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# The dependence of diamond growth rate on hydrogen dissociation in a d.c. arcjet plasma

D. A. RUSSELL, P. TABOREK
*Department of Physics, University of California, Irvine, Irvine, CA 92717, USA*

A calorimetric technique was used to measure the plasma enthalpy in a d.c. arcjet diamond deposition system. Using these measurements, and a model based on the assumption of local thermal equilibrium (LTE), the temperature of the plasma emerging from the torch nozzle could be calculated. By controlling the electrical power into the torch, the plasma temperature could be varied from 2900 to 4500 K. This range of plasma temperatures corresponded to a fraction of dissociated $H_2$ ($\alpha$) which ranged from 0.19 to 0.98. Surprisingly, this variation in the concentration of atomic hydrogen had no effect on the diamond growth rate.

## 1. Introduction

Chemical vapour deposition (CVD) of diamond always involves hydrogen in the gas phase. Atomic hydrogen is considered to be crucial to CVD diamond growth for several reasons. One important function of atomic hydrogen is to suppress graphite formation [1–6] by preferentially etching $sp^2$ bonds over $sp^3$ bonds. Atomic hydrogen is known to satisfy dangling $sp^3$ bonds on the diamond surface and is thought to activate surface sites by abstracting hydrogen atoms from the growth surface [7–11], as well as from hydrocarbons in the vapour phase [12]. One growth model [13] predicts that diamond growth rate is dependent on the mole fraction of atomic hydrogen ($\chi_H$) up to a point, but that the effect saturates at some critical value of $\chi_H$. Other models [9, 14] suggest that molecular hydrogen is critical because it suppresses formation of aromatics in the gas. Although several techniques have been developed to detect atomic hydrogen in diamond CVD reactors [15–19], the effect of [H] or $\chi_H$ on diamond growth rate has not been quantitatively investigated. In this paper, results from an experiment to determine the effect of varying the fraction of dissociated hydrogen molecules, $\alpha = [H]/([H] + 2[H_2])$, on the growth rate of diamond in a plasma jet reactor are presented.

In this d.c. arcjet plasma system, an arc was driven between a tungsten cathode and an annular water cooled copper anode, which also served as a nozzle. The arc heated a flowing mixture of 25 slm of argon, 5–10 slm of hydrogen and 50–100 sccm of methane. The heated gas was then accelerated out of a small orifice (4.72 mm diameter) into a background pressure of $1.333 \times 10^3$ Pa and impinged on a molybdenum substrate. Under typical operating conditions, the pressure inside the torch was approximately $1.013 \times 10^5$ Pa. This high pressure, along with the small electric field ($\sim 25\ \mathrm{V\,cm^{-1}}$) which drove the arc, and the long transit time ($\sim 2$ ms) through the arc and nozzle, ensured that the gas inside the torch was in local thermodynamic equilibrium (LTE) [20].

## 2. Theory

The heat capacity and other thermodynamic properties of the gas mixture inside the torch were determined primarily by the extent of dissociation of molecular hydrogen via the reaction $H_2 \rightarrow 2H$, which absorbed 4.48 eV per molecule [21]. Due to this large heat of reaction, in the temperature range 2000–5000 K, most of the heat transferred to the gas was utilized in converting $H_2$ into H, rather than increasing the temperature of the gas. Because the thermal energy of the molecules in this temperature range was approximately 1 eV, measuring the power absorbed by the gas was equivalent to counting the number of dissociated hydrogen molecules.

Estimating the temperature of the gas jet was complicated by the fact that, under normal operating conditions, the flow was highly supersonic. Since the ratio of the pressure inside the torch to the ambient pressure was approximately 75, it was estimated [22] that the maximum Mach number (M) of the jet was 3.5. This meant that the kinetic energy of the flow had to be taken into account when calculating the gas temperature because, in supersonic flow, velocity and temperature are strongly coupled, with high velocities corresponding to low temperatures. Furthermore, the velocity and temperature varied rapidly with position: as the gas left the nozzle, it expanded and accelerated, and then recompressed and decelerated in the stagnation zone near the substrate. These adiabatic expansions and compressions were accompanied by corresponding variations in temperature. When the flow stagnated near the substrate boundary layer, however, the temperature approached the temperature inside the torch where the fluid velocity was also small. Although the spatial variation of the fluid velocity, temperature and pressure was quite complicated, the conditions at the exit of this converging nozzle were specified by general principles of gas dynamics [22] and were independent of the details of the system geometry. The exit velocity was the local velocity of sound $c(T^*, P^*)$ ($\sim 10^5\ \mathrm{cm\,s^{-1}}$),

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where $P^* \approx 0.5P_0$ ($P_0$ was the pressure in the torch).

