Measurement and modeling of Ar/H₂/CH₄ arc jet discharge chemical vapor deposition reactors II: Modeling of the spatial dependence of expanded plasma parameters and species number densities

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Detailed methodology and results are presented for a two-dimensional (r,z) computer model applicable to dc arc jet reactors operating on argon/hydrogen/hydrocarbon gas mixtures and used for chemical vapor deposition of micro- and nanocrystalline diamond and diamondlike carbon films. The model incorporates gas activation, expansion into the low pressure reactor chamber, and the chemistry of the neutral and charged species. It predicts the spatial variation of temperature, flow velocities and number densities of 25 neutral and 14 charged species, and the dependence of these parameters on the operating conditions of the reactor such as flows of H₂ and CH₄ and input power. Selected outcomes of the model are compared with experimental data in the accompanying paper [C. J. Rennick et al., J. Appl. Phys. 102, 063309 (2007)]. Two-dimensional spatial maps of the number densities of key radical and molecular species in the reactor, derived from the model, provide a summary of the complicated chemical processing that occurs. In the vortex region beyond the plume, the key transformations are CH₄ → CH₃ → C₂H₂ ↔ large hydrocarbons; in the plume or the transition zone to the cooler regions, the chemical processing involves C₂H₄ ↔ (CH₃ and CH₂), C₃H₄ ↔ (CH₄ and C₂H₂), (C₂H₄ and C₃H₄) → C₂H₆ ↔ (CH₂ and C₂H). Depending on the local gas temperature T and the H/H₂ ratio, the equilibria of H-shifting reactions favor C, CH, and C₂ species (in the hot, H-rich axial region of the plume) or CH₃, C₂H, and C₂H₂ species (at the outer boundary of the transition zone). Deductions are drawn about the most abundant C-containing radical species incident on the growing diamond surface (C atoms and CH radicals) within this reactor, and the importance of chemistry involving charged species is discussed. Modifications to the boundary conditions and model reactor geometry allow its application to a lower power arc jet reactor operated and extensively studied by Jeffries and co-workers at SRI International, and comparisons are drawn with the reported laser induced fluorescence data from these studies. © 2007 American Institute of Physics. [DOI: 10.1063/1.2783891]

I. INTRODUCTION

The accompanying paper described the latest results and analysis of our extensive experimental studies of the properties of a 6.4 kW dc arc jet reactor operating on an Ar/H₂/CH₄ gas mixture and used to deposit thin films of polycrystalline diamond. This reactor has been the subject of many prior experimental and computational studies and comparisons of spectroscopic data with the outputs of a computer model have enabled the model to develop in sophistication and accuracy. In turn, the insights provided by analysis of the model results inform our understanding of the physical and chemical processes that occur in the nozzle, gas expansion, and free-plume region of this and, by extension, other arc jet reactors. Here, we describe in detail the various components of the model, which builds upon prior computational studies of diamond deposition arc jet reactors and our previous work on Ar/H₂ expansions. The latter improvements come through the incorporation of the H/C chemistry ensuing from CH₄ addition to the plume, an improved treatment of the role of charged species, and several other important refinements. The model was tested by comparison with experimental data, and the preceding paper presents selected outcomes of this intercomparison. Although some discrepancies remain between absolute values and spatial profiles of calculated and measured number and column densities of H(n=2), C₂, and CH, the level of agreement serves to justify the key features of the model. In this paper, further details are provided of the calculated number densities of numerous species (for example, H atoms, C atoms, C₂, C₂H, CH, C₃, CH₄, C₂H₂, CH₃, and electrons) and their dependence on spatial location in the plume and the operating parameters of the reactor. From the radial variations of number densities of several radical species in proximity to the substrate, we can speculate about the relative importance of these compounds on the growth of polycrystalline diamond films. The versatility of the model is demonstrated by the calculations conducted for the conditions of operation of a lower power dc arc jet reactor operated and extensively studied by Jeffries and co-workers at SRI International.

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II. COMPUTER MODELING OF DC ARC JET CVD REACTORS

A. Overview of the model

The improved computer simulation of the arc jet discharge chemical vapor deposition (CVD) reactor consists of three main phases: (I) determination of plasma parameters in the region of the arc discharge, the intermediate torch head chamber, and at the nozzle into the reaction chamber (we focus on the primary N-torch nozzle); (II) a two-dimensional model of the expansion of the plasma into the reaction chamber; and (III) incorporation of C/H/Ar plasma chemistry and gas-surface deposition processes at the substrate. The gas temperature, gas pressure, flow velocity, and degree of ionization of an activated Ar/H₂ feedstock gas are calculated in phase (I) from power and mass balances and experimental measurements of the difference between the supplied power and the power coupled into the plasma. The corresponding plasma and flow parameters at the primary nozzle are used as boundary conditions for the two-dimensional model of the expanding plasma.

Phases (I) and (II) for an argon-hydrogen plasma have been fully described in our preceding paper and are only briefly summarized here. The first two phases of the model address the activation within the primary nozzle of an Ar/H₂ feedstock gas flow and the expansion of the resultant, partially ionized mixture into the reaction chamber. The model incorporates analytical procedures for the argon excitation in the region of the arc discharge, based on the energy deposited and use of the Saha equation to compute the degree of ionization, and the results of mixing with further Ar and H₂ flow in the intermediate nozzle chamber (including complete thermal dissociation of H₂). The treatment includes the expansion of the Ar, H, Ar⁺, H⁺, and electrons through the primary nozzle into the reactor chamber, formation of a shock front at small ż, ~6 mm, generation of the plasma plume, its interaction with nearby cold gas, and various plasma-chemical and radiative transfer processes.

