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Unsteady heat and mass transfer on the codeposition of SiO_2/GeO_2 during the modified chemical vapor deposition process

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Abstract

A numerical analysis of unsteady heat and mass transfer on the codeposition of SiO_2 and GeO_2 in the modified chemical vapor deposition has been carried out. An earlier study showed that the optimized torch speed variation could be used to enhance the deposition uniformity of single component SiO_2 particle. However, this optimized torch speed resulted in the deterioration of GeO_2 deposition uniformity for multi-component SiO_2/GeO_2 deposition in the present study. To ensure the uniformity of both SiO_2 and GeO_2 , a control strategy may need variations of two parameters at least. Parametric studies, varying three different operating conditions over time (maximum wall temperature, torch speed and in-take amount of GeO_2 can be obtained by increasing the in-take flow rate of $GeCl_4$ over time. \bigcirc 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

The modified chemical vapor deposition (MCVD) process is utilized to manufacture high-quality optical fibers [1]. In the process, a fire polished silica tube is rotated and heated by a slowly traversing oxy-hydrogen torch. A mixture of gases, such as silicon tetra-chloride (SiCl₄), germanium tetrachloride (GeCl₄), and oxygen (O₂) flow into the rotating silica tube and are heated to high temperatures. Chemical reactions occur and result in fine particles; e.g. silicon dioxide (SiO₂),

germanium dioxide (GeO₂). These particles move axially with the gases and are deposited on the inner wall of the tube due to thermophoresis; that is, from the net force that a suspended particle experiences in the direction of decreasing temperature in a nonisothermal medium [2]. The deposited particles are consolidated into a glassy thin layer by sintering. When the torch completes its traverse to the end of the tube, one layer of deposition is obtained. By controlling the dopant chemical composition, desired refractive index profile is obtained. Germanium is the most common dopant used to increase the refractive index of SiO₂ to form a guiding core. After 10–40 layers are deposited, the tube is collapsed into a solid preform rod and then drawn into a long thin fiber.

The high-temperature chemical reactions, deposition and consolidation steps are interrelated and are

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Nomenclature

С	gas concentration (mol m^{-3})	S_i	source term in Eq. (6)	
C_p	specific heat of gas at constant	T	temperature (K)	
	pressure (J mol ^{-1} K ^{-1})	t	time	
D_i	diffusivity $(m^2 s^{-1})$	и	radial velocity	
E_i	activation energy for oxidation (J	v	axial velocity	
	mol^{-1})	\vec{V}	velocity (u, v)	
ΔH_i	heat of reaction of species i (J mol ⁻¹)	$ec{V}_{ ext{T}}$	thermophoretic velocity of par- ticles (m s^{-1})	
h	heat transfer coefficient (W m ⁻²	X_i	mole fraction in the gas phase	
	K^{-1})	X	axial coordinate	
k	thermal conductivity (J $m^{-1} K^{-1} s^{-1}$)	Y_i	mole fraction in the particle phase	
$k_{\rm GC,0}$	frequency factor for GeCl ₄ oxi-	Greek symbols		
<i>,</i>	dation (s^{-1})	α	absorption coefficient	
$k_{\rm GC}, k_{\rm SC,0}, k_{\rm SC,1}$	constants for oxidation reaction	δm_i	deposition mass of particle i	
k_0, k_1, k_2	constants to calculate thermal		(GeO_2, SiO_2) per unit area	
	conductivity	γ	activity coefficient of GeO2 in	
Κ	thermophoretic coefficient		GeO ₂ /SiO ₂ particle phase	
$K_{\rm EQ}$	equilibrium constant of GeCl ₄ oxi-	3	emissivity	
	dation	λ	control parameter for torch heat	
M	molecular weight		flux	
n	refractive index	V	kinematic viscosity (m ² s ^{-1})	
n _i	moles of <i>i</i> species particles per	ρ	density	
	mole of carrier gas	σ	Stefan–Boltzmann constant	
р	pressure			
q_{max}	control parameter for torch heat	Subscripts		
	flux	CL	Cl ₂	
r	radial coordinate	GC	GeCl ₄	
r _i	rate of formation of particle i	GO	GeO ₂	
	(GeO ₂ , SiO ₂) by oxidation (m^{-3})	O2	O_2	
	s^{-1})	SC	SiCl ₄	
$R_{ m i}$	inner tube radius	SO	SiO ₂	
$R_{\rm G}$	gas constant	0	inlet condition	
Ro	outer tube radius			

