Simulation of morphological instabilities during diamond chemical vapor deposition

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Abstract

The diamond chemical vapor deposition (CVD) process has been investigated theoretically and the morphological instabilities associated with the growth of diamond films have been examined with a model based on the continuum species conservation equation coupled to surface reaction kinetics. A linear stability analysis and numerical calculations have been carried out to determine critical parameters affecting the diamond deposition layer morphology. A two-dimensional model describes the evolution of the gas–solid interface. The dynamic behavior of the interface depends on the reactants' diffusivity and surface kinetics. These factors depend upon the reactant material properties and film growth conditions such as the reactor temperature and pressure. From the analyses, it has been found that the ratio ($\mathcal{D}/k$) of gas phase diffusivity ($\mathcal{D}$) to the surface reaction rate constant (k) plays the critical role in promoting diamond morphological instabilities because the film morphology stabilizing processes of surface diffusion and re-evaporation are absent or negligible during diamond CVD. It is found that the film nonuniformity increases as the ratio ($\mathcal{D}/k$) decreases. Increasing growth rates also result in increasing morphological instability, leading to rough surfaces. It is shown that increasing reactor pressure and decreasing gas-phase temperature and/or substrate temperature promote deposition layer nonuniformity. An approach to avoiding these instabilities is proposed. © 1997 Elsevier Science S.A.

Keywords: Diamond growth; Morphology evolution; Modeling

1. Introduction

The synthesis of diamond at low pressures is a current topic of intense worldwide interest due to the inherent physical properties of this material [1]. The feasibility of synthesizing diamond at low pressures enables the exploitation of these properties in a large range of applications such as semiconductor devices, cutting and grinding tools, and windows for visible and infrared transmission.

Diamond films may be synthesized using a variety of low-pressure techniques whereby mixtures of hydrocarbons such as methane, and hydrogen are activated with energetic sources such as microwaves to generate plasmas, direct current (DC) glow discharges, hot filaments, combustion flames and arcjets. Broadly speaking, diamond synthesis processes may be classified by rates at which diamond can be synthesized. The low growth rate methods include the hot filament [2] and many types of microwave plasma [3], which typically have

growth rates less than $1 \mu\text{m h}^{-1}$, whereas the high growth rate techniques, such as DC or radio frequency (RF) arc discharges [4] and atmospheric combustion synthesis devices [5], have growth rates of $30\text{--}150 \mu\text{m h}^{-1}$. Ideally, it is desirable to obtain the highest deposition rate possible, but it has been found that the film uniformity often decreases with increasing deposition rate. A “fingerlike” morphology develops as a result of surface instabilities which accompany higher deposition rates of diamond [6] and these instabilities are magnified with time. The control of film quality and morphology is strongly coupled to the control of conditions in the deposition chamber, that is, the processing time, reactor throughput, and related economic considerations. The characterization of diamond film morphology and its control have become increasingly important because the thermal and electrical properties of a polycrystalline diamond film is adversely affected by factors such as porosity, inhomogeneities and inclusions, and zones of differing morphology.

In this work, a numerical model is developed to analyze the factors which control diamond film morphol-

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ogy, and therefore contribute to morphological instabilities during diamond CVD. By morphological instability it is meant that small random fluctuations in interface shape grow with time, leading to nonuniformity in the deposition layer which promote columnar growth of films, voids in films, and deposition of nondiamond phases. The model presented in this work does not include any information regarding facets, crystal orientation or defects such as twins or dislocations. Before a numerical solution is presented, a linear stability analysis is performed, based on the work of Oh et al. [7], in order to quantify the growth rate limits beyond which planar deposition is not possible, as well as to identify the influence of the system parameters on the stability limits. The numerical model, presented after the stability analysis, is based on continuum species conservation equations, and coupled to surface reaction kinetics.

2. Background

Often in the growth of a solid film, from either a liquid or vapor phase, a critical objective is to achieve a planar solid–liquid or solid–gas interface, and for the interface to advance uniformly in a direction normal to itself as growth proceeds. Film smoothness is critical even for nonplanar films, where the film is locally planar on the scale of grains. However, in real crystal growth processes, and particularly at high growth rates, such quiescent interfaces are difficult to obtain. Typically, small, random fluctuations at the interface may grow in time, leading to morphological instabilities. This situation can lead to extremely rough surfaces, shadowing, trapping of voids and discontinuities, and the incorporation of impurities and second phases into the growing material. Basically, there are two transport mechanisms of the gas particles to the gas–solid interface for vapor growth processes: (1) diffusive transport of gas species [8]; and (2) ballistic transport of gas species [9,10], which occurs if the mean free-path of the gas species is greater than the characteristic length in the reactor.

Several studies have been undertaken to explain the experimentally observed phenomenon of morphological instability. These studies have been theoretical, taking the form of computer simulations and Monte Carlo studies of the ballistic (nondiffusive) transport of particles to the gas–solid interface [11–14] or continuum models [15–18] for the study of diffusive processes. Van den Brekel and Jansen [19] examined the stability of a flat interface during CVD processes using analytical techniques. Their model included a stagnation boundary layer, but assumed the gas-phase was isothermal, and the surface reaction was assumed proportional to the supersaturation. In that model, capillarity is the only stabilizing factor and the effect of surface diffusion is neglected. Van den Brekel and Jansen found that vapor

