Optical Emission from C\textsuperscript{2−} Anions in Microwave-Activated CH\textsubscript{4}/H\textsubscript{2} Plasmas for Chemical Vapor Deposition of Diamond

E. J. D. Mahoney, † B. S. Truscott, † M. N. R. Ashfold, ‡ and Yu. A. Mankelevich*,‡

1School of Chemistry, University of Bristol, Bristol, U.K. BS8 1TS
2Skobeltsyn Institute of Nuclear Physics, Lomonosov Moscow State University, Leninskie gory, Moscow 119991, Russia

ABSTRACT: Visible emission from C\textsuperscript{2−}(B\textsuperscript{3}Σ\textsuperscript{u+}) anions has been identified underlying the much stronger Swan band emission from neutral C\textsubscript{2}(d\Pi\textsubscript{g}) radicals (henceforth C\textsuperscript{2−} and C\textsuperscript{2+}, respectively) in MW-activated C/H/(Ar) plasmas operating under conditions appropriate for the chemical vapor deposition (CVD) of diamond. Spatially resolved measurements of the C\textsuperscript{2−} and C\textsuperscript{2+} emissions as functions of the C/H/(Ar) ratio in the input gas mixture, the total pressure, and the applied MW power, together with complementary 2-D(r, z) plasma modeling, identifies dissociative electron attachment (DEA) to C\textsubscript{2}H radicals in the hot plasma as the dominant source of the observed C\textsuperscript{2−} emission. Modeling not only indicates substantially higher concentrations of C\textsubscript{2}H\textsuperscript{−} anions (from analogous DEA to C\textsubscript{2}H\textsubscript{2}) in the near-substrate region but also suggests that the anion number densities will typically be 3–4 orders of magnitude lower than those of the electrons and partner cations, i.e., mainly C\textsubscript{2}H\textsuperscript{+} and C\textsubscript{2}H\textsubscript{3}\textsuperscript{+}. The identification of negatively charged carbon-containing species in diamond CVD plasmas offers a possible rationale for previous reports that nucleation densities and growth rates can be enhanced by applying a positive bias to the substrate.

1. INTRODUCTION

Optical emission spectroscopy (OES) has found widespread use as a relatively straightforward and easy-to-implement probe of DC arc-jet and microwave (MW) plasmas used for the chemical vapor deposition (CVD) of diamond. Species amenable to study in this way in traditional dilute carbon/hydrogen (C/H) plasmas include electronically excited H atoms (via the Balmer emissions), H\textsubscript{2} molecules (typically via lines within the Fulcher system), and CH and C\textsubscript{2} radicals. To this list can be added electronically excited Ar atoms (when Ar is added to the process gas mixture), CN and N\textsubscript{2} (when N\textsubscript{2} is present, either by design or as an impurity), CN and N\textsubscript{2} and BH (if a B-containing dopant is added), B and BH (if a B-containing dopant is added), CN and N\textsubscript{2} and OH and CO (when, for example, CO\textsubscript{2} is used as the carbon source). The emitting species are generally formed by electron impact excitation (EIE) either of the corresponding ground-state species, or of a low-lying excited state in the case of C\textsubscript{2}. Thus, the emission intensities are sensitive not just to the respective lower state populations but also to the electron temperature, \textit{T}_{\text{e}}, and number density, \textit{n}_{\text{e}}, and the variation of all of these quantities with changes in process conditions, e.g., in the gas composition and mixing ratio, total pressure \textit{p}, applied MW power \textit{P}, sign and magnitude of any substrate bias voltage, etc., and with location within the plasma volume. Several studies have investigated the correspondence (or otherwise) between measured OES intensities and absolute densities measured by absorption methods. OES measurements made with high spectral resolution can provide estimates of the temperature of the emitting species, either through the measured Doppler broadening of a single spectral line (e.g., of the H Balmer-\alpha line) or from the relative intensities of a series of rotational lines in, for example, the emission spectrum of H\textsubscript{2} or C\textsubscript{2}. Given the typical pressures prevailing in these plasmas, excited-state temperatures determined in this way are generally considered reliable proxies for the local gas temperature, \textit{T}_{\text{g}}.

Electron impact excitation is the dominant, but not the sole, mechanism by which emission species arise in MW-activated gas mixtures used for diamond CVD. Spatially resolved measurements of both the BH radical emission in MW-activated B\textsubscript{2}H\textsubscript{6}/H\textsubscript{2}/(Ar) gas mixtures and the CH and C\textsubscript{2} emissions from MW-activated CH\textsubscript{4}/CO\textsubscript{2}/H\textsubscript{2} plasmas reveal chemiluminescence from these species, formed as products of exothermic atom-radical and radical-radical reactions, most clearly in regions of low electron density at the periphery of the plasma. Resonant collisional energy transfer from metastable triplet CO molecules in C/H/O plasmas has also been proposed as a contributor to the observed OH emission.

Received: January 25, 2017
Revised: March 10, 2017
Published: March 20, 2017

DOI: 10.1021/acs.jpca.7b00814
Here we report the first identification of optical emission from the electronically excited \( C_2^- (B^2\Sigma_g^+) \) anion (henceforth \( C_2^- \)) in a MW-activated C/H/(Ar) plasma operating under conditions appropriate for diamond CVD. To the best of our knowledge, this is the first charged species (anion or cation) to be observed by OES in such plasmas. The finding is noteworthy for several reasons. One centers on the \( C_2^- \) production mechanism, which we deduce to be dissociative electron attachment (DEA) to the \( C_2 \) radical on the basis of plasma-chemical modeling. This modeling is informed by spatially resolved OES measurements comparing the variation of the optical emissions from \( C_2^- \) and from neutral \( C_2 \) radicals in their \( d^3\Pi_g \) state (henceforth \( C_2^* \)) with the \( C/H/(Ar) \) ratio in the input process gas mixture, the total pressure, and the applied MW power. Second, the presence of anions may have implications for the detailed modeling of such plasmas. Previous analyses of MW-activated C/H/(Ar) containing plasmas \(^{60,61}\) have assumed that the negatively charged particles partnering the cations (assumed to be mainly \( C_2H_2^+ \) and \( C_2H_3^+ \) in our previous work \(^{60}\)) are exclusively electrons. Lastly, the presence of negatively charged carbon-containing species in diamond CVD plasmas offers a possible rationale for previous findings that nucleation densities and growth rates can be enhanced by applying not just a negative \(^{14,46,65}\) bias voltage to the substrate.

