Self-consistent modeling of microwave activated N$_2$/CH$_4$/H$_2$ (and N$_2$/H$_2$) plasmas relevant to diamond chemical vapor deposition

Michael N R Ashfold$^{1,*}$ and Yuri A Mankelevich$^{2,*}$

$^1$ School of Chemistry, University of Bristol, Bristol, BS8 1TS, United Kingdom
$^2$ Skobeltsyn Institute of Nuclear Physics, Moscow State University, Leninskie gory, Moscow, 119991, Russia

E-mail: mike.ashfold@bristol.ac.uk and ymankelevich@mics.msu.su

Received 28 September 2021, revised 29 November 2021
Accepted for publication 7 December 2021
Published 15 March 2022

Abstract

The growth rate of diamond by chemical vapor deposition (CVD) from microwave (MW) plasma activated CH$_4$/H$_2$ gas mixtures can be significantly enhanced by adding trace quantities of N$_2$ to the process gas mixture. Reasons for this increase remain unclear. The present article reports new, self-consistent two-dimensional modeling of MW activated N$_2$/H$_2$ and N$_2$/CH$_4$/H$_2$ plasmas operating at pressures and powers relevant to contemporary diamond CVD, the results of which are compared and tensioned against available experimental data. The enhanced N/C/H plasma chemical modeling reveals the very limited reactivity of N$_2$ under typical processing conditions and the dominance of N atoms among the dilute ‘soup’ of potentially reactive N-containing species incident on the growing diamond surface. Ways in which these various N-containing species may enhance growth rates are also discussed.

Keywords: diamond, chemical vapor deposition, microwave plasma, plasma chemistry, self-consistent modeling, nitrogen, methane and hydrogen

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

1. Introduction

Diamond production by chemical vapor deposition (CVD) from microwave (MW) plasma activated methane/hydrogen gas mixtures is now an established technology. It is now also widely recognized that the diamond growth rate can be accelerated and the morphology of the as-grown (polycrystalline diamond (PCD) or single crystal diamond (SCD)) material affected by adding trace amounts of molecular nitrogen to the process gas mixture, to extents that vary with process conditions (e.g. plasma composition, pressure, temperature, substrate, etc) [1–18]. Enhancing growth rates without compromising quality is important for established applications of PCD and SCD and, potentially, for emerging applications such as the production of diamond spheres for inertial confinement fusion [19]. The causes of the growth rate enhancement remain less clear, however. N$_2$ addition to the process gas mixture affects the chemistry and composition of the MW activated N/C/H gas mixture adjacent to (and sampled by) the growing diamond surface. Our earlier combined experimental/modeling study of MW activated dilute N/H [20] and
N/C/H\cite{21} plasmas showed that the vast majority of the \( N_2 \) introduced in the typical dilute N/C/H gas mixtures used in diamond CVD is exhausted from the reactor unchanged. Of the small fraction that undergoes chemical transformation, most is converted to HCN. The relative abundances of all other N-containing species were predicted to be at least an order of magnitude lower than that of HCN and, focusing on the near substrate (ns) region, the gas phase number density of atomic nitrogen, \([N]_{ns}\), was deduced to be higher than that of the radical species \([\text{NH}]_{ns}\), \([\text{NH}_2]_{ns}\) and \([\text{CN}]_{ns}\)\cite{21}.

Knowledge of the gas phase species incident on the growing diamond surface is necessary but not sufficient information to account for the observed enhanced growth rates. Which of these potentially ‘reactive’ N-containing species are preferentially adsorbed and accommodated? Quantum mechanical and hybrid quantum mechanical/molecular mechanical cluster modeling has identified plausible nitrogen incorporation routes involving N, NH or CN addition to a surface radical site associated with a C–C dimer bond on the C(100):H2\times1 diamond surface\cite{22}, each of which proceeds via a ring-opening/ring-closing reaction mechanism analogous to that identified previously for the case of CH3 addition (and CH2 incorporation) in diamond growth from a pure C/H plasma\cite{23–25}. Based on the relative abundances close to the growing diamond surface, N atoms were identified as the probable carrier of the nitrogen appearing in CVD-grown diamond\cite{22}.

This still leaves the question of how incorporated N atoms lead to accelerated diamond growth rates. Several earlier \textit{ab initio} studies explored the extent to which sub-surface N atoms might lower the energy barriers to H-terminated diamond (100) growth\cite{26–29}, and another showed how a four-atom cluster (including an N atom) could serve to nucleate (and thereby accelerate) growth on the diamond (111) surface\cite{30}. However, the recent theoretical study by Oberg \textit{et al}\cite{31} is the first to demonstrate a route whereby N incorporation might lead to substantially accelerated growth rates. Specifically, these authors show that the energetics of the classic CH3 addition (CH2 incorporation) process via the ring-opening/ring-closing reaction on the H-terminated 2\times1 reconstructed diamond (100) surface are much more favourable for a surface C–N bond (rather than the traditional C–C dimer bond), predict two-order of magnitude rate enhancements for this particular reaction sequence and note that such a localised nucleation picture would accord with the experimentally observed morphological change (from step-flow to nucleation dominated) with increasing \( N_2 \) content in the process gas mixture. Thus, the last few years have witnessed considerable progress in resolving longstanding questions regarding the role of \( N_2 \) in promoting diamond CVD. But, as pointed out by Oberg \textit{et al}\cite{31}, \textit{ab initio} data alone are not sufficient to fully describe the interactions of surface embedded N and the many possible growth mechanisms within the complex diamond CVD environment.

Several factors stimulate us to revisit the earlier combined experimental/modeling study of MW activated \( N_2/H_2 \) and \( N_2/\text{CH}_3/H_2 \) gas mixtures used for the CVD of N-doped diamond\cite{20,21}. First, the recently developed self-consistent 2D(r, z) model, supplied by a block describing the electromagnetic fields, offers an opportunity to trace the influence of \( N_2 \) additions on plasma parameters and the various species detected experimentally (by optical emission spectroscopy (OES) and cavity ring down spectroscopy (CRDS)), directly, without invoking external parameters like a plasma volume (which had to be assumed in our previous modeling). Second, the lack of high temperature kinetic data relating to N/C coupling reactions and \( N_2 \) decomposition meant that the primary sources and losses of NH\((x = 1, 2)\) radicals were not fully resolved in references\cite{20,21}. Recent calculations for the reaction of metastable \( N_2 \) molecules with H atoms (i.e. the \( N_2(A^3\Sigma_u^+) + H \rightarrow NH + N \) reaction)\cite{32,33} and for the quenching of \( N_2(A^3\Sigma_u^+) \) molecules by \( H_2 \)\cite{34}, along with more detailed N/C/H plasma-chemical kinetics involving higher excited states of \( N_2 \), allow some refinement of this issue. Third, the debate concerning the more important gas phase source(s) of potentially active nitrogen (e.g. N atoms, NH\(_x\) or CN radicals, etc)\cite{21,35} merits further study in light of the recently recognized role of metastable N atoms in initiating the reactive transformation of surface Si–CH\(_3\) groups on SiOCH low-k dielectrics\cite{36}. Thus, the present study also explores the extent to which metastable nitrogen atoms (e.g. \( N(2D) \)) or molecules (\( N_2(A) \)) might act as N-doping sources in diamond CVD.
electron impact ionization (EII), excitation (EIE) and dissociation (EID) of N₂, and ion conversion reactions involving NHₓ⁺ and HₓCNᵧ⁺ ions, etc) [20, 21], all of which require consideration in any full N/C/H reaction mechanism involving ground and excited states of neutral species. Again, to aid orientation, the most important reactions and their rates under representative plasma conditions are listed in tables 1 and 2. The full reaction mechanisms involve, respectively, 19 species and 155 reactions for the N/H plasma and 53 species and 2. The full reaction mechanisms involve, respectively, 19 species and 155 reactions for the N/H plasma and 53 species and 535 reactions for the N/C/H plasma. The electromagnetic block introduced in the more recent 2D model has been further refined by calculating an effective collisional frequency using equation (21) in Peterson et al [43]. For our H₂-dominated plasma conditions this effective e-H₂ collision frequency is slightly higher than the collision frequency vₑ(Tₑ) for electron momentum transfer (vₑ=[(1.16 − f × (Tₑ − 0.9)), with the factor f = 0.07 and 0.12 for electron temperatures in the ranges 0.3 ≤ Tₑ < 0.9 eV and 0.9 ≤ Tₑ ≤ 1.6 eV, respectively), which leads to a comparable relative increase in the maximal electron number densities. For H atoms, the effective e-H collision frequency is close to vₑ(Tₑ). The remainder of this article addresses, in order, the deceptively complex N/H plasma chemistry, then the yet richer N/C/H plasma chemistry, before offering a refined description of the gas phase environment sampled by the growing surface during diamond CVD.

2. N/H plasma modeling

2.1. N₂ addition to an H₂ plasma: changes in plasma parameters and ion distributions

N₂ and H₂ have similar ionization cross-sections and ionization potentials: IP(N₂) = 15.6 eV vs IP(H₂) = 15.4 eV. Thus, in contrast to the case of introducing hydrocarbons (e.g. CₓHᵧ, with a much lower IP of 11.4 eV) into an H₂ plasma, adding a few percent of N₂ to an H₂ plasma has only minor effect on the total ionization rate (reactions (1)–(5) in table 1). More serious disruptions of the balance between charge production and loss processes upon N₂ addition can be anticipated from the changes in the various ion concentrations (reactions (6)–(9) in table 1) and the increased overall rate of electron–ion recombination (reactions (10)–(12)) due to the appearance of N₁Hₓ⁺ ions. The branching ratios and cross-sections for the recombination reactions (10) [44, 45], (11) [43, 46] and (12) [47] used in the modeling are from experimental data collected at near room gas temperatures. The cross-sections for N₁Hₓ⁺ listed in table 1 were therefore scaled by a factor of b(Tₑ) to accommodate the expected drop in the effective recombination rate coefficients at higher gas temperatures [48]. The rate coefficients kₑ of the electron reactions in the 2D model are calculated from the respective cross-sections and the local electron energy distribution function (EEDF). For illustration, table 1 presents the approximations of these kₑ values as functions of electron temperature Tₑ (valid in the limited 0.8 ≤ Tₑ ≤ 1.5 eV range relevant to the present study). The minor production of nitrogen ions by EII of N₂ (and NHₓ) species is followed by the fast ion conversion reactions N₂⁺ + H₂ ↔ N₂H⁺ + H and NHₓ⁺ + H₂ ↔ NHₓ₋₁⁺ + H (x = 0–3) [49], but the main sources of these ions are the reversible reactions of Hₓ⁺ with N₂ and NHₓ (reactions (7) and (8) from table 1, plus the additional interconversion N₁Hₓ⁺ → NHₓ⁺ via reaction (9)). With regard to the N₂H⁺ concentration, it is important to note that the fast and weakly exothermic (∆E = 0.55 eV) direct reaction H₁⁺ + N₂ ↔ N₂H⁺ + H₂ is in strong equilibrium with the reverse reaction and that the ratio of the forward to backward rate coefficients k_f/k_b ∼ 17 at the gas temperature prevailing in the hot plasma core, Tₑ ≈ 3200 K. (The reverse reaction rate coefficients were determined from thermochemical data [50].)
Table 1. The most important reactions (and rate coefficients, $k_i$) of ionization, ion interconversion, electron–ion recombination, electron impact excitation and dissociation of N$_2$(X) and reactions of electronically excited N$_2$ molecules with H atoms and H$_2$ molecules, and plasma parameters in an MW activated N/H plasma. Reaction rates $R_i (r = 0, z)$ (in cm$^{-3}$ s$^{-1}$) and specified plasma conditions are presented for a 1.2% N$_2$/H$_2$ gas mixture in the regions of maximal reduced electric field and power density (at $z$ ~ 1.5 mm) and maximal gas temperature $T_g$ (at $z$ ~ 10.5 mm) for base pressure ($p = 150$ Torr) and power ($P = 1.5$ kW). The quoted $k_i$ are in units of cm$^3$ s$^{-1}$, $T_g$ is in K, $T_e$ is in eV, and N$_2$, N, H$_2$ and H denote the respective ground states.

| $i$ | Main ionization processes | Rate coefficient, $k_i$ | $R_i (z = 1.5$ mm) | $R_i (z = 10.5$ mm) |
|-----|---------------------------|------------------------|-------------------|-------------------|
| 1   | H$(n = 2) + H_2 \rightarrow H_3^+ + e$ | $3.82 \times 10^{-8} T_e^{0.5}$ | $2.05 \times 10^{13}$ | $9.47 \times 10^{14}$ |
| 2   | H$(n = 3) + H_2 \rightarrow H_3^+ + e$ | $3.82 \times 10^{-8} T_e^{0.5}$ | $7.56 \times 10^{13}$ | $6.42 \times 10^{14}$ |
| 3   | H$_2^+ + e \rightarrow H^+ + 2e$ | $5.0 \times 10^{-7} T_e \exp(-15.6/T_e)$ | $7.90 \times 10^{13}$ | $4.86 \times 10^{14}$ |
| 4   | H$^+ + e \rightarrow H^+ + 2e$ | $3.0 \times 10^{-7} T_e \exp(-13.8/T_e)$ | $1.01 \times 10^{13}$ | $2.97 \times 10^{14}$ |
| 5   | N$_2^+ + e \rightarrow N_2^+ + 2e$ | $2.3 \times 10^{-9} T_e^2 \exp(-15.6/T_e)$ | $2.37 \times 10^{13}$ | $8.14 \times 10^{11}$ |