growth is essentially an unstable process because the gas phase transport favors enhancement of surface protrusions during vapor growth. The work was extended to nonisothermal conditions, and it was found that the results remained qualitatively the same. Van den Brekel and Jansen's study suggested that nonisothermal conditions had maximal effect when the process was mass-transfer limited. Bales et al. [17] performed a numerical treatment of the Van den Brekel–Jansen model and considered cases where the process was either mass-transfer limited or surface kinetics limited. Under mass-transfer limited growth conditions, Bales et al. found the morphology to be “fingerlike”, as illustrated in Fig. 1a. In cases where growth was surface kinetics limited, the morphology consisted of “circular arcs”, illustrated in Fig. 1b, which exhibited the same growth–death phenomenon observed in many vapor deposition processes. In their studies of morphological instabilities in CVD, Palmer and Gordon [20,21] also neglected the effect of a temperature gradient in the gas and in the growing film. They did include the effects of surface diffusion, gas diffusion and reevaporation. It was assumed that the reactions took place in the gas-phase; only adsorption and re-evaporation took place on the surface. Gas diffusion was identified as the destabilizing

Fig. 1. (a) Schematic of “finger-like” morphology; (b) schematic of “circular-arc” morphology.

factor for a mass-transfer limited process, while surface diffusion and reevaporation were the stabilizing factors.

Work has been performed to derive analytical solutions using linear stability analysis to study the: (1) morphological stability of a deposition layer during CVD [7,22,23]; and (2) stability of the shape of a phase boundary enclosing a solidification front during solidification processes [24,25]. The stability analysis has demonstrated its own significance by providing useful information on morphology control in many practical CVD and solidification processes. One of the first successful treatments of the problem of linearizing the entire system of equations was the pioneering work of Mullins and Sekerka [24,25] who used linear stability analysis to characterize the stability of a planar interface and a spherical particle growing in an undercooled melt. The question of stability is studied by introducing a perturbation in the original interface shape and determining whether this perturbation will grow or decay. The Mullins and Sekerka problem (liquid–solid phase) is analogous to vapor deposition and the growth of a solid film into the gas-phase. The solidification process can be controlled by the liquid-phase temperature gradient, and thus diffusion of heat, which is similar to solid film growth in a diffusion-limited CVD process. In the CVD process, however, there is a diffusion of reactants to the growing interface. The solidification model of Mullins and Sekerka includes heat diffusion and capillarity. More examples of analogies between different systems where the dynamics of curved interfaces have been studied can be found in the literature [26].

Oh et al. [7] have carried out a stability analysis to examine the behavior of small disturbances imposed on a flat interface during the growth of a deposition layer in a CVD process. The deposition layer is said to be morphologically unstable if the imposed disturbance is amplified with time and to be morphologically stable if it is damped out with the passage of time. The model of Oh et al. included gas-phase diffusion of a single reactant species to the surface, surface migration and *n*th-order surface reaction kinetics. An expression was derived for change in amplitude of the imposed disturbance. The derived expression suggests that surface migration/diffusion plays a stabilizing role in controlling the morphology of films, whereas gas-phase diffusion has a destabilizing effect in a mass-transfer limited regime. In the present work, the linear stability analysis results derived by Oh et al. [7] will be used to analyze the factors responsible for controlling diamond film morphology.

3. Model formulation

In this work, a convective diamond CVD process such as the DC arcjet or combustion torch is studied using a two-dimensional model. These systems typically

consist of a downward stagnation flow which transports the reactant species to the top of the boundary layer by convection. Within the boundary layer, the species are transported to the substrate surface primarily by diffusion. The model developed in this work is applicable to the boundary layer of such convective systems. To satisfy mass conservation, the flow inside the control volume, shown in Fig. 2, is two-dimensional, with horizontal (*x*) and vertical (*y*) components. Once the species are transported to the surface, they undergo surface reactions such as H atom abstraction and termination, and adsorption of CH₃ on the surface [27]. A description of such a chemical vapor deposition process must therefore contain four elements: (1) mass transport to the surface; (2) incorporation of mass onto the surface by thermally activated kinetic processes; (3) mass transport along the solid surface by surface diffusion; and (4) re-evaporation of the adsorbed species into the gas phase.

In the case of diamond deposition, re-evaporation or desorption is expected to be negligible since the diamond phase of carbon is very stable and gasification of diamond, once it has been formed, will occur very slowly, if at all. The etching rates of diamond during diamond synthesis ambients are orders of magnitude smaller than the deposition rates as has been mentioned by Ravi [6]. Thus, the re-evaporation process is neglected in the model formulation in this work.

In the present work, the following assumptions are made to simplify the mathematical treatment:

1. The gas-phase consists only of CH₃, H, and H₂.
2. The gas-phase species are transported solely by diffusion in the boundary layer and deposited on the surface under isothermal conditions. It is shown in Table 1 that the Knudsen numbers of H in H₂ at pressures and temperatures typical of diamond CVD process are significantly less than unity, thereby justifying the use of a continuum equation within the boundary layer to describe the diffusive transport of species to the gas–solid interface. The Knudsen number is defined as the ratio of the mean free path to the characteristic reactor scale, taken

Fig. 2. Schematic of the problem domain. The diamond surface is represented by $x(s, t)$ and $y(s, t)$ where s is the arclength and t is the time. δ is the boundary layer thickness.