2. EXPERIMENT

The experiments employ the previously described MW plasma-activated (PA) CVD reactor \(^{64}\) with a new setup for imaging the optical emission from the plasma. Base conditions were chosen as \( P = 1.5 \) kW and \( p = 150 \) Torr, with flow rates \( F(CH_4) = 19 \) standard cm\(^3\) per minute (sccm) and \( F(H_2) = 300 \) sccm (i.e., 6\% \( CH_4 \) in \( H_2 \)). Power, pressure, and \( F(CH_4) \) were varied individually over the respective ranges \( 0.7 \leq P \leq 1.86 \) kW, \( 50 \leq p \leq 275 \) Torr, and \( 2 \leq F(CH_4) \leq 30 \) sccm, while keeping the other parameters at their base values. The effect of adding Ar to the process gas mixture was investigated over the range \( 0 \leq F(Ar) \leq 60 \) sccm, with \( F(H_2) \) reduced in a compensatory way so as to ensure that \( F(H_2)+F(Ar) = 300 \) sccm.

Optical emission from the plasma was coupled into a Czerny–Turner spectrograph (Newport MS127i) using a 250 mm focal length, \( f/6 \) objective lens and dispersed using an 1800 grooves \( mm^{-1} \) grating, yielding a spatial resolution of \( 0.5 \) mm and a spectral resolution of \( \approx 0.11 \) nm (full width at half-maximum, fwhm) when a 13 \( \mu \)m entrance slit is used. The effects of adding Ar were investigated at lower spectral resolution (25 \( \mu \)m entrance slit) wherein, under base conditions, the recorded \( C_2^* (0,0) \) and \( C_2^- (0,0) \) emission intensities, henceforth \( I_{mm}(C_2^*) \) and \( I_{mm}(C_2^-) \), were both increased \( \approx 2\)-fold. The diffracted radiation was imaged onto a cooled CCD detector (Andor Newton 970) with an overall spatial magnification of \( \approx 0.1 \), and each image was scaled to the equivalent of a 2048 s. accumulation for direct comparability of the intensities. The lens aperture was closed right down in these studies, so the data reported here effectively include emission from the whole thickness of the plasma.

3. RESULTS AND DISCUSSION


After a number of low-resolution survey scans, attention was concentrated on the wavelength range 489–566 nm, which under the present conditions is dominated by the \( \Delta \nu = 0 \) and \( \Delta \nu = -1 \) progressions of the \( C_2^* (d^3\Pi_g^+ \rightarrow a^3\Pi_u) \) transition but also includes the much weaker \( C_2^- (B^2\Sigma_u^- \rightarrow X^2\Sigma_g^+) \) \( \Delta \nu = 0 \) emission of current interest. The measured images comprise spatially and wavelength-resolved emission intensities \( I_{mm}^z(\lambda, \nu) \).

![Figure 1](image-url) shows an illustrative image recorded under base conditions, after postprocessing to correct for vertical skew in the raw image. The height scale spans the range \( -3 \leq z \leq 27 \) mm, where \( z = 0 \) corresponds to the substrate surface and the scale is calibrated by imaging a test target placed at the substrate center position. The spectroscope parameters for the \( d^3\Pi_g \) and \( a^3\Pi_u \) states of \( C_2 \) are known to sufficient precision that fitting to the \( C_2(d-a) \) line positions calculated using PGOPHER \(^{66}\) constitutes the best means of calibrating the wavelength scale.

Figure 2a shows the \( I_{mm}(\lambda) \) plot obtained by binning all intensity values measured for the range \( 9 \leq z \leq 12 \) mm in the image shown in Figure 1, along with a best-fit simulation of the relevant part of the \( C_2(d-a) \) spectrum that assumes that each spectral feature is broadened with a Gaussian line shape having \( 0.11 \) nm fwhm. The fit returns a rotational temperature \( T_{rot} = 2900 \) K, in good accord with previous studies of such plasmas in this reactor \(^{62,59,64}\) and supports the assumption that the rotational population distribution in the emitting state is in local thermodynamic equilibrium. The (observed – calculated) difference plot over the limited wavelength range shown in Figure 2b highlights an obvious feature around 541.5 nm, which matches with the P-band head of the \( C_2^- (B^2\Sigma_u^- \rightarrow X^2\Sigma_g^+) \) (Herzberg–Lagervist system) \(^{67}\) \( (\nu' = 0 \rightarrow \nu'' = 0) \) transition. The PGOPHER simulation of both this and the overlapping (1,1) band using the appropriate spectroscopic constants \(^{68}\) and \( T_{rot} = 2900 \) K is shown in Figure 2c; nuclear spin statistics account for the absence of alternate lines in each branch. Many previous studies have reported optical emission...
in this spectral region from similar MW activated gas mixtures but, as far as we can see, none have been recorded with sufficient spectral resolution/signal-to-noise ratio or analyzed in sufficient detail to reveal the weak C2⁻⁺⁺ features.

Clearly, the difference plots are very sensitive to the high-ν and high-J tail of the overlapping C2(d–a) Δν = −1 progression, the appearance of which depends on Tgas (which, as before, is assumed to be a reliable measure of Tgas). Tgas peaks in the core of the plasma and decreases both with increasing z and, more steeply, as z → 0.60 Much of the following analysis is based on the relative emission intensities Iem(C2⁺⁺⁺) and Iem(C2⁺⁺), and their variation with spatial position and changes in process conditions. As it is important to separate the relative contributions from the two species as reliably as possible, we analyze the Iem(λ) data using either Δz = 1.5 mm (higher spatial resolution) or Δz = 3 mm (lower resolution) vertical strips, each with its own best-fit Tgas. Under base conditions, for example, the higher resolution analysis shows Tgas ≈ 2750 ± 20 K at z ≈ 2.25 mm, rising to a maximum of ≈2900 ± 20 K at z ≈ 11.25 mm and declining again to ≈2640 ± 30 K at z ≈ 24.75 mm. The comparative intensities presented below are normalized against the respective (0,0) bands in the best-fit PGOPHER simulations, with all other band intensities given by their relative transition probabilities and the vibrational partition function with Trot = Tgas. To convert these intensities to relative excited-state populations requires scaling by the respective Einstein A-coefficients, for which we take 7.63 × 10⁶ s⁻¹ for the C2(d–a) (0,0) band65 and 9.1 × 10⁶ s⁻¹ for the C2⁻⁺⁺(B–X) (0,0) transition. This latter value was derived using literature values for the radiative lifetime of the B(ν′=0) level60,60 and the relevant Franck–Condon factors.70 Thus, if we consider the emission intensities as indicative of relative number densities, the values for Iem(C2⁻⁺⁺) given here should be reduced by a factor of 1.2 to obtain the relative excited-state number densities.