affected by the details of thermal processing and control, as well as by the specific chemical mixture used. Thus, most previous studies of the MCVD have been numerical analyses. The previous investigations focused on various aspects of the problems: thermophoresis [2], correlation between overall efficiency and minimum temperature [3], laser-enhanced MCVD [4,5], chemical kinetics and silica aerosol dynamics [6], tapered entry region reduction [7,8], three-dimensional effect [9,10], codeposition of SiO₂ and GeO₂ [11], two torch model [12], oxidation of SiCl₄ and GeCl₄ and buoyancy [13], measurement of deposited film thickness and tube wall temperature [14]. However, there has been relatively little attention on the processing control for the optimum performance such as tapered entry region reduction and uniform deposition thick-

ness. The reason of intactness in the control of the processing conditions may be found on the quasisteady assumption used in previous works. Recently, Park and Choi [15] extended their work to the unsteady analysis and found out that unsteady calculations significantly improved the prediction of SiO₂ particle deposition profile in the entire region by comparing their results with the existing experimental study. They also examined the effects of torch speed variation on deposition performance for silica particles and identified that the linearly varying torch speed case resulted in a much shorter tapered entry than the constant torch speed case. For the codeposition of silica and germanium dioxide, very precise compositional and processing control is necessary to ensure the desired refractive index structures, especially for

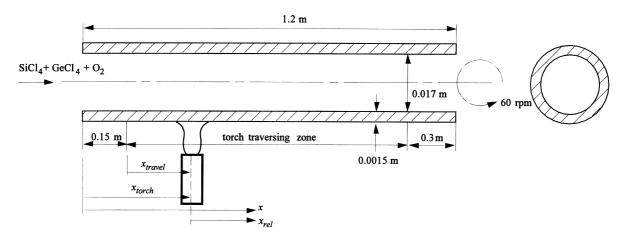


Fig. 1. Schematic diagram of the MCVD system.

multi-mode fiber manufacture, and optimum operating conditions will be considerably different from single component particle generation and deposition. Therefore, time dependent operating conditions such as torch speed, chemical gas flow rate and tube wall temperatures, etc. should be considered and, correspondingly, the unsteady analysis is prerequisite in its modeling.

In this paper, we extend our earlier work [15] to the unsteady analysis of multi-component (SiO₂ and GeO₂) MCVD. For the present unsteady calculation, the quartz tube is included in the calculation domain and the effects of chemical reactions for oxidations of both SiCl₄ and GeCl₄ and variable properties are also included. The time dependent operating conditions for the reduction of tapered entry and uniform deposition of both SiO₂ and GeO₂ are also examined.

2. Analysis

Fig. 1 depicts the geometric configuration considered in this study. A mixture of reactants (SiCl₄, GeCl₄ and O_2) is fed into a silica tube (reactor) as a fully developed laminar flow at the inlet. The mixture is heated by an external heat source and exothermic oxidations of SiCl₄ and GeCl₄ take place forming SiO₂, GeO₂ and Cl₂. From previous studies on the oxidation chemistry of SiCl₄ and GeCl₄ [16,17], it is well known that SiCl₄ oxidizes to form SiO₂ and its reverse reaction can be neglected, but the reverse and forward reaction of GeCl₄ oxidation should be considered:

$$SiCl_4 + O_2 \rightarrow SiO_2 + 2Cl_2, GeCl_4 + O_2 \leftrightarrow GeO_2 + 2Cl_2$$
 (1)

Fractions of newly formed silica and germanium dioxide particles are deposited onto the relatively low-

temperature tube wall mostly by thermophoresis, while the rest exit the tube by convection.