Conservation of energy at the nozzle exit can be written as:

$$\dot{m}h(T^*, P^*) + \frac{1}{2}\dot{m}c^2(T^*, P^*) = \dot{m}h(T_0, P_0) + \dot{Q} \tag{1}$$

where $\dot{m}$ is the total mass flux of the input gas, $h(T, P)$ is the enthalpy per unit mass of the gas, $T_0$ is the initial gas temperature (298 K) and $T^*$ is the temperature of the gas leaving the nozzle. For a given value of the absorbed power, $\dot{Q}$, mass flux $\dot{m}(= \dot{m}_{H_2} + \dot{m}_{Ar})$ and pressure $P^*$, Equation 1 determines the exit temperature $T^*$, which in turn determines the fraction of dissociated hydrogen $\alpha(T^*, P^*)$ using a standard chemical equilibrium calculation [23]. A typical plot of $\alpha$ versus $\dot{Q}$ is shown in Fig. 1.

$\dot{Q}$, the rate of gas enthalpy flowing out of the torch nozzle, can be determined calorimetrically [24] (see Fig. 2). The total amount of power supplied to the torch is $\dot{Q}_e = IV$. The waste power, $\dot{Q}_w$ (typically of the order $\dot{Q}_e/2$), is the power transferred to the inner walls of the torch and removed by the cooling water. $\dot{Q}$ is determined by measuring the flow rate, $J$, and temperature rise ($T_h - T_c$) of the cooling water as shown in Fig. 2. Because the hot gas inside the torch was enclosed in water cooled copper, and was leak tight, there were no other channels for energy transfer. At steady state, the input power was balanced by the gas enthalpy flux out the torch nozzle and the heat removed by the cooling water, with $\dot{Q} = \dot{Q}_e - \dot{Q}_w$. The mass flux, $\dot{m}$, was determined with precisely calibrated mass flow controllers. $P_0$ was measured through a small orifice in the torch body. The experimentally determined values of $\dot{Q}$, $P_0$ and $\dot{m}$ were used to determine the gas temperature $T^*$ and $\alpha$ at the nozzle exit.

Although the gas temperature varied considerably as it flowed from the nozzle to the top edge of the boundary layer near the substrate (2 cm away), $\alpha$ was essentially constant. This was a consequence of the fact that the recombination of atomic hydrogen was limited by slow three-body collisions [12]. At a typical nozzle temperature and pressure, the frequency of this type of three-body collision was less than 2500 $s^{-1}$ per hydrogen atom. Since the flow time from the nozzle to the boundary layer was approximately 20 μs (assuming $v_{ave} = c(T^*, P^*)$), $\alpha$ could not respond to the temperature variations in the flow, and was frozen at its value at the nozzle. This conclusion was corroborated by detailed chemical kinetic calculations [25]. In contrast to the temperature, $\alpha$ was constant along lines of flow in the supersonic part of the jet.

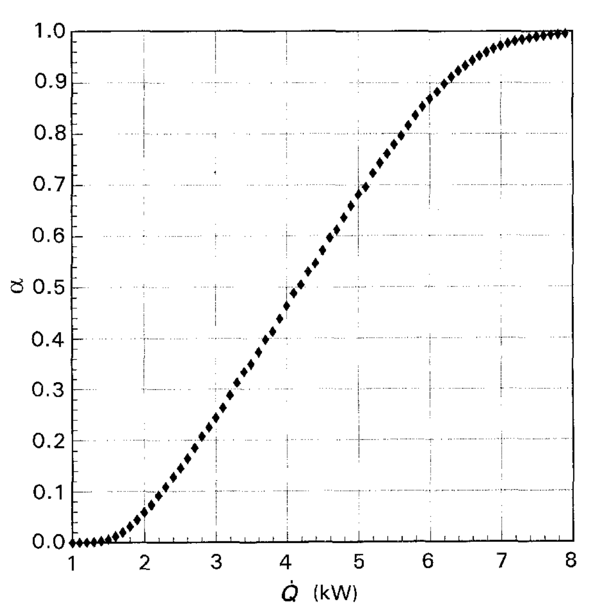

*Figure 1* $\alpha$ versus $\dot{Q}$ for a gas mixture consisting of 25 slm Ar, 10 slm $H_2$, $P = 5.065 \times 10^3$ Pa and M = 1.

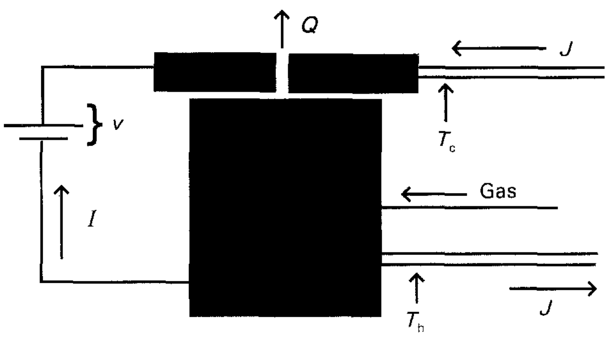

*Figure 2* Schematic of the torch calorimetry. $T_c$ and $T_h$ are the incoming and outgoing cooling water temperatures: $J$ and $C$ are the cooling water flow rate and specific heat per unit volume, respectively. $\dot{Q}_e = IV = \dot{Q} + CJ(T_h - T_c)$.