Table 1
Knudsen number for typical diamond CVD conditions

Temperature (K)	Pressure (torr)	Boundary layer thickness (cm)	Mean free path (cm)	Kn
800	30	0.2722	0.00491	0.018
1200	30	0.3689	0.00736	0.0199
1800	30	0.5	0.01104	0.0221
2300	30	0.6	0.0141	0.0235
1800	5	1.225	0.0663	0.054
1800	60	0.3536	0.00552	0.01561
1800	760	0.1	0.000436	0.00436

to be the boundary layer thickness, δ . The mean free path, λ , of a mixture is defined as [28]:

$$\lambda = \frac{4}{4\sqrt{2}\pi n_1 \sigma_1^2 + \pi n_2 (\sigma_1^2 + \sigma_2^2)}, \quad (1)$$

where the subscript “1” denotes the minor gas species and subscript “2” denotes the major (bath) gas, n_1 and n_2 are the number density of molecules, and σ is the collision diameter of the molecules. For the stagnation flow geometry, boundary layer thickness may be evaluated using [29],

$$\delta = \frac{L}{Re^{1/2}} \left[\frac{0.24}{Re^{1/2}} + \left(1.89 + \frac{0.056}{Re} \right)^{1/2} \right], \quad (2)$$

where L is the transport length of the reactant species measured as the distance between the inlet of the reactor to the substrate and Re is the Reynolds number. The boundary layer thickness is a function of temperature and pressure in the reactor, such that $\delta \propto T^{3/4}$ and $\delta \propto P^{-1/2}$, where T is the temperature and P is the pressure. Therefore, on the basis of a predicted value of $\delta = 0.5$ cm at 1800 K and 30 torr, δ for other combinations of reactor temperatures and pressures are computed in this work.

3. Homogeneous gas phase reactions during diffusion are excluded.

Based on the assumptions stated above, the governing equations and boundary conditions for the problem may be derived, and these are described below. The reactants are transported to the top of the concentration boundary layer, $y = \delta$, by convection. In the boundary layer, the reactants are assumed to be transported primarily by diffusion. The diamond surface position is described using an arclength representation, i.e. $x = x(s, t)$ and $y = y(s, t)$ (Fig. 2), where s is the arclength along the interface measured from a reference point on the surface and t is time. The governing equations for the transport of H and CH_3 in the boundary layer are obtained from the species conservation equations, which reduce to the following form:

$$\frac{\partial C_i}{\partial t} = \mathcal{D}_i \nabla^2 C_i, \quad (3)$$

where $\mathcal{D}_i$ is the binary diffusivity of species i in H_2 ; the subscript i refers to either CH_3 or H. Although this is a multicomponent system, the transport of H and CH_3 may be treated as binary due to the large excess of H_2 present in the boundary layer.

The boundary condition for CH_3 and H at $y = \delta$ is given by:

$$C_i = C_i^0, \quad (4)$$

where C_i^0 are obtained from detailed stagnation flow calculations.

The boundary conditions on H and CH_3 at either side of the problem domain, that is, at $x = 0$ and $x = x_{\max}$ (where $x_{\max}$ is the length of the substrate over which deposition is studied) are given by:

$$\mathcal{D}_i \mathbf{n} \cdot \nabla C_i = C_i \mathbf{n} \cdot \mathbf{v}. \quad (5)$$

This expression accounts for the mass of H and CH_3 that is swept out of the control volume due to the horizontal velocity component, evaluated as $\mathbf{n} \cdot \mathbf{v}$, where $\mathbf{n}$ is the unit normal to the control volume and $\mathbf{v}$ is the velocity.

Methyl radicals transported to the surface by diffusion may be adsorbed, leading to the growth of diamond films. Therefore, from mass balance, the flux of CH_3 to the surface must be equal to the incorporation rate of CH_3 at the surface. The boundary condition for CH_3 at the interface is then given by:

$$-\mathcal{D}_{\text{CH}_3} \mathbf{n} \cdot \nabla C_{\text{CH}_3}^s = k_{\text{CH}_3} \frac{C_{\text{CH}_3}^s C_{\text{H}}^s}{b + C_{\text{H}}^s}, \quad (6)$$

where the superscript s denotes that the concentrations are evaluated at the surface and the values of the parameters are taken from the literature [30], i.e. $k_{\text{CH}_3} = 1469.5 \text{ cm s}^{-1}$ and $b = 5 \times 10^{-9} \text{ mol cm}^{-3}$.

Hydrogen atoms transported to the surface undergo abstraction and termination reactions. Mass conservation at the surface requires that the diffusive flux of H to the surface is equal to the surface/heterogeneous recombination rate of atomic hydrogen [31]. The boundary condition for H at the interface is given by:

$$-\mathcal{D}_{\text{H}} \mathbf{n} \cdot \nabla C_{\text{H}}^s = k_{\text{H}} C_{\text{H}}^s = \frac{\gamma_{\text{H}} \gamma'_{\text{H}}}{4} C_{\text{H}}^s, \quad (7)$$

where γ_H is the recombination coefficient, that is, the probability that an H atom recombines when striking the surface, v_H is the mean thermal speed of an H atom, given by $\sqrt{8RT/\pi m_H}$, m_H is the molecular weight of H, R is the gas constant, and T is the effective temperature of the gas-phase, such that $T = (T_s + T_g)/2$, where T_s is the temperature of substrate and T_g is the temperature of the gas at the top of the boundary layer. The transport parameters used in this work are taken from Dandy and Yun [29] and the kinetic parameters from Dandy and Coltrin [27].