Since uniform deposition in the circumferential direction can be assumed for normal rotational speeds (60–120 rpm) [10], the axisymmetric, two-dimensional unsteady governing equations can be written as

Continuity equation

$$\frac{\partial C}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}(Crv) + \frac{\partial}{\partial x}(Cu) = 0$$
(2)

Momentum equation

$$C\left(\frac{\partial u}{\partial t} + v\frac{\partial u}{\partial r} + u\frac{\partial u}{\partial x}\right)$$

= $-\frac{1}{M}\frac{\partial p}{\partial x} + \frac{1}{M}\left[\frac{2}{3}\frac{\partial}{\partial x}\left\{\mu\left(2\frac{\partial u}{\partial x} - \frac{\partial v}{\partial r} - \frac{v}{r}\right)\right\}$
+ $\frac{1}{r}\frac{\partial}{\partial r}\left\{\mu r\left(\frac{\partial u}{\partial r} + \frac{\partial v}{\partial x}\right)\right\}\right]$ (3a)

$$C\left(\frac{\partial v}{\partial t} + v\frac{\partial v}{\partial r} + u\frac{\partial v}{\partial x}\right)$$

$$= -\frac{1}{M}\frac{\partial p}{\partial r} + \frac{1}{M}\left[\frac{\partial}{\partial x}\left\{\mu\left(\frac{\partial u}{\partial r} + \frac{\partial v}{\partial x}\right)\right\}\right]$$

$$+ \frac{2}{3r}\frac{\partial}{\partial r}\left\{\mu r\left(2\frac{\partial v}{\partial r} - \frac{\partial u}{\partial x} - \frac{v}{r}\right)\right\}$$

$$+ \frac{2\mu}{3r}\left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial r} - \frac{2v}{r}\right)$$
(3b)

Energy equation for gas

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Table 1 Simulation conditions used for the MCVD process with SiCl₄ and GeCl₄

$E_{\rm SC}$ (J mol ⁻¹)	4.02×10^{5}
$E_{\rm GC}$ (J mol ⁻¹)	2.63×10^5
$\Delta H_{\rm SC} (\rm J \ mol^{-1})$	2.51×10^5
$\Delta H_{\rm GC} (\rm J \ mol^{-1})$	4.6×10^4
$k_{\rm SC,0} (\rm s^{-1})$	1.7×10^{14}
$k_{\rm SC,1} \ ({\rm m}^3 \ {\rm mol}^{-1} \ {\rm s}^{-1})$	3.1×10^{13}
$k_{\rm GC,0} \ ({\rm m}^3 \ {\rm mol}^{-1} \ {\rm s}^{-1})$	2.3×10^{9}
v_0^{a}	1.39×10^{-9}
$k_0, k_1, k_2^{\rm b}$	$4.52 \times 10^{-3}, 7.62 \times 10^{-5}, -9.80 \times 10^{-9}$
$C_{p,0}, C_{p,1}, C_{p,2}^{c}$	7.16, 1.0×10^{-3} , -0.4×10^{5}
$D_{\rm SC,0}, D_{\rm GC,0}, D_{\rm CL,0}^{\rm d}$	$6.32 \times 10^{-10}, 6.0 \times 10^{-10}, 1.12 \times 10^{-9}$

^a
$$v = v_0 T^{1.64874}$$
.
^b $k = k_0 + k_1 T + k_2 T^2$.
^c $C_p = C_{p,0} + C_{p,1} T + C_{p,2} T^{-2}$
^d $D_i = D_{i,0} T^{1.6561}$.

$$CC_{p}\left(\frac{\partial T}{\partial t} + v\frac{\partial T}{\partial r} + u\frac{\partial T}{\partial x}\right)$$
$$= \frac{1}{r}\frac{\partial}{\partial r}\left(kr\frac{\partial T}{\partial r}\right) + \frac{\partial}{\partial x}\left(k\frac{\partial T}{\partial x}\right) + r_{SC}\Delta H_{SC}$$
$$+ r_{GC}\Delta H_{GC}$$
(4)

Energy equation for quartz tube

$$\rho C_p \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(k r \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right)$$
(5)