Main ion interconversions

| $i$ | Electron–ion recombination reactions | Rate coefficient, $k_i$ | $R_i (z = 1.5$ mm) | $R_i (z = 10.5$ mm) |
|-----|--------------------------------------|------------------------|-------------------|-------------------|
| 10a | H$_3^+ + e \rightarrow 3H$ | $2.35 \times 10^{-9} T_e^{0.5}$ | $2.44 \times 10^{14}$ | $6.06 \times 10^{14}$ |
| 10b | H$_3^+ + e \rightarrow H + H_2$ | $2.05 \times 10^{-9} T_e^{0.5}$ | $2.13 \times 10^{14}$ | $5.29 \times 10^{14}$ |

Dissociations and excitations of N$_2$ by electron impact

| $i$ | $N_2 (v = 0) + e \rightarrow N_2^+ + e$ | $2.84 \times 10^{-10} \exp(-11.2/T_e)$ | $2.84 \times 10^{14}$ | $2.89 \times 10^{13}$ |
|-----|--------------------------------------|------------------------|-------------------|-------------------|
| 14  | $N_2 (v = 1) + e \rightarrow N_2^+ + e$ | $2.7 \times 10^{-10} \exp(-9.7/T_e)$ | $1.39 \times 10^{14}$ | $2.81 \times 10^{13}$ |
| 15  | $N_2 (v \geq 2) + e \rightarrow N_2^+ + e$ | $1.5 \times 10^{-10} \exp(-9.3/T_e)$ | $5.38 \times 10^{13}$ | $2.40 \times 10^{13}$ |

Reactions of electronically excited N$_2$ with H atoms and H$_2$ molecules

| $i$ | $N_2(A^3\Sigma^+u) + H \rightarrow NH + N$ | $2.84 \times 10^{-10} \exp(-2721/T_e)$ | $2.85 \times 10^{14}$ | $3.10 \times 10^{13}$ |
|-----|--------------------------------------|------------------------|-------------------|-------------------|

Plasma parameters and species concentrations

- Gas temperature, $T_g$ (K): 2005
- Electron temperature, $T_e$ (eV): 1.26
- Averaged reduced electric field (Td): 37
- Absorbed power density (W cm$^{-3}$): 89
- Electron concentration, $n_e$ (cm$^{-3}$): $4.4 \times 10^{11}$
- H atom concentration, [H$(n = 1)$] (cm$^{-3}$): $3.3 \times 10^{16}$
- N atom concentration, [N] (cm$^{-3}$): $2.7 \times 10^{22}$
- NH concentration, [NH] (cm$^{-3}$): $4.9 \times 10^{11}$
- N$_2^+$ concentration, [N$_2^+$] (cm$^{-3}$): $3.4 \times 10^{15}$
- N$_2$(A$^3\Sigma^+u$) concentration, [N$_2$(A)] (cm$^{-3}$): $1.2 \times 10^{10}$
- N$_2^+$ concentration, [N$_2^+$] (cm$^{-3}$): $1.1 \times 10^{10}$
The most important NH₂ production and CN/N coupling reactions (and rate coefficients, \(k_i\)) and plasma parameters in an MW activated N/C/H plasma. Reaction rates \(R_i(r = 0; z)\) (in \(\text{cm}^3\ \text{s}^{-1}\)) and specified plasma conditions are shown for a 0.6% N₂/4% CH₃/H₂ mixture in the regions of maximal reduced electric field (at \(z \sim 1.5\) mm) and maximal gas temperature \(T_g\) (at \(z \sim 10.5\) mm) for base pressure (\(p = 150\) Torr) and power (\(P = 1.5\) kW). The quoted \(k_i\) are in units of \(\text{cm}^3\ \text{s}^{-1}\). \(T_g\) is in eV, and N₂, H, N, and H₂ denote the respective ground states.

### Decomposition of N₂ molecules

\[
\begin{align*}
19 & \quad \text{N}_2(\text{A}^3\Sigma^+) + \text{H} \rightarrow \text{NH} + \text{N} \\
21 & \quad \text{N}_2^+ + \text{H} \rightarrow \text{NH} + \text{N} \\
26 & \quad \text{N}_2 + e \rightarrow 2\text{N} + e
\end{align*}
\]

\[
\begin{align*}
\text{Rate coefficient, } k_i & = 2.84 \times 10^{-11} \times \exp(-2721/T_g) \\
R_i(z = 1.5\ \text{mm}) & = 9.74 \times 10^{13} \\
R_i(z = 10.5\ \text{mm}) & = 1.83 \times 10^{13}
\end{align*}
\]

### N/C coupling reactions

\[
\begin{align*}
27 & \quad \text{CH} + \text{N} \rightarrow \text{CN} + \text{H} \\
28 & \quad \text{CH}_3 + \text{N} \rightarrow \text{HCN} + \text{H} \\
29 & \quad \text{C}_2\text{H}_2 + \text{N} \rightarrow \text{HCN} + \text{C} \\
30 & \quad \text{C}_2\text{H}_3 + \text{N} \rightarrow \text{CH}_2\text{CN} + \text{H} \\
31 & \quad \text{CH}_3 + \text{NH} \rightarrow \text{H}_2\text{CN} + \text{H} \\
32 & \quad \text{CH}_2 + \text{NH} \rightarrow \text{HCN} + 2\text{H} \\
33 & \quad \text{CH}_2 + \text{NH} \rightarrow \text{HCN} + 2\text{H}
\end{align*}
\]

\[
\begin{align*}
\text{Rate coefficient, } k_i & = 1.35 \times 10^{-11} \times T_g^{0.41} \\
R_i(z = 1.5\ \text{mm}) & = 5.96 \times 10^{12} \\
R_i(z = 10.5\ \text{mm}) & = 1.38 \times 10^{13}
\end{align*}
\]

### Key H-shifting reactions for NH, CN and CH concentrations

\[
\begin{align*}
37 & \quad \text{NH} + \text{H} \rightarrow \text{N} + \text{H}_2 \\
38 & \quad \text{N} + \text{H}_2 \rightarrow \text{NH} + \text{H} \\
39 & \quad \text{CN} + \text{H} \rightarrow \text{HCN} + \text{H} \\
40 & \quad \text{CH} + \text{H}_2 \rightarrow \text{CH}_2 + \text{H}
\end{align*}
\]

\[
\begin{align*}
\text{Rate coefficient, } k_i & = 3.51 \times 10^{-11} \times \exp(-166/T_g) \\
R_i(z = 1.5\ \text{mm}) & = 3.84 \times 10^{16} \\
R_i(z = 10.5\ \text{mm}) & = 4.74 \times 10^{16}
\end{align*}
\]

### Plasma parameters and species concentrations

| Parameter | Value |
|-----------|-------|
| Gas temperature, \(T_g\) (K) | 2035 |
| Electron temperature, \(T_e\) (eV) | 1.19 |
| Averaged reduced electric field (Td) | 36.5 |
| Absorbed power density (W cm⁻³) | 86 |
| Electron concentration, \(n_e\) (cm⁻³) | \(4.5 \times 10^{11}\) |
| H atom concentration, [H(n = 1)] (cm⁻³) | \(3.1 \times 10^{16}\) |
| N atom concentration [N] (cm⁻³) | \(1.2 \times 10^{11}\) |
| NH concentration [NH] (cm⁻³) | \(2.5 \times 10^{10}\) |
| CN concentration [CN] (cm⁻³) | \(4.4 \times 10^{10}\) |
| CH concentration [CH] (cm⁻³) | \(1.6 \times 10^{11}\) |
| HCN concentration [HCN] (cm⁻³) | \(2.1 \times 10^{13}\) |
| N₂ concentration [N₂] (cm⁻³) | \(1.65 \times 10^{15}\) |

Figure 2 shows the net effect of these various reactions on the various ion concentrations, the \(H(n = 1)\) concentration and the \([H(n = 2, 3)]\) column densities: \(H_3^+\) (the main ion in a pure \(H_2\) plasma) is progressively replaced by \(NH_4^+\) and \(N_2H^+\) (the main two N-containing ions) upon introducing \(N_2\) into an \(H_2\) plasma. The enhanced rates of the electron–ion recombination reactions (11) and (12) upon \(N_2\) addition as compared to the \(H_3^+ + e\) recombination reaction (10), throughout the whole reactor including the ‘cool’ peripheral regions beyond the hot plasma core, leads to significant (more than two-fold) reductions in the plasma density in the peripheral regions (figure 3(a)) and in the total charge content. By way of illustration, the calculated total numbers of ions are \(2.06 \times 10^{13}\) and \(1.73 \times 10^{13}\) for the \(0.66\% N_2/H_2\) and \(6\% N_2/H_2\) mixtures, respectively. \(N_2\) addition also leads to some spatial redistribution of the averaged reduced electric fields \(|E|/(N \times a)\)
[38] (with the factor \( a = (1 + \omega^2/\nu_{\text{eff}}^2)^{0.5} \) for the MW frequency \( \omega = 2\pi \times 2.45 \) GHz in the ns region (figure 3(a)), of the absorbed power density, PD, (in favor of the ns region and to a lesser extent the plasma core, figure 3(a)) and a progressive increase in the rates of the main ionization reactions (i.e. the associative ionizations (AIs) \( H(n \geq 2) + H_2 \rightarrow H_3^+ + e \) and EII of \( H_2, H \) and \( N_2 \), reactions (1)–(5) in table 1) in the plasma core and, especially, near the substrate, which more than compensate for the \( N_2 \)-induced increases in the electron–ion recombination rates in these regions. In summary, the quasi-neutral plasma becomes more confined and shifts toward the substrate with increasing \( N_2 \) input mole fraction, \( X_0(N_2) \). These trends and redistributions under base conditions (pressure, \( p = 150 \) Torr and input MW power, \( P = 1.5 \) kW) are illustrated by the predicted values and locations of the following quantities in, respectively, 0.06\% \( N_2/H_2 \) and 6\% \( N_2/H_2 \) mixtures: maximal plasma densities, \( n_e \approx \sum n_i = 6.25 \times 10^{11} \) cm\(^{-3}\) (at \( r = 0, z = 6.5 \) mm) vs \( 6.8 \times 10^{11} \) cm\(^{-3}\) (at \( r = 0, z = 5.5 \) mm); maximal gas temperatures, which increase from \( T_{\text{max}} = 3160 \) to \( 3215 \) K, and maximal H atom concentrations, which increase from \( [H]_{\text{max}} = 6.6 \times 10^{16} \) to \( 8 \times 10^{16} \) cm\(^{-3}\). The maximal electron temperatures are consistently found at \( z \approx 1.5 \) mm, remain within the narrow range \( 1.24 \pm 0.03 \) eV and show no clear trend with \( X_0(N_2) \), whereas increasing \( N_2 \) causes a minor reduction of \( T_e \) in the hot plasma region, e.g. \( T_e(r = 0, z = 10.5 \) mm) is predicted to decline from \( 1.08 \) to \( 1.05 \) eV upon increasing \( X_0(N_2) \) from 0.06\% to 6\%. 

Figure 2. (a) Calculated and measured \( [H(n = 2)](z = 8 \) mm) column densities and the calculated concentrations (at \( r = 0, z = 8 \) mm) of the main ions for various \( N_2/H_2 \) mixtures. (b) Calculated \( [H(n = 1)](r = 0, z = 0.5 \) and 7 mm) concentrations and \( [H(n = 3)](z = 7 \) mm) column densities vs the measured \( H_{\alpha} \) intensities (at \( z = 7 \) mm [20]) for various \( N_2/H_2 \) mixtures (solid lines). All data are for base pressure, \( p = 150 \) Torr, and power, \( P = 1.5 \) kW. Also shown (long and short dashed lines) are the \( [H(n = 2, 3)] \) values calculated with all exponents \( b \) in the electron–ion recombination coefficients \( k \sim T^{b} \) set to, respectively, \( b = 0 \) or \( b = 0.4 \) to illustrate deviations from base case where \( b = 0 \) for \( H_3^+ \) and \( b = 0.4 \) for \( NH_4^+ \) and \( N_2H^+ \) ions (table 1). Reproduced from [21]. CC BY 4.0.
No simple explanation for the predicted changes with increasing $X_0(N_2)$ is evident under the prevailing conditions. Rather, these changes are best viewed as the result of several closely coupled processes. To confirm the role of ion conversion effects, test calculations were run for the 6% $N_2/H_2$ plasma using the 2D model with the cross-sections of the nitrogen ion–electron recombination reactions (11) and (12) artificially set equal to that of the $H_3^+ + e$ recombination reaction (10). These calculations returned plasma parameters and electromagnetic fields that are essentially the same as those for the pure $H_2$ plasma. We highlight that the described effects provide a salutary illustration of how plasma parameters can respond, seemingly indirectly, to an external perturbation (here, minor $N_2$ additions). Without such modeling, the observation of $\sim 20\%$ increase in the ns $H$ atom concentration, $[H]_{ns}$, upon adding 6% $N_2$ to an $H_2$ plasma (figure 2(b)) might most plausibly be attributed to a reduced plasma–surface interaction. These effects do not appear to be related to the observed enhanced diamond deposition rates when trace amounts of $N_2$ are added to a C/H plasma, however. Many other peculiarities are revealed by modeling these three element plasmas, as discussed in section 3.

