

Thermal plasma synthesis of diamond

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Abstract: A numerical model was used to examine experimental data in which a gas chromatograph measured the composition of gas sampled through a 70- μm orifice in the growth substrate during atmospheric-pressure RF plasma diamond CVD. Substantial discrepancies were found between the measurements and the predicted species mole fractions at the surface, but the data were in much better accord with predicted mole fractions ~ 0.2 mm above the surface. This may possibly be due to the perturbation caused by the orifice. The model was also used to examine the predicted effects of freestream and substrate temperatures on the surface concentrations ratios of H, CH₃ and C₂H₂. Different trends versus substrate temperature were found according to whether the freestream temperature was 3000 K or 4000 K.

INTRODUCTION

Atmospheric-pressure plasmas generated by RF inductive coupling are one of the more promising methods for diamond CVD. Among the advantages of this method are high growth rates (10–100 $\mu\text{m}/\text{h}$), the absence of electrode contamination (compared to DC arcjets), and the relative ease of atmospheric-pressure operation. Nevertheless, although there is a general understanding that the gas-phase chemical composition near the diamond growth surface crucially affects film growth, remarkably few experimental measurements have been reported for chemical species mole fractions in this environment. For atmospheric-pressure inductively-coupled RF plasmas, the only reported measurements are boundary-layer profiles of CH (1) and C₂ (2) obtained by Owano *et al.* using degenerate four-wave mixing spectroscopy, and our recently reported measurements (3) of several stable hydrocarbon species using a gas chromatograph for samples obtained through a small orifice located in the center of the deposition substrate. The CH measurements of Owano *et al.* were shown to be in good agreement with a numerical model, whereas their measured C₂ mole fractions closest to the surface lay two orders of magnitude above the predictions of the model (2).

In this paper we consider two aspects of the experiments in which our recent GC measurements were obtained. First, we examine the agreement of the measured species mole fractions with a detailed numerical model. Secondly, we use the numerical model to consider the discrepancy which was reported in Ref. 3, concerning the effect of substrate temperature on film morphology—namely, that different diamond CVD environments appear to produce opposite trends regarding the effect of temperature on film morphology.

EXPERIMENTAL

The flow configuration for the experiments reported in Ref. 3 was the "central jet injection" geometry of Refs. 4 and 5, in which reactants are coaxially injected through a probe inserted directly into the coil region of an RF plasma, forming a jet which impinges on the growth substrate. Operating pressure was 1 atm, and the RF generator operated at 2.9 MHz with a plate power of 13

kW. Flow rates were 40 slm for the main argon introduced at the torch inlet, and 4 slm for both argon and hydrogen introduced through the injection probe, with methane injected through the probe at 1-5% of the hydrogen flow rate. The temperature of the molybdenum substrate was controlled using a previously described cooling system (6).

The GC measurements were obtained by sampling gas through a 70- μm -diameter (before diamond growth) sonic orifice located in the center of the substrate. The pressure of the sampling line was maintained at 20 Torr, dropping to 6 Torr across the sample loop in the GC. The GC was equipped with both flame ionization and thermal conductivity detectors, and provided calibrated measurements of the mole fractions of stable species including Ar, H₂, CH₄, C₂H₂, C₂H₄ and C₂H₆.

Because we wish to compare the experimental data to the numerical calculations discussed below, it is necessary to note that the interpretation of the GC measurements is complicated by two effects: (1) the perturbation and finite spatial resolution introduced by the sampling orifice, and (2) chemistry in the line which delivers the sample to the GC. Suction close to the orifice causes the flow to lose its one-dimensional character. Gas in this region is rapidly accelerated from close-to-zero velocity to sonic velocity, effectively freezing the chemical composition at its value some distance above the orifice. A simple analysis using as a criterion that the Peclet number equals unity (transition from diffusion-dominated flow close to the surface to convection-dominated flow for the gas accelerating toward the orifice) at the edge of a "hemisphere of influence" indicates that the radius of this hemisphere is approximately twice the orifice diameter, or about 140 μm before diamond growth. However this analysis neglects two complicating effects: (1) the effect of viscous drag close to the surface for fluid drawn laterally toward the orifice, which may cause the geometry of the affected region to be effectively more conical than spherical; and (2) the fact that isotherms, which in the absence of the orifice would be flat and parallel to the surface, would tend in the region above the orifice to be depressed toward the orifice. Thus about 200 μm may be a more realistic estimate for the distance from the orifice for which the composition is effectively sampled.