This paper focuses on the incorporation of the consequences of downstream addition of CH₄ to the plasma, which is described in greater detail here. The associated chemical kinetics model includes 25 neutral and 15 charged species, more than 170 neutral reactions (direct and reverse), and 110 reactions with charged species. The key atoms, radicals, and molecules are C, CH, CH₂, CH₃, CH₄, C₂H, C₂H₂, C₂H₃, C₂H₄, C₂H₅, C₂H₆, C₂H₇, C₃H, C₃H₂, C₃H₃, C₄H, C₄H₂, C₄H₃, C₄H₄, H, H₂, Ar, and (Ar) (a limited number of calculations were carried out for an expanded set of neutral species also including the heavier hydrocarbons C₅H, C₆H, C₇H, and C₈H). The charged species that are included are electrons, ions Ar⁺, ArH⁺, H⁺, the negative ion H⁻, and 10 hydrocarbon ions CHₓ⁺ (y=0−3), CₓHₓ⁺ (y =0−3), and CₓHₓ⁺ (y=0,1). Thermochemical data and the reaction kinetics data are taken from the GRI-Mech mechanism for H, H₂, CH₄, and CₓHₓ reactions, pyrolysis mechanisms of C₂H₂ and CH₄ (for reactions up to C₄Hₓ compounds; C₂H₄ is treated as a sink representing all higher hydrocarbons which are not explicitly described), and additional electronic state specific rates for Cₓ(a) and Cₓ(X) reaction and interconversion. In addition, atomic hydrogen recombination at the reaction chamber walls, with a probability γ=0.15 that is typical for metal surfaces, is incorporated along with the following gas-surface processes at the substrate: atomic hydrogen recombination and sinks of CHₓ, x =0−3 and C₂Hₓ, x=0−2. The complete plasma-chemical reaction mechanism is provided as electronic supplementary information. The temperature dependence of chemical reaction rates and thermochemical data should capture not only the chemistry up to 5000−6000 K in high power plasma reactors (corresponding to the well-studied range of temperatures arising in combustion), but also the higher temperature range above 6000 K, for which data are more scarce. Several aspects of the coupled chemistry and flow are discussed in this section. Comparisons of the model outputs with experimental data for the Bristol arc jet are presented in the accompanying paper and for the SRI reactor in Sec. III.

To simulate the plasma expansion and formation of a plasma plume, the conservation equations for mass, species, energy, and radial and axial momenta were numerically integrated, simultaneously, using thermal and caloric equations of state and initial and boundary conditions in two dimensions, i.e., the cylindrical (r,z) coordinate space. The calculations incorporate heat, mass and radiation transfer, formation of a shock wave and gas flow recirculation, plasma-chemical kinetics, gas viscosity, diffusion, thermodiffusion, and barodiffusion (species diffusion due to a pressure gradient) processes. Power-law temperature dependences as approximations of tabular data are used for the viscosity and thermal conductivity of the Ar/H mixture. Neutral species thermodiffusion and diffusion (D) coefficients are calculated for different Ar/H/C mixtures using species specific Lennard-Jones parameters, and diffusion coefficients are approximated as D_i=α_i T^β_i/ρ, where α_i is a constant for species i. Charged species diffusion is ambipolar for the arc jet conditions, and ion diffusion fluxes and coefficients in a multicomponent mixture are calculated taking into account the energy dependence of various ion-neutral and ion-charged species collisions.

The outcomes of this phase of the calculations are gas temperature, gas pressure, flow velocities, mole fractions, and number densities of plasma species, with two-dimensional (r,z) resolution. A positive column plasma in a high (atmospheric) pressure arc discharge is a dense hot equilibrium system, so the electron temperature in the expanded plasma is taken to be the same as that of the heavy particles at the same location. The explicit conservative numerical integration scheme employed time steps of 6–20 ns and a grid size of Δr=0.5 mm in r and Δz=2.1 mm in z and continued until steady state conditions were attained. A limited number of test calculations were carried out for Δz =1 mm to check that the numerical results were insensitive to the larger chosen Δz. The reactor chamber is approximated as two cylinders in series, with respective radii of 19 and 72.5 mm and lengths of 82 and 92 mm. The center of the substrate, a disc with radius of 13 mm, is located at (r =0,zₑ). In this study, the base value of zₑ was 155 mm to...
match the experimental configuration. In all the calculations, the (water-cooled) substrate temperature was constrained to be 1200 K.

B. Further details and refinements of the model

Several modifications and corrections have been made in the present version of the two-dimensional model. First, barodiffusion has been taken into account as an additional term in species mass diffusional fluxes \( j_i \). For a two-component mixture, diffusional, thermodiffusional, and barodiffusional terms in \( j_i = 1 \) are expressed as follows:

\[
j_1 = \frac{m_1 m_2}{m_{12}} D_{12} \left[ - \nabla X_1 + \frac{k_{T1}}{T} \nabla T + \frac{(m_2 - m_1) X_2}{m_{12} P} \nabla P \right].
\]

(1)

Here, \( T, N, \) and \( P \) are the gas temperature, the total number density, and pressure, respectively, \( m_i \) and \( X_i = N_i / N \) are the \( i \)-th species mass and mole fractions, \( m_{12} = m_i X_i + m_2 X_2 \), and \( D_{12} \) and \( k_{T1} \) are the diffusional and thermodiffusional coefficients. The most prominent effects of barodiffusion are observed for atomic hydrogen near the nozzle and in the region of the shock front. In particular, H-atom mole fractions \( X_{H} \) just after the shock front are increased by factors of 2–3 compared with the initial mole fraction \( X_H^0 \) at the primary nozzle (\( X_{H} \approx 3 X_H^0 \) for \( X_H^0 = 6 \% \) and \( X_{H} \approx 2 X_H^0 \) for \( X_H^0 = 20 \% \)). Quantitatively, similar H-atom behavior was experimentally observed by Mazouffe et al., and we suggest that this anomalous behavior is more likely caused by barodiffusional processes rather than from any plasma-surface interactions as proposed in Ref. 23.