3.2. Trends in C2⁺⁺⁺ and C2⁻⁺⁺ Emission Intensities with Changes in Process Conditions. Figure 3 illustrates the similarity of the Iem(C2⁺⁺⁺) and Iem(C2⁻⁺⁺) profiles, analyzed at the higher spatial resolution, measured at pressures p = (a) 75, (b) 150, and (c) 225 Torr and otherwise base conditions. The respective profiles at any given p are similar, declining to near zero at small and large z. The maxima of both distributions shift to smaller z with increasing p, more noticeably in the case of...
Figure 4. Solid symbols: variation in $I_{em}(C_2^*)$ and $I_{em}(C_2^{-*})$ intensities from the $9 \leq z \leq 12$ mm region from a MW-activated CH$_4$/H$_2$ plasma operating under base conditions of $P$, $F$(CH$_4$), and $F$(H$_2$), plotted as a function of total pressure over the range $50 \leq p \leq 275$ Torr. The intensities so derived have been reduced by a factor of 2 prior to display (on the inner y-axis scales) to allow direct comparison with the values shown in Figure 3. The solid line through the $I_{em}(C_2^*)$ data is a cubic $p$ function, and the solid blue line simply connects the $I_{em}(C_2^*)$ data points. Open symbols: respective $I_{em}(C_2^*)_{calc}$ and $I_{em}(C_2^{-*})_{calc}$ emission rates (outer y-axis scales) returned by the 2-D modeling described in section 3.4.

$I_{em}(C_2^{-*})$, and the profiles visibly narrow. Closer inspection reveals that the ratio of emission intensities is a sensitive function of pressure. As Figure 4 shows, the $C_2^*$ emission intensity observed from the $z = 10.5 \pm 1.5$ mm strip exhibits an approximate $p^3$ dependence, similar to that observed previously over a smaller range of pressures, whereas $I_{em}(C_2^{-*})$ scales near-linearly with $p$. These data have been derived using the lower ($Δz = 3$ mm) spatial resolution, to minimize any effects from the peaks of the respective distributions shifting with $p$. The binned intensities so derived have then been halved prior to display to allow direct comparison with the intensities in the higher resolution ($Δz = 1.5$ mm) profiles shown in Figure 3b.

Panels a and b of Figure 5 show $I_{em}(C_2^*)$ and $I_{em}(C_2^{-*})$ profiles measured at $p = 0.9$ and 1.85 kW, respectively, with all other parameters maintained at their base values and analyzed at the higher ($Δz = 1.5$ mm) spatial resolution. As expected, reducing (increasing) $P$ results in a smaller (larger) emitting volume, and again, the spatial distributions of the two emissions appear similar. Nonetheless, the $I_{em}(C_2^*)/I_{em}(C_2^{-*})$ ratio determined by (lower resolution) analysis of the $z = 10.5 \pm 1.5$ mm strip exhibits a marked $P$-dependence. This is quantified in Figure 6, which shows that (as with $p$, Figure 4) increasing $P$ results in a near-cubic growth in $I_{em}(C_2^*)$, whereas $I_{em}(C_2^{-*})$ shows only a roughly linear increase. Again, the binned intensities have been halved prior to display for direct comparability with the intensities shown in Figures 3 and 5. The spectra also reveal a modest increase in $T_{gas}$ from $\approx 2830$ K at $P = 0.7$ kW to $\approx 2920$ K at $P = 1.85$ kW.

The final variables investigated were $F$(CH$_4$) and $F$(Ar). Figure 7 shows the variations in $I_{em}(C_2^*)$ and $I_{em}(C_2^{-*})$ determined by (lower resolution) analysis of the $z = 10.5 \pm 1.5$ mm strip when (a) $F$(CH$_4$) varies across the range 2–30 sccm (or, in terms of input mole fractions, $0.66 \leq X_0$(CH$_4$) $\leq 9.1\%$) with all other parameters held at their base conditions, and (b) $F$(Ar) varies over the range 0–60 sccm (input mole fractions 0 $\leq X_0$(Ar) $\leq 18.8\%$), with $F$(CH$_4$), $p$ and $P$ fixed at their base values. As Figure 7a shows, both emissions increase linearly at small $F$(CH$_4$) and then somewhat less steeply at higher $F$(CH$_4$). Figure 7b shows that adding Ar also results in (modest) increases in both $I_{em}(C_2^*)$ and $I_{em}(C_2^{-*})$, more so in the former case, such that the $I_{em}(C_2^{-*})/I_{em}(C_2^*)$ ratio increases from $\approx 40$ at $X_0$(Ar) = 0% to $\approx 56$ when $X_0$(Ar) = 18.8%.

3.3. $C_2^{-*}$. Formation Mechanism. We start by reprising some of the plasma characteristics established in our previous optical diagnosis and modeling studies of dilute CH$_4$/H$_2$ plasmas produced in this same CVD reactor at equivalent (base) power and pressure. The supplied MW power is expended mainly on gas heating by rotational and vibrational excitation of H$_2$ and C$_2$H$_6$ species by electrons driven in the MW field, with subsequent vibrational- and rotational-to-translational ($V \rightarrow T$ and $R \rightarrow T$) energy redistribution, and by elastic collisions of electrons with atoms and molecules.