Regarding the effect of chemistry in the probe line, we conducted kinetic calculations, similar to those described in Ref. 7. If, following the discussion above, we assume that the gas composition entering the probe corresponds to the species mole fractions predicted by our numerical model at a location 200 μm above the surface, then these calculations indicate that the mole fractions of methane and acetylene are virtually unaffected by chemistry in the sampling line. As in Ref. 7, methyl radicals are predicted to recombine in the sampling line to form C₂H₄ and C₂H₆.

NUMERICAL MODEL

Our general approach to modeling this system (4, 8) involves both a two-dimensional "global" plasma model and a one-dimensional model for the chemically-reacting boundary layer above the substrate. The plasma model solves the continuum fluid conservation equations coupled to the electromagnetic field equations, using the induction coil current rather than the plasma power as a boundary condition (9). The injected hydrocarbon (which comprises less than 0.2% of the total flow rate) is neglected in the two-dimensional model. One outcome of this calculation is the location of the 4000 K isotherm above the substrate, which we take to define the edge of the chemically reacting boundary layer. For the argon and hydrogen flow rates corresponding to the experimental values, the calculation predicts that this boundary layer is 2.0 mm thick, and that the axial velocity at the boundary layer edge is 9.7 m/s.

These outputs of the two-dimensional model are used as inputs to the boundary-layer model, which utilizes the Sandia SPIN code (10) to solve the transformed one-dimensional conservation equations for stagnation-point flow, including both homogeneous gas-phase chemistry and diamond growth chemistry at the surface. Both the gas-phase reactions considered and our model for surface chemistry are described in detail in Ref. 8.

The boundary condition for species mole fractions at the boundary layer edge is based on an equilibrium calculation. In doing this calculation we use the elemental inputs of argon, hydrogen and carbon measured by the GC, rather than those which one would use if the reactor were assumed to be fully mixed. In fact the GC measurements indicated that the gas composition on the flow axis was hydrogen-enriched by a factor of 3.0, and carbon-enriched by a factor of 4.5, relative to complete mixing. This can be explained by the high velocity of the reactant jet (~ 100 m/s shortly past the injector exit compared to ~ 10 m/s for the surrounding argon) and by the higher diffusivity of hydrogen compared to hydrocarbons. Using these actual H and C inputs, instead of the global reactor inputs, has a substantial effect on the predicted boundary layer chemistry.

RESULTS AND DISCUSSION

Figure 1 shows the boundary-layer mole fraction profiles of several species, predicted by the numerical model for the case of 2% input methane-hydrogen ratio and a substrate temperature of 1200 K. Hydrogen and hydrocarbons are predicted to be more than 90% dissociated at the boundary layer edge. The H-atom profile drops steeply near the surface due to hydrogen recombination. The predicted C_2H_2 profile is rather flat near the substrate, whereas the profiles of the other hydrocarbons shown are all relatively steep close to the surface.

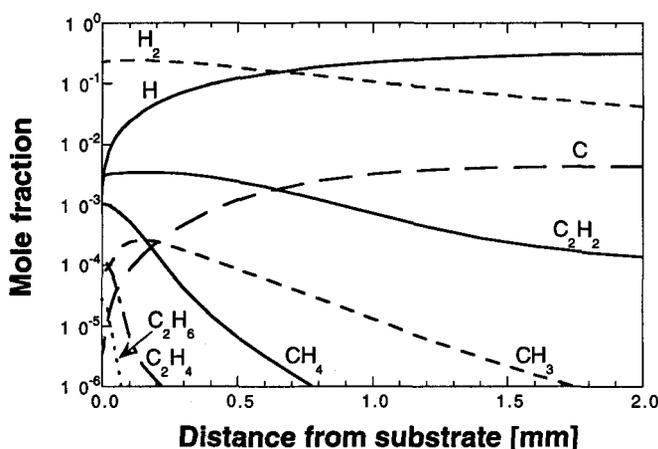


Fig. 1. Calculated mole fraction profiles of selected species for an input methane-hydrogen ratio of 2%; substrate temperature = 1200 K.