A second significant modification is that \( H^+ \) ions are assumed to be present in the expanded plasma. As was estimated in our earlier work, the residence time of \( H \) atoms in the hottest core region of the plasma stream in the intermediate nozzle chamber is \( \approx 30 \% \) of the characteristic ionization time; we therefore assume that the \( H^+ \) mole fraction \( X_{H^+} \) in the plasma at the primary nozzle is about 30% of the equilibrium Saha values, e.g., \( X_{H} \approx 0.67 \% \) for a base \( H_2 \) flow rate of 1.8 SLM (SLM denotes liter per minute at STP) and a gas temperature \( T = 120 \) K. Hydrogen ions are long-lived species in the hot plume because of low recombination rates (requiring three-body mechanisms) and an absence of fast charge transfer processes with the main plume species (Ar and, downstream, \( H_2 \)) because the \( H \)-atom ionization potential is less than those of \( H_2 \) and Ar. Thus, \( H^+ \) ions survive in the plume and affect \( H(n=2) \) concentrations downstream where the \( Ar^+ \) ion concentrations have fallen to zero as a result of their charge transfer reactions with \( H_2 \) molecules,

\[
Ar^+ + H_2 \rightarrow ArH^+ + H.
\]

(2)

This fast reaction (its rate coefficient, \( k \approx 1.4 \times 10^{-9} \) cm\(^3\) s\(^{-1}\) is \( \approx 10^4 \) times bigger than the rate coefficient of \( H_2 \) thermal dissociation, \( H_2 + Ar \rightarrow 2H + Ar \), at a gas temperature \( T = 6000 \) K) suppresses the \( H_2 \) concentrations in the plume. The ion kinetics in a H/Ar plasma and radiation transfer and reabsorption via the \( H(n=2) \rightarrow H(n=1) \) resonance line have been analyzed in our previous papers.7,8 Radiation transfer is an important mechanism for the loss of excited \( H(n>2) \) atoms, with consequences for ion kinetics, including \( ArH^+ \) ion production, and it was simulated previously by incorporation of \( C_{ij} \) coefficients into the calculations (where \( C_{ij} \) is a probability of the radiation from grid cell \( i \) being absorbed in cell \( j\)). In the present calculations, the appropriate \( C_{ij} \) coefficients were calculated using a high resolution division (into 400 frequency intervals) of the (Voigt profile) emission and absorption line shapes. In the presence of a hydrocarbon process gas, the suppressed \( H_2 \) concentration will affect the \( C_{ij} \) transformations. In addition, various \( C_{ij} \) ions with low ionization potentials (\(~9–13 \) eV) will appear in the plume as a result of charge transfer reactions between primary ions, \( Ar^+ \) and \( H^+ \), and \( C_H \) species, e.g.,

\[
\begin{align*}
Ar^+ + CH_j \rightarrow & CH_j^+ + Ar, \\
Ar^+ + CH_j \rightarrow & CH_{j-1}^+ + H + Ar, \\
H^+ + CH_j \rightarrow & CH_{j-1}^+ + H, \\
H^+ + CH_j \rightarrow & CH_{j-1}^+ + H_2.
\end{align*}
\]

(3–6)

The resulting \( C_{ij} \) ions can also participate in further charge transfer reactions with \( C_H \) species and are destroyed in dissociative recombination reactions with electrons, such as

\[
CH_j^+ + e \rightarrow CH_{j-1} + H(n).
\]

(7)

Calculations show that the concentration of the most abundant carbon-containing ion, \( C^+ \) (present at high levels because of its low electron-ion recombination rate) reaches \( \approx 2.9 \times 10^{15} \) cm\(^{-3}\), whereas the maximum concentrations of other \( C_{ij} \) ions (e.g., \( CH^+, CH_2^+, \) and \( C_2H_2^+ \)) are lower than \( \approx 2 \times 10^{12} \) cm\(^{-3}\). All of these values are much lower than the concentrations of primary ions at the nozzle (\( Ar^+ \approx 4 \times 10^{16} \) cm\(^{-3}\) and \( H^+ \approx 3 \times 10^{15} \) cm\(^{-3}\)), and the most important effect of the hydrocarbon ion kinetics on the neutral \( C_H \) species transformations is the loss of \( C_H \) species in the charge transfer reactions (3–6). This loss becomes dominant for some species, e.g., \( C_2 \) molecules, in regions of the plume where the \( H_2 \) concentration is much lower than the \( Ar^+ \) concentration, and such conditions are realized over the whole plume length at low \( H_2 \) flow rates (\( F_{H_2} \leq 0.5 \) SLM) and in the conical part of the plume at small \( z \) for high \( H_2 \) flow rates (\( F_{H_2} \approx 1 \) SLM, see below). In addition, the \( C_{ij} \) ions enhance the total rate of ion-electron recombination and loss of primary ions, compressorizing the radial profiles of electrons and \( ArH^+ \) ions and, as a consequence, affecting \( H(n>1) \) number density distributions [because \( ArH^+ + e \rightarrow Ar + H(n) \) reactions are an important source of excited \( H(n=2,3) \) atoms]. There is some additional loss of primary ions by recombination with negative ions, as illustrated by the reduction of \( H^+ \) ion concentrations. We only considered the effects of \( H^- \) ions, as these are among the most abundant negative ions under standard operating conditions. For base reactor conditions, the maximum concentrations of \( H^- \) (\( \approx 3 \times 10^{12} \)–\( 7 \times 10^{12} \) cm\(^{-3}\)) occur in the conical part of the plume at \( z < 100 \) mm, where the number densities of other nonprimary ions are also the greatest. \( H^- \) ion concentrations are
controlled by a balance of production by dissociative electron attachment to H₂ molecules and loss by detachment in collisions with electrons, associative detachment in collisions with H atoms, and recombination with positive ions.