Species equations

$$C\left(\frac{\partial X_i}{\partial t} + v\frac{\partial X_i}{\partial r} + u\frac{\partial X_i}{\partial x}\right)$$
$$= \frac{1}{r}\frac{\partial}{\partial r}\left(CD_i r\frac{\partial X_i}{\partial r}\right) + \frac{\partial}{\partial x}\left(CD_i \frac{\partial X_i}{\partial x}\right) + S_i$$
(6)

where ΔH_i represents the reaction enthalpy of oxidation of species *i* (SiCl₄, GeCl₄) and X_i and D_i denote mole fraction and diffusion coefficient of species *i* (SiCl₄, GeCl₄, Cl₂), respectively. The source term S_i in species equation is expressed as

$$S_{\rm SC} = -r_{\rm SC}, \quad S_{\rm GC} = -r_{\rm GC}, \quad S_{\rm CL} = 2r_{\rm SC} + 2r_{\rm GC}$$
(7)

Kim and Pratsinis [11] and Powers [16] suggested the following equations for $r_{\rm SC}$ and $r_{\rm GC}$

$$r_{\rm SC} = (k_{\rm SC,0} + k_{\rm SC,1}CX_{\rm O2})\exp(-E_{\rm SC}/R_{\rm G}T)CX_{\rm SC}$$
(8)

$$r_{\rm GC} = k_{\rm GC,0} \exp(-E_{\rm GC}/R_{\rm G}T)C^{2}(X_{\rm GC}X_{\rm O2} - \gamma Y_{\rm GO}X_{\rm CL}^{2}/K_{\rm EQ})$$
(9)

where the particle phase is assumed to be an ideal sol-

ution ($\gamma = 1$) and particle surface reaction is assumed to be negligible.

Since relatively dilute suspensions in an excess oxygen flow are employed, the mixture gas properties are calculated as properties of the carrier gas, O_2 . These are given as a function of T and p using literature expressions for viscosity and diffusion [18], heat capacity [19] and thermal conductivity [20]. The details are summarized in Table 1.

The particle size of SiO_2 and GeO_2 is O (0.1 µm). Thus, diffusion is negligible compared with thermophoresis and bulk gas motion [2,3]. The mass balance equation for SiO_2 and GeO_2 are written as

$$C\frac{\partial n_i}{\partial t} + C[(\vec{V} + \vec{V}_T) \cdot \nabla]n_i = r_i$$
(10)

where V_T denotes the thermophoretic velocity defined by $V_T = -K(v/T)\nabla T$ [21] and n_i s are moles of species *i* particles per mole of carrier gas. The boundary conditions are

$$x = 0, r \le R_{i}: u = 2u_{0}[1 - (r/R_{i})^{2}], v = 0, T$$
$$= T_{0}, X_{SC} = X_{SC,0}, X_{GC} = X_{GC,0}, X_{CL}$$
(11)

$$= 0; n_{SO} = n_{GO} = 0$$

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$$x = 0, R_{\rm i} < r \le R_{\rm o}: \frac{\partial T}{\partial x} = 0 \tag{12}$$

$$x = L, r \le R_{\rm i}: \frac{\partial^2(u, v, T, X_{\rm SC}, X_{\rm GC}, X_{\rm CL})}{\partial x^2} = 0$$
(13)

$$x = L, R_{i} < r \le R_{0}: \frac{\partial T}{\partial x} = 0$$
(14)

$$r = 0: \frac{\partial(u, v, T, X_{\text{SC}}, X_{\text{GC}}, X_{\text{CL}}, n_{\text{SO}}, n_{\text{GO}})}{\partial r} = 0$$
(15)

$$r = R_{\rm i}: u, v = 0, \frac{\partial(X_{\rm SC}, X_{\rm GC}, X_{\rm CL})}{\partial r} = 0$$
(16)

and continuity of temperature and heat flux

The localized heating by the torch is modeled as Gaussian distribution and dissipated by convection and radiation at the outer tube wall [12];

$$r = R_{\rm o}: q_{\rm max} \exp[-\lambda^2 (x - x_{\rm torch})^2]$$
$$= k \frac{\partial T}{\partial r} + h(T - T_{\infty}) + \varepsilon \sigma (T^4 - T_{\infty}^4)$$
(17)

where x_{torch} is the torch location and h is the temperature-dependent heat transfer coefficient on the rotating

cylinder [22]. Two parameters, λ and q_{max} , control the width and the maximum value of the heating profile [12]. The emissivity of the quartz tube, ε , is calculated from a band approximation [23], with the assumption that the quartz is transparent below 4.5 µm wavelength and behaves like a black body above that.