The gas temperature in the plasma core is $T_{gas} \approx 2900$ K, resulting in an [H]$e(z,r)$ distribution as shown in Figure 8a, a maximal H atom density [H] $\approx 4.4 \times 10^{16}$ cm$^{-3}$, and an H atom mole fraction X(H) $\approx 9.1\%$. These H atoms participate in
I and larger species, depending on the local
z
C2H2 is the most stable carbon-containing species in the hot
plasma region, and >97% of all the carbon in this region is
predicted to be in the form of C2H2. Figure 8b shows the
calculated electron density (n(rz)) distribution; the peak
electron density and temperature are, respectively, n0 = 1.8 \times 10^{11} \text{cm}^{-3} and T_e \approx 1.26 \text{eV}. Both of these values are relatively
flat across the plasma volume but fall steeply very close to the
substrate and at large r and z. The radical species C2H and,
particularly, C2 are concentrated in the hot plasma region, as
illustrated by the 2-D(rxz) model outputs in Figure 8c,d. The
dominant cations ensuring quasi-neutrality for our assumed ion
chemistry are C2H+ and C2H3+. The presence of anions has not
can not be considered hitherto.

Several possible mechanisms for forming C2−* anions are
now considered. The first involves electron attachment to
neutral C2, stabilized by the presence of a third body (M), i.e.

\[ \text{C}_2 + e^- + M \rightarrow \text{C}_2^{-*} + M \]  

Figure 6. Solid symbols: variation in Iem(C2−*) and Iem(C2−*) intensities from the 9 \leq z \leq 12 \text{mm region from a MW-activated CH}_4/H_2 plasma operating under base conditions of P, F(CH4), and F(H2) plotted as a function of applied power over the range 0.7 \leq P \leq 1.85 \text{kw}. Again, the intensities so derived have been reduced by a factor of 2 prior to display (on the inner y-axis scales) to allow direct comparison with the values shown in Figures 3 and 5, and the solid black and blue lines simply connect the
Iem(C2−*) calc and Iem(C2−*) data points. Open symbols: respective Iem(C2−*) calc and Iem(C2−*) emission rates (outer y-axis scales) returned by the 2-D modeling described in section 3.4.

Figure 7. Variation in Iem(C2−*) and Iem(C2−*) intensities from the 9 \leq z \leq 12 \text{mm region from (a) a MW-activated CH}_4/H_2 plasma operating under base conditions of P, F(CH4) and F(H2) plotted as a function of F(CH4), and (b) a MW-activated CH4/H2/Ar plasma operating under base conditions of P, F, and F(CH4) plotted as a function of F(Ar). Again, the intensities so derived have been reduced by a factor of 2 prior to display to allow direct comparison with the values shown in Figures 3 and 5, and the solid black and blue lines simply connect the
Iem(C2−*) calc and Iem(C2−*) data points, respectively.

Numerous H addition and abstraction reactions, summarized as a family of H-shifting equilibria that rapidly redistribute the
input CH4 into a whole range of CHx (x = 0–4), C2Hx (y = 0–6) and larger species, depending on the local T gas and X(H). C2H2 is the most stable carbon-containing species in the hot plasma region, and >97% of all the carbon in this region is predicted to be in the form of C2H2. Figure 8b shows the
which are excited by electron impact.\textsuperscript{22,42} DEA to C\textsubscript{2}H\textsubscript{2} has \( >10 \) eV, as evidenced by the ubiquitous H Balmer emissions, Maxwellian and possesses a heavy high-energy tail extending to electron energy distribution function (EEDF) is not identically \( T \)

Although

For this reaction to be significant under the present process conditions.

As noted above, C\textsubscript{2}H\textsubscript{2} is the dominant carbon-containing species in the hottest part of the plasma, so it is logical to consider possible C\textsubscript{2}\textsuperscript{−} production routes starting from C\textsubscript{2}H\textsubscript{2}. Although \( T \approx 1.22 \pm 0.04 \) eV under base conditions, the electron energy distribution function (EEDF) is not identically Maxwellian and possesses a heavy high-energy tail extending to \( >10 \) eV, as evidenced by the ubiquitous H Balmer emissions, which are excited by electron impact.\textsuperscript{22,42} DEA to C\textsubscript{2}H\textsubscript{2} has been investigated previously, with known channels yielding both C\textsubscript{2}\textsuperscript{−} and C\textsubscript{2}H\textsuperscript{−}:

\[
C\textsubscript{2}H\textsubscript{2} + e^- \rightarrow C\textsubscript{2}^- + 2H \tag{3}
\]

\[
C\textsubscript{2}H\textsubscript{2} + e^- \rightarrow C\textsubscript{2}H\textsuperscript{−} + H \tag{4}
\]

The calculated threshold energy for the three-body fragmentation process (3) is 7.4 eV, but the first resonance in the DEA spectrum of C\textsubscript{2}H\textsubscript{2} that yields C\textsubscript{2}\textsuperscript{−} as the dominant product is centered at \( \approx8.1 \) eV, with a cross-section of \( 4.1 \pm 1 \) pm\textsuperscript{2}.\textsuperscript{67} Reaction 4 has a calculated threshold of 2.7 eV and a reported DEA cross-section of 3.6 \pm 0.9 pm\textsuperscript{2} at 2.95 eV, with C\textsubscript{2}H\textsuperscript{−} as the dominant product. Combining the literature cross sections\textsuperscript{8} with the EEDF calculated in our modeling allows estimation of rate coefficients for reactions 3 and 4, as functions of \( T \) under the present plasma conditions, as shown in Table 1.

Figure 8. False color 2-D\((r, z)\) plots showing the calculated number density distributions of (a) H, (b) \( n_e \), (c) C\textsubscript{2}H, (d) C\textsubscript{2}(a), (e) C\textsubscript{2}\textsuperscript{−}, and (f) C\textsubscript{2}\textsuperscript{−}\textsuperscript{8}, and (f) C\textsubscript{2}\textsuperscript{−} from a MW-activated CH\textsubscript{4}/H\textsubscript{2} plasma operating under base conditions. The vertical distance from the substrate to the quartz window at the top of the reactor is 5.7 cm, and the reactor radius is 6 cm.