As a third modification, the numerical approximation of power balance was corrected. In the previous version of the numerical model, the finite difference approximation of the boundary conditions at the primary nozzle underestimated the power coupled into the plasma. The revised two-dimensional model incorporates a much-improved treatment of the power utilization within the plasma. In our previous paper, we developed an analytical approach that allows determination (when provided with experimental measurements of power losses) or estimation of plasma parameters (temperature, pressure, ionization degree, and flow velocity) at the exit of the primary nozzle of the Bristol (or any other) arc jet reactor as a function of known experimental data of charged species mole fractions the feed gas mixture energies of argon and atomic hydrogen. The parameters of power losses at the exit of the primary nozzle of the Bristol/H₂O849 Ar, primary nozzle to be related via

\[ N = \frac{N^0 (m_{H_2} F_{H_2}^0 + m_{Ar} F_{Ar}^0)}{S' \sqrt{\gamma k T} \sqrt{m_i (X_{H_i} + X_{H_{i+1}}) + m_{Ar} (X_{Ar} + X_{Ar})}}, \]  

\[ F (\text{cm}^3 \text{s}^{-1}) = \frac{(2 F_{H_2}^0 + F_{Ar}^0) N^0}{N} \]  

\[ X_{H_i} = \frac{2 F_{H_2}^0 N^0}{FN} - X_{H_{i+1}}, \]  

and

\[ X_{Ar} = \frac{F_{Ar}^0 N^0}{FN} - X_{Ar+}, \]  

where \( N^0 \) (cm⁻³) is the number density at STP, \( \gamma = C_p/C_v \) is a ratio of heat capacities, and \( k \) is the Boltzmann constant. The effective area of the nozzle aperture, \( S' \), is smaller than the physically measured cross-sectional area of the orifice, \( S \), because of edge effects on the gas flow, and \( S'/S \approx 0.85 \). Charged species mole fractions \( X_{Ar^+}, X_{H_{i+1}}, \) and \( X_i = X_{Ar^+} + X_{H_{i+1}} \) can be estimated at any gas temperature using the Saha equation. The temperature \( T \) is determined from power balance arguments,

\[ \frac{3}{2} k T = \frac{P_{total} - P_{loss}}{FN} \times 10^7 \left[ \frac{1}{2} X_i D_0 (H_2) + I_{Ar} X_{Ar^+} + I_{H_i} X_{H_{i+1}} \right] + T_0 \left( C_V^0 X_{H_2}^0 + \frac{3}{2} k X_{Ar}^0 \right), \]  

where \( \frac{1}{2} D_0 (H_2) \) gives the heat of formation of a H atom in terms of the bond dissociation energy of H₂ (complete dissociation of H₂ is implicit), and \( I_{Ar} \) and \( I_{H_i} \) are the ionization energies of argon and atomic hydrogen. The parameters of the feed gas mixture \( C_V^0, X_{H_2}^0, X_{Ar}^0 \), and \( T_0 \) are, respectively, the heat capacity \( [C_V^0 (\text{erg/K}) \approx 2.47 k] \) and mole fraction of molecular hydrogen, the argon mole fraction, and the initial gas temperature. Note that the last term of Eq. (12) was neglected in our prior analysis.7

The model does not explicitly simulate the behavior of the plume in the thin boundary layer above the substrate. For typical gas flow conditions above the boundary layer (flow velocity \( v_r \approx 10^5 \text{ cm/s}, \) gas density \( \approx 7 \times 10^{-6} \text{ g/cm}^3 \), gas temperature \( \approx 6000 \text{ K} \), the thermal boundary layer thickness is estimated to be \( \delta (\text{cm}) \leq 0.1 R \), where \( R = \pm 1.3 \text{ cm is the substrate radius}, \) and \( \delta \) is comparable to, or lower than, the chemical mean free path for hydrocarbon species. The number densities of radicals computed for the region just preceding the boundary layer are thus taken to be representative of the number densities at the surface of the substrate, allowing inferences to be drawn about the chemical identity of the principal contributors to growth of diamond films. The extreme temperature gradient across the narrow boundary layer, whose thickness is only \( \approx 70 \) elastic collision mean free paths, and the high plume velocity, which is comparable to Ar atom thermal velocities, suggest that local thermal equilibrium will not be established, preventing integration of a chemical mechanism with temperature-dependent reaction rates. In their model of diamond CVD, Yu and Girshick10 considered chemical transformations within a boundary layer, and the effect of the thickness of this layer on the dominant diamond growth precursor species; their model, however, treated an atmospheric pressure plasma for which collisions in the boundary layer will be much more frequent than for the low pressure arc jets considered here.