In studies of optical fiber drawing, Homsy and Walker [24] and Paek and Runk [25] considered the effect of radiation in a silica solid rod by using the Rosseland diffusion approximation [23]. The same approximation is utilized in the present study:

$$k = k_{\text{cond}} + k_{\text{rad}} = k_{\text{cond}} + 16n^2 \sigma T^3 / 3\alpha$$
(18)

where the Rosseland mean absorption coefficient, α and the refractive index, *n*, take the values of 4 and 1.5 cm⁻¹, respectively [24,25].

The above set of governing equations subject to the given boundary conditions were solved in terms of the primitive variables by employing the finite volume technique along with power law scheme and SIMPLE algorithm [26]. The pressure correction equation is solved with the MCGS solver [27] and other discretized equations are solved with CGS solver [28]. Convergence is assumed when the summed residual over the domain falls below a prescribed tolerance (10^{-3}) . More stringent convergence criteria did not reveal noticeable changes in the solution. After the solution converges, the deposition masses of SiO₂ and GeO₂ per unit area at a certain axial location are evaluated from the mass fluxes onto the inner surface of tube, as follows:

$$\delta m_i(x,t) = \int_0^t (-CM_i n_i K v \partial \ln T / \partial r)_{r=R_i} d\tilde{t}$$
(19)

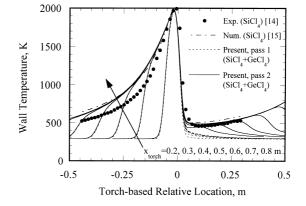
The deposition thicknesses for fully sintered particle layers can be obtained by dividing δm_i by the solid density of SiO₂ and GeO₂.

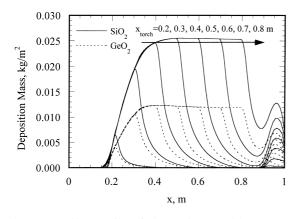
The grids near the reaction zone should be denser due to steep changes resulting from the chemical reaction. Therefore, non-uniform grids are generated each time step with the torch movement. From the preliminary grid sensitivity test, grid spaces chosen are maximum axial grid space, $\Delta x_{\text{max}} = 5$ mm, minimum axial grid space, $\Delta x_{\text{min}} = 1$ mm, radial grid space, $\Delta r = 0.7$ mm and time interval, $\Delta t = 1$ s. Deposition masses of SiO₂ and GeO₂ in this grid system differ from the denser grid system ($\Delta x_{\text{max}} = 2.5$ mm, $\Delta x_{\text{min}} = 0.5$ mm, $\Delta r = 0.7$ mm and $\Delta t = 1/3$ s) by less than 3 and 4%, respectively.

3. Results and discussion

In order to make a proper assessment of our numerical implementation, the previous numerical and Fig. 2. Distribution of tube wall temperature with respect to the torch based relative axial coordinate for different torch locations (different times).

experimental studies for single component SiO₂ deposition [14,15] have been compared with the present calculations. The in-take flow rate of carrier gas, O₂, is 2 1 min^{-1} and the flow rate of SiCl₄ and GeCl₄ is 3 and 1.9 mol m⁻³ (Table 1). Since overall efficiency can be expressed as a function of minimum temperature [3], a proper prediction of wall temperature is a prerequisite condition for a correct estimation of efficiency. Fig. 2 shows the spatial wall temperature variation at several different times (i.e. different torch locations) using the relative coordinate that moves with the torch, $x_{rel} =$ $(x - x_{torch})$. Reasonably good agreement was obtained compared with quasi-steady experiments [14] at later times (i.e. larger distance of torch movement). However, at early times, the discrepancies between the present unsteady and previous quasi-steady calculations are shown to be significant, which indicates the importance of unsteady analysis, especially at early times. It is also noted that the previous calculation considering only the effect of SiCl₄ oxidation agrees very well with the present calculation considering both chemical reactions of SiCl₄ and GeCl₄. Therefore, the effect of GeCl₄ reaction on the wall temperature would be small. The dashed and solid lines represent temperature distributions for the first pass and second pass of the torch traverse, respectively. The wall temperature ahead of the torch for the second pass is higher than that of the first pass and there exists an axial region where the wall temperature increases ahead of the torch. This is a consequence of the residual heat from the first pass. This temperature increase coincides with experiment [14] and was also predicted by a two-torch quasi-steady model suggested by Park and Choi [12]. At early times, wall temperature distributions in the region behind the torch do not fall onto a single curve even when they are plotted using the relative moving coordinate, x_{rel} and are much different from quasi-