In this work, it is assumed that the growth of diamond is due to both surface reaction and surface migration. Therefore, the kinematic equation for the growth rate of the deposited diamond film in the direction normal to the surface is:

$$\tilde{n} \cdot \mathbf{v}_d = v(-\mathcal{L}_{CH_3} \tilde{n} \cdot \nabla C_{CH_3}^s) + \left(\frac{D_s \zeta \Omega^2 \Gamma}{k_B T_s} \right) \nabla_s^2 \kappa, \quad (8)$$

where: v_d is the linear growth velocity; v is the molar volume of diamond; D_s is the surface diffusivity of C atoms on diamond; ζ is the interfacial energy of diamond per unit area; Ω is the molecular volume of diamond; Γ is the number of atoms per unit area; k_B is the Boltzmann constant; ∇_s^2 is the surface Laplacian operator; and κ is the total curvature at a point on the interface. In Eq. (8), the second term on the right-hand side derived for the surface diffusion effect is similar to the one used by Mullins [32].

After nondimensionalization with characteristic scales of $t_c = \delta$, $C_c = C_{CH_3}^0$ and $t_c = (t_c^2 / \mathcal{L}_{CH_3}) / (v C_{CH_3}^0)$, the governing Eq. (3) for CH_3 and H species becomes:

$$v C_{CH_3}^0 \frac{\partial \tilde{C}_{CH_3}}{\partial \tilde{t}} = \tilde{\nabla}^2 \tilde{C}_{CH_3}, \quad (9)$$

$$v C_{CH_3}^0 \frac{\mathcal{L}_{CH_3}}{\mathcal{L}_H} \frac{\partial \tilde{C}_H}{\partial \tilde{t}} = \tilde{\nabla}^2 \tilde{C}_H, \quad (10)$$

where the overbar denotes a dimensionless quantity. Typical values of $v C_{CH_3}^0$ for diamond CVD are in the range 10^{-6} – 10^{-10} , and because this quantity is significantly less than unity, the governing Eqs. (9) and (10) may be reduced to a quasi-steady state system, that is:

$$\tilde{\nabla}^2 \tilde{C}_{CH_3} = 0, \quad (11)$$

$$\tilde{\nabla}^2 \tilde{C}_H = 0. \quad (12)$$

The corresponding dimensionless boundary conditions for CH_3 and H at the top of the boundary layer, that is, at $\tilde{y} = 1$ become:

$$\tilde{C}_{CH_3} = 1, \quad (13)$$

$$\tilde{C}_H = \frac{C_H^0}{C_{CH_3}^0}. \quad (14)$$

The boundary conditions at the sides of the domain become:

$$\left(\frac{\mathcal{L}_{CH_3} t_c}{\ell_c^2} \right) \frac{\partial \tilde{C}_{CH_3}}{\partial \tilde{x}} = \tilde{v}_x \tilde{C}_{CH_3}, \quad (15)$$

$$\left(\frac{\mathcal{L}_H t_c}{\ell_c^2} \right) \frac{\partial \tilde{C}_H}{\partial \tilde{x}} = \tilde{v}_x \tilde{C}_H, \quad (16)$$

where $\tilde{v}_x$ is the dimensionless velocity of the gas in the x -direction and the expression for $\tilde{v}_x$ is obtained from Dandy et al. [29].

The boundary conditions at the interface, Eqs. (6) and (7), transform to:

$$-\left(\frac{1}{Da_{CH_3}} \right) \frac{\partial \tilde{C}_{CH_3}^s}{\partial \tilde{n}} = \frac{\tilde{C}_{CH_3}^s \tilde{C}_H^s}{\tilde{b} + \tilde{C}_H^s}, \quad (17)$$

$$-\left(\frac{1}{Da_H} \right) \frac{\partial \tilde{C}_H^s}{\partial \tilde{n}} = \tilde{C}_H^s, \quad (18)$$

where $Da_{CH_3} = (k_{CH_3} t_c) / \mathcal{L}_{CH_3}$, $Da_H = (k_H t_c) / \mathcal{L}_H$, and $\tilde{n}$ denotes the dimensionless coordinate normal to the deposition surface. The kinematic condition for growth is given by:

$$\tilde{v}_d = - \frac{\partial \tilde{C}_{CH_3}^s}{\partial \tilde{n}} + \beta \tilde{\nabla}_s^2 \tilde{\kappa}, \quad (19)$$

where $\tilde{v}_d$ is the dimensionless velocity of the surface in the normal direction, $\tilde{\kappa}$ is the dimensionless curvature at a point on the interface, and

$$\beta = \left(\frac{D_s}{\mathcal{L}_{CH_3}} \right) \frac{(\zeta v)(\Gamma / N_0)}{(N_0 k_B T) C_0 t_c^2}, \quad (20)$$

where N_0 is the Avogadro's number.

The dimensionless equations above contain three dimensionless parameters denoted by Da_{CH_3} , Da_H , and β . Physically, Da is analogous to the Damköhler number and is a measure of the relative rates of surface reaction and gas-phase diffusion. A small value of Da indicates a kinetically limited process, while a large value of Da indicates a mass-transfer limited process. The dimensionless parameter β represents the relative importance of surface diffusion rate to the gas phase diffusion rate. A small value of β implies that the surface diffusion rate is negligible compared with the gas phase diffusion rate. The value of β is calculated for typical diamond CVD conditions to evaluate the importance of surface diffusion in diamond growth.