C. Outcomes of the model

Equations (8)–(12) provide a detailed specification of the conditions prevailing in the throat of the primary nozzle, a schematic diagram of which is provided in Fig. 1 of Ref. 7. For example, under the base operating conditions, such as are favored for CVD diamond growth conditions (i.e., parameters for the N torch of \( P_{total} = 6250 \text{ W}, F_{Ar}^0 = 190 \text{ SCS} \) (11.4 SLM) and \( F_{H_2}^0 = 30 \text{ SCS} \) (1.8 SLM), and a power \( P_{total} - P_{loss} = 4450 \text{ W} \) coupled into the N-torch plasma), we find \( T = 12100 \text{ K} \) and \( P \approx 900 \text{ Torr}; \) the gas velocity at the throat of this nozzle (denoted by NZRC in Ref. 7), where the cross-sectional diameter is 2.5 mm, will be \( \approx 2.5 \text{ km/s} \). The preceding analysis also gives insight into the utilization of the high input power (corresponding to \( \approx 5 \text{ eV per particle} \); ionization is the dominant sink of this power (consuming \( \approx 2100 \text{ W} \), and causing a degree of ionization, \( X_i = 0.1 \)). H₂ dissociation accounts for \( \approx 670 \text{ W} \), and the balance is partitioned into thermal energy of the constituent particles.

The fully developed two-dimensional model was used for systematic study of the Bristol (see accompanying paper) and SRI (Sec. III) dc arc jet reactors under various operation conditions to reveal key plasma-chemical and transport processes, to compare with ours and others’ published experimental data, and to resolve several surprising experimental observations and challenges. In the Bristol CVD reactor, for example, the model calculations clarify (i)
the observed thousandfold drop of detected H-α emission with increased H₂ flow rates (for 0.5 and 1.8 SLM), which was reported in Ref. 7; (ii) the question of how to treat measured column densities and rotational temperatures of CH and C₂(a) in conditions of sharp gradients of temperature and species number densities, addressed in detail in the accompanying paper; (iii) which species are most likely to be responsible for the observed, extremely high (~100 μm/h) and nonuniform diamond film growth rates; and (iv) an apparent increase in electron number density with CH₄ flow rates, contrary to the decrease expected because of enhanced recombination rates of produced hydrocarbon ions, which will be discussed further below.

To illustrate the global heat and mass transfer processes occurring in the Bristol reactor, Fig. 1 shows two-dimensional (r,z) plots of the calculated Tgas and flow field for the base operating conditions (i.e., FH₂₀ = 1.8 SLM and FA = 11.4 SLM flowing through the N torch, with a further FCH₄₀ = 80 SCCM (SCCM denotes cubic centimeter per minute at STP) entering through the downstream injection ring, and a total power W = 4450 W coupled into the N-torch plasma). The hot central core of the jet is strikingly evident in the former plot, as are a local minimum at small z and the rapid temperature rise within ~1 cm of the substrate. The arrow lengths in the flow field plot are merely indicative of, and not directly proportional to, the absolute velocities. Nonetheless, this plot clearly illustrates the directed flow from the nozzle to the substrate and the importance of gas recirculation through the main body of the chamber and back into the narrower bore section. Such recirculation is crucial for efficient processing of hydrocarbon gases injected into the reactor when used for diamond CVD because the annulus, through which hydrocarbon process gas is injected, is located within the recirculation vortex.

The gas temperature distribution (consisting of a hot plume, a transition zone, and a cold surrounding gas) and interaction of the hot plasma with the cold gas generate extremely complicated and nonuniform distributions of all species concentrations. As an example, Fig. 2 shows the calculated two-dimensional mole fraction profiles of some important species C, CH, C₂(a), C₂H₂, H, and H₂. Figures 1 and 2 clearly demonstrate that experimentally measured temperatures, obtained by line-of-sight spectroscopy, should be treated with special care (issue ii). Indeed, a measured C₂(a) rotational temperature characterizes the plume boundary temperature rather than higher temperatures near the z axis (r ~ 0). In contrast, CH rotational temperature measurements probe the hotter central regions and should be higher than C₂(a) rotational temperatures, but still lower than the maximum axial temperatures. Experimental and calculated rotational temperatures, the latter averaged over the radial direction, at distances z = 145–120 mm (i.e., d = 10–25 mm from the substrate) confirm these observations: the temperature derived from rotational structure in the C₂ Swan-band experimental absorption spectrum is Texp[C₂(a)] ~ 3300 K, whereas the temperature derived from rotationally resolved CH spectra is Texp(CH) ~ 4000 K; from the two-dimensional model outputs, the corresponding values are Tcalc[C₂(a)] = 3870 K and Tcalc(CH) = 4300–4670 K.

Figures 1 and 2 also allow the main stages of the chemical processing, and the regions in which they occur, to be traced. CH₄ is released from the injection ring into the recirculation vortex region and is very rapidly decomposed by reaction with abundant H atoms (with local concentrations of ~5 × 10¹⁴ cm⁻³) under conditions of elevated Ar/H₂ gas temperatures (~1300–1800 K). The CH₃ radicals so produced undergo further chemical transformations into C₂H₂, which is more stable under these conditions, as well as other
FIG. 2. Calculated two-dimensional percentage mole fraction profiles of selected important species C, CH, C$_2$/H$_2$, C$_2$H$_2$, H, and H$_2$ for the Bristol arc jet reactor operating under standard base conditions. The profiles are each plotted for half the reactor and are symmetric about the center line. The nozzle and substrate are located, respectively, at the top and bottom centers of each figure.
heavier species. As a result, quasiequilibrium distributions of various hydrocarbon species are established in the vortex region. For our base conditions of reactor operation, typical calculated concentrations (in cm⁻³) of the more abundant species in the central part of the vortex are as follows:

\[ \text{C}_2\text{H}_2 \sim 1.2 \times 10^{13}, \quad \text{CH}_4 \sim 4.5 \times 10^{13}, \quad \text{CH}_2 \sim 1.3 \times 10^{13}, \quad \text{C}_2\text{H}_4 \sim 5.7 \times 10^{12}, \quad \text{C}_2 \sim 1.2 \times 10^{13}, \quad \text{C}_3\text{H}_2 \sim 4.7 \times 10^{13}, \quad \text{C}_2\text{H} \sim 1.2 \times 10^{13}, \quad H \sim 8.3 \times 10^{14}, \quad H_2 \sim 4.5 \times 10^{16}, \quad \text{and Ar} \sim 3 \times 10^{17}. \]

Upwind flow near the wall of the narrower bore section and species diffusional flows deliver \( \text{H}_2 \) molecules and various \( \text{C}_x\text{H}_y \) species back to the plume, where they are incorporated into the main stream and decompose into atoms (C and H) and simple molecules, e.g., \( \text{CH} \) and \( \text{C}_2 \), in regions of higher temperature \((T > 5000 \text{ K})\) towards the center of the plume. An important reactive and highly nonequilibrated transition zone is observed at the boundary of the hot plume in computed two-dimensional distributions of \( \text{C}_2 \) (see Fig. 2) and other species such as \( \text{C}_3\text{H} \) and \( \text{C}_5 \). The fastest reactions with \( \text{C}_3\text{H}_y \) species in the plume and transition zone are the H-shifting reactions, such as

\[
\text{CH}_y + \text{H} \leftrightarrow \text{CH}_{y-1} + \text{H}_2, \quad y = 1, 2, \tag{13}
\]

\[
\text{C}_2\text{H}_y + \text{H} \leftrightarrow \text{C}_2\text{H}_{y-1} + \text{H}_2, \quad y = 1, 2. \tag{14}
\]

The acetylene diffuses radially towards the hotter plume core and is chemically processed first to \( \text{C}_2\text{H} \) and then \( \text{C}_2 \). Wills \textit{et al}. \textsuperscript{4} made \textit{cw} diode laser cavity ring down spectroscopy (CRDS) measurements of the acetylene content of the reactor, and demonstrated clearly that it is principally located in the cooler parts away from the plume and at number densities consistent with the model calculations. Various reactions involving the interconversion between \( \text{CH}_y, \text{C}_2\text{H}_y, \text{C}_3\text{H}_y, \text{C}_4\text{H}_y, \) and higher hydrocarbon species and thermal decompositions of \( \text{C}_x\text{H}_y \) species are slower (by one to several orders of magnitude in different regions of the reactor) than the H-shifting reactions. A consequence of the variety of local conditions (gas temperature, \( H, H_2, \) and \( \text{C}_x\text{H}_y \) concentrations) is that the chemical mechanism cannot be reduced to a limited number of prevailing exchange reactions; instead, we identify several important reactions of this type, including

\[
\text{C} + \text{C}_2\text{H} \leftrightarrow \text{C}_3 + \text{H}, \tag{15}
\]

\[
\text{C} + \text{C}_2\text{H}_2 \leftrightarrow \text{C}_3 + \text{H}_2, \quad y = 1, 2. \tag{16}
\]

\[
\text{C} + \text{C}_2\text{H} \leftrightarrow \text{C}_3 + \text{H}_2, \tag{17}
\]

\[
\text{C} + \text{C}_3 \leftrightarrow \text{C}_2 + \text{C}_2. \tag{18}
\]

\[
\text{C} + \text{CH} \leftrightarrow \text{C}_2 + \text{H}, \tag{19}
\]

\[
\text{C}_2 + \text{C}_2\text{H} \leftrightarrow \text{C}_4\text{H} + \text{H}, \tag{20}
\]

\[
\text{C}_2\text{H} + \text{C}_2\text{H}_2 \leftrightarrow \text{C}_4\text{H}_2 + \text{H}. \tag{21}
\]

Thus, we observe a very complicated picture of \( \text{C}_x\text{H}_y \) transformation in the Bristol reaction chamber, which can be summarized as follows: in the vortex region, \( \text{CH}_4 \rightarrow \text{CH}_3 \rightarrow \text{C}_2\text{H} \rightarrow \text{heavier hydrocarbons} \); in the plume and transition zone, \( \text{C}_2\text{H}_4 \rightarrow \text{CH}_3 \rightarrow \text{C}_3 + \text{H}_2 \rightarrow \text{C}_4\text{H}_2 \rightarrow \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_3 \rightarrow \text{CH}_4 \).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Calculated radial distributions of the diamond film growth rate and \( \text{CH}_x \) species distributions just above the substrate. (a) C atoms. (x) CH, (a) \text{C}_2\text{H}_2, (b) \text{C}_3\text{H}, \quad \text{(c) CH}_2, \quad \text{(d) CH}_3, \quad \text{(e) C}_2\text{H}, \quad \text{(f) C}_2\text{H}_2, \quad \text{and (g) C}_2\text{H}_3. \quad \text{Growth rate} \quad \text{(right-hand axis).}}
\end{figure}
$\sim 100 \mu\text{m/h}$, could be accounted for, within the model of Ref. 19, simply in terms of the contributions of $\text{C}_1\text{H}_4$ species. Calculations for other $\text{H}_2$ flow rates (500, 1000, and 1500 SCCM) show that the concentrations of CH and C atoms increase and decrease, respectively, with greater $\text{H}_2$ flow rate, but the total contribution of $\text{C}_1\text{H}_4$ species and, thus, the modeled growth rate remain in the same general range (with $G \sim 40\text{--}150 \mu\text{m/h}$).