600 torch=0.2m torch=0.3m torch=0.4m Wall Temperature, K 550 torch=0.5m torch=0.6m 500 450 400 0 0.05 0.1 0.15 0.2 Torch-based Relative Location, m

Fig. 3. Deposition profiles of SiO_2 and GeO_2 with respect to torch traversing.

steady results. This means that the quasi-steady assumption is not valid at early times. We also note that previous discrepancies in the deposition profile between quasi-steady state predictions and measurements near the inlet region were significantly improved by using a full unsteady calculation for the case of single component SiO₂ particle deposition [15]. It is now extended to consider the unsteady heat and mass transfer for multi-component SiO₂ and GeO₂ particle deposition.

Fig. 3 shows the deposition mass profiles of SiO_2 and GeO_2 for the constant torch speed case. Note the axially non-uniform deposition for both SiO_2 and GeO_2 deposition near the entry. Since this tapered entry must be eliminated before drawing the preform of optical fiber, it is desirable to reduce the tapered length. Therefore, there is a great need to find out the operating condition reducing this non-uniform deposition of multi-component SiO_2/GeO_2 particles.

Fig. 4 shows the thermophoretic flux to the wall, defined as $\vec{V}_T Cn_i$. \vec{V}_T is the thermophoretic particle

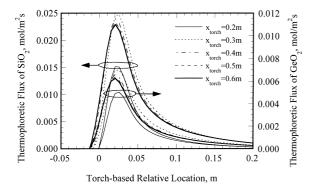


Fig. 4. Thermophoretic fluxes of SiO_2 and GeO_2 to the tube wall for different torch locations (different times).

Fig. 5. The variations of minimum wall temperature for different torch locations (different times).

velocity and C and n_i are gas concentration and moles of species SiO₂ and GeO₂ per mole of carrier gas. The deposition efficiency is low at the beginning of torch traverse compared to when torch moves enough to reach steady state. At the beginning of torch traverse, the narrow region of high wall temperature (shown in Fig. 2) causes this low deposition efficiency. Note that there is a maximum deposition efficiency at $x_{\text{travel}} =$ 0.3 m before it reaches steady state. The decrease of deposition efficiency beyond $x_{\text{travel}} = 0.3 \text{ m}$ is due to the increase of the minimum wall temperature ahead of the torch. Fig. 5 shows the wall temperature distribution ahead of the torch for different torch travel locations (or different times). The minimum wall temperature is about 435 K at the beginning of torch traverse and becomes steady near 500 K as the torch moves on. The effects of exothermic chemical reactions would cause the increase of the minimum wall temperature as the torch travels and a similar effect was observed experimentally [14]. As the wall temperature becomes higher, the particle deposition is suppressed due to lower thermophoretic particle velocity. On the other hand, as the torch moves on, particle formation in a tube becomes more active, which would tend to increase the deposition flux. Therefore, there are two mechanisms of which each has the opposite effect: the increasing minimum temperature to reduce the deposition flux and the increasing particle formation to increase the deposition flux. Correspondingly, the maximum deposition flux may exist as the torch moves. Note also that the broad range of particle deposition occurs, which should cause the undesirable tapered entry. This means that there would be the area of non-uniform deposition that is equivalent to the broad particle deposition area, even if quasi-steady state is reached.

