EXPERIMENTAL STUDY OF DIAMOND FILM MORPHOLOGY AND SURFACE CHEMISTRY IN RF INDUCTION PLASMA CVD

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Abstract. Measurements were made using a gas chromatograph of several hydrocarbon species concentrations during chemical vapor deposition of diamond films in an atmospheric-pressure RF plasma. The measurements were little affected by whether carbon was introduced into the reactor as methane or acetylene. Measurements are compared to a model for the reactor and probe chemistry. Studies were conducted in which the film morphology was characterized for a range of methane/hydrogen ratios and substrate temperatures. The results indicate a qualitative shift compared to similar results reported for microwave systems.

Introduction

Detailed models have been developed for the chemistry in the boundary layer above the diamond growth surface during chemical vapor deposition (CVD) in atmospheric or near-atmospheric radio-frequency (RF) induction plasmas [1-5]. To our knowledge, however, the only measurements of species concentrations in these systems are CH and C_2 profiles by Kruger, Zare and coworkers [2,6,7] using degenerative four-wave mixing . In this paper we report measurements, using a gas chromatograph (GC), of several stable species—CH_4, C_2H_2, C_2H_4 and C_2H_6—in an atmospheric-pressure RF plasma under diamond CVD conditions.

Diamond film morphology can be characterized in terms of the growth parameter $\alpha \equiv \sqrt{3}(V_{100}/V_{111})$, where V_{100} and V_{111} are respectively the growth rates in the <100> and <111> directions [8-10]. Previous investigators [11,12] constructed empirical maps showing the variation of α with surface temperature T_s and with the CH_4/H_2 ratio introduced into their microwave plasmas. To our knowledge α-maps have not been reported for any environment other than a microwave plasma. In this paper we show experimental results for the effect on α of CH_4/H_2 and T_s for an atmospheric pressure RF plasma.

Surface chemistry

The measurements presented here were made in an RF reactor described previously [3,4]. The reactor pressure was 1 atm, the main plasma gas was argon at 40 slm, and H_2 and additional argon were each introduced at 4 slm through a central injection tube. These conditions (depending on the added CH_4 flow rate and T_s) have produced diamond growth at up to ~20 μm/h. The substrate holder was equipped for both active temperature control [13] and gas sampling.

Gas was sampled through a 50-μm sonic orifice machined into the center of each substrate. The sampled gas passed to the GC system through a sample line inserted into the substrate holder. The GC system used was a Hewlett Packard 5890, series 2, equipped with a flame ionization detector and a sample loop and sampling valve to transport gas to the GC analysis system. The sampling line pressure was 20 torr, dropping across the sample loop to 6 torr.

It is typically assumed that reactants injected into a thermal plasma are completely dissociated before undergoing recombination chemistry in the cold boundary layer. To test this hypothesis we ran two experiments, in which the C-carrying reactant was either CH_4 (at 80 sccm) or C_2H_2 (at 40 sccm). The experiments were run for 150 minutes, with GC measurements taken at approximately 6 minute intervals. During these experiments four species were detected, CH_4, C_2H_2, C_2H_4 and C_2H_6.

Results for the case where C_2H_2 was injected are shown in Fig. 1. There are noticeable transient trends, which we found to be reproducible and not affected by whether C_2H_2 or CH_4 was injected. There are two possible explanations for these transients. First, as the film grows the orifice size shrinks. Results for separate experiments with various orifice sizes were consistent with this explanation for C_2H_2, C_2H_4 and C_2H_6, but not for CH_4. A second possible explanation is that the gas composition at the surface is affected by the changing nature of the surface, which evolves over the sampling time from bare molybdenum to a continuous diamond film.

The total mole fraction of C-containing species indicated in Fig. 1, approximately 4.5×10^{-3}, is ~5 times greater than would be expected if the C-containing species were well-mixed into the argon-hydrogen plasma. This indicates that the hydrocarbons in the central injection jet have had relatively little time to diffuse radially before reaching the substrate.

The averages (over each run) of the measurements are shown in Fig. 2, for both CH_4 and C_2H_2 injection, and are compared to the predictions of a numerical model. The two sets of data show little difference between CH_4 and C_2H_2 injection, supporting the assumption that reactants are fully dissociated in the hot plasma. This conclusion is further supported by measurements, reported elsewhere in these proceedings [14], in which a quadrupole mass spectrometer was used to measure species concentrations in a virtually identical reactor, operating at about 200 torr.

