Diamond deposition by atmospheric pressure induction plasma: effects of impinging jet fluid mechanics on film formation

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Abstract

The effect of boundary layer thickness on diamond film formation in an atmospheric pressure plasma was investigated by adding argon to the methane–hydrogen reactant jet so as to increase the jet momentum. It was found that argon addition significantly increased the range of conditions over which well-faceted, continuous diamond film could be grown. A numerical model was developed to predict the two-dimensional temperature and flow fields in the reactor and the one-dimensional chemical kinetics in the substrate boundary layer. An interesting outcome of these calculations is that the largest effect of thinning the boundary layer by adding argon to the central jet is a significant enhancement in the flux of monatomic carbon vapor to the substrate, and the experimentally observed results can be correlated with the calculated carbon fluxes.

1. Introduction

An important difference between atmospheric pressure "thermal" plasmas and other environments for diamond deposition is that reactants (e.g. hydrogen and methane) introduced into the plasma core are almost completely dissociated at the high plasma temperatures. In the usual geometry a relatively cold stagnation point boundary layer exists above the substrate, which in the case of thermal plasmas must be actively cooled to maintain a temperature (about 1000 °C) conducive to diamond growth. In the hot "freestream" outside this boundary layer chemical equilibrium is a reasonable approximation. Although the peak reactant temperature depends on various factors, it is at least 4000 K. For typical hydrogen and methane inputs an equilibrium calculation at 4000 K indicates that hydrogen is about 90% dissociated and, furthermore, about 90% of all available carbon atoms are in the form of monatomic carbon vapor. This level of dissociation qualitatively distinguishes thermal plasmas from other types of diamond chemical vapour deposition (CVD) systems.

Of course, the dissociated plasma must traverse the cold boundary layer, and diffusion and chemical reactions in this boundary layer determine the actual species fluxes to the substrate. If the boundary layer is too thick, substantial recombination can occur and the advantage of using a thermal plasma may be lost. Thus boundary layer thickness may be an important issue for diamond deposition using a thermal plasma.

In this paper we report both experiments and numerical modeling relating to diamond CVD using an atmospheric pressure induction plasma. A series of experiments was conducted in which several parameters were varied, particularly including the addition of argon to the central reactant jet so as to manipulate the boundary layer thickness: for constant-property stagnation point flow the fluid boundary layer thickness scales as the inverse square root of jet momentum [1].

2. Description of experiments

The experiments were conducted with the apparatus shown schematically in Fig. 1, which is essentially the same as described previously [2, 3]. The plasma was driven by inductive coupling to an r.f. power generator operating at 2.9 MHz with a typical plate power for these experiments of 12–14 kW. The water-cooled quartz plasma tube had an inner diameter of 44 mm. The main plasma gas was argon at a flow rate of 40 sLpm (standard 1 min⁻¹), introduced through the top of the plasma tube as a swirling sheath gas. Reactants were introduced through a water-cooled stainless steel injection probe with an inner diameter of 1.8 mm, which was inserted coaxially directly into the plasma, terminating at the midplane of the induction coil. The reactants were methane and hydrogen and in some cases additional argon was introduced through the central injection probe so as to increase the jet momentum. The peak velocity of the reactant jet was much higher (100–200 m s⁻¹) than that of the surrounding argon plasma (about 10 m s⁻¹).

The reactant jet impinged in stagnation point flow on a water-cooled substrate assembly with a total diameter
of 27.4 mm. In these experiments molybdenum disks were used as substrates and were pretreated by scratching with 0.25 µm diamond paste followed by cleaning in methanol. Substrate temperatures were measured using a two-color optical pyrometer (Ircon Modline Series R). For a given set of run conditions we varied the substrate temperature by inserting various thicknesses of stainless steel between the substrate and the water-cooled cylinder.

A series of 16 depositions lasting 4 h each were conducted with variation of four parameters: hydrogen flow rate, either 4 or 8 slpm; methane:hydrogen ratio, either 1% or 2%; flow rate of argon through the central injection tube, either 0 or 4 slpm; and substrate temperature, either "low" or "high" within the range 830–1070°C. Detailed results of all 16 cases have been reported separately [4].

We focus here on four cases which illustrate the general trend of the experimental results and present new results of the numerical modeling which are correlated with these experimental results. The conditions of these four cases are listed in Table 1. All four cases involved a hydrogen flow rate of 4 slpm. In cases A and B the methane:hydrogen ratio was 1% and the surface temperature was maintained at about 900°C, but in case A no argon was added through the central injection probe whereas 4 slpm was added in case B.