\textsuperscript{8}\textsuperscript{8} is rather slow \( (k < 10^{-33} \text{ cm}^3 \text{ s}^{-1}) \). Thus, we conclude that H-shifting from C\textsubscript{2}H\textsuperscript{−} cannot be an important source of C\textsubscript{2}−.

Processes 3 and 4 can also be ruled out as (indirect) sources of C\textsubscript{2}\textsuperscript{−} through consideration of the observed spatial distributions. The C\textsubscript{2}H\textsubscript{2} number density (indicated using \{ \} brackets, i.e., \{ C\textsubscript{2}H\textsubscript{2} \}) increases at small \( z \) as an inevitable consequence of the fall in \( T \) upon approaching the substrate.\textsuperscript{60} The spatial distributions of the products of reactions 3 or 4 will closely resemble the product of the \{ C\textsubscript{2}H\textsubscript{2} \} and \( n_e \) distributions, and the C\textsubscript{2}H\textsuperscript{−} and C\textsubscript{2}\textsuperscript{−} column densities (indicated using \{ \} brackets) predicted on this basis peak close to the substrate and decline with increasing \( z \) as a result of the fall in, first, [C\textsubscript{2}H\textsubscript{2}] and, at larger \( z \), \( n_e \). Consequently, this predicted \{ C\textsubscript{2}\textsuperscript{−}(v''=0) \} distribution bears no resemblance to that of the C\textsubscript{2}(v''=0) neutrals, \{ C\textsubscript{2}(v''=0) \}, formed by the well-established\textsuperscript{78} sequence of thermally driven H-shifting reactions. We emphasize that the contributions from reactions 3 and 4 still outweigh those from reactions 1 and 2 and are non-negligible C\textsubscript{2} sources under the present conditions, but the observed spatial distributions allow us to exclude electron impact with the ground-state anion as the progenitor of the observed C\textsubscript{2}\textsuperscript{−} species.

Similar arguments will apply to any other formation processes starting from a stable precursor. For example, we have investigated the possible direct formation of C\textsubscript{2}\textsuperscript{−}:

\[
C\textsubscript{2}H\textsubscript{2} + e^- \rightarrow C\textsubscript{2}\textsuperscript{−} + 2H \tag{3a}
\]

proposed by Locht\textsuperscript{78} to account for an increase in the cross-section for forming C\textsubscript{2}\textsuperscript{−} ions in the DEA of C\textsubscript{2}H\textsubscript{2} at incident electron energies \( \geq 11.6 \) eV. Again, however, the \{ C\textsubscript{2}\textsuperscript{−} \} distributions predicted assuming the participation of process 3a are very different from the present observations, particularly at low pressures (75 Torr) and powers (0.7 kW), where the inclusion of this reaction leads to very obvious enhancements in \{ C\textsubscript{2}\textsuperscript{−} \} in the near-substrate region, in contradiction with the experimental measurements.
Table 1. Anion Reactions: Rate Coefficients (in cm$^3$ s$^{-1}$ Unless Explicitly Shown Otherwise) and Rates (in cm$^3$ s$^{-1}$), Calculated for Base Conditions at $z = 10.5$ and 1.5 mm, and $r = 0$.

<table>
<thead>
<tr>
<th>reaction</th>
<th>rate coefficient/cm$^3$ s$^{-1}$ (if no other unit is indicated)</th>
<th>$z = 10.5$ mm</th>
<th>$z = 1.5$ mm</th>
<th>number</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_2 + e^- + M \rightarrow C_2^{-*} + M$</td>
<td>$k_{-c} = 3 \times 10^{-29}$ cm$^3$ s$^{-1}$</td>
<td>2.33 $\times 10^{12}$</td>
<td>1.05 $\times 10^{10}$</td>
<td>(1)</td>
</tr>
<tr>
<td>$C_2^{*} + e^- + M \rightarrow C_2 + e^- + M$</td>
<td>$k_{-c} = 7.5 \times 10^{-10} \times \exp(-11605/T_{gas})$</td>
<td>1.53 $\times 10^{12}$</td>
<td>9.72 $\times 10^9$</td>
<td>(-1)</td>
</tr>
<tr>
<td>$C_2H_2 + e^- \rightarrow C_2^{-*} + H + H$</td>
<td>$k_5 = 2.28 \times 10^{-11} \times \exp(-93907/T_{gas})$</td>
<td>1.77 $\times 10^{13}$</td>
<td>4.57 $\times 10^{13}$</td>
<td>(3)</td>
</tr>
<tr>
<td>$C_2H_2 + e^- \rightarrow C_2H^* + H$</td>
<td>$k_4 = 4.62 \times 10^{-12} \times \exp(-34201/T_{gas})$</td>
<td>2.48 $\times 10^{14}$</td>
<td>5.57 $\times 10^{14}$</td>
<td>(4)</td>
</tr>
<tr>
<td>$C_2H^* + H \rightarrow C_2H_2 + e^-$</td>
<td>$k_{-4} = 1.6 \times 10^{-9}$</td>
<td>2.48 $\times 10^{14}$</td>
<td>5.56 $\times 10^{14}$</td>
<td>(-4)</td>
</tr>
<tr>
<td>$C_2H + e^- \rightarrow C_2^{-<em>} + H^</em>$</td>
<td>$k_9 = 1.9 \times 10^{-13} \times \exp(-34777/T_{gas})$</td>
<td>1.04 $\times 10^{13}$</td>
<td>2.52 $\times 10^{11}$</td>
<td>(5)</td>
</tr>
<tr>
<td>$C_2H + e^- \rightarrow C_2^{-*} + H$</td>
<td>$k_{6} = 3.87 \times 10^{-11} \times \exp(-20218/T_{gas})$</td>
<td>6.00 $\times 10^{13}$</td>
<td>1.41 $\times 10^{12}$</td>
<td>(6)</td>
</tr>
<tr>
<td>$C_2^{-*} + H \rightarrow C_2H + e^-$</td>
<td>$k_{-6} = 7.7 \times 10^{-10}$</td>
<td>7.92 $\times 10^{12}$</td>
<td>1.13 $\times 10^{11}$</td>
<td>(-5)</td>
</tr>
<tr>
<td>$C_2^{-*} + H \rightarrow C_2H + e^-$</td>
<td>$k_{-5} = 7.7 \times 10^{-10}$</td>
<td>8.09 $\times 10^{13}$</td>
<td>4.71 $\times 10^{13}$</td>
<td>(-6)</td>
</tr>
<tr>
<td>$C_2^{-<em>} \rightarrow C_2^{-</em>} + h\nu$</td>
<td>$A_4 = 1.3 \times 10^7$ s$^{-1}$</td>
<td>3.26 $\times 10^{12}$</td>
<td>1.40 $\times 10^{11}$</td>
<td>(7)</td>
</tr>
<tr>
<td>$C_2 + e^- \rightarrow C_2^{-*} + e^-$</td>
<td>$k_4 = 10^{-8} \times \exp(-29065/T_{gas})$</td>
<td>1.96 $\times 10^{14}$</td>
<td>5.88 $\times 10^{11}$</td>
<td>(8)</td>
</tr>
<tr>
<td>$C_2^* \rightarrow C_2 + h\nu$</td>
<td>$A_5 = 1.02 \times 10^7$ s$^{-1}$</td>
<td>1.60 $\times 10^{14}$</td>
<td>5.43 $\times 10^{11}$</td>
<td>(9)</td>
</tr>
<tr>
<td>$C_2^{-*} + H_2 \rightarrow C_2H_2 + e^-$</td>
<td>$k_{10} = 1.5 \times 10^{-11} \times \exp(-3012/T_{gas})$</td>
<td>3.74 $\times 10^{13}$</td>
<td>1.16 $\times 10^{11}$</td>
<td>(10)</td>
</tr>
</tbody>
</table>