Torch speed control was shown to be effective to result in a much shorter tapered entry for single com-

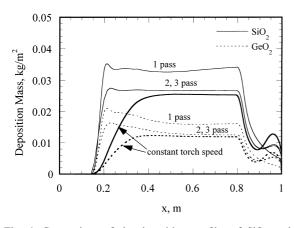


Fig. 6. Comparison of the deposition profiles of SiO_2 and GeO_2 between cases of variable torch speed (thin lines) and constant torch speed (bold lines).

ponent SiO₂ deposition than the constant torch speed case [15]. This may be also true for multi-component SiO₂/GeO₂ particle deposition. To examine the validity of torch speed variation on the enhancement of deposition performance, calculations with the same torch speed variation utilized previously in single component SiO_2 deposition [15], which is linearly increased up to 120 s and then maintains at 0.2 m/min, have been done for the multi-component particle deposition case. Fig. 6 shows the deposition profiles of SiO_2 and GeO_2 during three passes. The deposition masses of both SiO₂ and GeO₂ during the first pass are more than those during the second or third pass because the minimum wall temperatures of the latter are approximately 200 K higher than the former, due to the heat remaining from the first pass. There is no difference between second and third passes, which indicates calculations for further passes are not necessary. For SiO₂ deposition, the uniformity has been much improved compared to the case of constant torch speed (bold solid line) as already confirmed by Park and Choi [15]. The reason for this improvement was that the deposited mass near the torch starting position increased due to the longer duration of torch heating for the case of linearly varying torch speed and thus the tapered entry region was greatly reduced by less than 0.1 m. The uniformity of deposition of GeO2, however, becomes worse by the excessive particle deposition at the beginning. Note that for the constant torch speed case, the deposition of GeO₂ becomes steady earlier ($x \approx 0.35$ m) than SiO₂ ($x \approx 0.45$ m) shown in Fig. 3, because the activation energy of GeCl₄ oxidation is lower than that of SiCl₄ oxidation. Therefore, the strategy of slowing down the torch speed for the enhancement of SiO₂ uniformity may cause excessive particle deposition of GeO₂ over a broad zone. Thus, the different characteristics in chemical reactions between SiCl₄ and GeCl₄ pose a difficulty in achieving both uniformity of SiO_2 and GeO_2 simultaneously by the use of only one control method, e.g. the variation of torch speed in time.

To ensure the uniformity of both SiO_2 and GeO_2 , a control strategy may need the variation of at lease two parameters, rather than changing only one parameter. For this purpose, parametric studies have been conducted varying three operating parameters over time, i.e. maximum wall temperature, torch speed and intake amount of GeCl₄, independently or varying a set of two parameters simultaneously. The conditions for the base case are $T_{\text{max}} = 1973 \text{ K}$, $V_{\text{torch}} = 0.2 \text{ m min}^{-1}$ and $C_{\text{GC},0} = 1.9 \text{ mol m}^{-3}$. Case A is the variation of torch speed which is linearly increased from zero to 0.2 m min⁻¹ for 120 s and then maintains uniform as 0.2 m min⁻¹ after 120 s. Case B is similar to case A, except for beginning the torch speed with an initial torch speed, 0.0667 m min⁻¹. Case C and D are variations of maximum wall temperatures with the same torch speed variation as case A. Case C lowers the maximum wall temperature from T_0 by about 50°C as

Table 2

	T_{\max} (K)	$V_{\rm torch} \ ({\rm m} \ {\rm min}^{-1})$	$C_{\mathrm{SC},0} \ (\mathrm{mol} \ \mathrm{m}^{-3})$	$C_{\mathrm{GC},0} \ (\mathrm{mol} \ \mathrm{m}^{-3})$
Base	$T_{\rm max}$	V_0	C_1	<i>C</i> ₂
А	$T_{\rm max}$	$\min[V_0 t/t_0, V_0]$	C_1	C_2
В	$T_{\rm max}$	$\min[V_0(2t/t_0+1)/3, V_0]$	C_1	C_2
С	$-a_T(x_{\text{travel}}/x_{\text{sweep}}) + T_{\text{max}}$	$\min[V_0 t/t_0, V_0]$	C_1	C_2
D	$a_T(x_{\text{travel}}/x_{\text{sweep}}-1) + T_{\text{max}}$	$\min[V_0 t/t_0, V_0]$	C_1	C_2
E	$T_{\rm max}$	$\min[V_0 t/t_0, V_0]$	C_1	$a_x(x_{\text{travel}}/x_{\text{sweep}}-1)+C_2$
F	$T_{\rm max}$	$\min[V_0 t/t_0, V_0]$	C_1	$b_x x_{\text{travel}} / x_{\text{sweep}} + C_2$