Cases C and D both involved a 2% methane:hydrogen ratio and a surface temperature of about 1040°C. Again the only difference between these two cases was that no argon was added through the central injection probe in case C while 4 slpm was added in case D.

### 3. Experimental results

By far the most striking trend of the full set of experiments was the effect of adding argon to the reactant jet. Of the eight cases without argon addition only two produced well-faceted crystallites and only one of these was a continuous film. In contrast, all eight cases with argon addition produced well-faceted crystallites and seven of the eight produced continuous films. The four cases discussed here highlight this trend. In all cases the film characteristics were qualitatively uniform over the entire substrate.

A scanning electron microscopy (SEM) image of the film deposited in case A is shown in Fig. 2. This appears to be a non-diamond carbon deposit consisting of clumps of submicron grains, even though the conditions—1% methane:hydrogen ratio and a substrate temperature of 890°C—are known to be conducive to diamond growth.

Figure 3 shows an SEM image of case B. With all conditions the same except for adding 4 slpm argon to the reactant jet, we find a continuous diamond film with a predominantly octahedral structure and typical crystallite dimensions of about 10 µm. The film thickness in this case (as determined by cross-sectioning and microscopy) was 32 ± 3 µm, indicating an average growth rate of 8 µm h⁻¹.

Figures 4 and 5 show SEM images of cases C and D. Case C, without argon addition, produced 5–10 µm balls covered with what appear to be graphite fibers. Case D, with argon addition, produced a dense, continuous
diamond film with crystallite dimensions as large as 50 $\mu$m. The film thickness was determined to be 65–70 $\mu$m, indicating an average growth rate of about 17 $\mu$m h$^{-1}$.

4. Plasma model

Our plasma model assumes two-dimensional (axisymmetric) laminar flow and local thermodynamic equilibrium, except that the finite rate kinetics of hydrogen dissociation and recombination are considered. The equations solved are the continuum fluid conservation equations, including the continuity equation, all three components of the momentum equation and the energy equation, coupled to the two-dimensional electromagnetic field equations and to species diffusion equations for H, H$_2$ and Ar. The computational domain corresponded to the experimental reactor including the reactant injection probe and the deposition substrate assembly. Boundary conditions were based on measured induction coil current and frequency, measured substrate temperature and wall coolant temperatures and measured flow rates of argon and hydrogen both as main plasma gas and through the central injection tube. Hydrogen atoms were assumed to recombine at all surfaces. The methane flow through the central injection tube was neglected in this part of the model since it comprised only about 0.1% of the total flow rate and therefore would not be expected to significantly affect the temperature and flow pattern in the reactor. For further details of the model and numerical methods see refs. 3, 5 and 6.

Typical results for the temperature distribution in the
reactor are shown in Fig. 6, which was calculated for the conditions of case D. Peak temperatures exceed 10,000 K. A relatively cold central channel is seen downstream of the reactant injection tube due to the energy sink represented by heating the central flow and dissociating the hydrogen. However, it should be noted that hydrogen diffuses rapidly (i.e., it is not confined to the central channel) and that in any case the flow along the center-line reaches a temperature exceeding 4500 K, still hot enough to achieve a very high degree of molecular dissociation.

5. Boundary layer chemistry model

We modeled the chemistry in the hydrogen–carbon–argon system over a region extending from the substrate to a location at which the temperature equalled 4000 K, as determined by the plasma model. For cases A and C (without argon addition) this location was about 5 cm from the substrate; for cases B and D (with argon addition) it was about 2 cm. Our reason for choosing 4000 K is that above that temperature chemical rate constants are extremely uncertain but thermochemical equilibrium is a reasonable assumption. Thus we perform an equilibrium calculation at 4000 K based on the inputs of argon, hydrogen and methane and use that composition as an initial condition for the kinetics calculations.

The kinetics calculation was based on the approach of Coltrin et al. [7], which has been employed by Goodwin and coworkers to model several types of diamond CVD reactors [8, 9]. The fluid conservation equations for stagnation point flow are recast as ordinary differential equations under a simple similarity transformation. The equations we solved are the continuity and momentum equations and a set of species diffusion equations. Since the temperature profile was taken from the plasma solution, the energy equation was not re-solved.