The predicted changes in plasma parameters upon $N_2$ addition to an $H_2$ plasma also translate into increases in the predicted maximal concentrations of excited species (i.e. electronically excited $H_2$ molecules ($H_2^*$) and $H(n > 1)$ atoms) that accord well with the earlier OES and CRDS measurements [20] (figures 2 and 3(b)). Unless specified otherwise, all measured data reprised in this work were recorded under base conditions ($p = 150$ Torr and $P = 1.5$ kW). The measured $H_\alpha$ emission intensity at $z = 7$ mm increases more steeply at low $X_0(N_2)$ ($<1\%$) and tends to saturate at higher $X_0(N_2)$
(figure 2(b)). Similar saturations are observed for the measured and the calculated \{H(n = 2)\} column density (figure 2(a)). As these figures show, the measured trends and axial profiles are in broad agreement with the calculated \{H(n = 2, 3)\} (z, X₀(N₂)) column densities. (Note, the measured \{H(n = 2, 3)\} column densities measured at the lowest X₀(N₂) are likely to be perturbed by ion conversions into H₂O⁺ via reactions with H₂O molecules within trace air impurities in the process gas mixture [20].) It is also important to note that the calculated saturation of the \{H(n = 2, 3)\} column density with X₀(N₂) is only achieved for a relatively narrow range of \(k_{i0}/k_i\) ratios, i.e. of the total electron–ion coefficients for the major \(H^+\) and \(NH_4^+\) ions. As noted above, the electron–energy dependent recombination cross-sections employed here were measured at or near room temperature and their \(T_x\)-dependencies up to 3000 K have been assumed to vary as \((300/T_x)^6\) where the exponent \(b\) ranges between 0 and 1 for different ions [48].

The present modeling finds that the measured behavior of \{H(n = 2, 3)\} (figure 2) can be reproduced well with \(b(H^+) = 0\) and \(b(NH_4^+) = 0.4\) (table 1). As figure 2 also shows, assuming a common exponent (e.g. \(b = 0\) or \(b = 0.4\)) for all ions results in more serious deviations from the experimental data. In the absence of detailed data, we have adopted the same \(b = 0.4\) value for electron recombination with \(N_2H^+\) ions and note that assuming \(b = 0.4\) for other \(H\), \(C\), \(N\), ions in the N/C/H plasmas also allows us to reproduce the measured doubling of \{H(n = 2)\} upon adding \(\sim 1%–4\%\) CH₄ into an H₂ plasma [51]. We speculate that the much weaker \(T_x\)-dependence adopted for \(H^+\) may be related with the enhanced recombination with vibrationally excited ions, i.e. \(k(e + H^+(v = 1)) \gg k(e + H^+(v = 0))\) [52].

The effects of \(N_2\) addition (and the induced interconversion of ions) provide further illustration of the importance of calculating ion and electron concentrations throughout the whole reactor, i.e. in the ‘cool’ plasma regions also, so as to correctly partition the absorbed power in the ‘hot’ and ‘cool’ plasma regions—as shown and described in more detail for the case of Ar/H₂ plasmas [38] and (more briefly) for an H₂ plasma with some air contamination [37]. These early studies also emphasized the potential importance of energy transfer (ET) processes between excited state manifolds (in particular \(H^+ \leftrightarrow H_2^+\) excitation transfer) for adequate calculation of the excited species concentrations, their spatial distributions and their \(p\) and \(P\) dependences. \(H^+ \leftrightarrow H_2^+\) coupling in the present study was realized by including the direct and reverse reactions \(H(n = 3) + H_2(X^1\Sigma_g^+) \leftrightarrow H(n = 1) + H_2(a^3\Sigma_g^+)\), with respective rate coefficients \(k_{direct} = 10^{-9}\) and \(k_{reverse} = 3.8 \times 10^{-10}\) \(\exp(-3481/T_x)\ cm^3 s^{-1}\) [37]. Including such ET processes results in a discernible improvement in the agreement between the calculated \{H(n = 3)\}(z) column density and measured \(H_2^+\) emission intensity profile shown in figure 3(b).

As before [37, 38], other EIE, ET and quenching reactions were included in the calculations of excited \(H^+\) and \(H_2^+\) species within the frame of the present N₂/H₂ plasma model. Given the appearance of various electronically excited states of nitrogen \(N_2^*\) (and \(NH_4^*\)) in the N/H plasma [20], it is not possible to rule out other potential reactions and ET processes between other excited state manifolds (e.g. \(H^+ \leftrightarrow N_2^*\) and \(H_2^+ \leftrightarrow N_2^*\)), or AI reactions (e.g. \(H + N_2^* \rightarrow N_2H^* + e\), and \(H^+ + N_2 + M \rightarrow N_2H(n) + M\) followed by \(N_2H(n) + M \rightarrow N_2H^* + e + M\), where \(N_2H(n)\) represents high lying Rydberg states of the radical). Unfortunately, there is as yet little reliable data for such reactions (especially at high gas temperatures) and it is important to try and ensure that this does not lead to the neglect of potentially significant processes. As an example, the possible importance of H atom reactions with electronically excited \(N_2^*\) molecules could be a significant \(N_2\) decomposition route (and a major source of NH radicals) under the prevailing conditions, as argued in the next paragraph.

2.2. \(N_2\) decomposition mechanisms, the balance between \(NH_x\) production and loss processes and heterogeneous loss

The balance of the production and loss processes for the various \(NH_x\) \((x = 0–3)\) species is neither trivial nor completely clear. Thermal dissociation of \(N_2\) is negligible even at the highest relevant gas temperatures \(T_g \sim 3200\ K\). Non-thermal \(N_2\) decomposition as a primary source of \(N\) atoms (and NH radicals) is concentrated within the hot plasma region, but the primary products are redistributed within the \(NH\) group throughout the whole reactor volume by the fast \(H\)-shifting reactions \((NH_{x+1} + H \leftrightarrow NH_x + H_2\ (x = 0–2))\) and by diffusional transfer [20]. The two- and three-body recombination reactions of \(NH\) species into \(N_2\) (and \(N_2H\)) are unable to balance the local \(NH\) production rates in the plasma region and overall balance is only reached by \(NH\) recombination in off-plasma regions and at the internal reactor surfaces (i.e. at the metal side walls and base plate, Mo substrate holder and quartz window shown schematically in figure 1). Plasma sources are expected to be main sources of \(N\) atoms in the present MW plasma conditions.

The non-thermal \(N_2\) decomposition reactions (13)–(15) are modeled using available vibrational \((v)\) level-dependent cross-sections [53–55] for EIE of ground state \(N_2(X^1\Sigma_g^+)\), \(v\) molecules and subsequent dissociation and predissociation of different triplet and singlet excited states (e.g. the \(N_2(B^3\Pi_g, v > 12), N_2(C^3\Pi_u, v > 4)\) and \(N_2(a^3\Pi_g, v > 6)\) states), with given dissociation fractions [54, 55]. Predissociation via \(N_2(a^3\Pi_g, v > 6)\) molecules, with a low threshold energy \((E < 10\ eV)\) and large cross-sections in the near threshold region [55], is considered a major dissociative pathway under the prevailing experimental conditions. Dissociative excitations of vibrationally excited \((v > 3)\) ground state \(N_2(X)\) molecules were identified as the major \(N\) atom source in previous studies of \(N_2\) direct current discharges [56], but such vibrationally excited species are relatively much less important in the present N/H plasma due to the fast vibration–translation (V–T) relaxation of \(N_2(v)\) molecules in collision with H atoms [57]. Under the present conditions, dissociative excitations from the \(v = 0, 1\) and \(2\) levels of \(N_2(X)\) are predicted to make comparable contributions to the \(N\) atom yield in the hot plasma region, with the differences in population (i.e. \(\sim 67\%, \sim 22\%\) and \(\sim 11\%\) of the population in levels with \(v = 0, 1\) and \(2\), respectively, at \(T_g \sim 3000\ K\)) compensated by the progressive...
increase in cross-section with increasing vibrational quantum number [54].

The previous combined experimental and theoretical study of MW activated N/H plasmas [20] and the present modeling both find this N atom source insufficient to reproduce the measured \([\text{NH}(v = 0)]\) column densities. An additional mechanism, EIE of N2 molecules into the lowest metastable \((A^3\Sigma^+u)\) state, followed by reaction (19) (i.e. \(\text{N}_2(A^3\Sigma^+u) + \text{H} \rightarrow \text{NH} + \text{N}\)), was thus proposed in [20]. The rate coefficient \(k_{19}\) of this process at room temperature was determined by re-modeling data reported by Hack et al [58], but there were no data available to allow direct determination of the temperature dependence \(k_{19}(T_g)\) over the range 300–3300 K. The recent calculations of \(k_{19}(100 < T_g < 2000 \text{ K})\) [32] and the rate coefficient \(k_{20}(300 < T_g < 3000 \text{ K})\) [34] for the reaction \(\text{N}_2(A^3\Sigma^+u) + \text{H}_2 \rightarrow \text{products}\) (e.g. \(\text{N}_2 + 2\text{H}\), as in reaction (20) in table 1) offer an opportunity to refine the previous parametrization of \(k_{19}(T_g)\). Specifically, the rate coefficient \(k_{20}(T_g)\) listed in table 1 (from [34]) is much higher at the core plasma temperatures than previously assumed. Implementing this new expression for \(k_{20}(T_g)\) in the 2D modeling greatly suppresses the contribution of reaction (19) to N2 decomposition. The rate coefficients \(k_{19}(T_g)\) reported by Borges et al [32] (which increase from \(k_{19}(298 \text{ K}) = 7 \times 10^{-13}\) to \(k_{19}(2000 \text{ K}) = 7.3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}\) are also higher than those used in [20], but Borges et al [32] note that the formation of NH + N products via reaction (19) is a rare event (especially at low \(T_g\)), which complicates the calculation. What is clear, however, is that these recent calculations [32] overestimate \(k_{19}(T_g)\) at low temperatures, since the reported \(k_{19}(298 \text{ K})\) value is some two orders of magnitude larger than the value (2.8 \(\times 10^{-15}\) \(\text{ cm}^3 \text{ s}^{-1}\) used to accommodate the data of Hack et al [58]. Mota et al [33] predict a barrier in the entrance channel to reaction (19). Adopting the \(k_{19}(2000 \text{ K})\) value from [32] and the above value of \(k_{19}(298 \text{ K})\) leads to the \(k_{19}(T_g)\) expression listed in table 1, with an activation energy of 2721 K (0.235 eV) somewhat larger than the reaction endothermicity (~0.18 eV).

Implementing these new expressions for \(k_{19}(T_g)\), \(k_{20}(T_g)\) and the aforementioned plasma sources of N atoms in the 2D self-consistent model results in total N2 decomposition rates that are substantially less (by factors of two to three) than that required to reproduce the measured \([\text{NH}(v = 0)]\) column densities in N2/H2 plasmas [20]. The predicted \([\text{NH}(v = 0)](z)\) profiles were also much flatter than those measured by CRDS. This evident mismatch served to stimulate a search for additional N2 decomposition mechanisms, involving other excited states of N2, and their ultimate inclusion into an expanded 2D model. The calculations showed that only a sub-set of N2 excited states (the \(B^3\Pi_g\), \(W^1\Delta_u\), \(B^3\Sigma^-\) at \(\alpha\)), \(\Pi_g\) and \(W^1\Delta_u\) states, henceforth bulked as \(N_2^+\) with excitation energies in the limited range 7.35 \(\leq E^* \leq 8.9\) eV have sufficiently high EIE rates to provide significant contributions to N2 decomposition in further reactions with H. The \(N_2^+ + H \rightarrow \text{NH} + \text{N}\) reactions (21) are exothermic (with respect to ground state products), could well be barrier-free, and will pass through regions of high N2-H Rydberg state density that could serve to boost the \(N_2^+ + H\) collision cross-section—all of which factors encourage the view that these reactions are likely to be faster than reaction (19) for \(N_2(A^3\Sigma^+u)\).

