

# Relationship between diamond growth rate and hydrocarbon injector location in direct-current arcjet reactors

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A series of detailed calculations have been carried out using a stagnation flow model to examine the dependence of diamond growth rate on hydrocarbon injector location in dc arcjet reactors. It is predicted that, for methane feed, growth rate can be increased by as much as 75% by relocating the injector from a position near the plasma torch exit to one near the diamond surface, but outside the boundary layer. As the injector is moved towards the surface from the plasma torch, the concentrations of C and CH<sub>3</sub> present at the surface increase. When the injector is located within the boundary layer, the lower atomic hydrogen concentration and short residence time leave most of the injected CH<sub>4</sub> unreacted, causing growth rates to drop. © 1995 American Institute of Physics.

Of the high growth rate deposition technologies for the synthesis of diamond via low-pressure (<1 atm) chemical vapor deposition, direct current (dc) arcjet reactor systems have been demonstrated to be extremely robust at producing high quality, relatively large area films.<sup>1,2</sup> While growth rates in dc arcjet systems are indeed high, ranging from 10  $\mu\text{m/h}$  up to over 100  $\mu\text{m/h}$ , the growth rate is achieved at a significant materials cost. Carbon capture efficiencies are estimated to lie between 0.1% and 5%, depending on the details of the reactor system and operating conditions, where capture efficiency is simply the measure of rate of carbon uptake into a film compared to the rate at which carbon is introduced into the reactor as a gaseous feed. The low carbon capture efficiency translates into anywhere from 40 to 100 h of continuous reactor operation to produce an 0.5 mm thick film; increases in carbon uptake efficiency may potentially reduce the growth time by a corresponding amount.

A means of improving the carbon utilization is to exploit the disparate time scales for the physical processes occurring in the dc arcjet reactor. Specifically, characteristic time scales associated with convection of mass, energy, and momentum, as well as diffusion of these quantities (the transport time scales), compete with the characteristic time scales associated with each of the homogeneous and heterogeneous reactions taking place in the reactor (the chemical kinetic time scales). If all gaseous hydrocarbon species were equally likely to adsorb and incorporate into the diamond film, there might not exist a competition between the transport and chemical kinetic time scales; if the time scales associated with the delivery of material to the diamond surface were smaller than the rate at which carbon species could react, the kinetic limit, then the rate of diamond growth would depend solely on the rate-limiting incorporation step(s).

However, there is significant evidence that a small subset of the gas-phase hydrocarbon distribution actually leads to diamond growth. One piece of evidence is based on isotope labeling experiments,<sup>3</sup> with an additional body of work based on numerical modeling studies. The models predict that, for reasonable adsorption and abstraction rates, experimentally

observed growth rates in a variety of reactor systems can be reproduced by gas-surface chemical kinetic models in which CH<sub>x</sub> ( $x=0-3$ ) are the species leading to diamond growth.<sup>4-7</sup> One of these numerical studies included C<sub>2</sub>H<sub>2</sub> as a potential growth species,<sup>4</sup> but concluded that it contributed negligibly to diamond growth.

In dc arcjet reactors where CH<sub>4</sub> is the feed and there are no oxygen bearing species present, conditions leading to a favorable growth environment—that is, large atomic hydrogen concentrations—also result in the formation of appreciable amounts of C<sub>2</sub>H<sub>2</sub>. Even though large H concentrations quickly strip hydrogen from the CH<sub>4</sub> feed to form CH<sub>x</sub> radical species, subsequent reactions among these radicals lead to the formation of C<sub>2</sub>H<sub>2</sub>. For example, if a dc plasma torch can produce 30 mol % atomic hydrogen at 2500 K, the dominant hydrocarbon species over 80% the region between the torch exit and the substrate are C and C<sub>2</sub>H<sub>2</sub>, in comparable concentrations. Inside the several-millimeter-thick boundary layer adjacent to the substrate, heterogeneous hydrogen recombination chemistry drives the homogeneous hydrocarbon chemistry to the extent that the concentration of C<sub>2</sub>H<sub>2</sub> is five times higher than that of the second most prevalent carbon species, C atoms.<sup>4</sup> For systems with less H present, the concentration of C<sub>2</sub>H<sub>2</sub> at the surface is higher.