The chemical rate equations are solved using the Chemkin database and software package [10]. We considered 23 species in the C–H–Ar system, accounting for 60 reactions, with reaction rates obtained from recent compilations [11–15]. Species transport by convection, ordinary diffusion and thermal diffusion is included.

For our present purposes we did not model the surface chemistry in detail but assumed the following simple set of boundary conditions at the substrate: hydrogen atoms were assumed to recombine to H₂; carbon vapor species (C and C₂) were assigned a sticking probability of unity (equivalent to assuming that they “condensed” on the cold substrate); and all hydrocarbon species were assigned a sticking probability of zero. These conditions would not be expected to be strictly accurate but reflect the fact that C atoms are expected to encounter a much lower energy barrier as a diamond growth species than CₓHₓ species.

Figure 7, which corresponds to case D, shows typical results for the species profiles. With reference to Fig. 6 it is not obvious how one should choose the most pertinent measure of boundary layer thickness. One appropriate measure of boundary layer thickness for diamond CVD is the region over which the H atom concentration deviates by more than 1% from its equilibrium value. We find that this “hydrogen non-
equilibrium boundary layer" has a thickness of 3.5 mm in cases A and C compared with 1.0 mm in cases B and D.

The equilibrium calculations at 4000 K are affected by the methane:hydrogen ratio, but all cases show extremely high concentrations of monatomic carbon vapor. For example, the C atom concentration at the right edge of Fig. 7 is more than 70 times higher than the most abundant hydrocarbon (CH) at the same location.

In discussing the boundary layer chemistry in filament-assisted diamond CVD, Goodwin and Gavillet [8] noted that although the total system was far from equilibrium, several important reactions were close to being in partial equilibrium. The overall non-equilibrium was maintained by species with long characteristic diffusion lengths. In our case we find a similar analysis to be particularly pertinent for understanding why the carbon vapor concentration remains so high across the boundary layer. (The drop in the C atom profiles close to the substrate is a consequence of the boundary condition that atoms have unity sticking probability.)

The characteristic diffusion length (average distance over which a molecule diffuses before experiencing destruction by a chemical reaction) for C atoms over most of the boundary layer is only about 0.05 mm. It may thus seem surprising that the C atom concentration does not quickly decay from its freestream value. However, a particularly important reaction for C atoms is

\[ \text{CH} + \text{H} = \text{C} + \text{H}_2 \]

We find that this reaction is in almost perfect partial equilibrium over almost the entire boundary layer. H atoms have a much longer average diffusion length in this boundary layer, almost 1 mm, and therefore stay virtually frozen at the high concentration they attained in the hot plasma. Thus the equilibration of this reaction together with the superabundance of H atoms (and an adequate supply of CH) maintain the high concentration of C atoms in this system.

### 6. Comparison of model and experiment

We now consider the films produced in the four cases in light of the modeling results. The two most prominently discussed diamond "growth species" have been methyl (e.g. ref 16) and acetylene (e.g. ref.17). Our model results indicate that both these species have higher concentrations in the cases without argon addition (A and C) than in the cases with argon addition (B and D), yet only the latter grew diamond. In contrast, the cases with argon addition had a higher flux of monatomic carbon vapor to the surface. Under our assumption that carbon atoms had unity sticking probability, one can calculate the film growth rates in the four cases. The results are given in Table 2.

It should be recalled that the experimental growth rates were 8 \( \mu \text{m h}^{-1} \) in case B and 17 \( \mu \text{m h}^{-1} \) in case D. Considering that the ratio of these growth rates is about the same as the ratio of the calculated carbon fluxes for these two cases and that diamond did not grow in cases A and C, a rather facile hypothesis presents itself: the main growth species in this system was monatomic carbon vapor with a sticking probability of about 0.1. For cases A and C the resulting diamond growth rate was too low and competing non-diamond carbon growth mechanisms dominated.

Recent semiempirical quantum chemical calculations have shown that the energetics of diamond growth by addition of monatomic carbon are quite favorable [18], although it also seems reasonable to suppose that the sticking probability for C atoms would not be unity, as they could react with hydrogen or other species at the surface and return to the gas phase.

We do not suppose that this mechanism is important other than in thermal plasma systems, because to our knowledge only thermal plasmas generate enough carbon vapor for it to be a significant factor. However, for thermal plasmas the present results do appear to suggest this route as an explanation for diamond growth, in which case the mass transfer of carbon atoms through the boundary layer becomes a crucial consideration in reactor design.

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### References

1. S. L. Girshick et al., Diamond deposition by atmospheric pressure plasma