The numerical model considered chemical reactions in the boundary layer above the substrate and in the GC probe system. Following our

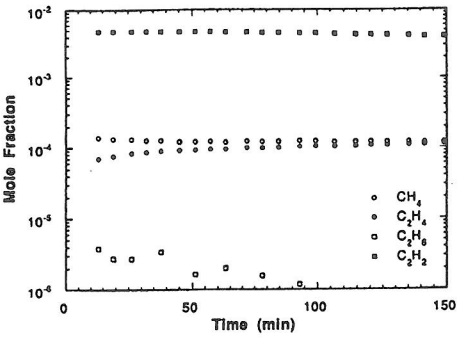

Figure 1. Transient GC measurements during diamond growth.

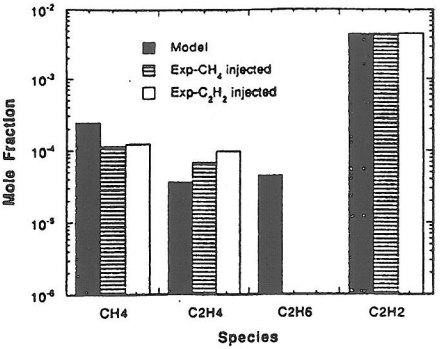

Figure 2. A comparison of modeling and GC measurements during diamond growth.

previous work [3-5] the boundary layer was defined as extending to the 4000 K isotherm in the plasma. At that point chemical equilibrium was assumed, for a gas mixture in which Ar and hydrogen were assumed to be well-mixed, while the C-species mass fraction was set equal to the average of the values measured by the GC. Calculations were performed using the Sandia SPIN software package [15]. In the C-H-Ar system only the C_1 and C_2 hydrocarbon species were included. The surface boundary condition was a set of surface reactions which accounted for diamond growth from C_1H_m radical species, m = 0-3 [5]. The composition calculated at the surface was used as input to a one-dimensional model of the sampling probe. This model calculated the pressure, temperature and velocity profiles in the sample line. These profiles were input to the probe chemistry model. For these calculations we assumed that H atoms recombined instantaneously on the walls of the 2-mm ID sample line [16]. Agreement between the model and the measurement for the C_2H_2 concentration is excellent, while the predicted CH_4 concentration is about twice as high as measured. C_2H_2 and CH_4 are predicted by the model to be virtually unaffected by probe chemistry, so that the results directly represent their concentrations at the surface. The results for C_2H_4 and C_2H_6 are somewhat more complicated, in that they are affected by probe chemistry. For C_2H_4 the model predicts a surface concentration of 26 ppm, rising in the sample line to 36 ppm as a result of probe reactions. The experimental results are 2-3 times higher than this. For C_2H_6 the discrepancy between the model and the measurement is large. The model predicts that about 90% of the C_2H_6 is produced in the probe, primarily from self-scavenging of CH_3. Thus a C_2H_6 measurement here should serve as a surrogate for a CH_3 measurement. However the experimental measurement was only about 1 ppm, close to the lower limit of the GC

sensitivity, whereas the model predicted 45 ppm. A possible explanation for this discrepancy is that the freestream temperature on the jet axis was lower than the 4000 K value assumed by the model. Calculations to test the sensitivity of the model to freestream temperature indicate that a colder-than-assumed freestream would also explain the trend of the discrepancies for CH_4 and C_2H_4, while the predicted C_2H_2 concentration is virtually unaffected by freestream temperature.

Film morphology

Diamond growth studies were conducted to relate the substrate temperature T_s and the feed gas composition to the film morphology. The