## 3. Experiment and results

The calorimetric technique described above was used to study the effect of $\alpha$ in the gas jet on the growth rate of diamond films. A sequence of diamond depositions was performed on electrically isolated molybdenum substrates in which the electrical power supplied to the torch was varied over a wide range, but all other process parameters were held constant. In particular, the substrate temperature, as measured with an infrared pyrometer, was 1000 ± 20 °C; variations in the heat flux to the substrate were compensated for by adjusting the thermal impedance to a water cooled block. The ambient pressure was maintained at 1.333 × $10^3$Pa, and the initial ratio $\chi_{CH_4}/\chi_{H_2}$ in the feed gas was fixed at 0.01. $T^*$, determined from Equation 1, was varied between 2900 and 4500 K, corresponding to the range $0.19 \leq \alpha \leq 0.98$. Instability of the arc at low power prevented exploration of the range of $\alpha$ below 0.19. The diamond film thickness was determined using a calibrated optical microscope. Figs 3 and 4 show the diamond growth rate versus $\alpha$ for two different values of the initial molar ratio $\chi_{Ar}/\chi_{H_2}$, however, voltage and current limitations of the instrument and the arc prevented a complete scan over all $\alpha$ at a single $\chi_{Ar}/\chi_{H_2}$. The most significant feature of the figures is that, over the entire range of $\alpha$ accessible with this torch, the diamond growth rate was independent of $\alpha$.

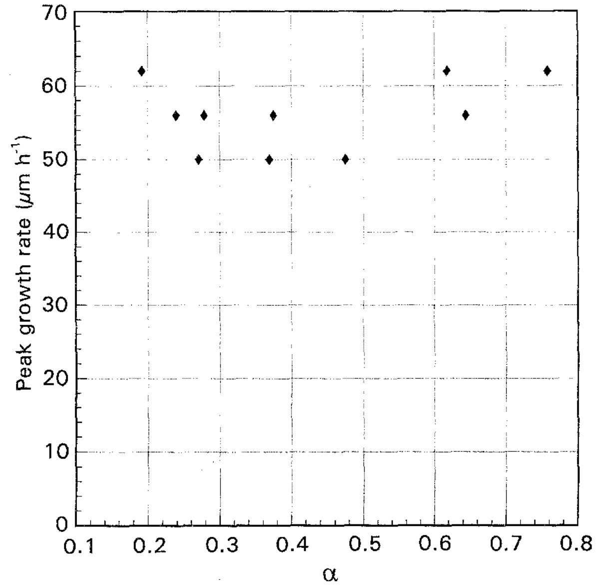

*Figure 3* Diamond growth rate versus α for a gas mixture consisting of 25 slm Ar, 10 slm $H_2$ and 100 sccm $CH_4$.

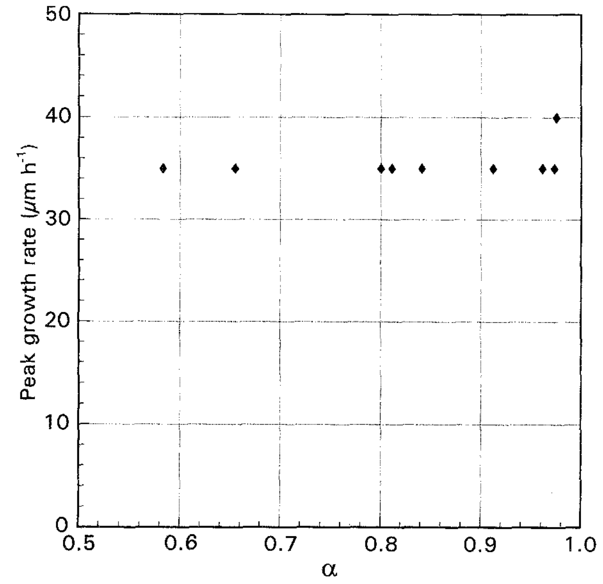

*Figure 4* Diamond growth rate versus α for a gas mixture consisting of 25 slm Ar, 5 slm $H_2$ and 50 sccm $CH_4$.

## 4. Conclusion

The observation that wide variations in the input power, the plasma temperature, and α had no effect on the diamond growth rate has at least two important practical implications. Firstly, there is apparently no benefit in maximising the input power in arcjet diamond deposition systems; high input power only aggravates electrode erosion and substrate cooling problems without increasing the diamond growth rate. Secondly, since the growth rate was independent of α in the bulk gas phase throughout the range investigated, it is concluded that whatever the role of atomic hydrogen in diamond growth, the effect is saturated for $\alpha > 0.19$. Reactions involving hydrocarbons, which can proceed via two-body collisions, are more difficult to analyse than the recombination of H, but the concentrations of various hydrocarbon species are expected to have a strong temperature dependence in the range investigated [10, 25]. The observation that variations in $T^*$ by nearly a factor of two have no effect on the diamond deposition rate shows that the deposition process is remarkably insensitive to the conditions in the bulk gas phase. This suggests that the rate determining steps for diamond growth in an arcjet reactor takes place either at the substrate surface or in the boundary layer region.

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