When adding \(N_2^+\) as an effective ‘reactant’ in the 2D model, it is important also to recognize the potentially important quenching of \(N_2^+\) in collision with H2 molecules and H atoms (reactions (22)–(24)). For reaction (22), we assume the same \(T_g\)-dependent rate coefficient as for reaction (20). Reaction (23) was studied by Piper [59] and, simply on statistical grounds, we assume \(k_{24} = 0.5 \times k_{21}\). The main sources of electronically excited N2 molecules are the EIE processes (table 1, reactions (16)–(18) with cross-sections from [60]). The EIE rates for the two lowest states within the \(N_2^+\) family (the \(B^3\Pi_g\) and \(W^1\Delta_u\) states, with \(E^* = 7.35\) eV and 7.36 eV, respectively) provide the main contributions under the plasma conditions of current interest (~45% and ~28% of the total EIE probability to \(N_2^+\), respectively). The higher energy, emitting \(C^3\Pi_u\) state of N2 (with \(E = 11\) eV) was also included in the model but found to make only minor contribution to the total N2 decomposition rate and the NH concentration due to its low EIE rate coefficient \(k_{18}\) (cf \(k_{17}\) for \(N_2^+\) (table 1)). As table 1 also shows, the formation rate for \(N_2^+\) by EIE (reaction (17)) is substantially larger that the rates of the \(N_2\) dissociation reactions (13)–(15).

The 2D model was run with the expanded N/H kinetic scheme based on the previous N/H kinetics for charged and neutral species [20] along with the additions and modifications of the important reactions listed in table 1, in order to establish a value for the unknown rate coefficient \(k_{21}\) that would return calculated \([\text{NH}(v = 0)]\) column densities consistent with the measured values. Figure 4 shows the \([\text{NH}(v = 0)](z)\) column density profiles returned for different \(X_9(N_2)\) values when adopting a rate coefficient \(k_{21} = 3.5 \times 10^{-11}\) \(\text{ cm}^3 \text{ s}^{-1}\). In deriving these profiles, the modeling assumes the following N atom recombination probabilities, which are typical of those for glass and metal surfaces [61]: \(\gamma_{\text{quartz}} = 0.0001\) for the quartz window and \(\gamma_{\text{metal}} = 0.01\) for the aluminum side walls and the Cu base plate of the reactor.

Experimentally, the surfaces are exposed to simultaneous fluxes of H and N atoms (\(F_{\text{H}}\) and \(F_{\text{N}}\), respectively, with \(F_{\text{N}} \ll F_{\text{H}}\). The actual recombination probabilities could be \(F_{\text{N}}\)- and \(F_{\text{H}}\)-dependent and the effective \(\gamma\) values very different from those determined under conditions where surfaces are exposed just to a flux of N atoms. Thus, the effects of lower \(\gamma_{\text{metal}} = 0.001\) (and higher \(\gamma_{\text{metal}} = 0.1\) recombination probabilities have also been explored. These changes cause predictable increases and decreases, respectively, in the concentrations of all \(\text{NH}_x\) species (mainly in the near surface regions), but only modest (~5%–10%) variations in the predicted \([\text{NH}(v = 0)](z)\) column densities. Removing all surface losses in the 2D model (i.e. setting all \(\gamma = 0\)) leads to a build-up of \(\text{NH}_x\) species in the cool, near surface regions. The possible loss of \(\text{NH}_x\) and \(\text{NH}_2\) species or their conversions on the surfaces are less important, since the fast H-shifting equilibria ensure that their near-surface concentrations \([\text{NH}_x]\), \((x = 1, 2)\) are an order of magnitude lower than the N atom concentration.
Due to its proximity, the predicted NH column densities are most sensitive to N atom recombination on the Mo substrate and the modeling showed an additional decline of [NH(z)] at smaller z (z < 5–8 mm) when γsub > 0.001. The efficient two-stage recombination process (e.g. addition of a nitrogen atom, Mo + N → MoN, followed by nitrogen abstraction MoN + N → Mo + N2) requires suitable nitrogen sites (e.g. MoN, MoNH, MoN2H). Experimentally, Fsub ≫ FNI, so the reaction MoNH → H → Mo + NH0,0 (x = 0, 1) is likely to be the main destruction route for MoNHx sites. The steady-state fraction of MoNHx surface sites will be proportional to FNI, while the value of γsub for nitrogen recombination will be proportional to the local concentration of N atoms in the gas phase just above the substrate, [N]ns. This situation was realized in the 2D modeling by using an effective recombination probability γsub given by γsub = β × [N]ns, with a constant β = 2 × 10^{-16} cm^3 that provides γsub = 0.0013 for [N]ns = 6.6 × 10^{12} cm^{-3} (typical for the MW activated 1.2% N2/H2 plasma operating at p = 150 Torr and P = 1.5 kW). This surface loss causes a discernible reduction in the predicted NH concentration at high X0(N2). For example, the predicted maximal [NH(v = 0)] column density for X0(N2) = 3% decreases from ~3.4 × 10^{12} cm^{-2} when β = 0 (i.e. no substrate surface induced loss) to ~3 × 10^{12} cm^{-2} when β is set to be the base value adopted in this work. The ~30% drop in [NH](z = 0.5 mm) near the substrate is predictably higher. The maximal column density is in good accord with the experimental value: [NH(v = 0)](z = 8 mm) = 2.7 × 10^{12} cm^{-2} [20].

Heterogeneous recombination of N atoms offers a reason for the less than linear dependence of the measured [NH(v = 0)](z = 8 mm) ~ (X0(N2))^q, with q = 0.7 [20]. The present 2D modeling returns a slightly higher factor, q ~ 0.85 ± 0.05. (Excluding all N atom surface losses gives q close to 1.) The NH(A−X) emission, Iem(NH⁺), monitored by OES showed a similar X0(N2) dependence: q = 0.81 [20]. [NH(v, z)] concentrations estimated as part of the present modeling return a value q ~ 0.84, but we caution that these estimates are derived using a simplified model wherein NH(A) production (by EIE of NH(X)) is balanced by loss through radiative decay and reactive quenching by collisions with H2 and H atoms. This analysis thus makes no allowance for possible chemiluminescent reactions contributing to NH(A) production (e.g. N2(D) + H2 → NH(A) + H and/or NH2 + H → NH(A) + H2) and we note that a full chemical mechanism for NH⁺ merits further study. All these X0(N2) dependences with q ≥ 0.7 hint, indirectly, that the NH concentrations in the hot plasma region are not determined by local NH loss in binary reactions of the form NHn + NHn ↔ N2Hn + (x + y − z)H since, if such were to be the case, q should equal 0.5 as observed (experimentally and theoretically) for (CH(v = 0)) ~ (X0(CH4))0.5 in dilute CH4/H2 plasmas [62]. In contrast to NH and NH⁺, the earlier OES study [20] showed a linear relationship between N2(C2Πu) and X0(N2). Consistent with this, the present 2D modeling returns linear X0(N2) dependences for all N2 excited state populations. This reflects the intrinsic stability of N2. The concentration of N2(X) molecules in the hot plasma core is three orders of magnitude greater than the sum of all NH (x = 0–3) species. Thus [N2(X)] is essentially proportional to X0(N2) and, since the dominant route to forming N2(C) is the EIE of N2(X), the proportionality N2(C) ~ X0(N2) follows automatically (apart from any minor variations in the EIE rate coefficients and/or ne with X0(N2) (figure 3(a)) unless the N2(C) concentrations are significantly affected by excitation transfer between excited state manifolds (e.g. H2* ↔ N2*, H* ↔ N2*) as has been recognised for Ar/H2 plasmas under similar operating conditions [38].

We now return to the comparison of the measured and calculated [NH(v = 0)](z) axial profiles for the MW activated 1.2% N2/H2 mixture shown in figure 4. The absolute values

![Figure 4](image-url)
of the calculated column densities through the hot plasma core are within the spread of the measured column densities (e.g. [NH(v = 0)](z = 8 mm) ~ (1.32 ± 0.08) × 10^{12} cm^{-2} [20]). The local rise of the measured [NH(v = 0)] column density at z = 4 mm can be explained, in part at least, by the use of a constant gas (T_g) and NH rotational (T_rot) temperatures T_g = T_rot = 2900 K in the PGOPHER [63] simulations used to convert the integrated intensity of individual absorption lines measured at all z into absolute column densities [20]. Further simulations based on the calculated T_g(r, z) and [NH](r, z) distributions show that this becomes a progressively poorer assumption in the colder regions and that the column density values returned by the CRDS experiments (reproduced in figure 4) should be reduced by, e.g. ~11% at z = 2 mm and by ~5% at z = 4 mm, but that no corrections are needed at larger z (6 < z < 20 mm), where the measured [NH(v = 0)] column densities clearly decline more steeply than predicted by the modeling. The reason for this discrepancy is not clear. The calculated p and P dependencies of the [NH(v = 0)] and [H(n = 2)] column densities are broadly in accord with the respective CRDS results [20], apart from at high pressure (p = 180 Torr) where—as shown in figure S1 (https://stacks.iop.org/PSST/31/035005/mmedia) in the electronic supplementary information (ESI)—the predicted increase in [NH(v = 0)](z = 8 mm) is contrary to the weak decline observed experimentally.

Finally in this section we consider the extent to which N2 additions affect the substrate temperature T_s and the near-substrate gas temperature T_g(r, z = 0.5 mm). Briefly, the substrate heating due to the incident fluxes of NH radicals and excited N2 molecules is negligible in comparison with the contributions from heat conduction (from the hot plasma) and from H atom accommodation at radical surface sites [64]. Indirectly, however, the calculations clearly reveal the effect of the N2-induced redistribution of the reduced electric fields (figure 3(a)) on substrate heating (the total power loading to the substrate, P_s), T_s and T_g(r, z = 0.5 mm): e.g. P_s = 328 W, T_s = 915 K, T_g(r = 0, z = 0.5 mm) = 1316 K for a 0.06% N2/H2 mixture, cf P_s = 402 W, T_s = 1015 K, T_g(r = 0, z = 0.5 mm) = 1431 K for a 6% N2/H2 mixture.

3. N/C/H plasma modeling

2D self-consistent modeling with a refined and expanded N/C/H plasma-chemical mechanism was undertaken for a range of N2/CH4/H2 mixtures (focusing particularly on 0.4% CH4/3% N2/H2 and 4% CH4/0.6% N2/H2 base mixtures) to explore the effects of N additions and to compare with available data from the previous CRDS and OES experiments [21]. This modeling employed the updated N/H mechanism discussed in section 2 and various changes and additions to the previously introduced N/C coupling mechanism [21]. One key question is the necessity (and relative importance) of the newly proposed main N2 decomposition route in the N/H plasmas (reactions (17) and (21) in table 1) in the case of N/C/H plasmas. All direct molecular ion conversion reactions [49] are used together with the respective reverse reactions (with thermochemical data taken from reference [50]). H+ ions are efficiently converted into molecular ions via the three-body reaction H+ + 2H2 ↔ H3+ + H2 (reference [65], as in the N/H plasmas) and by fast reactions involving C2H2 species (mainly the H+ + C2H2 ↔ C2H3+ + H+ reaction). This section starts with a consideration of other ion conversions and changes in plasma parameters upon adding nitrogen or methane to a pre-existing plasma operating at base pressure (p = 150 Torr) and power (P = 1.5 kW).

3.1. Response of plasma parameters upon adding N2 to CH4/H2 mixtures

The dominant C2H4+ (x = 2, y = 2, 3) ions in a C/H plasma are initially produced by EII of C2H2 and by the reversible (and almost balanced) charge exchange reaction: H2+ + C2H2 ↔ C2H3+ + H2 [21, 62]. Further partitioning of the C2H3+ ions occurs via fast reversible reactions like C2H3+ + C2H2 ↔ C2H5+ + H2 and C2H2+ + C2H2 ↔ C2H3+ + H in the currently used reaction scheme results in a dominant role for the C2H5+ ion, with the [C2H5+]/[NH] fraction exceeding 70% in the hot plasma core. Further production of heavier ions cannot be excluded, however. Prior studies of C2H2+/C2H2 mixtures at low pressure and room temperature identified further conversions of primary C2H2+ (x = 2, 3) ions into C2H4+ ions via termolecular association reactions with M = C2H2 [66]. The survival probability of such heavy ions at the high gas temperatures and in the presence of the high H atom number densities prevailing in the MW activated plasmas of interest here is unknown, and the current modeling assumes that the inclusion of just these three C2H3+ (x ≥ 2) hydrocarbon ions does not lead to any serious loss of generality or perturbation of the C/H plasma chemistry.

In contrast to the case of N2 addition to a H2 plasma, no serious changes in the concentrations of C2H4+ ions (C2H4+, C2H3+, C2H2+) are observed upon introducing N-containing ions (via reactions (2) and (3) from table 1) to a C/H plasma. The biggest change is due to the reversible reaction C2H4+ + HCN ↔ HCNH + C2H2, the forward and reverse rate coefficients for which are both large (k_r = 2.9 × 10^{-9} cm^3 s^{-1} [49], k_f = 1.6 × 10^{-9} cm^3 s^{-1}) in the hot plasma core at T_g = 3200 K. N-containing ions (i.e. HCNH+, NH2+, N2H+) [21] are predicted to contribute no more than 1% of the total ion content in the hot plasma core of MW activated 0.6% N2/4% CH4/H2 gas mixtures (<20% in the case of a 3% N2/0.4% CH4/H2 gas mixture), however, but these fractions are predicted to increase to, respectively, ~4% and ~55% just above the growing substrate surface.