Figure 4 provides an explanation of an apparent paradox detected experimentally, denoted as (iv) in the earlier list: the deduced electron number density $N_e$ increases with addition of hydrocarbon ions, which undergo fast recombination reactions. The measured $N_e$ which is derived from Stark broadening of H Balmer-$\alpha$ or -$\beta$ absorption lines, characterizes the off-axis region where the number density of $\text{H}(n=2)$ maximizes. In this region, the electron number density is much lower than its maximum, on-axis value, and the measured value will be very sensitive to small ($\sim 1 \text{ mm}$) radial shifts of the position of the $\text{H}(n=2)$ concentration maximum because of the very sharp radial gradients of $N_e$. Thus, as the calculations show, an apparent increase in $N_e$ with $\text{CH}_4$ flow could be detected under conditions of an overall drop of $N_e$, if the addition of methane compresses the $\text{H}(n=2)$ radial distributions to increase the overlap of the radial profiles of electron and $\text{H}(n=2)$ number densities.

Figure 5 shows the calculated axial profiles of several neutral and charged species number densities at the plume centerline ($r=0 \text{ mm}$) and at the plume boundary ($r=6 \text{ mm}$). As is evident from the plots, many of the species number densities change by several orders of magnitude over the axial and radial extent of the plume, emphasising the above-mentioned complexity of plasma-chemical transformations within the plasma jet.

![Image 1](https://example.com/image1.png)

**FIG. 4.** Calculated radial profiles of $\text{H}(n=2)$ (triangles) and electron (circles) number densities for the arc jet reactor operating with flows of methane of 0 SCCM (white symbols) or 80 SCCM (black symbols) and otherwise standard conditions. The arrows indicate the axes against which the data are plotted. The black and white boxes with color coding as above indicate approximate electron number densities that would be derived from Stark broadening measurements of the H atom Balmer-$\alpha$ or -$\beta$ lines, which are sensitive to the electron densities in the regions of the plume where the $\text{H}(n=2)$ number densities are greatest. In this example, the higher $\text{CH}_4$ flow rate gives rise to a higher apparent electron density (see text for further discussion).

![Image 2](https://example.com/image2.png)

**FIG. 5.** Calculated $z$-dependent number density profiles at (a) $r=0 \text{ mm}$ and (b) $r=6 \text{ mm}$ for the Bristol dc arc jet reactor. Key: (\$) C atoms, (\%) CH, (\textcolor{red}{\circ}) CH$_4$, (\textcolor{blue}{\circ}) C$_2$, (\textcolor{green}{\square}) C$_2$H$_2$, (\textcolor{blue}{\textbullet}) C$_2$H$_4$, (\textcolor{black}{\textcircled{C}}) CH$_3$, (\textcolor{green}{\textcircled{C}}) CH$_2$, (\textcolor{red}{\textcircled{C}}) CH, (\%) $\text{H}(n=1)$, (\%) $\text{H}(n=2)$, (\%) $\text{H}_2$, (\%$\ll$) C$_2$H$_6$, (\%$\ll$) CH$_4$, (\%$\ll$) $e^-$, (\%)$\text{Ar}^+$, (\%) H$^+$, (\%) Ar$^+$, (\%) C$^+$, and (\%) H$^+$.

### III. CALCULATIONS FOR THE SRI REACTOR

The modeling approach developed for the Bristol arc jet reactor was also used for simulation of the SRI International dc arc jet CVD reactor.\textsuperscript{11--16} The SRI arc jet reactor has been intensively studied, with an abundance of experimental data collected on various aspects of characterization of the expanded plasma, including $(r, z)$ distributions of gas temperatures and flow velocities;\textsuperscript{13} CH, C$_2$, C$_3$, and H species number densities [determined by laser induced fluorescence (LIF)];\textsuperscript{11} the degree of hydrogen dissociation (determined by a calorimetry method);\textsuperscript{11} and excited state density distributions of H, C, CH, and C$_2$ (by optical emission spectroscopy).\textsuperscript{15} In this lower power ($\sim 1600 \text{ W}$, $\sim 2 \text{ eV/molecule}$) arc jet, the dc discharge was struck through a mixture of Ar and H$_2$ (rather than in a pure Ar flow as in the Bristol arc jet reactor), and methane was added to the activated gas mixture through orifices in the diverging part of the nozzle. The boundary conditions and geometry of...
the model reactor were thus specially adapted to reflect the different nozzle geometry in the SRI reactor (a nozzle throat diameter of 0.635 mm, with exit diameter of 9.53 mm, and a length of the diverging nozzle section of ~13 mm). A schematic diagram of the nozzle is available in Fig. 1 of Ref. 13.