Parametric studies for searching optimum operating parameters of time dependent maximum wall temperature, torch speed and intake amount of GeCl_4^a

^a $T_{\text{max}} = 1973 \text{ K}, a_T = 50 \text{ K}, x_{\text{sweep}} = 0.75 \text{ m}, t_0 = 120 \text{ s}, V_0 = 0.2 \text{ m} \text{min}^{-1}, C_1 = 3 \text{ mol m}^{-3}, C_2 = 1.9 \text{ mol m}^{-3}, a_x = 0.475 \text{ mol m}^{-3}, b_x = 0.665 \text{ mol m}^{-3}.$

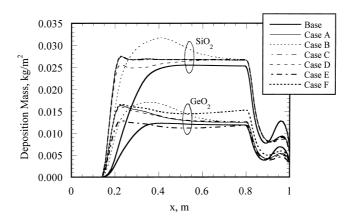


Fig. 7. Deposition profiles of SiO₂ and GeO₂ corresponding to the various operating parameters in Table 2.

the torch travels, while case D raises the maximum wall temperature by about 50°C from 1923 K at the starting position. Case E and F represent time dependent variations of in-take amount of GeCl_4 , which is linearly increased. The details on the variations of parameters used for each case are summarized in Table 2.

Fig. 7 shows the deposition profiles of SiO₂ and GeO₂ for seven different cases. In case A, the enhancement of deposition uniformity of SiO₂ is quite clear compared with the base case but the deterioration of deposition uniformity of GeO₂ is also found, as mentioned earlier. Slight change of torch speed profile (case B) makes it worse for the uniformity of both SiO₂ and GeO₂. Thus hereafter the torch speed variation is fixed with that of case A and then the change of another parameter has been studied to find uniform deposition of GeO_2 and SiO_2 . The effect of lowering the maximum wall temperature (case C) by 50°C would be negligible and resulted in almost the same depositions as case A. Case D has been carried out to examine that lower maximum wall temperature at the starting position may reduce the reaction rate of GeCl₄ and decrease the deposition amount of GeO_2 at entry region where excessive deposition was made for case A. This has a positive effect to some extent for the deposition uniformity of GeO₂. However, the low maximum wall temperature also reduces the reaction rate of SiCl₄ and makes the non-uniform deposition profile of SiO₂ near the entry region. Both cases E and F, where the in-take amount of $GeCl_4$ is linearly increased to suppress the initial high deposition of GeO₂, yielded considerable enhancement of deposition uniformity on both SiO2 and GeO2, while case F resulted not only in uniform GeO₂ deposition, but also a higher deposition rate than case E. Thus the uniformity of deposition thickness of SiO₂ can be maintained by torch speed variation over time and that of GeO_2 may be simultaneously obtained by increasing the in-take flow rate of GeCl_4 as the torch travels.

4. Conclusions

Unsteady heat and mass transfer analysis on the codeposition of SiO_2 and GeO_2 during the modified chemical vapor deposition process has been conducted. The present unsteady analysis has been shown to be an effective and versatile tool to examine the effects of the time dependent variations of different operating parameters on deposition performance for enhancement of uniform deposition profile and short tapered entry region.

The tapered entry region for SiO_2 deposition can be reduced by varying the torch speed in time, that is, linearly increasing speed up to a certain time and maintaining at constant speed beyond that time. However, this optimized torch speed, which was valid for SiO₂ deposition, resulted in the deterioration of GeO₂ uniformity. Therefore, to ensure the uniformity of both SiO₂ and GeO₂, a control strategy may need variations of at least two parameters, rather than changing only one parameter. Parametric studies varying three operating parameters over time, i.e. maximum wall temperature, torch speed and in-take amount of GeCl₄, independently or varying a set of two parameters simultaneously, have been conducted to find optimum operating conditions. The uniformity of deposition thickness of SiO₂ is obtained by linearly varying torch speed and at the same time, GeO₂ uniformity can be obtained by increasing the in-take flow rate of GeCl₄ over time.

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