For diamond, $\Gamma = 1.7544 \times 10^{15}$ atoms cm^{-2} , $v = 3.414 \text{ cm}^3 \text{ mol}^{-1}$, $\zeta = 7000 \text{ ergs cm}^{-2}$ [33]. The surface diffusion coefficient of carbon atoms on the diamond surface is calculated by [34]:

$$D_s = 0.25 \frac{\mu}{\Gamma} \exp \left(\frac{-E_d}{k_B T_s} \right), \quad (21)$$

where: μ is the effective surface vibration frequency of atoms such that $\mu \sim 10^{11} - 10^{13} \text{ s}^{-1}$ [34], taken as 10^{13} in the present study [35]; E_d is the surface diffusion energy, where $E_d \approx 1/4 E_a$ [36], and E_a is the desorption energy of a carbon atom on the diamond surface. In this work, E_a is assumed to be equal to the C–C covalent bond energy of carbon atoms in diamond, which is 711 kJ mol^{-1} [37]. Therefore, $E_d = 42.52 \text{ kcal mol}^{-1}$ is used in Eq. (21) to compute D_s . A typical value for β is estimated to be in the range $6.3 \times 10^{-18} - 4.3 \times 10^{-23}$ for $900 \leq T_s \leq 1300 \text{ K}$, $1500 \leq T \leq 3000 \text{ K}$, and $1 \leq P \leq 100 \text{ torr}$. For example, for a substrate temperature of 1173 K , a reactor pressure of 30 torr , and an average gas temperature of 1800 K , the values of C_0 and ℓ_c are reported to be $4.0 \times 10^{-10} \text{ mol cm}^{-3}$ and 0.5 cm , respectively [27]. Based on the above values of the physical parameters, the value of β is computed to be 1.8×10^{-19} . Since β is vanishingly small, the surface diffusion term is negligible compared with the gas phase diffusion rate, and hence the second term in Eq. (19) can be neglected. Therefore, the kinematic equation for the dimensionless growth rate of the deposited diamond film reduces to:

$$\bar{v}_d = - \frac{\partial \bar{C}_{\text{CH}_3}}{\partial \bar{n}}. \quad (22)$$

4. Linear stability analysis

Before obtaining numerical solutions to the above system of equations, it is desirable to carry out a stability analysis of the planar growth mode of a diamond film. A small shape perturbation is imparted to the planar surface and it is determined whether this perturbation will grow or dampen in time. This analysis may yield valuable information regarding limits beyond which planar deposition is not possible, as well as determining the influence of different parameters on these stability limits.

Physically, small perturbations on the growth surface may arise due to nonuniform nucleation of diamond on the substrate surface or nonuniformities on the substrate surface on a microscopic scale. Preferential growth of protrusions on the growing film will take place owing to (1) higher reactant concentrations at their tips than at their bases, and (2) higher temperature at their tips because temperature rises with height in the boundary layer. On the other hand, surface diffusion and capillarity tend to smooth any surface protrusions. Since in diamond CVD processes the stabilizing effects of surface diffusion and re-evaporation are negligibly small compared with gas phase diffusion, the diamond growth process is anticipated to be inherently unstable.

The planar surface is perturbed slightly by a sinusoidally varying function, and it is determined whether this perturbation grows or decays under specific diamond CVD reactor conditions. The general results of linear

stability analysis applied to a CVD process obtained by Oh et al. [7] are utilized in this work to determine the effect of diamond CVD reactor conditions on stability. The stability analysis is performed utilizing the governing Eq. (11), and the kinematic Eq. (22) for the growth of the diamond film, together with the boundary conditions [Eq. (13)] at the top of the boundary layer and Eq. (17) at the interface. For mathematical simplicity in the linear stability analysis, Eq. (17) may be reduced to:

$$-\left(\frac{1}{Da_{\text{CH}_3}}\right) \frac{\partial \bar{C}_{\text{CH}_3}}{\partial \bar{n}} = \bar{C}_{\text{CH}_3}, \quad (23)$$

if $C_H \gg b$; for diamond films grown at high growth rates using DC arcjet or combustion torch processes, C_H is typically greater than b [30,31].

Although Eq. (23) is valid for diamond films grown at high growth rates, the results obtained using this simplification may still be applied to low diamond growth rates since the stability limits predicted using Eq. (23) will be more restrictive than those predicted using Eq. (17) directly.

Suppose a small disturbance, $\epsilon h_1(x, t)$ is to be superposed on a planar or flat interface, such that:

$$\epsilon h_1(x, t) = \epsilon a(t) \sin \omega x, \quad (24)$$

where $a(t)$ represents the time dependent amplitude of the imposed disturbance. Using the results of Oh et al. [7] applied to the equations developed in this model, i.e. Eqs. (11), (13) and (22)–(24), an expression is obtained for the growth/decay rate of the amplitude of the disturbance:

$$\frac{\dot{a}(t)}{a(t)} = \left(\frac{Da_{\text{CH}_3}}{1 + Da_{\text{CH}_3}}\right) \frac{Da_{\text{CH}_3} \omega (1 + e^{-2\omega})}{\omega (1 + e^{-2\omega}) + Da_{\text{CH}_3} (1 - e^{-2\omega})} = \sigma, \quad (25)$$

where $\dot{a}$ denotes the time derivative of the amplitude a and σ has the following functional form:

$$\sigma = \left(\frac{Da_{\text{CH}_3}}{1 + Da_{\text{CH}_3}}\right) \frac{Da_{\text{CH}_3} \omega (1 + e^{-2\omega})}{\omega (1 + e^{-2\omega}) + Da_{\text{CH}_3} (1 - e^{-2\omega})}. \quad (26)$$

Integrating the expression in Eq. (25) with time yields:

$$a(t) = a_0 e^{\sigma t}, \quad (27)$$

where a_0 is the amplitude of the perturbation at $t=0$. The disturbance is said to be unstable if σ is positive and stable if σ is negative. The function σ is plotted in Fig. 3 for several values of reactor temperature and pressure, and wavenumber ω . It is to be noted from Fig. 3 that the σ values are positive for all pressures, temperatures and wavenumbers, indicating that a small perturbation on a diamond growth surface will always grow and therefore will not decay. This is due to two physical effects inherent to diamond growth: (1) surface diffusion which plays a stabilizing role on the diamond growth