In view of the discussion above regarding the sampling orifice effect, in Fig. 2 we compare the experimental measurements for the mole fraction ratio of methane to acetylene to the experimental predictions both at the surface and 0.2 mm above the surface, for a range of input methane-hydrogen ratios at a fixed substrate temperature of 1100 K. The measurements lie more than an order of magnitude below the predicted values at the surface, but are in good agreement with the values 0.2 mm above the surface. While the choice of 0.2 mm was somewhat arbitrary—and the actual effect of the orifice perturbation requires a more detailed two-dimensional analysis—it is clear that the orifice perturbation could possibly account for the discrepancy between the measurements at the predicted surface mole fractions. We ran a number of numerical experiments to examine other factors which could explain the discrepancy—including incorrectly predicted freestream temperature, velocity, and boundary layer thickness—and none of these could reasonably account for the order-of-magnitude difference between the CH_4 mole fraction measured and that predicted at the surface. Therefore, in the comparisons of measurements and model predictions which follow we use the predicted species mole fractions at $z = 0.2$ mm.

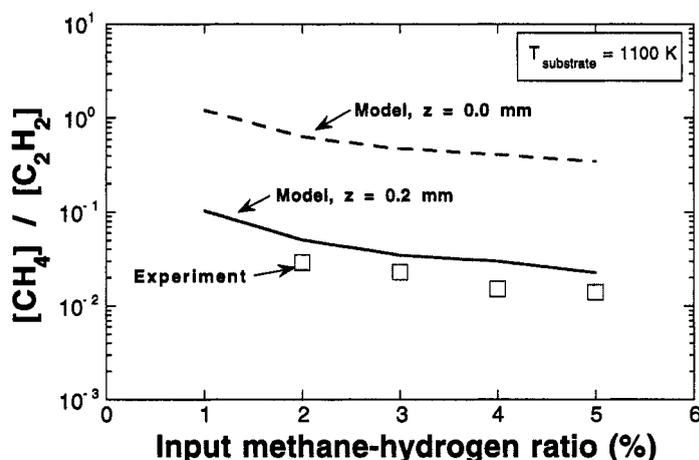


Fig. 2. Comparison of experimental measurements (3) for methane-acetylene ratio with model predictions at the surface and 0.2 mm above the surface.

In Figs. 3 and 4 we compare the GC measurements to predicted mole fractions both as the input methane-hydrogen ratio is varied at a fixed substrate temperature of 1100 K (Fig. 3) and as the substrate temperature is varied at a fixed input methane-hydrogen ratio of 2% (Fig. 4). Measurements of C_2H_6 are not shown because it was not measured in any of the experiments, indicating that its mole fraction was below the ~ 1 ppm detection limit of the GC.

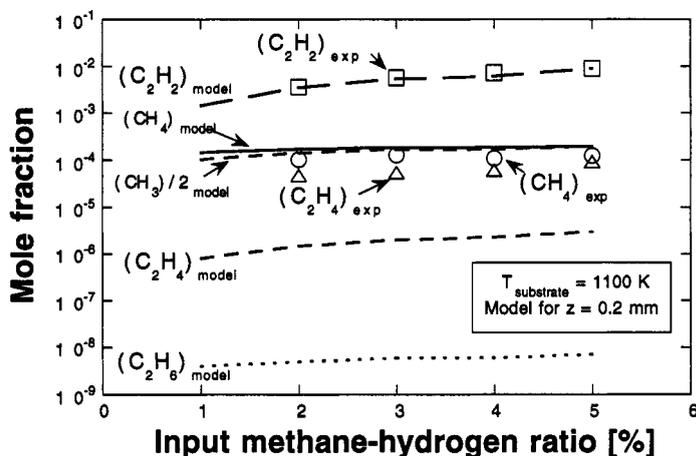


Fig. 3. Effect of input methane-hydrogen ratio on species mole fractions: comparison of experimental measurements (3) with model predictions 0.2 mm above the surface.

In both figures the agreement for acetylene is excellent, and close agreement is seen for methane as well. The predicted ethane mole fraction under all conditions is only a few ppb, far too low to be measured by the GC, and the predicted ethylene mole fraction is of the order ~ 1 ppm, low enough so that the measured C_2H_4 could plausibly be inferred as a surrogate for methyl. If one does that, then

the CH_3 mole fraction which would be inferred from the C_2H_4 data is within an order of magnitude of the predictions over the range of the experimental conditions. However it should be reiterated that our model for chemistry in the sampling line predicts that CH_3 recombination produces more ethane than ethylene. Thus the absence of detectable C_2H_6 in these experiments remains unexplained.