Because of the independence of the time scales associated with the chemical kinetics and the convective and diffusive transport, it may be possible to exploit the competition between the different scales to increase diamond growth rate for a given set of operating conditions. That is, the system might be manipulated to utilize the strongly convective nature of the dc arcjet systems to increase the amount of CH<sub>x</sub> growth species delivered to the diamond surface, relative to the rate at which these species are converted to C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>. A means of implementing this concept is to control the location of the hydrocarbon injector. Existing dc arcjet systems locate the hydrocarbon injector(s) immediately downstream of the plasma torch exit;<sup>1</sup> the resulting hydrocarbon species equilibrate within approximately 20  $\mu\text{s}$  around the H and H<sub>2</sub> composition issuing from the torch.

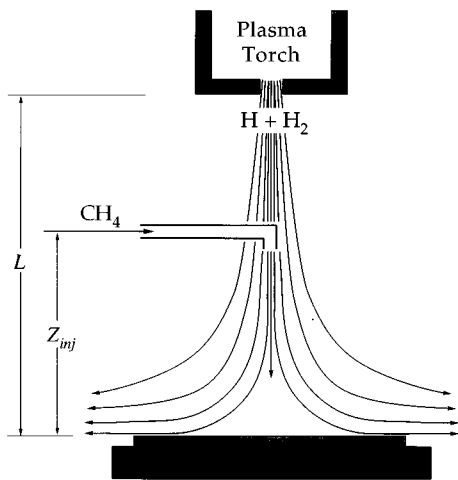


FIG. 1. Schematic diagram of the plasma torch/substrate configuration. Methane is injected into a mixture of H and H<sub>2</sub>, which exit the torch at 2500 K and a velocity of  $2 \times 10^5$  cm/s.

Depending on the torch power and operating conditions, the gas temperature ranges from 2000 to 3000 K. As the hydrocarbon species convect towards the substrate they are inexorably converted to C<sub>2</sub>H<sub>2</sub>. By moving the hydrocarbon injector closer to the substrate the amount of C<sub>2</sub>H<sub>2</sub> formed will be less due to the decreased residence time.

To demonstrate the utility of optimizing diamond growth rate through control of the hydrocarbon injector location, a set of calculations was performed based on the geometry illustrated in Fig. 1. A dc plasma torch, operated solely on H<sub>2</sub>, is located a distance  $L$  above the substrate. Methane is injected into the system, inside the jet, at a distance  $Z_{inj}$  above the substrate, and in the direction towards the substrate. The mole fraction of atomic hydrogen leaving the plasma torch,  $X_H^0$ , is assumed known. Analysis of this system leads to a set of ordinary differential equations describing the transport of mass, momentum, and energy in the region between the plasma torch exit and the substrate.<sup>8</sup> These equations contain multicomponent transport properties, and detailed gas-phase pyrolysis chemistry<sup>9</sup> and surface chemistry.<sup>4</sup> The diamond growth mechanism<sup>4</sup> used here provides for the deposition of C, CH<sub>3</sub>, and C<sub>2</sub>H<sub>2</sub>.

Calculations are presented here for a system similar to one studied previously,<sup>4</sup> for which  $L = 15$  cm, the reactor pressure is 30 Torr, and the H/H<sub>2</sub> mixture leaves the dc plasma torch at  $2 \times 10^5$  cm/s and 2500 K. In that study, CH<sub>4</sub> comprised 0.5 mol % of the gas mixture at the torch exit. For purposes of direct comparison between the results of this work, as well as with those of the previous study, the injected CH<sub>4</sub> flux  $\dot{M}_{CH_4}$  is chosen such that the local gas mixture in the vicinity of the injection position  $Z_{inj}$  is composed of 0.5% CH<sub>4</sub>; as  $Z_{inj}$  decreases, so does the value of  $\dot{M}_{CH_4}$ , because the total axial mass flux decreases as the substrate is approached. Also, the closer  $Z_{inj}$  is to the surface, the less hydrocarbon that is "swept by" without the possibility of encountering the surface.<sup>10</sup> Two sets of calculations are presented below for five different injector locations,  $Z_{inj} = 10,$