Two-dimensional model calculations have been carried out for the following basic operational parameters of the SRI reactor: an H2 flow rate of 3.27 SLM, an Ar flow rate of 3.63 SLM, a CH4 flow rate of ~0.016 SLM, a dc arc discharge input power of 1.6 kW, a gas pressure of ~5300 Torr for the initial flow (upstream of the discharge), a gas pressure in the reaction chamber of 25 Torr, and a substrate temperature $T_s=870$ K. We first determined analytically the plasma parameters for the nozzle throat cross section using experimental measurements of power loss of $475\pm55$ W into cooling water, assuming that additional (e.g., radiative) power losses do not exceed 50 W. Contrary to the analysis in Ref. 14, we do not include the kinetic energy of the plasma stream (~410 W) in the energy balance considerations for the calorimetry method. The high, near speed-of-sound, flow velocities are a result of the pressure difference of the initial flow (pressure=5300 Torr) and the gas that has expanded in the reaction chamber (25 Torr), and would be observed without any discharge input power. According to Eqs. (1) and (8)–(12), the remaining 1075 W of input power into the flowing plasma results in the following plasma parameters at the nozzle throat: gas temperature $T_{gas}=6000$ K; gas pressure $P\sim3700$ Torr and flow velocity $v_{z1}=1600$ m/s; and mole fractions $X_H=-0.34$, $X_{H2}=0.22$, $X_Ar=-0.44$. The low ionization degree ($X_i<0.01\%$ in the plume) does not affect the gas flow parameters. The degree of hydrogen dissociation, $[H]/([H]+2[H_2])$ ~ 0.436 returned by the analytical approach of Eqs. (1) and (8)–(12) and calorimetry data, is much lower than the equilibrium degree of dissociation at 6000 K (~0.977). This deviation is probably due to the short residence time of the mixture in the hot dc discharge region and/or hydrogen atom recombination processes at the metal surfaces of the arc jet apparatus. It is difficult to make a more accurate assessment of the inlet plasma parameters, so we have instead varied these parameters and further unknown conditions for the diverging nozzle surface within limits of ±20% from the stated values, and showed that the calculated results remain stable and are not seriously affected by such uncertainties. For the present calculations, we took 2000 K as a basic value of the surface temperature of the diverging tungsten nozzle and $\gamma=0.15$ for the atomic hydrogen recombination probability on the nozzle surface and reaction chamber walls.

The calculated results are in qualitative and satisfactory quantitative agreement with experimental measurements of gas flow parameters and species concentrations profiles. For example, the calculated flow velocity $v_{z1}\sim2400$ m/s at the plume center ($r=0$, $z=20$ mm) compares favorably with a measured value $v_{z1}\sim2600$ m/s, and the calculated gas temperature $T\sim2200$ K is only slightly lower than that measured experimentally ($T\sim2200–2400$ K). The calculated CH, C2, and C3 concentration profiles are compared with the LIF measurements of CH, C2, and C3 number densities distributions in Figs. 6 and 7. Figure 6 shows the species radial profiles at three plume cross sections: near the nozzle exit (at an axial coordinate $z=0$), near the plume center ($z=20$ mm), and at 1.2 mm from the substrate ($z=37$ mm). In this coordinate system for the model reactor, the nozzle throat cross section and CH4 injection ring nozzle were located at $z=-13$ mm and $z=-10$ mm, respectively. Reasons for the discrepancies in the measured and calculated profiles for CH at $z=20$ mm and around $r=0.4$ cm are not clear.

[FIG. 6. Calculated and measured radial number density profiles of CH, C2, and C3 for the SRI dc arc jet reactor: (a) $z=0.5$ mm, near the nozzle exit; (b) $z=20$ mm, at the middle of the plume; and (c) $z=37$ mm, in the boundary layer above the substrate. Key: experimental, LIF measurements of CH (⚫), C2(a) (●), and C3 (▲); model calculations of CH (☐), C2(a) (☐), C3 (△), and C2(X) (◇).]
of electronic excitations in the SRI reactor is electron-ion recombination. For example, the rate of dissociative recombination of ArH$^+$ with an electron,

$$\text{ArH}^+ + e^- \rightarrow \text{Ar} + \text{H}(n > 1),$$

is much higher (by many orders of magnitude) than the direct electronic excitation proposed in Ref. 15 as the predominant mechanism of formation of excited states of the H atoms.

IV. CONCLUSIONS

The approach developed for arc-jet CVD reactor simulations, described in detail in this paper, building on the content of Ref. 7, allows us to reproduce self-consistently many aspects of complex plasma-chemical and transport processes, not only in the Bristol dc arc jet reactor, but also in a similar, but lower power reactor operated and studied by Jeffries and co-workers at SRI, and for which extensive experimental measurements are available. Phase I of the model approach serves to determine accurately the plasma parameters (temperature, pressure, flow velocity, and degree of ionization and dissociation of an activated feedstock gas mixture) of the inlet high pressure gas flow. In the second and third phases, a two-dimensional model of the H/C/Ar plasma expanded into a low pressure chamber provides full characterization of all aspects of the gas-phase CVD processes: plasma-chemical kinetics, plume expansion and gas recirculation, radiation, heat and mass transfer, carbon feed gas decomposition, C,H$_4$ species transformation and diffusion, and potential diamond precursors capable of providing the extremely high growth rates ($\sim 100 \mu\text{m h}^{-1}$). As a result, the model calculations allow us to explore and understand key features of the deposition process and to explain numerous experimental observations and results, including spatial distributions of C,H$_4$ number densities, gas temperatures, and flow velocities; excited H($n > 1$) atom spatial profiles, the mechanisms of formation of species in excited electronic states, and associated OES measurement results; and to comment on diamond growth rates. The model calculations indicate that the experimentally observed high and nonuniform diamond growth rates are determined mainly by the contributions from C atoms and CH radicals in the high-power Bristol reactor, and C,H$_4$ ($y=0\text{–}3$) radical contributions in the lower power SRI reactor.

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Gri-Mech mechanism, http://www.me.berkeley.edu/gri_mech


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See EPAPS Document No. E-JAPIAU-102-096718 for details of the chemical mechanism used in the computer model. This document can be reached via a direct link in the online article’s HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).