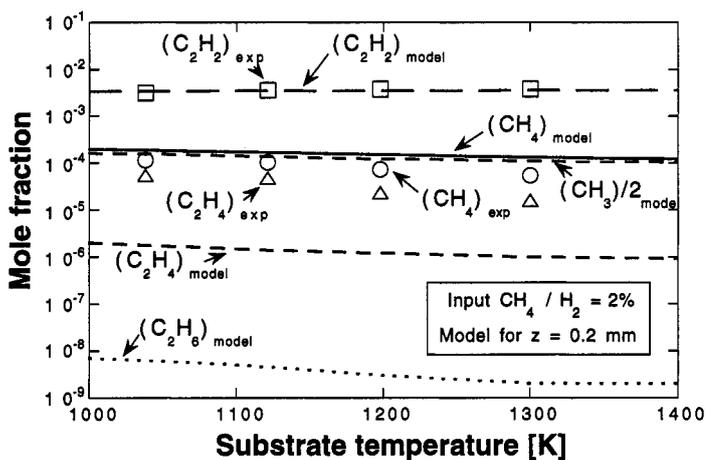


Fig. 4. Effect of substrate temperature on species mole fractions: comparison of experimental measurements (3) with model predictions 0.2 mm above the surface.

Insofar as the numerical model is at least not invalidated by the above comparisons, it is of interest to explore predictions of the model for radical species which cannot be measured by the GC. Of particular interest are the predicted surface mole fractions of CH_3 and H , as these are widely believed to be key species in diamond growth. In Fig. 5 we show the predicted surface mole fractions of CH_3 and H , both for the calculations discussed above and for a case where all else is the same except that the freestream temperature is reduced from 4000 K to 3000 K (and the velocity at the boundary layer edge is correspondingly lowered from 10 to 7.5 m/s to preserve mass continuity for a given flow rate). At a freestream temperature of 4000 K the surface mole fraction of H is virtually unaffected by substrate temperature, while the mole fraction of CH_3 drops by a factor of two as substrate temperature increases from 1000 K to 1400 K. In contrast, for a freestream temperature of 3000 K, the dependence of H and methyl on substrate temperature shows strikingly different trends, with the H mole fraction increasing and the methyl mole fraction decreasing as substrate temperature is increased.

Simple models of the incorporation of defects during diamond growth (e.g., (11)) have suggested that the defect density scales on $[\text{CH}_3]/[\text{H}]$ at the surface, and one study of film morphology (12) has indicated that $\{100\}$ - vs. $\{111\}$ -faceting is affected by $[\text{CH}_3]/[\text{H}]$. While these results are tentative, the result shown in Fig. 6 reinforces the plausibility of arguments that substrate temperature, in addition to its direct effect on diamond surface kinetics, may affect the gas-phase environment differently for different growth environments, which may explain some of the discrepancies which have been noted for the effect of substrate temperature on film morphology (3).

Further evidence for the crucial effect of substrate temperature on the gas-phase environment at the growth surface is shown in Fig. 7, which compares the predicted concentration ratios of methyl-to-acetylene for freestream temperatures of 3000 K and 4000 K. The consensus from a number of

studies, reviewed recently in Ref. 13, is that under most diamond CVD conditions the primary growth species is methyl, but that acetylene may contribute with a sticking coefficient about two orders of magnitude below that of methyl. If that is correct, then the results shown in Fig. 7 suggest that for relatively low freestream temperatures (*i.e.* 3000 K and lower) growth is dominated by methyl, but that for the high freestream temperatures accessible by thermal plasmas (4000 K or higher) acetylene may be expected to contribute about as much as methyl to diamond growth, especially when the substrate temperature is higher than about 1200 K.