These changes in the relative ion concentrations induce no discernible changes in the plasma parameters (n_e, T_e, T_g, E/]d(N × a)). The detected increase in the [CH(v = 0)] column density upon adding 0.1% N2 to a 4%/CH4/H2 plasma (from ~2.4 × 10^{12} to 3 × 10^{12} cm^{-2} at z = 8 mm) [21] cannot be explained by N/C coupling reactions involving neutral or charged species (discussed below) or by changes in the plasma parameters; it might reflect changes in gas–surface processes upon nitriding reactor surfaces. The calculated CN(v = 0) column densities scale linearly with X_N(N2), as observed in the CRDS measurements of {CN(v = 0)}
column densities [21]. The calculated concentrations of ground and excited states of N2, NH and other N-containing species also all show essentially linear dependencies on X0(N2).

3.2. Response of plasma parameters upon adding CH4 to N2/H2 mixtures

In contrast to the apparent insensitivity of the plasma parameters when small amounts of N2 are added to a C/H plasma, CH4 addition to an N/H plasma significantly reduces the fractions of all pre-existing ions (i.e. H3+, NH4+, N2H+, etc), mainly because of the aforementioned H2 + C2H2 ↔ C2H4 + H2 conversion. The decrease in the H3+ concentration induces similar declines in the concentrations of NH4+ and N2H+ ions, which are closely coupled with [H3+ as described in section 2 (table 1). For example, adding 0.1% CH4 to a pre-existing 0.6% N2/H2 plasma is predicted to result in a ~three-fold drop in [H3+] in the hot plasma core and C,H4+ species becoming the dominant (~70%) ions in this region. The direct nitrogen–hydrocarbon ion conversion reaction N2H+ + C2H2 ↔ C2H4+ + N2 is predicted to provide a (minor) additional contribution to this switch. This substantial change in the ion fractions upon transitioning from a 0.6% N2/H2 plasma to a 0.1% CH4/0.6% N2/H2 plasma (and the associated increase in the total electron–ion recombination rates) causes some modest changes in the plasma parameters, reminiscent of the changes of ns, Tε, Ts and |E|/(N x a) upon adding 0.6% N2 to an H2 plasma (figure 3(a)). For example, the maximal rises in ns and Ts upon adding 0.1% CH4 to a 0.6% N2/H2 plasma are ~3.4% and ~1%, respectively. Increasing X0(CH4) further results in a progressive growth in the C2H4+ fractions, but the effect of such additions on the plasma parameters saturates at X0(CH4) ~ 1% (figure S2 in the ESI, from [21])). At yet higher CH4 additions (X0(CH4) > 2%), ion production by EI of neutral C,H4 species (mainly C2H2) is predicted to start exceeding the sum of that from EI of H and H2, resulting in a slow and progressive decline in Tc. Such trends upon CH4 addition were also noted and discussed in [41].

These modest responses of the N/H plasma parameters to CH4 addition can be seen (indirectly) in the OES data measured at z = 7 mm varies non-monotonically within a narrow (±20%) range upon adding CH4 to a 0.6% N2/H2 plasma. The observed emission intensity (scaled to maximal intensity) initially increases from I(N2*) ~ 0.7 at X0(CH4) = 0 to I(N2*) ~ 1 at X0(CH4) = 1%–2%, then slowly declines to I(N2*) ~ 0.86 at X0(CH4) = 5%. The X(Zn(C), (v = 0))(z = 7 mm)/(1017 cm−2) values calculated in the present work show broadly similar behavior, i.e. 0.81, 1.05, 1.07 and 0.78 for X0(CH4) = 0, 0.1, 0.4 and 4%, respectively. The measured CN(B → X) emission intensities show an initial jump from near zero values at X0(CH4) = 0 but, thereafter, I(CN*) show a similar behavior to that of I(N2*), maximizing at X0(CH4) = 0.8% and then declining gently throughout the range 1% ≤ X0(CH4) ≤ 5% [21]. The measured NH(A → X) emission intensity, in contrast, declines nonlinearly with increasing X0(CH4) [21] but its behavior is mainly determined by the parent NH(X) concentration which, in turn, depends on N/C coupling reactions. The more important N/C coupling reactions are discussed in detail in section 3.3.

3.3. N/C coupling mechanism and variations in the NH, CN and CH concentrations

The main features of the N/C/H reaction mechanism (based on GRI Mech 3.0 [67]) in the MW activated CVD reactor conditions of current interest have been discussed previously [21]. Here this mechanism is revised and expanded on the basis of analyses of many initial data sources (collected in NIST [68] and astrochemical [69] databases). The present emphasis is on providing a detailed description of the N/C coupling mechanism and modifications to the N/C/H reaction mechanism that critically affect the NH, CN and CH concentrations for which there are relevant experimental data. The global balance within the NH family is discussed, along with the conversion of these species into the H2CN family and the relevance of the newly proposed N2 decomposition routes for modeling and understanding N/C/H plasmas (reactions (19), (21) and (26)) in table 2, where reaction (26) represents the sum of all N2 dissociations by EI, i.e. reactions (13)–(15) in table 1.

3.3.1. NH4 loss reactions. The net loss of NH4 is largely determined by the reactions of N atoms with CH4 (x = 1–3) species and with C2H (reactions (27)–(30) in table 2) and by the NH + CH3 radical–radical reaction (31). Relative to our earlier N/C/H plasma study [21], two additional and potentially important N atom loss processes—N + CH2 ↔ HCN + H and N + C2H ↔ products (reactions (28) and (30) in table 2)—have been added to the model, with rate coefficients from Loison et al [69]. The dominant (94%) products of the latter reaction are CCN + H radicals (with minor branching into HCN + C and HNC + C products). Most of the CCN products will undergo the fast conversion CCN + H ↔ HCN + C, with a minor (20%) rival channel leading to CNC + H [69]. The present 2D modeling shows that, under the prevailing plasma conditions, the reaction sequence N + C2H ↔ CCN + H and CCN + H ↔ HCN + C can be replaced by a single effective reaction N + C2H ↔ HCN + C, which serves as the most important sink of N atoms and (via the fast H-shifting reactions NH4 + H ↔ NH3 + H2 (x = 1–3)) of all other NHx species in the hot plasma core.

The exothermic CH3 + N ↔ H2CN + H reaction (29), which the previous modeling assumed as a major N atom loss process [21] merits further careful consideration. It remains an important sink of N atoms in the present modeling, particularly beyond the hot core regions and including the ns region. Theoretical studies suggest that this is essentially the only product channel, with calculated room temperature rate coefficients k29 = 9 × 10−12 cm3 s−1 [70] or 3.3 × 10−11 cm3 s−1 [71] and that the (minor) yield of HCN + H2 products may be the result of the secondary process H2CN + H ↔ HCN + H2. Other literature values for k29 with weak (or missing) temperature dependences span the range k29 ~ 5 × 10−11 up to 1.3 × 10−10 cm3 s−1; e.g. the value of k29(cm3 s−1) in [67] ranges from 1.1 × 10−10 at Tg = 300 K down to 8 × 10−11 at
$T_g = 3000$ K. A direct measurement of $k_{29}$ at high gas temperatures ($T_g \sim 1600$–2000 K), employing atomic resonance absorption spectroscopy at a wavelength of 119.9 nm to monitor the time-evolving N atom concentrations in shock tube studies of NO/C2H6/Ar gas mixtures, with ArF (193 nm) laser photolysis of the NO [72] yielded a broadly constant value: $k_{29}(T_g) \approx 1.2 \times 10^{-10}$ cm$^3$ s$^{-1}$.

Use of such a high value for $k_{29}$ in the present 2D modeling of the H/C/N plasma results in a poor match with experiment, as illustrated in figure 5: the maxima of the calculated [NH($v = 0$)](z) profiles peak further from the substrate (i.e. at larger z), at values that are typically only ~70% of the column densities returned by the CRDS measurements. This has encouraged a re-evaluation of the earlier shock tube data (for which the prevailing conditions were $T_g = 1725$ K, pressure, $p = 0.77$ bar and an initial gas mixture comprising 432 ppm NO, 100 ppm C2H6 in Ar) within the framework of a 0D model using the detailed H/C/N/O mechanism based on the GRI Mech 3.0 mechanism [67]. The experimental value for the rate coefficient $k_{29}$ was deduced from the slope of a plot of $\ln(X_S(t))$—the natural logarithm of the N atom mole fraction as a function of time during the short (~30 μs) period just after the photolysis laser pulse—and the $X_S(t)$ values were obtained from the measured absorption A(t) of the 119.9 nm probe radiation above a near-constant baseline absorption $A_{\text{base}}$ as described in section S2 of the ESI. The 0D modeling can reproduce a near-constant $A_{\text{base}}$ value with major contributions from NO absorption, and a progressively declining contribution from C2H6 photoabsorption (PA) that is compensated by photoionization and PA of the shock-produced CH3 molecules and C1H6 molecules (mainly C2H4)). However, as section S2 shows, the $\ln(X_S(t))$ function and thus the rate coefficient $k_{29}$ are extremely sensitive to even minor variations of a chosen $A_{\text{base}}$ value; e.g. a 10% decrease of the assumed $A_{\text{base}}$ value results in a ~two-fold reduction in the derived $k_{29}$ value. Thus the 2D modeling adopts a value $k_{29} = 1.3 \times 10^{-11} \times T_g^{0.17}$ cm$^3$ s$^{-1}$ (i.e. which assumes the same weak temperature dependence as for the rate coefficient $k_{29}$(CH$_2$ + N $\leftrightarrow$ HCN + H) = 3 $\times$ 10$^{-11}$ $\times$ $T_g^{0.17}$ [69]), gives $k_{29} \approx 4.7 \times 10^{-11}$ cm$^3$ s$^{-1}$ at 2000 K and provides much better agreement with the experimental [NH($v = 0$)](z) profile. This $k_{29}$ value is ~2.5 times lower than that recommended in the early shock tube study [72] but does not visibly contradict the re-evaluation of those results shown in section S2, which also details the species-dependent and total absorbances, and the total absorptions $A_i(t)$ returned by that modeling, and considers the possible effects of the build-up of photoinduced deposits on the LiF and fused silica windows in, respectively, the probe and photolysis axes of the shock tube experiment.

Apart from the important reactions (27)–(31) discussed above, other possible radical reactions (32) and (33) only make small additional contributions to the overall loss of NH$_x$ species, as can be seen from table 2. Loss of N atoms and other NH$_x$ radicals at the substrate surface (with probabilities near (or lower than) those prevailing in an N/H plasma discussed above) is insignificant in comparison with loss by gas phase reactions with C$_2$H$_6$ radicals (table 2).

### 3.3.2. NH$_x$ production reactions

The main NH$_x$ radical sources in the MW activated N/C/H gas mixtures are the same as in the N/H plasmas, i.e. the reactions of excited nitrogen molecules (N$_2^*$ and N$_2$(A)) with H atoms and EID of N$_2$ (reactions (19), (21) and (26) in table 2). The EI induced dissociation of N$_2$ is calculated to be maximal close to the substrate (z = 2 ± 1 mm) but even here its contribution does not exceed 25% of the N$_2$ decomposition. Additional sources specific to the N/C/H plasmas include the N$_2$ decomposition reactions CH$_x$ + N$_2$ $\rightarrow$ products ($x = 0$, 1), which serve as significant sources in the hot plasma core (reactions (34)–(36) in table 2), where the reverse reaction rate coefficients ($k_{-35}$ and $k_{-36}$) are presented as approximations of the relevant $k_i$ values calculated from thermochemical data. Following Faßheber et al [73], we treat the CH + N$_2$ interaction as two reversible reactions CH + N$_2$ $\leftrightarrow$ NCN + H and NCN + H $\leftrightarrow$ HCN + N, but the calculated concentrations of the NCN intermediate product never exceed 10$^8$ cm$^{-3}$ under the conditions of present interest.

The foregoing description of the main NH$_x$ production and loss reactions lays the necessary foundation for the following rationalization of the measured and calculated behavior of the NH column densities as functions of reactor parameters and gas mixtures.