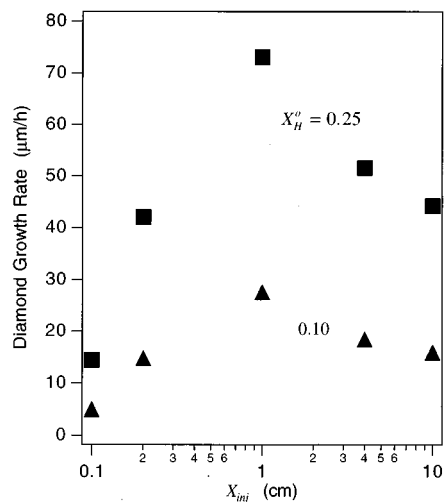


FIG. 2. Predicted diamond growth rate as a function of hydrocarbon injector height  $Z_{inj}$  for two initial mole fractions of atomic hydrogen.

4, 1, 0.2, and 0.1 cm. The last two injector locations were chosen specifically to lie within the boundary layer, which is approximately 0.5 cm thick for these conditions. At each injector location two values for  $X_H^0$  were used, 0.10 and 0.25. These values were chosen to be representative of H<sub>2</sub> dissociation fractions achievable in low and moderate power dc plasma torches. The values of  $\dot{M}_{CH_4}$  ranged from 2 mg/cm<sup>2</sup>/s at  $Z_{inj} = 10$  cm down to 0.011 mg/cm<sup>2</sup>/s at  $Z_{inj} = 0.1$  cm. The plasma torch/substrate gap  $L$  was maintained at 15 cm for all calculations.

The predicted diamond growth rate as a function of injector location is shown in Fig. 2 for the two different values of free-stream H mole fraction. The dependence of growth rate on injector location is qualitatively similar between the two values of  $X_H^0$ , but as can be clearly seen, the growth rate is higher when more H is produced by the plasma torch. Both sets of growth rate calculations show a local maximum, indicating that there is an optimal injector location near the substrate but outside of the boundary layer. And within the bounds set by the relatively few points computed, it appears that the optimal value of  $Z_{inj}$  is insensitive to the amount of H produced by the plasma torch. The percent increase in growth rate as the injector is moved from 10 cm down to 1 cm is larger for  $X_H^0 = 0.25$  than for  $X_H^0 = 0.10$ , primarily due to the differences in the relative amounts of C and CH<sub>3</sub> produced for the two cases. Figure 3 illustrates the major species mole fraction profiles for the injector located at  $Z_{inj} = 1$  cm. For  $X_H^0 = 0.10$  [Fig. 3(a)] little C is produced in the free stream, and much of this is converted back to CH<sub>4</sub> inside the boundary layer, driven by the drop in atomic hydrogen due to heterogeneous destruction. In contrast, when  $X_H^0 = 0.25$  [Fig. 3(b)] a significant fraction of the inject CH<sub>4</sub> is converted to C. Although the concentration of CH<sub>3</sub> at the surface in Fig. 3(a) is a factor of 2 and 3 higher than the concentrations of C and CH<sub>3</sub> in Fig. 3(b) the assumed reactivity of C with the surface results in a higher predicted growth rate for the case presented by Fig. 3(b).