$^{*}T_{gas}$ and $T_{gas}$ are in units of K (1 eV = 11605 K).

From here on, we therefore focus on electron-driven processes involving transient species—particularly the $C_2H$ radical, which sits between $C_2$ and $C_2$ in the sequence of $H$-shifting equilibria involving the $C_2H_2$ ($y = 0$–6) family. As Figure 8c shows, its number density is predicted to peak at $[C_2H] \approx 5 \times 10^{13}$ cm$^{-3}$ in the hot plasma region (i.e., to be $\approx 40$-fold higher than $[C_2]$) and thus to adopt a more spatially extensive distribution than that of $C_2$ (a), which is given in Figure 8d. As we now show, adding the set of negative ion reactions listed in Table 1 to the C/H reaction mechanism used in our previous 2-D(r,z) coupled kinetic and transport modeling enables near-quantitative replication of the measured $I_{em}(C_2H^{*})$ and $I_{em}(C_2^*)$ distributions, their relative intensities, and their respective variations with process conditions.

The dominant source of $C_2H^{*}$ is deduced to be

$$C_2H + e^- = C_2^{-*} + H \tag{5}$$

with DEA also being the main source of ground-state $C_2^{-*}$ in the hot plasma core according to

$$C_2H + e^- \rightarrow C_2^{-*} + H \tag{6}$$

The balance of reactions 5 and −5 and the radiative decay

$$C_2^{-*} \rightarrow C_2^{-*} + h\nu \tag{7}$$

largely determine the $C_2^{-*}$ concentration and thus the emission intensity, $I_{em}(C_2^{-*})$. Other possible quenching processes, e.g., $C_2^{-*} + H_2 \rightarrow$ products, are unimportant relative to the reactive quenching process −5 under the present conditions. In the quenching of $C_2^*$ species, however, the roles of $H$ and $H_2$ are completely different. $I_{em}(C_2^*)$ is modeled simply as the balance between EIE

$$C_2 + e^- \rightarrow C_2^{-*} + e^- \tag{8}$$

radiative decay

$$C_2^* \rightarrow C_2 + h\nu \tag{9}$$

and the quenching process $C_2^* + H_2 \rightarrow$ products, e.g.,

$$C_2^* + H_2 \rightarrow C_2H^{*} + H \tag{10}$$

where $C_2H^{*}$ represents $C_2H$ products possessing some, but undefined, internal excitation.

We have not found information on either the rates or the major products of reaction 10, which, as written, is exothermic by $\approx 3$ eV. Pasternack et al. reported a rate constant $k_{-12}$ (cm$^3$ s$^{-1}$) $\approx 1.5 \times 10^{-11} \exp(-3012/T_{gas})$ for the corresponding reaction of $C_2(a)$ radicals with $H_2$ (reaction −12 below) and, lacking alternative information, we have adopted a similar form for $k_{90}(T_{gas})$ in Table 1. The $C_2H^{*}$ products are assumed to be rapidly quenched by $H_2$ and $C_2H_2$ with rate coefficients in the range $(0.5$–1.5$) \times 10^{-10}$ cm$^3$ s$^{-1}$ (ref 81), so reaction −10 is not considered to be a source of $C_2^{*}$. Other possible $C_2^{*}$ loss processes such as the reactive quenching reaction

$$C_2^{*} + H \rightarrow \text{CH} + \text{H} \tag{11}$$

for which we deduce a rate coefficient $k(T_{gas}) < 3.7 \times 10^{-12}$ cm$^3$ s$^{-1}$ from the coefficient of the reverse chemiluminescent reaction, is too slow to be important under the prevailing plasma conditions. So, too, is the quenching of $C_2^{*}$ by $CH_4$ (with a reported rate coefficient $3.7 \times 10^{-12}$ cm$^3$ s$^{-1}$ at $T_{gas} = 298$ K) and other hydrocarbons.

The rate coefficient for the associative detachment reaction −4 is due to Barckholtz et al. We have not found reported DEA cross sections for reactions 5 and 6. The expression for $k_5$ was chosen to provide a value $k_5 \approx 1.5 \times 10^{-12}$ cm$^3$ s$^{-1}$ in the hot plasma region. Such a value, along with the appropriate rate coefficients $k_5$ and $A_5$ (Table 1), yields the calculated spatial distributions of $C_2^{-*}$ and $C_2^*$ shown in Figure 8ef and the $C_2^{*}(v=0)$ and $C_2^{-*}(v=0)$ column densities shown in Figure 9a. The respective profiles and the ratio of these column densities all match well with the measured $I_{em}(C_2^{-*})$ and $I_{em}(C_2^{*})$ profiles and $I_{em}(C_2^{-*})/I_{em}(C_2^{*})$ ratios. Changing the activation energy in the expression for $k_5$ has little impact on the predicted $C_2^{-*}(v=0)$ profile. The rate coefficient $k_5$ is also not known, but its value is unimportant from the viewpoint of $C_2^{-*}$ emission. Reaction 6 will contribute to $C_2^{*}$ production but, as discussed above, $C_2^{-*}$ is not a significant source of the observed $C_2^{-*}$ in the proposed mechanism.