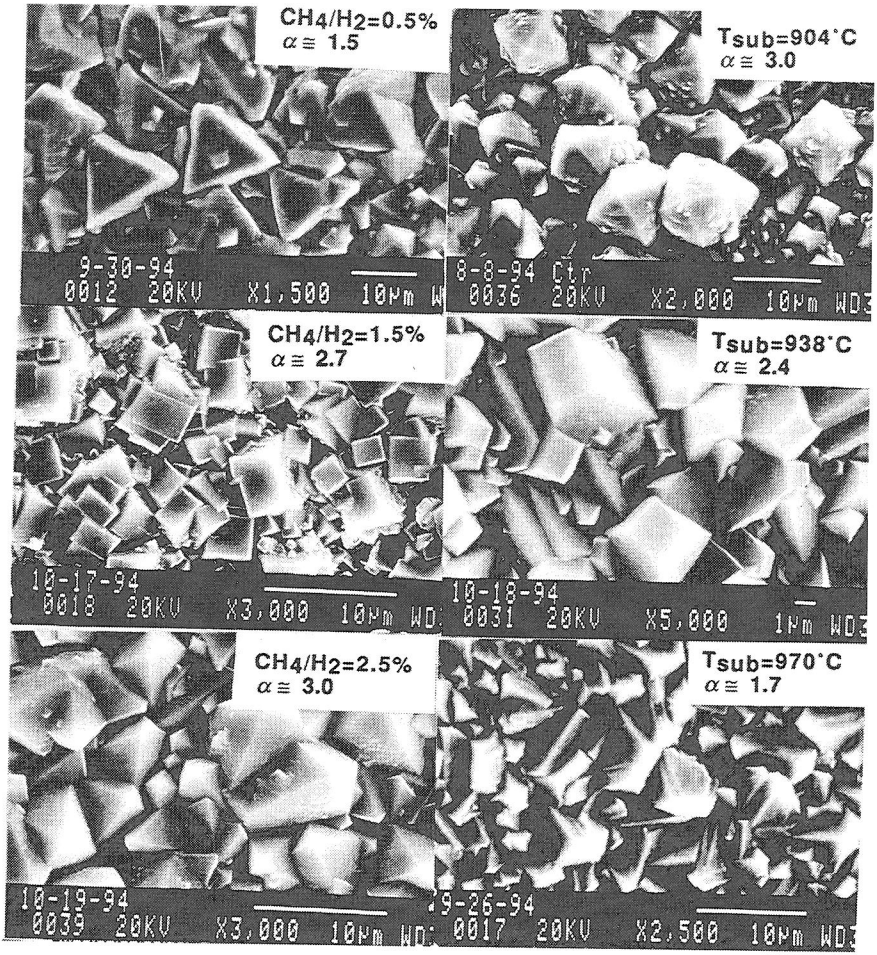

Figure 3. Micrographs showing the effect of substrate temperature and gas composition on the film morphology.

reactor used for these studies was similar to the reactor used for the GC studies with the exception that downstream of the RF coil a converging nozzle was used to accelerate the plasma toward the substrate. Two separate sets of experiments were conducted, both at 1 atm and with Ar and H_2 flow rates identical to the experiments described above. For the first set of experiments T_s was maintained at 970°C, and the CH_4/H_2 ratio was varied from 0.5 to 2.5%. For the second set of experiments CH_4/H_2 was maintained at 1.0%, and T_s was varied from 904 to 1165°C. Fig. 3 shows representative scanning electron micrographs of the resulting films. Values of the growth parameter α were assigned by visual inspection of the micrographs [12]. Increases in CH_4/H_2 and decreases in T_s caused α to increase, consistent with previously reported trends for microwave systems [11,12]. However there is an apparent shift between the results from the different systems, as shown in Fig. 4. Compared to the microwave plasma, the RF thermal plasma produces the same value of α for higher T_s and lower CH_4/H_2. As what actually determines α is not the feed gas inputs but actual surface concentrations, this shift is explained by the fact that the two types of systems produce different results for gas composition at the surface for the same reactant inputs.

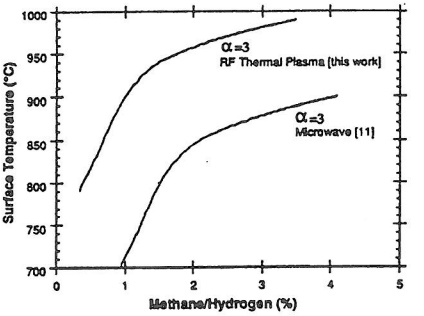

Figure 4. Graph showing the growth parameter shift between systems.

Conclusions

A gas chromatograph was used to obtain the first concentration measurements of several hydrocarbon species at the diamond growth surface in an RF thermal plasma. The measurements indicate that species concentrations are only slightly affected by whether the feed gas is CH_4 or C_2H_2, suggesting full dissociation in the hot freestream, and that the central jet in the reactor is carbon-rich relative to a fully-mixed assumption. A comparison of the data with a numerical model suggests that the freestream temperature on the central axis may be colder than the 4000 K value assumed. In separate experiments, also with a 1-atm RF plasma, the diamond growth parameter α was characterized for various values of CH_4/H_2 ratio and substrate temperature. The results followed the same trend as previously reported for microwave plasmas, but with a systematic shift in the growth parameter. This is presumably due to different species concentrations at the surface in the two types of systems for the same methane/hydrogen ratios. A long-term goal of this work is to relate film morphology to species concentrations at the film surface.

Acknowledgments

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