Figure 4 demonstrates that the mole fraction of C<sub>2</sub>H<sub>2</sub>

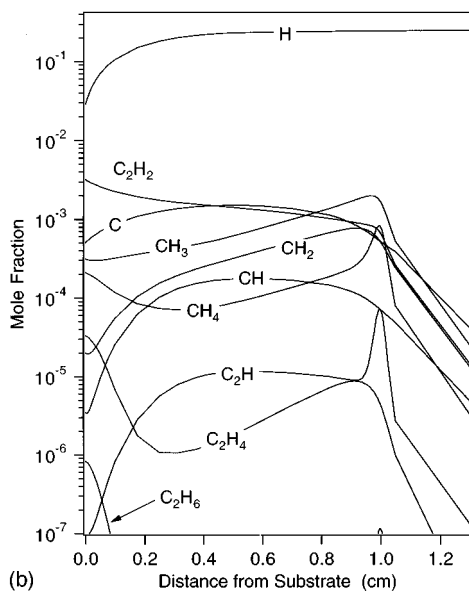
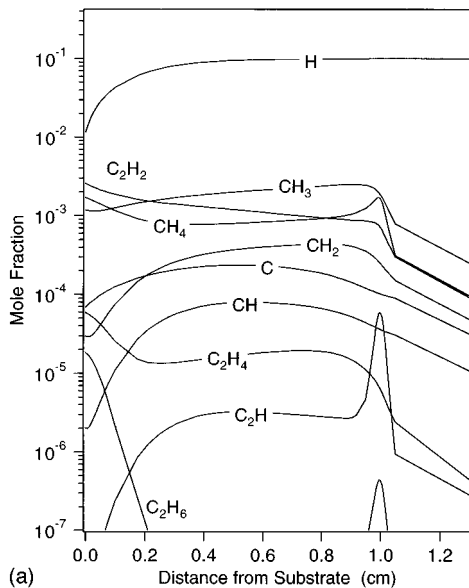


FIG. 3. Species mole fraction profiles for  $Z_{inj}=1$  cm and two free-stream atomic hydrogen mole fractions: (a)  $X_H^0=0.10$  and (b)  $X_H^0=0.25$ .

present at the surface is relatively insensitive to  $X_H^0$ . Also, over the injection position range for which the growth rate climbs, the level of  $C_2H_2$  at the surface remains nearly constant. The calculated growth rate does, however, scale directly with the concentrations of C and  $CH_3$  at the surface, both of which increase as  $Z_{inj}$  is decreased from 10 to 1 cm. For injector positions less than 1 cm, the amount of C present at the surface drops, as does the growth rate. There is less C at the surface because there is insufficient time to completely strip the hydrogen from the  $CH_4$  feed before the mixture enters the boundary layer; and once inside the

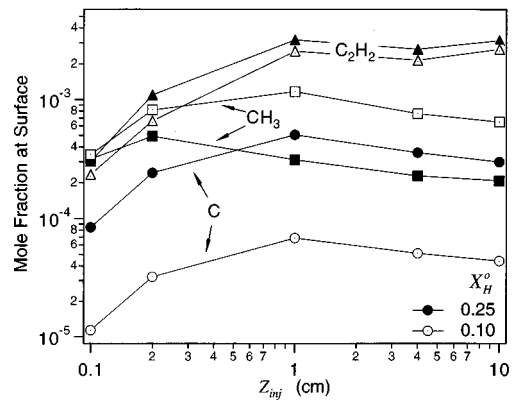


FIG. 4. Mole fractions at the growth surface as a function of hydrocarbon injector height  $Z_{inj}$  for two initial mole fractions of atomic hydrogen (closed symbols  $X_H^0=0.25$ ; open symbols  $X_H^0=0.10$ ).

boundary layer the chemistry is driven in a direction that produces  $CH_4$  and  $C_2H_2$  at the expense of C and  $CH_3$ . When the injector is located inside the boundary layer there is an order of magnitude less  $C_2H_2$  present at the surface than when the injector is located in the free-stream region ( $Z_{inj}>0.5$  cm in this case). However, this is because the atomic hydrogen concentration is between 2 and 10 times less than in the free stream, and little of the  $CH_4$  is converted to  $CH_x$  and  $C_2H_x$  species during its residence time within the boundary layer.

Thus the numerical simulations predict that diamond growth rate can be increased by moving the hydrocarbon injector to a position near the substrate, but outside the boundary layer. When the injector is located within the boundary layer there is insufficient time and insufficient H concentration to convert the injected  $CH_4$  to either reactive diamond precursors or to  $C_2H_2$ .

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