ H ₄	2.25-06	C ₂ H ₄	1.10-05	CH ₃	4.15-06	C ₂ H ₄	2.93-04
CH ₃	5.84-07	CH ₃	1.29-06	C ₂ H ₄	3.69-06	CH ₃	3.71-05
C ₂ H ₆	3.64-08	C ₂ H ₆	1.77-07	C ₂ H ₃	3.60-08	C ₃ H ₄	6.57-06
C ₂ H ₃	1.01-09	C ₃ H ₄	8.30-09	C ₂ H	1.80-08	C ₄ H ₂	5.94-06
C ₃ H ₄	7.63-10	Allene	5.31-09	C ₃ H ₄	9.23-09	Allene	4.70-06
H ₂	9.91-01	H ₂	9.89-01	H ₂	9.74-01	H ₂	9.81-01
H	6.55-06	H	6.57-06	H	1.77-04	H	1.80-04
SiH ₄	4.95-09	SiH ₄	9.63-04	SiH ₂	1.86-07	Si ₂ C	1.35-03
SiH ₂	1.96-09	Si ₂ C	5.50-04	SiH	2.28-08	SiH ₂	2.18-04
SiH	3.59-11	SiH ₂	3.83-04	SiH ₄	2.01-08	SiH	2.69-05
SiH ₃	3.09-11	Si ₃	1.87-04	Si	1.51-08	SiH ₄	2.31-05
Si	7.56-12	SiH	7.06-06	SiH ₃	1.66-09	Si	1.80-05
SiC ₂	6.93-15	SiH ₃	6.02-06	SiC ₂	1.44-10	SiC ₂	1.37-05
Si ₂ C	6.39-15	Si	1.49-06	Si ₂ C	1.09-10	Si ₃	8.25-06
C(gr)	2.14-03	Not allowed		C(gr)	2.22-02	Not allowed	
SiC(β)	3.00-03	Not allowed		SiC(β)	2.93-03	Not allowed	

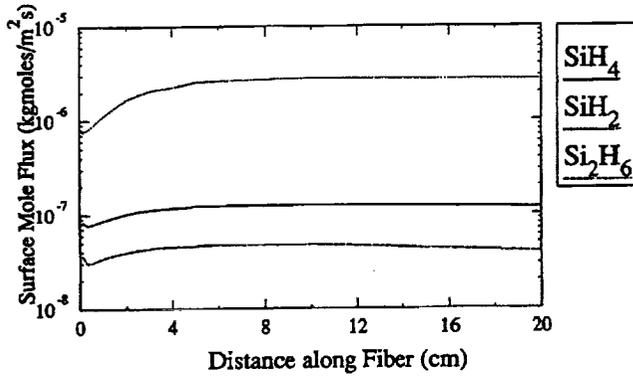
*No condensed phases are allowed in these calculations.



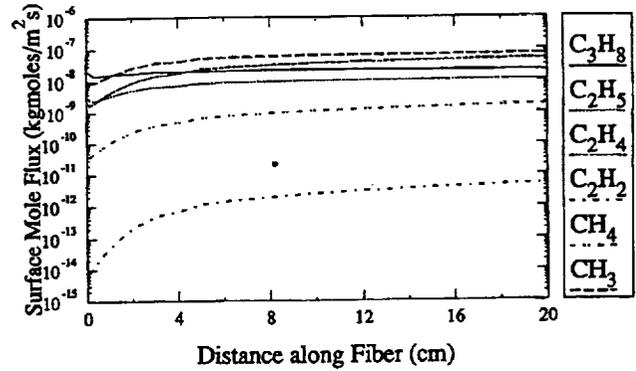
(a) Mole fractions of species along gas/fiber interface.



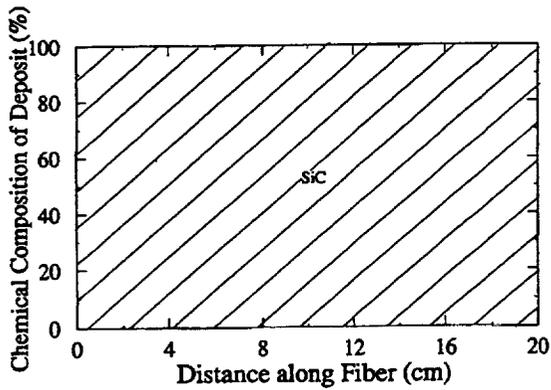
(b) Mole fractions of species along gas/fiber interface.



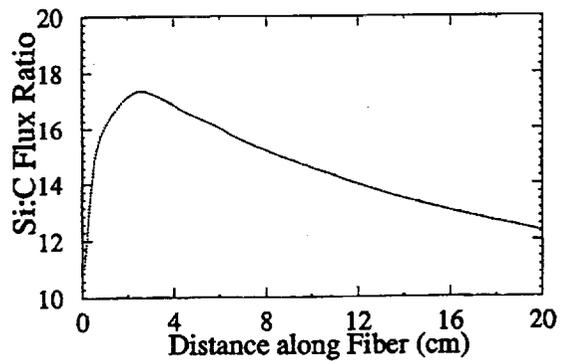
(c) Surface mole flux of species.



(d) Surface mole flux of species.