One aspect of the present data and its interpretation requires comment. The $C_2^{-*}$ species are deduced to be formed directly by DEA to $C_2H$. The radiative lifetime of the $C_2^{*}(B)$ state is short ($\approx 77$ ns$^{67,70}$), but more than an order of
1.85 kW at constant $p = 150$ Torr. For the ease of visualization, the $p = 75$ and 150 Torr (C$_2$$_2^-(v=0)$) data in (a) have been multiplied by factors of 8 and 2, respectively, and the $p = 0.7$ and 0.9 kW data in (d) have been multiplied by factors of 4 and 3, respectively, prior to display. To compare with the observed $I_m(C_2^+)$ and $I_m(C_2^{-})$ intensities (Figures 3 and 5), the column densities in (a) and (d) must be multiplied by the respective Einstein coefficients $A_d(v=0\rightarrow v'=0)$ and $A_d(v'=0\rightarrow v=0)$ (as in Figures 4 and 6 and described in section 3.4 and Table 2).

Figure 9. continued

The conclusion that reaction 3 is a dominant source of C$_2^-$ near the substrate (Table 1) is key to explaining the very different profiles for C$_2^-$ and C$_2^+$, which are reflected in the respective calculated column densities (Figure 9a,b, respectively). In contrast, the spatial similarity of $I_m(C_2^+)$ and $I_m(C_2^+)$ (recall Figure 3) is understandable given the similar $z$-profiles calculated for {C$_2$H}, Figure 9c, and {C$_2$H}$_2$), Figure 9b, these being the dominant sources of the respective electronically excited molecules (i.e., DEA to C$_2$H (5) and EIE of C$_2$ (8), respectively). Reactive quenching of C$_2^-$ by H atoms, reaction (−5), and of C$_2^+$ by H$_2$ molecules, reaction 10, also influences the calculated (C$_2^+$(v=0))/(C$_2^-$^−)(v=0)) ratios and, as we now show, can account for the major $p$- and $p$-dependent variations in the measured $I_m(C_2^+)$/$I_m(C_2^−)$ ratio.

3.4. Explaining the Process Condition Dependent Trends in $I_m(C_2^+)$ and $I_m(C_2^−)$. Analysis of the main C$_2^+$ and C$_2^-$ production/loss reactions provides a rationale for the quite different dependences of $I_m(C_2^+)$ and $I_m(C_2^−)$ on both pressure and power (Figures 4 and 6).

$I_m(C_2^+)$. As noted above, C$_2^+$ is produced by EIE of C$_2$(a) (reaction 8), balanced by radiative decay (9) and reactive quenching (10); its number density will be given by an expression of the form

$$[C_2^+]) \approx [C_2(a)] \times n_\lambda \times k_8/(A_9 + k_{10}[H_2])$$

The steady-state concentration of C$_2$(a) is established via fast, reversible H-shifting reactions

C$_2$H$_2$ + H $\rightleftharpoons$ C$_2$H + H$_2$

(The Journal of Physical Chemistry A)

DOI: 10.1021/acs.jpca.7b00814
C₂H + H ⇋ C₃(a) + H₂  \hspace{1cm} (12)

The aforementioned rate coefficient \( k_{-12}(T_{\text{gas}}) \) and thermochromic data were used in calculating the forward reaction coefficient \( k_{12}(T_{\text{gas}}) \approx (7.05 \times 10^{-8}/T_{\text{gas}}) \times \exp(-8180/T_{\text{gas}}) \). Balancing the direct and reverse H-shifting reactions 11 and 12 gives the following relation for \([C_2(a)]\):

\[
[C_2(a)] \approx [C_2H] \times (k_{12}/k_{-12}) \times ([H]/[H_2])
\]

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) with (units of cm⁻² s⁻¹) is then the product \( A_p \times \exp(\frac{n}{k_{12}/k_{-12}} \times ([H]/[H_2])^2 \times (k_{11}/k_{-11}) \times (k_{12}/k_{-12}) \times ([H]/[H_2])^2 \) \hspace{1cm} (13)

The 2-D model calculations show that the \([H]/[H_2]\) ratio in the plasma region is roughly proportional to both pressure and temperature. The 2-D model calculations show that the \([H]/[H_2]\) ratio in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.

The calculated intensity \( I_{\text{calc}}(C_{2\star}) \) in the plasma region is roughly proportional to both pressure and temperature.
Table 2. p- and P-Dependent Variations in the I_{em}(C2*)/I_{em}(C2^-) Ratio Measured for the Strip Centered at z = 11.25 ± 0.75 mm Compared with the Corresponding Ratios of the Respective Maximum Intensities Calculated Using the Reaction Mechanism in Table 1

<table>
<thead>
<tr>
<th>p/Torr</th>
<th>I_{em}(C2*)/I_{em}(C2^-)</th>
<th>P/kW</th>
<th>I_{em}(C2*)/I_{em}(C2^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>12</td>
<td>0.7</td>
<td>16</td>
</tr>
<tr>
<td>150</td>
<td>44</td>
<td>0.9</td>
<td>22</td>
</tr>
<tr>
<td>225</td>
<td>99</td>
<td>1.85</td>
<td>57</td>
</tr>
</tbody>
</table>

little, but T_y and, particularly, the [H]/[H2] ratio all increase with increasing X_{Ar}(Ar) (see, e.g., Figure 8 in ref 46). Given this increase in [H] and the inevitable decline in [H2] upon substitution by [Ar], the 2-D modeling predicts a steeper increase in {C2*}, which varies quadratically with ([H]/[H2])^2, eq 13, than in {C2^-}, which eq 14 shows to vary linearly with [H]/[H2]. Again, such predictions agree with the present experimental findings. Combining the present predictions with previous experimental studies of Ar-rich plasmas, we can predict much higher {C2*}/(C2^-) ratios in, for example, the 0.5%CH4/1%Ar mixtures used for depositing ultrananocrystalline diamond.