### 3.3.3. NH column densities

The total NH$_x$ ($x = 0$–3) content, which is mostly localized in the plasma region, is determined by the NH$_x$ production and loss reactions discussed above and by diffusional transfer of NH$_x$ into the off-plasma region. As described previously [21], local redistribution within the NH$_x$ family is provided by the fast H-shifting reactions NH$_x$ + H $\leftrightarrow$ NH$_{x+1}$ + H (x = 1–3), for which the various forward and reverse reaction rates are highly equilibrated (e.g. reactions (37) and (–37) in table 2). This ensures that the local partitioning of the various NH$_x$ species concentrations is controlled by the respective thermochemical data at the prevailing local gas temperatures and ensures a predominance of N atoms over the other NH$_x$ radicals (NH and NH$_2$), especially in the cooler regions including the region close above the substrate. As figure 5 shows, the present 2D modeling with $k_{29} = 1.3 \times 10^{-11} \times T_g^{0.17}$ cm$^3$ s$^{-1}$ (discussed above) provides very satisfactory agreement with the experimental [NH($v = 0$)](z) profile for a 3% N$_2$/0.4% CH$_4$/H$_2$ mixture operating at base $p$ and $P$ conditions. Broadly similar profiles can be obtained assuming other temperature dependences, however, (e.g. $k_{29} \approx T_g^b$ ($0 \leq b \leq 0.5$), provided similar $k_{29}$/cm$^3$ s$^{-1}$) values are ensured in the plasma region (e.g. $k_{29} \approx 9.5 \times 10^{-13} \times T_g^{0.5} \approx 4.3 \times 10^{-11}$ cm$^3$ s$^{-1}$ at $T_g \approx 2000$ K). Note also that calculated [NH($v = 0$)] profiles peaking closer to the substrate (as in figure 4) can only be obtained by including plasma sources of NH radicals and N atoms (i.e. reactions (19), (21) and (26)) that dominate the thermal sources of these species. For illustration, figure 5 also shows the much lower [NH($v = 0$)](z) profile calculated without including the main source reaction (21): N$_2^*$ + H $\rightarrow$ N + NH.

Table 3 collects calculated NH radical and N atom densities for various reactor parameters and process gas mixtures. Variations in the former are illustrated by listing the maximal value...
of the \{NH(v = 0)\}(z) profile (\{NH\}_\text{max}), while variations in the radial dependent N atom concentration just above the substrate are illustrated via the calculated \{N\}(r = 0, z = 0.5 mm) and \{N\}(r = 9.5 mm, z = 0.5 mm) values. The former values are of interest for comparison with the earlier CRDS data [21], while the latter inform the later discussion (section 5) of the possible diamond-growth-enhancing effects of N atoms and their radial non-uniformity. The predicted trends in \{NH(v = 0)\} are in reasonable accord with the respective CRDS results. The maximum column densities in the \{NH(v = 0)\}(z) profiles for the various N/C/H mixtures and pressures match (typically within \sim 20\%) the experimental data [21]. The data in table 3 show the \(X_0(\text{N}_2)\) dependences of \{NH(v = 0)\}_\text{max} for various \(X_0(\text{CH}_4)\): 0.4\% (rows 1–3), 0.1\% (rows 4 and 5) and 4\% (rows 6, 7 and 9). In all cases, \{NH\}_\text{max} and \{N\} are linearly proportional to \(X_0(\text{N}_2)\). This is to be expected, given that all the main NH\text{X} radical sources are proportional to the concentration of \text{N}_2 molecules and, since \sim 1\% of the input \text{N}_2 is decomposed under the present plasma conditions, \[\text{N}_2 \sim X_0(\text{N}_2)\] throughout the whole reactor. Note that the local mole fractions are not preserved at the initial \(X_0(\text{N}_2)\) values, however; as with other minority heavy species (e.g. hydrocarbons [62], Ar [38], etc) in a light gas (\text{H}_2), thermodiffusive transfer and, to a lesser extent, \text{H}_2 dissociation ensure that \(X(\text{N}_2)\) in the hot plasma core is less than 40\% the \(X_0(\text{N}_2)\) value.

The \(X_0(\text{CH}_4)\) dependence of \{NH(v = 0)\}_\text{max} (rows 4, 2 and 9 for \(X_0(\text{N}_2)\) = 0.6\% and rows 1 and 7 for \(X_0(\text{N}_2)\) = 0.06\%) is more interesting. Consistent with the CRDS measurements (figure S3 in the ESI [21]), the present modeling predicts the dependence \[\text{NH}_\text{max} \sim 1/(X_0(\text{CH}_4))^{0.5}\]. This functional form can be understood by recognizing that the main loss mechanism for NH\text{X} radicals (integrating over the whole reactor volume) is reaction with CH\text{X} radicals, whose concentrations scale as \((X_0(\text{CH}_4))^{0.5}\) [62]. In the hot plasma core region, however, the loss of NH\text{X} radicals is determined by reaction with C\text{H} radicals, the concentration of which (as with all other C\text{H} species, including the dominant hydrocarbon, C\text{H}_2) is proportional to \(X_0(\text{CH}_4)\) [62]. The predicted maximal C\text{H}(\text{a}) radical column densities, \{C\text{H}(\text{a})\}_\text{max} included in table 3 clearly show such a linear dependence on \(X_0(\text{CH}_4)\). This can also be expressed via the relationships \[C\text{H}(\text{a}) \sim \text{C}[\text{CH}]/\text{H}/\text{H}_2 \sim \text{C}[\text{H}_2] \times ([\text{H}]/[\text{H}_2])^2 \sim X_0(\text{CH}_4) \times ([\text{H}]/[\text{H}_2])^2\], which reflect the partitioning between the various C\text{H} species as a result of the fast H-shifting reactions [40]. Such relationships are also revealed by the stronger than linear dependence of \{C\text{H}(\text{a})\} on \(X_0(\text{CH}_4)\) and its insensitivity to \text{N}_2 additions, as shown in table 3.

The \(p\) and \(P\) dependences of \{NH(v = 0)\}_\text{max} also merit brief discussion. Focusing first on a 0.6\% \text{N}_2/4\% \text{CH}_2/\text{H}_2 mixture (rows 8 to 11 in table 3), \{NH\}_\text{max} increases only weakly with increasing \(p\) (in clear contrast to \{CN(v = 0)\}_\text{max}) and saturates at \(p \geq 150\) Torr. This reflects the rapid increase in C\text{H} radical density with increasing \(p\); the current modeling suggests that reaction (30) becomes a major N atom loss process by \(p = 200\) Torr. This is understandable given the dependence \[\text{C}[\text{CH}]/\text{H}/\text{H}_2 \sim [\text{C}[\text{H}_2] \times ([\text{H}]/[\text{H}_2])\text{ and the steep increase in the maximal }[\text{H}]/[\text{H}_2]\text{ ratios with increasing }p\ \sim [\text{H}]/[\text{H}_2] \sim p^{1.35 \pm 0.1},\text{ which shows even more strongly (near cubically) in the }p\text{-dependent }\{\text{C}[\text{H}(\text{a})]\}\text{ max values (table 3).}\]

Comparing rows 13 and 3 in table 3 (3\% \text{N}_2/0.4\% \text{CH}_2/\text{H}_2 mixture) shows \{NH\}_\text{max} increasing almost linearly with input power \(P\), \[\text{NH}_\text{max} \sim 9.54 \times 10^{11} \times (P/1500)^{0.85}\text{, though the 2D modeling of }\text{N}_2\text{-lean, }\text{CH}_2\text{-rich mixtures (lines 12 and 9 in table 3) shows a closer to square root }P\text{-dependence. These predicted variations reflect the complex }P\text{-dependence of several factors: the NH\text{X} loss and production rates and their }P\text{-dependent spatial dependences (maximal production shifts...}]}
to smaller \( z \) with increasing \( P \) and the partitioning within the NH\(_3\) family (the maximal [H]/[H\(_2\)]) ratios in the case of the 3\% N\(_2\)/0.4\% CH\(_3\)/H\(_2\) mixture are predicted to increase from 0.12 to 0.204 upon raising \( P \) from 0.75 to 1.5 kW). The previous CRDS probing of an MW plasma activated 3\% N\(_2\)/0.4\% CH\(_3\)/H\(_2\) gas mixture (\( p = 150 \) Torr) at \( z = 8 \) mm found a not dissimilar \( P \)-dependence: [NH(\( v = 0 \)] (\( z = 8 \) mm) \( \approx 7.2 \times 10^{11} \times (P/1500)^{1.17} \) (figure S4 in the ESI [21]).

### 3.3.4. H\(_2\)CN (\( x = 0–2 \)) production and loss reactions and the non-local global balance of HCN in MW activated CVD reactors

Table 2 and the foregoing discussion show net conversion of NH\(_3\) radicals via N/C coupling reactions (e.g. CH\(_2\) + NH\(_3\), C\(_2\)H\(_4\) + NH\(_3\), CH\(_3\) + N\(_2\)) into H\(_2\)CN (\( x = 0–2 \)) species, particularly HCN. The concentration of this stable product exceeds the sum of all NH\(_3\) concentrations and the CN concentration by an order of magnitude in the hot plasma core and by several orders of magnitude in the off-core regions for all N/C/H mixtures investigated. Fast H-shifting reactions establish the following partitioning within the H\(_2\)CN family: [H\(_2\)CN] \( \ll \) [CN] \( \ll \) [HCN] [21]. The global balance of the H\(_2\)CN family (and the minor related species: H\(_2\)C\(_2\)NH, H\(_2\)CHNH, H\(_3\)CN) is highly non-local: fast production reactions in the hot plasma region and slower (but non-negligible) production in the cooler regions are followed by diffusional expansion of these species (mainly HCN) throughout the whole reactor. Without substantial chemical losses of HCN, its total concentration (in the entire reactor volume) rises to an equilibrium level whereupon the HCN outflow from the reactor comes into balance with the global net-production of the H\(_2\)CN family.

### 3.3.5. CN column densities and peculiarities of the CN + H\(_2\) \( \leftrightarrow \) HCN + H conversion

One model has invoked CN radical addition as key in explaining enhanced diamond CVD rates upon adding trace N\(_2\) [30]. The CN concentrations just above the substrate (and throughout the whole reactor volume) are determined by fast exothermic reaction (38), CN + H\(_2\) \( \leftrightarrow \) HCN + H, which is strongly equilibrated with the reverse conversion (−38). As before [21], the measured [CN(\( v = 0 \))] column densities (figure 6) can only be reproduced by invoking an enhanced reverse reaction rate due to a non-thermalized vibrational state population distribution of HCN(v\(_1\), v\(_2\), v\(_3\)) molecules. Support for this assumption comes from previous observations of vibrationally excited HCN(v\(_1\), 0, v\(_3\)), v\(_1\) + v\(_3\) > 0 products in reaction (38) [74] and theoretical predictions that HCN vibrational excitation enhances the rate of reaction (−38) [75]. To reproduce the measured [CN(\( v = 0 \))(\( z \)) column densities in the present 2D modeling (figure 6), it is necessary to increase the rate coefficient \( k_{38a} \) by reducing the activation energy from \( E_a \approx 2.92 \) eV (derived using the recommended value for \( k_{38a} \) [67] and the relevant thermochemical data) to ~0.77 eV, i.e. by an amount less than the energy of the nascent vibrationally excited HCN(v\(_1\), 0, v\(_3\))) products of the forward reaction (38). Some fraction of these product molecules will relax via V−T ET, but a comparable fraction will have a chance to undergo the fast reverse reaction (−38).

The predicted trends in [CN(\( v = 0 \))] with changes in process conditions are in quantitative accord with the earlier CRDS measurements [21]. The [CN(\( v = 0 \))] values listed in table 3 generally increase linearly with \( X_0(N_2) \) (rows 1–3, 4–5 and 6, 7 and 9), reflecting the simple relation [CN] \( \sim \) [HCN] \( \times ([H]/[H\(_2\)]) \sim X_0(N_2) \times ([H]/[H\(_2\)])\). Tendencies toward [CN] max saturation are observed, however, in the limits of high N\(_2\) additions (\( X_0(N_2) \gg X_0(CH\(_3\)) \), reflecting a shortage of carbon species, rows 4 and 5) but not at high CH\(_3\) additions (\( X_0(CH\(_3\)) \gg X_0(N_2) \)), rows 6, 7 and 9 in table 3 and figure S3). The rates of the critical reactions (38) and (−38) are
highly equilibrated (table 2) and the calculated pressure dependence $\{CN\}_{\text{max}} \approx 6.5 \times 10^{11} \times (P/150)^{1.1}$ reflects the complex $p$-dependences of all three terms in the relation $[CN] \sim [HCN] \times ([HI]/[H_2]) \times (k_{38}/k_{39})$ and their variation with $r$. For $r = 0$, the calculated $p$-dependences are, respectively, near quadratic for $[HCN]$, $[HI]/[H_2] \sim p^{1.4}$ and, due to the variations in $T_g$, $(k_{38}/k_{39}) \sim p^{0.15}$. This predicted $p$-dependence is similar to, but somewhat steeper than, the observed experimental trend for $\{CN(v = 0)\} (z = 8 \text{ mm}) \approx 5.54 \times 10^{11} \times (P/150)^{1.45}$ (figure S5 in the ESI [21]). A similar analysis of the current model outputs return the following $P$-dependence $\{CN\}_{\text{max}} \sim 6.5 \times 10^{11} \times (P/1500)^{1.85}$ (with the input power $P$ in W), cf. the steeper experimental dependence $\{CN(v = 0)\} (z = 8 \text{ mm}) \approx 5.6 \times 10^{11} \times (P/1500)^{1.07}$ (figure S4 [21]). The different power dependencies (with exponents 1.85 vs 3.27) may indicate that the relative efficiency of the reactive pathways (−38), cf. V−T relaxation of vibrationally excited HCN molecules, increases with $P$. Such could be realized if other collision partners (e.g. H2 molecules) are more efficient than H atoms at driving V−T relaxation of HCN molecules [76]. (The maximal $[HI]/[H_2]$ ratios are nearly linearly proportional to $P$, implying that $[H_2]$ in the plasma core will decrease with increasing $P$.)