Fig. 3. A plot of stability function, σ , for various frequencies of the imposed disturbance, ω , versus temperature of the gas and pressure of the gas.

surface is negligible compared with the gas phase diffusion as shown earlier; and (2) even the highly convective diamond CVD processes may be mass-transfer limited, as indicated by the fact that Da_H and Da_{CH_3} are both greater than unity for typical diamond CVD process parameters (Table 2). Therefore, the reactant species do not have time to rearrange or move about on the surface before they are incorporated into the diamond lattice. It is also found that, for a fixed pressure and temperature, σ increases monotonically with increasing feature wavenumber for lower temperatures and higher pressures or high Da_{CH_3} , but σ is almost independent of ω for higher temperatures and lower pressures or low Da_{CH_3} . Therefore, it may be concluded that a disturbance becomes more unstable as the wavenumber increases when the process is diffusion limited. For a fixed wavenumber, ω , it is found that the σ value decreases with increasing temperature and decreasing pressure, that is, increasing reactant diffusivity; conversely, σ increases with decreasing reactor temperature and increasing reactor pressure (decreasing reactant diffusivity), indicating that the more the diamond CVD process is diffusion limited, the more unstable it is. Therefore, an increase in

temperature and decrease in reactor pressure will reduce instability of the planar mode.

An important point about these results is that linear stability analysis cannot predict what the morphology of the interface will be under general conditions far from conditions of stable planar growth. It can be used only to determine when the basic solution will become unstable. The next section addresses the problem of solving the model equations numerically in order to evolve the morphology of the growing diamond interface with time.

5. Numerical solution

The purpose of obtaining numerical solutions to the model equations is to be able to follow interface evolution with time and deduce the morphological phenomena which are observed experimentally during diamond CVD. Such results will allow prediction of film morphology and uniformity under chosen deposition conditions. Numerical solution of the problem is described below.

The governing Eqs. (11) and (12) together with the boundary conditions Eqs. (13)–(18) represent a set of

Table 2

Process parameters of diamond CVD process at which simulations are run

Run	Temperature (K)	Pressure (torr)	CH ₃ mole fraction	H mole fraction	$\mathcal{D}_{\text{CH}_3}$ (cm ² s ⁻¹)	$\mathcal{D}_{\text{H}}$ (cm ² s ⁻¹)	Da_{CH_3}	Da_{H}
I	1800	30	0.0015	0.15	422.23	1531.01	1.74	5.04
II	1200–2400	30	0.0015	0.15	422.23 ^a	1531.01 ^a	1.74 ^a	5.04 ^a
III	1800	5	0.0015	0.15	2533.38	9186.43	0.71	2.06
IV	1800	60	0.0015	0.15	211.115	765.51	2.46	7.13
V	1800	760	0.0015	0.15	16.57	60.435	8.82	25.51
VI	800	30	0.0015	0.15	102.15	370.39	3.92	7.56
VII	1200	30	0.0015	0.15	207.68	753.04	2.61	6.17
VIII	2300	30	0.0015	0.15	648.4	2351.12	1.36	4.45
IX	1800	30	0.00015	0.15	422.23	1531.01	1.74	5.04
X	1800	30	0.015	0.15	422.23	1531.01	1.74	5.04

^aThe values are calculated at the effective temperature.

coupled, nonlinear partial differential equations which cannot generally be solved using analytical techniques. To make this system tractable, a two-dimensional growth model is considered with only one horizontal direction. The model then becomes two-dimensional in the gas-phase and on the gas–solid interface.

Numerical techniques for solving this kind of problem can be divided into two classes: the first is where the interface shape and the field variables (in this case reactant concentration) are decoupled and solved with successive approximation; the second is simultaneous iteration for interface shape and field variables. Another distinction between different methods concerns the solution domain. One option is to transform the original coordinate system onto a domain with fixed boundaries, of which the interface is one. Grid or mesh generation is then simple, but the field equations become more complex. Alternatively, the problem can be solved in the original coordinates, where the grid or mesh changes with time. Generation of a new irregular mesh at each iteration becomes necessary. In this work, the interface shape and the concentration field are decoupled and solved in original coordinates with successive approximation. A new mesh is therefore generated after every iteration.

The steady-state gas phase problem is solved by the Newton–Raphson method. The horizontal coordinate is discretized into an equidistant grid and spatial derivatives are approximated with finite difference formulae. The vertical or growth direction coordinate is discretized in a nonuniform manner such that the grid is finer near the interface than at the top of the boundary layer. The governing Eqs. (11) and (12) are linear but the problem becomes coupled and nonlinear because of the boundary condition Eq. (17). The Jacobian matrix in the Newton–Raphson method becomes a sparse matrix for this problem. The sparse matrix solver, MA42AD, of the Harwell Subroutine Library [38], is used to solve the set of equations.

The solution procedure outlined above enables a study of the evolution of the diamond–gas interface starting

from an arbitrary initial interface shape. In order to examine the effects of interface shape perturbation, for simplicity the initial interface shape is considered as a sinusoid with an amplitude of 25 μm and wavenumber of 4π . One can, in principle, choose any horizontal length of substrate on which to study deposition. However, if this length is too small, the results may not be representative of an actual system [39,40]. Therefore, the horizontal length in each computation is chosen to be of the same length as δ . The binary diffusion coefficients, $\mathcal{D}_{\text{CH}_3}$ and $\mathcal{D}_{\text{H}}$, are calculated using Chapman–Enskog theory [28].