3.5. Further Implications for Plasma Activated Diamond CVD. C2 is not the only radical species present in C/H plasmas that has a large electron affinity (E_{ea} = 3.269 ± 0.006 eV). The electron affinity of C2H is almost as large as E_{ea} = 2.969 ± 0.006 eV, and that of the CN radical (which will be present if the plasma includes, whether by design or by accident, any nitrogen-containing precursor) is even larger (E_{ea} = 3.862 ± 0.004 eV). Of the resulting anions, only C2^- is an open-shell species, with bound excited electronic states capable of supporting OES in the visible spectral region. C2^+ and CN^- are isoelectronic with N2; their excited electronic states all lie at much higher energies, above the respective E_{ea} values. As Table 1 shows, the steady-state concentrations of anions like C2^- and C2H^- in a MW-activated C/H plasma are largely determined by DEA reactions 3, 4, and 6, balanced by associative attachment reactions −4 and −6. The rates of all other anion production and loss mechanisms (e.g., photoattachment, recombination with positive ions, electron detachment by electron impact, etc.) are orders of magnitude lower. As panels a, c, and d of Figure 9 show, the spatial profile of the C2^- anions revealed by OES is not representative of the majority anions. These are predicted to be C2H^+(X), from reaction 4, supplemented by ground-state C2^- anions from reactions 3 and 6. The column densities of these ground-state anions are predicted to peak at small z ≈ 1.5 mm, as with the main cations (C2H^+ and C2H^-), but to be 3−4 orders of magnitude smaller than those of the cations under base conditions.

We can also predict (perhaps surprisingly) high abundances of CN^- anions in the case of N-containing C/H plasmas. As shown in our recent combined experimental and modeling studies of MW and DC activated CH4/N2/H2 plasmas, HCN is by far the most abundant N containing species (besides N2) in the near substrate region.69,84 DEA to HCN, i.e.

\[
\text{HCN} + e^- \rightarrow \text{CN}^- + \text{H} \quad (15)
\]

has a huge cross-section at near threshold energies (reaching 940 pm² at incident electron energies ≥1.85 eV), attributable to a ‘H shape resonance.70 Combining the reported cross-section with the calculated EEDF translates into a dissociative attachment coefficient k_{15} ~ 2 \times 10^{-10} cm^3 s^{-1}. This coefficient, and an associative detachment coefficient k_{-15} ~ 6.3 \times 10^{-10} cm^3 s^{-1} (from ref 90), allows us to predict number densities [CN^-] ~ 10^7 cm^-3 (cf. neutral [CN] ~ 10^7 cm^-3) in the near substrate region and [CN^-] ~ 10^7 cm^-3 (cf. [CN] ~ 10^11 cm^-3) in the plasma core for the base 4%CH4/0.6%N2/H2 plasma considered in our recent study.90 Extrapolating to lower N2 input mole fractions, even with X_{Ar}(Ar) = 100 ppm, we predict that CN^- anions from process 15 could account for ~5% of the total near substrate anion concentration (which will then be dominated by [C2H^-] < 3 \times 10^7 cm^-3) from process 4).

We reiterate, however, that this anion number density is still 3 or more orders of magnitude lower than the concentrations of electrons and the positive ions ni ~ \Sigma[C2H^+] ~ 10^13 cm^-3.

Negative bias enhanced nucleation (BEN) has long been recognized as a route to accelerating diamond film growth on silicon substrates62 and is generally rationalized in terms of impacting C/H-containing cations yielding an interfacial SiC layer that facilitates subsequent diamond growth.91–94 The present identification of C2^- anions in a MW activated C/H plasma typical of those used for diamond CVD, and the deduction that other anions (e.g., C2H^+, and CN^- in the presence of adventitious N2) must also be present in the near substrate region, offer a plausible explanation for the (fewer) previous reports31,40,63 that the application of a positive bias voltage to the substrate can also lead to enhanced nucleation densities and growth rates. Negative BEN exploits the majority anions: as shown above, the cation densities in these plasmas are several orders of magnitude higher than those of the anions. But the dominant anions identified in the present work have much higher average C/H ratios, which may be beneficial for developing a carbon-rich seed layer.

4. CONCLUSIONS

Electronically excited C2^- anions have been identified, by spatially resolved imaging of their optical emission, in a MW-activated C/H/(Ar) plasma operating under conditions appropriate for diamond CVD. Various possible formation mechanisms have been modeled, only one of which (DEA to C2H2) is generally rationalized in terms of impacting C/H-containing cations yielding an interfacial SiC layer that facilitates subsequent diamond growth. The same 2-D model of the Respective Maximum Intensities Calculated Using the Reaction Mechanism in Table 1
previous findings that nucleation densities and diamond growth rates can be enhanced by using a positive substrate bias.

**AUTHOR INFORMATION**

**Corresponding Authors**
*M. N. R. Ashfold. E-mail: mike.ashfold@bris.ac.uk.*
*Y. A. Mankelevich. E-mail: ymankelevich@mics.msu.su.*

**ORCID**

M. N. R. Ashfold: 0000-0001-5762-7048

**ACKNOWLEDGMENTS**

The authors are grateful for financial support from the Engineering and Physical Sciences Research Council (EPSRC) through grant no. EP/K018388/1, the EPSRC Centre for Doctoral Training in Diamond Science and Technology (EP/L015315/1), and Element Six Ltd. The authors are also grateful for the many and varied contributions from colleagues Drs. Colin Western and James Smith. 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.

**REFERENCES**

A. Determination of Gas Temperature and C2 Absolute Density in Ar/Nanocrystalline Diamond Microstructures from Ar/H2/CH4-Plasma


(66) Western, C. M. PGOPHER, a Program for Rotational, Vibrational and Electronic Spectra (version 9.0, 2015), University of Bristol. Available at http://pgopher.chm.bris.ac.uk/.