3.3.6. CH column densities and peculiarities of $CH + H_2 \leftrightarrow CH_2 + H$ conversion. The literature [77–81] contains a broad spread of values for the rate coefficients of the $^3\text{CH}_2 + H \leftrightarrow \text{CH}_2^* \leftrightarrow \text{CH} + \text{H}_2$ conversions, which determine the CH concentrations under the prevailing conditions. The uncertainty in these rate coefficients hampers interpretation of the measured $\{CH\}$ column densities. That the forward and reverse reactions proceed via an intermediate $\text{CH}_2^*$ complex ensures that their rates are $p$ and $T_g$ dependent [79], suggesting that it may be inappropriate to treat reactions (39) and (40) in table 2 as a simple reversible $^3\text{CH}_2 + H \leftrightarrow \text{CH} + \text{H}_2$ conversion or to estimate the $k_{39}/k_{40}$ ratio from thermochemical data, as in [67]. The present modeling confirms that these conversions should be treated as two separate reactions (39) and (40), with associated rate coefficients measured under similar high $T_g$ conditions. Otherwise, simply assuming the relationship $k_{39}/k_{40} = K_{T_g}$ (thermochemical data) results in a substantial (~three-fold) overestimation of the calculated $\{CH(v = 0)\}$ column density (cf that measured by CRDS, as discussed in the supplementary information of [39]).

The literature values for $k_{40}$ are broadly self-consistent [78–80] and similar to the $k_{40} = 2.39 \times 10^{-10} \times \exp(-1760/T_g) \text{ cm}^3 \text{s}^{-1}$ dependence listed in table 2. The reported values of $k_{39}(^3\text{CH}_2 + H \rightarrow \text{CH} + \text{H}_2)$ at high gas temperatures $T_g \approx 1500–3000 \text{ K}$, in contrast, vary by more than an order of magnitude (from a low value of $1.3 \times 10^{-11} \text{ cm}^3 \text{s}^{-1}$ in [77], up to $\sim2 \times 10^{-10} \text{ cm}^3 \text{s}^{-1}$ [79]). The low value [77] is noteworthy in that it was measured at the high gas temperatures of current interest. This stimulated us to recalculate (again using a 0D model and the full C/H/O GRI Mechanism [67]) the kinetic data from the Frank et al experiments at $T_g = 1670, 2205$ and 2240 K (figures 3, 5 and 6 from [77]) to explore the correlations with measured $[\text{HI}(i)]$ and $[\text{CO}(i)]$. This re-evaluation, summarized in section S3 of the ESI, shows that the measured data can be accommodated with an increased value of $k_{39} = 6.28 \times 10^{-11} \text{ cm}^3 \text{s}^{-1}$ that is more consistent with the other available data. As figure 6 shows, using this value (listed in table S1) in the current 2D modeling yields similar maximal $\{CH(v = 0)\}$ column densities to those measured experimentally [21] but the calculated $\{CH(v = 0)\}$ profile peaks at higher $z$ than the measured profile.

The $\{CH\}_{\text{max}}$ values listed in table 3 are almost independent of $X_0(\text{N}_2)$ (compare rows 1–3 and 6, 7 and 9) and show only minor drops at extreme $X_0(\text{N}_2)/X_0(\text{CH}_4)$ ratios $\gg 1$ (rows 4 and 5). $\{CH\}_{\text{max}}$ shows an $X_0(\text{CH}_4)$ dependence that is slightly less steep than a square root dependence (compare rows 4, 2 and 9). The reasons for this (particularly the deduced relation $[\text{CH}_2] \sim (X_0(\text{CH}_4))^{1/2}$) have been detailed previously.

Figure 6. Measured (by CRDS [21]) and calculated $\{CH(v = 0)\}(z)$ and $\{CN(v = 0)\}(z)$ column density profiles for an MW activated 4% CH4/0.6% N2/H2 gas mixture at base conditions ($p = 150 \text{ Torr}, P = 1.5 \text{ kW}$).
The rates of fast and critical reactions (39) and (40) are in near balance (table 2), with the mis-balance (less than 10%) accommodated by the $^1\text{CH}_2 + \text{H} \leftrightarrow \text{CH} + \text{H}_2$ reaction (which is not of sufficient importance under the present conditions to merit inclusion in table 2). Similar to $\{\text{CN}\}_{\text{max}}(p)$, the calculated pressure dependence $\{\text{CH}\}_{\text{max}} \approx 3.4 \times 10^{12} \times (p/150)^{2.25}$ cm$^{-2}$ (with $p$ in Torr, table 3) is induced by the complex $p$-dependences of all three terms in the relation $[\text{CH}] \sim [^3\text{CH}_2] \times ([\text{H}] / [\text{H}_2]) \times (k_{39}/k_{40})$. This predicted $p$-dependence is in good agreement with the experimental results for $[\text{CH}(v = 0)](z = 8$ mm) $\approx 3.4 \times 10^{12} \times (p/150)^{2.25}$ cm$^{-2}$ (figure S5). A similar analysis returns the predicted $P$-dependence $\{\text{CH}\}_{\text{max}} \sim 3.4 \times 10^{12} \times (P/1500)^{1.3}$ cm$^{-2}$ (with the input power $P$ in W) which, again, compares well with that found experimentally: $[\text{CH}(v = 0)](z = 8$ mm) $\approx 3.35 \times 10^{12} \times (P/1500)^{1.5}$ cm$^{-2}$ (figure S5). We caution that the real $p$ and $P$ dependences will surely be more complex than the simple exponential functions assumed here, which have been used simply to illustrate the observed trends.

4. Summary of main differences between present and previous modeling

Before progressing to discussing the potential role(s) of nitrogen in enhancing diamond CVD rates it is worth summarizing the key differences introduced in the present 2D modeling. The charged species distributions and their maximal concentrations are most affected by the transition from the earlier non-self-consistent model [20, 21] (which employed an externally specified plasma volume for indirect determination of the reduced electric fields) to the present model. The self-consistent calculation of the electromagnetic fields ($E(r, z)$ and $H(r, z)$) along with the full plasma-chemical kinetics has resulted in some radial confinement of the glowing plasma volume, which is now more spherical and more localized above the substrate holder as illustrated by the false color plot of the $(r, z)$ distribution of the electron concentration $n_e$ in figure 7. This change, along with the introduction of the effective electron–molecule collision frequencies, $v_{\text{eff}}$, has resulted in increases in the calculated input power densities (PDs) and maximal electron and ion concentrations.

Our recent self-consistent modeling of $\text{H}_2$ and $\text{H}_2/\text{Ar}$ plasmas [37, 38], with simultaneous calculations of EEDFs throughout the whole reactor, has led to some refinements of the plasma-chemical kinetics for various excited states of $\text{H}^+$, $\text{H}_2^+$ (and $\text{Ar}^+$) and identified AI reactions of $\text{H}(n \geq 2)$ atoms with $\text{H}_2$ and $\text{H}(n = 1)$ as important additional ionization sources. The $\text{N}/\text{H}$ and $\text{N}/\text{C}/\text{H}$ reaction mechanisms used in the present modeling have been expanded and refined, and the $T_{\beta}$- (as well as the $T_{\alpha}$-) dependences of the electron–ion dissociative recombination coefficients are now explicitly included. All of these modifications have resulted in changes to the previously predicted [20, 21] plasma parameters and species concentration distributions. Arguably the most significant change is in the maximal electron concentration $n_{e,\text{max}}$, which is now predicted to reach $\sim 6.3 \times 10^{11}$ cm$^{-3}$ for a 0.6% $\text{N}_2/\text{H}_2$ mixture operating at base pressure $p = 150$ Torr and input power $P = 1.5$ kW (cf $n_{e,\text{max}} \sim 2 \times 10^{11}$ cm$^{-3}$ in [21]).

This predicted increase maps through into higher maximal gas temperatures ($T_{\text{g,\text{max}}}$ $\sim 3170$ K, cf $\sim 2900$ K in the previous modeling). Similar changes for these parameters are also observed for other $x\% \text{N}_2/4\% \text{CH}_4/\text{H}_2$ mixtures and in the $\text{N}/\text{H}$ plasma modeling. Reassuringly, we note that Derkaoui et al. [82] have reported very similar electron densities ($n_e \sim (7 \pm 2) \times 10^{11}$ cm$^{-2}$, measured using a 35.2 GHz MW interferometer) and temperatures ($T_e \sim 1.18 \pm 0.07$ eV, estimated from the ratio of $\text{H}_2/\text{H}_\alpha$ emission intensities) in MW activated 4% $\text{CH}_4/\text{H}_2$ plasmas operating under similar conditions ($p \sim 150$ Torr, $P = 3$ kW) to the calculated values reported in table 2 and figure 7.

5. Nitrogen-containing species just above the substrate and the effects of nitrogen on diamond growth

These refinements of the N/C/H plasma modeling all serve to reinforce previous conclusions [21] regarding the relative abundances of different N-containing species just above the growing diamond surface. The present 2D modeling reiterates that most (~99.7%) of the trace amount of $\text{N}_2$ introduced in the process gas mixture is immune to chemical processing under the MW plasma conditions prevailing in typical diamond CVD reactors and passes through the reactor unaltered. But a small fraction (~0.3%) of the input $\text{N}_2$ undergoes chemistry, primarily via reaction with $\text{CH}_3$ ($x = 0, 1$) species or (when electronically excited) with $\text{H}$ atoms. Further bimolecular collisions lead to a dilute ‘soup’ of N-containing (NH$_x$ ($x = 0–3$) and HCN ($x = 0–2$) species, among which the stable HCN molecule is dominant (accommodating almost all the decomposed nitrogen), with all other N-containing species two or more orders of magnitude less abundant still.
Figure 7 shows, in the form of false color (r, z) plots, the spatial distributions of the electrons and of three of the more abundant and potentially more reactive N-containing species at the growing diamond surface (N atoms, and NH and CN radicals) returned by the present 2D modeling for an MW activated 0.006% N2/4% CH4/H2 gas mixture operating in the Bristol CVD reactor at \( p = 150 \) Torr and \( P = 1.5 \text{ kW}. \) This gas mixture equates to 60 ppm N2 content, which has been shown to be sufficient to significantly enhance the growth rates of both polycrystalline and SCD by MW plasma assisted CVD methods. Necessarily, the precise form of the distributions shown in figure 7 will be reactor specific (reflecting, e.g. the spatial dependences of the electric fields, \( T_e, \) etc), but nothing in the present modeling contradicts the previous conclusions that the N atom concentration just above the growing diamond surface will be at least an order greater than that of CN, NH (or NH3). For example, the calculated concentrations of these species at \( r = 0, \ z = 0.5 \text{ mm} \) for the conditions shown in figure 7 are \([N] = 1.8 \times 10^4 \text{ cm}^{-3}, [NH] = 7.4 \times 10^4 \text{ cm}^{-3}, [NH_2] = 8.4 \times 10^5 \text{ cm}^{-3}\) and \([CN] = 6.9 \times 10^7 \text{ cm}^{-3}. \) Among this sub-set, the prevalence in favor of N atoms is even greater than predicted in our previous modeling [21] and this bias will only increase further upon approaching the substrate due to the sharp thermochemically driven increase of \([\text{N}](\text{z})\) as \( z \to 0 \) [20]. The current modeling shows that the fractionation among these various potentially active N-containing species is also independent of the chosen \( X_0(\text{N}_2) \) value. For completeness, we also note that the concentration of N atoms in the lowest metastable (2D) state (calculated here as a balance between EIE-induced pumping \( N + e \to N(2D) + e \) and \( N(2D) \) quenching by collision with H2 molecules, \( N(2D) + H_2 \leftrightarrow NH + H \)) are far too low to be important (e.g. \([N(2D)] = 6 \times 10^5 \text{ cm}^{-3} \) at \( r = 0, \ z = 0.5 \text{ mm} \) for the 0.006% N2/4% CH4/H2 gas mixture at base pressure and power).