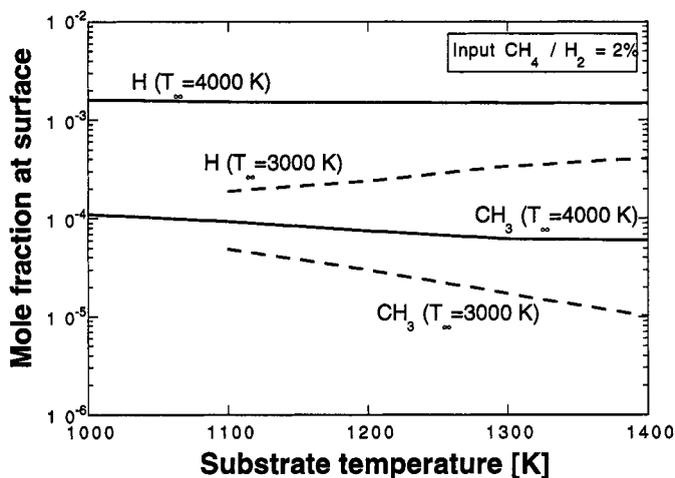


Fig. 5. Model predictions for the effect of substrate temperature on the surface mole fractions of H and CH₃, or two different freestream temperatures.

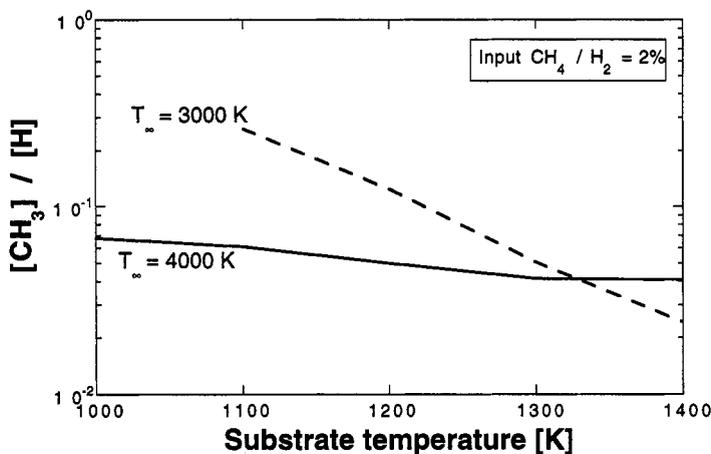


Fig. 6. Model predictions for the effect of substrate temperature on the ratio of methyl radicals to H-atoms at the surface, or two different freestream temperatures.

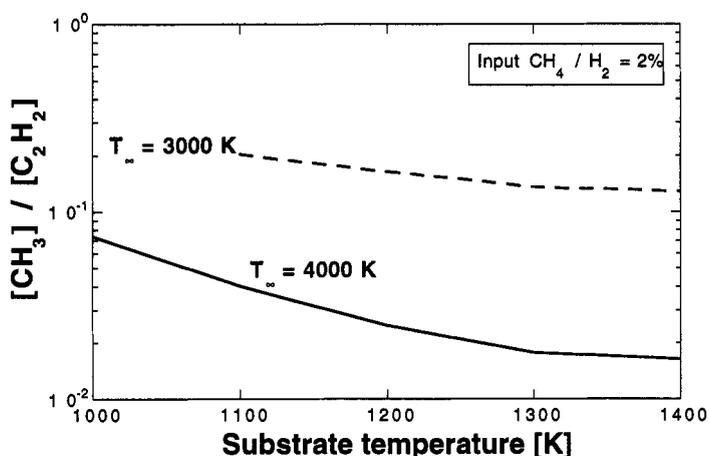


Fig. 7. Predicted effect of substrate temperature on surface concentration ratios of methyl to acetylene, for two different freestream temperatures.

CONCLUSIONS

Numerical calculations were conducted to simulate recently reported experiments involving atmospheric-pressure inductively-coupled RF plasma diamond CVD. Experimental data obtained with a gas chromatograph of species mole fractions were compared to the model predictions. It was found in general that the measurements agreed poorly with predicted species mole fractions at the growth surface, but that agreement was considerably improved if the data were compared to predicted species mole fractions 0.2 mm above the surface. These results may indicate that the numerical model is significantly in error, perhaps due to uncertainties in one more of the rate constants assumed, or that the presence of the gas sampling orifice in the experiments perturbs the flow directly above it, thereby sampling gas at some effective location above the surface. The numerical model was also used to examine the effect of freestream temperature on mole fractions of H atoms, methyl and acetylene at the surface. Quite different trends were found for the effect of substrate temperature on the H and CH₃ mole fractions, according to whether the freestream was assumed to be either 4000 K or 3000 K. These calculations also suggested that acetylene may be an important growth species for a combination of high freestream temperature (~4000 K) and high substrate temperature (greater than ~1200 K).

ACKNOWLEDGMENTS

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