Several calculations were performed at different reactor temperatures, pressures and CH₃ mole fractions at the top of the boundary layer. One calculation was carried out for nonisothermal conditions, assuming that the temperature varied linearly with height (as would be the case for conduction dominated energy transport within the boundary-layer) in order to illustrate that the results obtained for nonisothermal and isothermal conditions in the reactor are qualitatively the same. Several runs were carried out for different reactor temperatures at a constant pressure to examine the effect of temperature on morphological stability of films. Similarly, runs were conducted at different reactor pressures with a constant temperature to explore the effect of pressure on the uniformity of the deposited diamond film. To examine whether the CH₃ mole fraction had an effect on the uniformity of deposited film, two different runs were performed for different CH₃ mole fractions at the top of the boundary layer for the same reactor temperature, reactor pressure and H mole fraction. The run parameters for each run, that is, the reactor temperature, pressure, CH₃ and H concentrations, $\mathcal{D}_{\text{CH}_3}$, $\mathcal{D}_{\text{H}}$, Da_{CH_3} and Da_{H} are listed in Table 2.

6. Results and discussion

Several simulations were performed to examine the effects of system variables such as reactor temperature,

reactor pressure and CH_3 concentration on the morphology of the deposition layer. The results are categorized into three areas based on the variation of the system variables in different runs. In each run, the amplitude of the initial disturbance is considered to be $25\text{ }\mu\text{m}$ and the run is stopped after the tip of the protrusion reaches $500\text{ }\mu\text{m}$.

Two simulations, runs I and II, were performed at identical reactor pressures, and identical CH_3 and H mole fractions. The process parameters for both the runs are given in Table 2. In run I, the temperature was kept constant at 1800 K throughout the domain and in run II the temperature was varied linearly between 2400 K at the top of the boundary layer and 1200 K at the substrate. It is to be noted that the effective temperature in run II is 1800 K . The results for runs I and II are shown in Figs. 4 and 5, respectively. The deposition time and growth ratio of the tip of the protrusion to the base of the protrusion are given in Table 3 for runs I and II. It is found that the results obtained for both runs I and II are qualitatively the same. This is primarily because the diffusivity of reactants, although a function of temperature, does not change appreciably by considering a linear temperature profile in the boundary layer as compared with an effective temperature. Therefore, in the following runs, an effective temperature will be used for each simulation.

6.1. Effect of reactor pressure

Four runs — I, III, IV and V — were performed at the same temperature and the same inlet CH_3 mole fraction of 0.0015 and H mole fraction of 0.15 , but using different pressures. Run parameters for each simu-

Fig. 4. Evolution of the diamond-gas interface with time for a gas temperature of 1800 K , a gas pressure of 30 torr and an inlet CH_3 mole fraction of 0.0015 . Conditions correspond to run I.

Fig. 5. Evolution of diamond-gas interface with time for a gas pressure of 30 torr , an inlet CH_3 mole fraction of 0.0015 and a linear variation of the temperature of the gas from 2400 K at the top of the boundary layer to 1200 K at the substrate. Conditions correspond to run II.

lation are given in Table 2. Figs. 4 and 6–8 correspond to runs I, III, IV and V, respectively. The deposition time, growth ratio of the tip of the protrusion to the base of the protrusion are given in Table 3 for runs I, III, IV and V. It is found, when Table 3 and Figs. 4 and 6–8 are compared, that as the pressure increases, so does the rate of growth of the tip of the protrusion relative to the base, leading to instability of the deposition layer. In such a case, the deposition process is termed unstable. This unstable growth is evident from the prominent finger-like morphology of the diamond film at 760 torr pressure, as shown in Fig. 8. The tip-to-base growth ratio is comparatively lower at 5 torr , as illustrated in Fig. 6. The explanation for this trend is that, as pressures increases both Da_{CH_3} and Da_{H} increase, which is due to the fact that at higher pressures the diffusion rate of reactants to the interface decreases. Since the values of Da_{CH_3} and Da_{H} are greater than unity for runs I, IV and V, the diamond CVD process operates in a mass-transfer limited regime. Therefore, in a mass-transfer limited regime for diamond deposition, increasing the pressure will have an adverse effect on the stability of a growing film. Another factor worth noting from Table 3 is that, with increasing pressures, the time required to grow the tip of the protrusion by $475\text{ }\mu\text{m}$ decreases due to higher concentrations of reactants. The time required for growth of a $500\text{ }\mu\text{m}$ -thick diamond films in a commercial system is of the order of 100 h ; hence, the time required for growth calculated in most of the runs is comparable with typical durations of diamond deposition in industries, indicating that the changes in morphology predicted by the simulation results may take place during normal operating times.

Table 3
Simulation results at various process conditions

Run	Da_{CH_3}	Da_H	Deposition time growth (h)	Growth ratio (growth of tip: growth of base)
I	1.74	5.04	52.5	1.218
II	1.74 ^a	5.04 ^a	50	1.267
III	0.71	2.06	497.22	1.1515
IV	2.46	7.13	33.64	1.277
V	8.82	25.51	4.45	2.967
VI	3.92	7.56	39.4	1.439
VII	2.61	6.17	46.72	1.291
VIII	1.36	4.45	66.34	1.175
IX	1.74	5.04	577.2	1.218
X	1.74	5.04	6.26	1.218

^aThe values are calculated at the effective temperature.

Fig. 6. Evolution of diamond-gas interface with time for a gas pressure of 5 torr, a gas temperature of 1800 K and an inlet CH_3 mole fraction of 0.0015. Conditions correspond to run III.