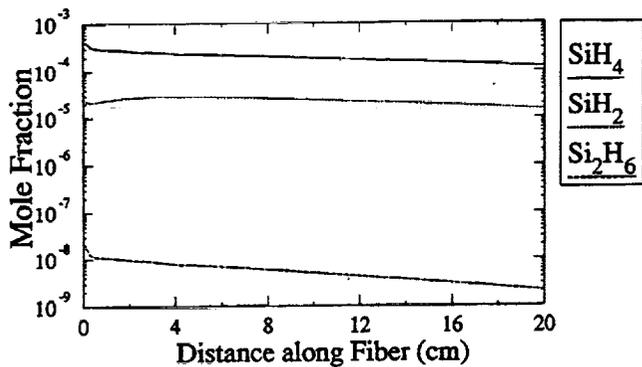


(e) Inferred composition of deposit - transport/kinetic calculations.

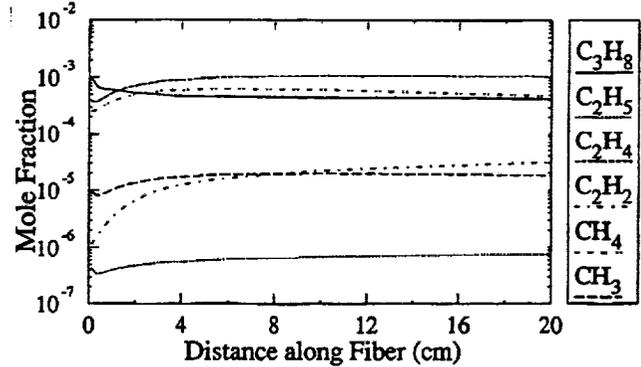


(f) Composition of deposit - equilibrium calculations.

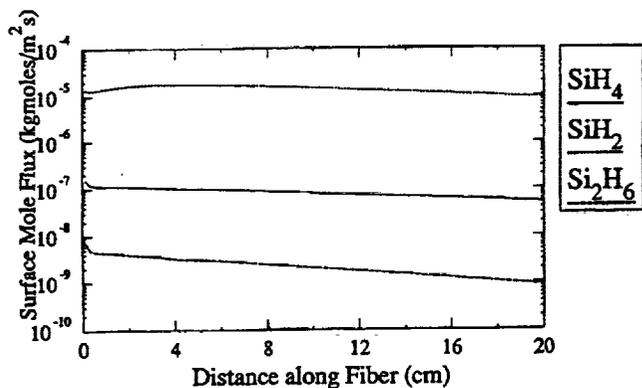
Figure 2.—T = "1150 °C", 0.3% SiH₄, 0.3% C₃H₈ (L/L case).



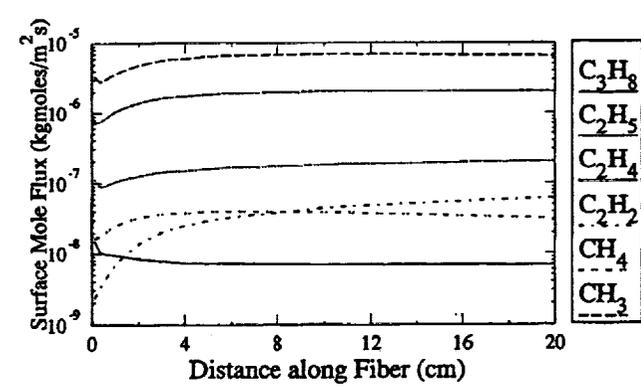
(a) Mole fractions of species along gas/fiber interface.



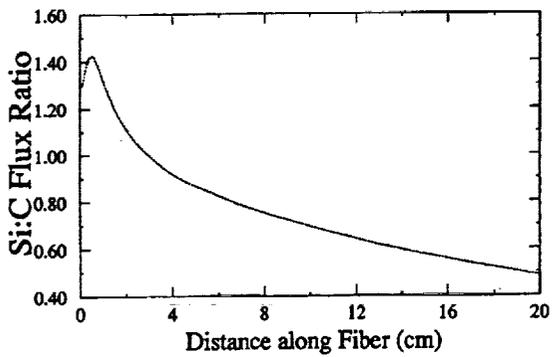
(b) Mole fractions of species along gas/fiber interface.



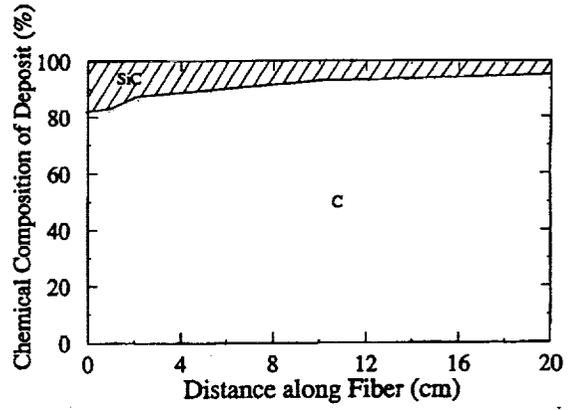
(c) Surface mole flux of species.



(d) Surface mole flux of species.



(e) Inferred composition of deposit - transport/kinetic calculations.



(f) Composition of deposit - equilibrium calculations.

Figure 3.—T = "1450 °C", 0.3% SiH₄, 0.9% C₃H₈ (H/Hcase).

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