Armed with this information, we return to the longstanding and intriguing issue of how and why small (even down to the level of a few ppm) additions of N2 (or other N-containing sources, e.g. NH3) to the base C/H plasma can lead to significantly enhanced CVD diamond growth rates, \( G \) [1–17]. Is there a key N-containing species that catalyzes growth? The near-surface relative abundances predicted here and previously [21] and the demonstrated availability of energetically plausible N atom incorporation pathways [22] encourage suggestions that N atoms are the most likely species responsible for the measured enhancement of \( G. \) As noted above, however, a CN-radical catalyzed scheme wherein an N-containing four-atom cluster nucleates (and thereby accelerates) growth on the diamond (111) surface has been proposed also [30], and Zaitsev et al [16] have suggested that \( G \) may be enhanced by the incorporation of N-terminated carbon nanoclusters formed in the plasma.

The relative concentrations of these various ‘active’ nitrogen species are all low. In the standard model of CVD diamond growth, \( G \) is determined by the incorporation rate of carbon incident in the form of CH3 radicals [23–25]. Thus, a key metric is the ratio of the concentrations of gas phase active nitrogen species to that of CH3 radicals incident on the growing surface. The present 2D modeling of the 0.006% N2/4% CH4/H2 plasma (i.e. a plasma containing 60 ppm of N2) returns \([N](\text{CH}_3) \sim 2 \times 10^{-5} \text{ at } r = 0, \ z = 0.5 \text{ mm} \). The calculated \([CN]/[CH_3]\) ratio at this position is \( \sim 25 \) times lower and the different \( T_e \)-dependences of \([N]\) and \([CN]\) will ensure that this relative difference becomes yet larger as \( z \to 0 \). The present plasma chemical calculations are silent on carbon nano-clusters.

These small \([N]/[\text{CH}_3]\) and \([CN]/[\text{CH}_3]\) ratios serve to emphasize the on-going curiosity as to how such a low fraction of incident active nitrogen species can enhance \( G \) for both single crystal [13] and polycrystalline [12] diamond by factors of 5 or more. Is there a dominant nitrogen-promoted growth mechanism, and is it necessarily the same for both material types? The more plausible scenarios assume that an incorporated N-atom (or N-containing species) acts as an ‘anchor’ site that boosts the local probability of carbon incorporation relative to that prevailing in nitrogen-free surface regions. This is the principle underlying both the proposed CN-radical catalyzed scheme for growth on the diamond (111) surface [30] and the recent findings of Oberg et al [31] that carbon insertion into a ‘C–N dimer’ bond (the N-analogue of the C–C dimer bond on the C(100))/H2 x 1 diamond surface) has significantly reduced energy requirements (cf the standard all carbon analogue) and could result in a \( \sim 400\)-fold increase in the rate of the key dimer ring-opening, ring-closing carbon insertion process.

In both cases, the presence of the N-containing group is proposed to immobilize adjacent CH2 groups on the diamond surface and thereby facilitate the growth of small islands that can act to nucleate next layer growth and provide step-edges at which surface migrating CH2 groups can accommodate, rather than these being etched (by H atoms) during the typically more extended migration required under N-free conditions. The present 2D modeling shows no discernible violations of plasma parameters or deposition conditions (e.g. CH3 radical and H atom concentrations just above the substrate, and the fraction of radical surface sites, \( C^* \)) upon trace (i.e. \( \sim \text{hundreds ppm} \)) additions to N2 to the process gas mixture. The deduced preservation of deposition conditions together with the ‘anchor’ effect imply that the observed substantial increases in \( G \) upon minor additions of N2 is likely attributable to the reduced probability that surface migrating CH2 groups will be etched during their random walk prior to accommodating at such islands. The low growth rate in N-free conditions, in comparison with the saturated or maximal rates (e.g. \( G(X_0(\text{N}_2) = 0) \sim 0.1 \times G(X_0(\text{N}_2) \sim 100 \text{ ppm}) [12] \)), would be realized if the vast majority (e.g. \( \geq 90\% \)) of surface CH2 groups deriving from the initially adsorbed CH3 radicals are etched back into the gas phase. In contrast, under saturated conditions \( X_0(\text{N}_2) \geq 100 \text{ ppm} \), a much higher (by an order of magnitude) fraction of the surface CH3 groups would successfully reach the nearby anchor sites (or the pre-extended islands) and be irreversibly accommodated.

Increasing \( X_0(\text{N}_2) \), under otherwise constant process conditions, will increase the near surface concentrations of all gas phase N-containing reactant species (recall table 3) and thus, plausibly, the density of N-based surface anchor sites and the re-nucleation rate—consistent with reported increases in the
surface roughness of material grown from process gas mixtures containing a higher N₂ fraction [7, 12, 13]. The finding that increasing $P$ allows use of a higher $X_0$($N_2$) fraction before the onset of discernibly lower-quality diamond growth (at least in the case of PCD) [12] can be traced to the increase in $[H_{ns}]$ with increasing $P$. Higher $[H_{ns}]$ increases the etching rate of surface adsorbed species, particularly species assembled into non-diamond phases.

Figure 8 shows that the present 2D modeling of the Bristol reactor predicts that the ns N atom and CN and CH₃ radical concentrations all show marked radial dependences. The $[N](r, z = 0.5 \text{ mm})$ distribution under base conditions (figure 8 and table 3) is predicted to maximize at $r = 0$ and drop by more than an order of magnitude by the edge of the substrate ($r = 16 \text{ mm}$), the $[CN](r, z = 0.5 \text{ mm})$ distribution shows a similar though less steep radial profile, whereas the $[CH_3](r, z = 0.5 \text{ mm})$ distribution shows the opposite dependence, increasing ~four-fold between $r = 0$ and $r = 16 \text{ mm}$. As figure 8 also shows, these differences are exacerbated by increasing $P$ (which leads to a contraction of the whole plasma volume [40] as illustrated in figure S12), leading to even greater radial variations in the near-substrate $[N]/[CH_3]$ (and $[CN]/[CH_3]$) ratios—which should be expected to map through as $r$ dependent N incorporation efficiencies in any large area diamond sample grown under such conditions.

Note, these predictions are reactor specific, and need not be such an issue in contemporary reactors operating at higher $P$. Additionally, as noted previously, growth rates and material quality depend on, but are not determined solely by, the local N (and/or CN) and CH₃ concentrations. Other quantities, notably $[H](r, z = 0.5 \text{ mm})$ and $T_s$, will also be critical in determining the radial uniformity of the as-grown material.
As figure 8(b) shows, both the magnitude and the radial variation of [H](r, z = 0.5 mm) are predicted to increase markedly with increasing p. The total power loading to the substrate, $P_s$, and $T_s$ are also both predicted to increase strongly with $p$: $P_s = 284, 395, 461, 542$ W and $T_s = 840, 1015, 1120, 1265$ K, for $p = 100, 150, 200, 350$ Torr, respectively. The main contribution to substrate heating is conduction from the hot gas, but H atom adsorptions at C* sites become increasingly important at higher $p$. The present modeling suggests that the latter process contributes, respectively, 13, 21, 27, 32% to $P_s$ at $p = 100, 150, 200, 350$ Torr. Sources of substrate heating and typical gas-surface loss probabilities of ~0.1 for incident H atoms (from H addition and H abstraction reactions at the substrate surface) have been discussed previously (e.g. [62, 64]), as has the reduction of gas phase [H] (along with the much smaller drop in [CH3]) from such gas–surface processes (section 3.4.2 of [40]).

Clearly, how trace N2 additions to a CH4/H2 process gas mixture promotes diamond growth remains an on-going issue. The present study provides the most comprehensive picture yet available for the gas phase processing induced by MW plasma activation and the relative abundances of potentially reactive N-containing species just above the growing diamond surface, and one can be reasonably confident about extrapolating the present plasma chemical modeling to other reactor geometries and process conditions. Both the gas–surface chemistry involved in N incorporation and the full range of ways in which incorporated N atoms (or N-containing moieties) promote carbon incorporation requires further study, however, and more experimental growth studies under well characterized process conditions, preferably with detailed characterization of the as-grown material would also be very beneficial.

6. Conclusions

2D self-consistent modeling of MW plasma activated N/H and N/C/H gas mixtures, using an extended N/C/H plasma chemistry mechanism, operating at input powers are pressures relevant to contemporary diamond CVD confirm and extend many of the conclusions reached in previous non-self-consistent modeling. The current modeling confirms that most (~99.7%) of the input N2 eludes chemical processing and is exhausted unaltered from the reactor. However, a small fraction of the input N2 reacts, primarily via reaction with CHx ($x = 0, 1$) species or (when electronically excited) with H atoms. This triggers a sequence of reactions that result in a dilute ‘soup’ of N-containing (NHx, ($x = 0–3$) and HxCN ($x = 0–2$)) species, among which the stable HCN molecule is dominant. The near surface N atom concentration is calculated to be at least one order of magnitude larger than that of other potentially reactive N-containing species like NH, NH2 or CN. The near-surface gas phase [N]/[CH3] and [CN]/[CH4] concentration ratios under base conditions are shown to scale with the N/C ratio in the input gas mixture, and both ratios increase with increasing pressure or MW power. Nonetheless, the near-surface [N]/[CH3] ratios are so low (e.g. $\sim 2 \times 10^{-5}$ for a not atypical 4% CH4/H2 plasma with 60 ppm added N2 operating under base $p$ and $P$ conditions for the Bristol reactor) that it remains challenging to envisage a mechanism wherein the incorporation of such small concentrations of any N-containing precursor can result in up to an order of magnitude increases in growth rate. The current discussion supports the view that an N-containing species on the diamond surface can act as an anchor site, that boosts the local probability of carbon incorporation (relative to that prevailing in N-free surface regions) and thereby facilitates growth of a small island that acts to nucleate next layer growth and provide step-edges at which surface migrating CH2 groups can accommodate. The low growth rates under N-free conditions (i.e. $G(X_0(N_2) = 0) \ll G(X_0(N_2) > 100$ ppm)) could be understood if the large majority of the surface CH2 groups produced from the initially adsorbed CH2 radicals are etched back into the gas phase whereas, under ‘saturated’ conditions (e.g. $X_0(N_2) > 100$ ppm), a much higher fraction of these migrating surface CH2 groups succeed in reaching the nearby anchor sites (or the pre-extended islands) and are irreversibly accommodated.

Acknowledgments

MNRA is grateful to many past research group members who helped in gathering the experimental data against which the current self-consistent 2D model outputs are tensioned. YuAM acknowledges support from RFBR for Grant No. 19-08-01250. The work was performed within the Cooperation in Science and Technology Agreement between Lomonosov Moscow State University, Skobeltsyn Institute of Nuclear Physics, and the University of Bristol.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Conflict of interest

The authors declare no conflict of interest.

ORCID iDs

Michael N R Ashfold  https://orcid.org/0000-0001-5762-7048
Yu A Mankelevich  https://orcid.org/0000-0002-7383-1396

References

[1] Locher R, Wild C, Herres N, Behr D and Koidl P 1994 Appl. Phys. Lett. 65 34–6
[2] Jin S and Moustakas T D 1994 Appl. Phys. Lett. 65 403–5
[3] Samlenski R, Haug C, Brenn R, Wild C, Locher R and Koidl P 1995 Appl. Phys. Lett. 67 2798–800
[4] Müller-Siebert W, Wörner E, Fuchs F, Wild C and Koidl P 1996 Appl. Phys. Lett. 68 759–60
[68] Manion J A NIST Chemical Kinetics Database, NIST Standard Reference Database 17, Version 7.0 (Web Version), Release 1.6.8, Data version 2015.09, National Institute of Standards and Technology, Gaithersburg, Maryland NIST kinetics database (https://kinetics.nist.gov/kinetics/Search.jsp)

[69] Loison J-C, Wakelam V and Hickson K M 2014 Mon. Not. R. Astron. Soc. 443 398–410 and references therein

[70] Cimas A and Largo A 2006 J. Phys. Chem A 110 10912–20

[71] Pearce B K D, Ayers P W and Pudritz R E 2019 J. Phys. Chem A 123 1861–73

[72] Davidson D F and Hanson R K 1990 23rd Int. Symp. Combustion (The Combustion Institute) pp 267–73

[73] Faßheber N, Bornhorst L, Hesse S, Sakai Y and Friedrichs G 2020 J. Phys. Chem A 124 4632–45

[74] Bethardy G A, Northup F J, He G, Tokue I and Macdonald R G 1998 J. Chem. Phys. 109 4224–36

[75] Takayanagi T and Schatz G C 1997 J. Chem. Phys. 106 3227–36

[76] Cannon B D, Francisco J S and Smith I W M 1984 Chem. Phys. 89 141–50

[77] Frank P, Bhaskaran K A and Just T 1986 J. Phys. Chem. 90 2226–31

[78] Zabarnick S, Fleming J W and Lin M C 1986 J. Chem. Phys. 85 4373–6

[79] Fulle D and Hippler H 1997 J. Chem. Phys. 106 8691–8

[80] González M, Saracibar A and Garcia E 2011 Phys. Chem. Chem. Phys. 13 3421–8

[81] Garcia E, Jambrina P G and Laganà A 2019 J. Phys. Chem A 123 7408–19

[82] Derkaoui N, Rond C, Gries T, Henrion G and Gicquel A 2014 J. Phys. D: Appl. Phys. 47 205201