Fig. 7. Evolution of diamond-gas interface with time for a gas pressure and temperature of 60 torr and 1800 K and an inlet CH_3 mole fraction of 0.0015. Conditions correspond to run IV.

6.2. Effect of temperature

Runs I and VI–VIII are carried out at the same reactor pressure of 30 torr and at different effective temperatures ranging from 800 to 2300 K. The run parameters for each simulation are listed in Table 2. The results for the runs I, VI, VII and VIII are illustrated in Figs. 4 and 9–11, respectively. It can be seen in Figs. 4 and 9–11 and Table 3 that increasing temperatures tend to stabilize the growing film. This is again due to increasing diffusion rate of reactants to the interface with increasing temperatures, once again illustrating the mass-transfer limited nature of diamond deposition. It may also be noted that higher temperatures lead to lower growth rates owing to decreasing concentrations of reactants. Therefore, it may be concluded that the smaller the value of Da , the more uniform is the deposition. In addition, as the growth rate increases so

do the morphological instabilities in the growing film, and these instabilities are manifested as a finger-like morphology.

6.3. Effect of CH_3 concentration

Figs. 4, 12 and 13, corresponding to runs I, IX, and X, compare film growth at the same reactor pressure and temperature, and H mole fraction, but for different CH_3 mole fractions. It is shown in Table 3 that increasing CH_3 mole fraction increases the growth rate of the films, while keeping the morphology of films qualitatively and quantitatively the same. The increase in growth rate of diamond films with increasing CH_3 mole fractions is the result of a linear dependence of the diamond growth rate on the CH_3 concentration at the surface, as indicated by Eqs. (17) and (22). For diamond deposition, it is recognized that although film growth

Fig. 8. Evolution of diamond-gas interface with time for a gas pressure and temperature of 760 torr and 1800 K and an inlet CH_3 mole fraction of 0.0015. Conditions correspond to run V.

Fig. 10. Evolution of diamond-gas interface with time for a gas pressure and temperature of 30 torr and 1200 K and an inlet CH_3 mole fraction of 0.0015. Conditions correspond to run VII.

Fig. 9. Evolution of diamond-gas interface with time for a gas pressure and temperature of 30 torr and 800 K and an inlet CH_3 mole fraction of 0.0015. Conditions correspond to run VI.

Fig. 11. Evolution of diamond-gas interface with time for a gas pressure and temperature of 30 torr and 2300 K and an inlet CH_3 mole fraction of 0.0015. Conditions correspond to Run VIII.

rate does increase with hydrocarbon concentration, this quantity cannot be increased beyond certain limits because of the unacceptable increase in graphitic and nondiamond carbon present in the film. Therefore, while increasing CH_3 is not predicted to have an inverse effect on film growth stability, it will adversely affect film quality.

The numerical results obtained compare well, in a qualitative sense, with linear stability analysis results, indicating that the film morphological stability decreases with decreasing temperature and/or increasing pressure in a mass-transfer limited regime. It is proposed that the reactor effective temperature should be increased

and reactor pressure decreased in order to promote film uniformity and prevent thermal instabilities in diamond films. There appears to be a trade-off between diamond film growth rate and film uniformity, i.e. film uniformity has to be sacrificed to obtain higher growth rates. It has been shown experimentally that at high growth rates ($\geq 50 \mu\text{m h}^{-1}$), a finger-like morphology develops, with the taller regions shadowing the shorter regions [6]. Once formed, these projections are enhanced because they experience higher temperatures and reactant concentrations; thus, these processes may be magnified with time, resulting in extremely convoluted and complex diamond film morphologies. These mechanisms of com-

Fig. 12. Evolution of diamond-gas interface with time for gas pressure and temperature of 30 torr and 1800 K, respectively, and an inlet CH_3 mole fraction of 0.00015. Conditions correspond to Run IX.

Fig. 13. Evolution of diamond-gas interface with time for gas pressure and temperature of 30 torr and 1800 K and an inlet CH_3 mole fraction of 0.015. Conditions correspond to run X.

petitive shadowing and nutrient starvation are a dramatic feature of high-rate diamond synthesis [6].

7. Summary

Numerical solution of a continuum model derived for the evolution of diamond film-gas interface for typical diamond growth conditions is described. The model equations represent a system of coupled nonlinear partial differential equations which cannot be solved analytically. However, a linear stability analysis of a planar solution was carried out to obtain a qualitative descrip-

tion of the stability of films grown at temperatures and pressures characteristic of diamond CVD. The numerical and analytical results obtained were qualitatively similar. Simulation results showed that the deposition morphology is strongly dependent on the Damköhler number, Da . A significant decrease in film uniformity was observed for increasing values of Da_{CH_3} and Da_{H} , which indicates that film uniformity decreases with a decrease in the diffusion rate of reactants under mass-transfer limited conditions. A decrease in film uniformity results in thermal instabilities in the film, e.g. a film morphology with finger-like protrusions that overshadow the slower growth regions. Under diffusion-limited conditions, film uniformity is improved if the diffusion limitations could be decreased by decreasing system pressure and/or increasing reactor effective temperature. The numerical results suggest that better film uniformity may be achieved by changing operating conditions in such a way that the lowest value of Da for reactants is achieved. Another important observation is that the diamond film growth rate is predicted to increase with increasing system pressure and/or decreasing reactor temperature, that is, under conditions which do not favor uniform film deposition. Therefore, in order to achieve high diamond growth rates, the film uniformity must be compromised.

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