IN-SITU DETECTION OF GASEOUS SPECIES IN THE FILAMENT-ASSISTED DIAMOND GROWTH ENVIRONMENT

F. G. CELII, P. E. PEHRSSON, H.-t. WANG, H. H. NELSON, and J. E. BUTLER

Chemistry Division, Naval Research Laboratory, Washington, D.C. 20375-5000, U.S.A.

In-situ gas phase diagnosis of the filament-assisted diamond deposition environment has been performed. We report the identification and concentrations of gaseous species present in the growth environment as determined by infrared diode laser absorption, laser-excited fluorescence and multiphoton ionization spectroscopies. From a reactant mixture of 0.5% methane in hydrogen, C$_2$H$_2$ ($2 \times 10^{14}$ mole/cc), C$_2$H$_4$ ($6 \times 10^{15}$) and CH$_3$ ($2 \times 10^{15}$) were detected above the growing surface. Concentration limits for undetected species were estimated. The results are discussed in terms of simple models for species formation and consumption, as well as the implications for the diamond growth mechanism.

1. Introduction

The growth of diamond from the vapor phase has been the subject of intense interest over the last ten years because of its potential for diverse industrial applications. The various techniques and historical development of diamond growth from the vapor phase have been reviewed recently.

Diamond, the cubic crystalline form of carbon, is metastable with respect to graphite at the low pressures involved in these techniques. What is not yet well established is why diamond can be grown at all. A common characteristic of each of these techniques is a supersaturation of carbon species in the gas phase and the presence of molecular and atomic hydrogen. But which molecules, radicals or atoms are crucial to the deposition of diamond as opposed to other forms of carbon? To obtain a detailed understanding of the diamond deposition processes it will be necessary to understand the gaseous chemistry, the transport of species to/from the growing surface, and the surface chemical processes. To date, most characterization has focused on the deposited material itself.

Optical emission from the excited states of gaseous species has been reported, but little evidence is given to substantiate the importance or concentration of the detected species. In this work we report the use of in-situ optical diagnostics to characterize the various gaseous species present in the filament-assisted diamond deposition environment that has been well established by many laboratories.

We employed tunable infrared (IR) diode laser absorption spectroscopy, UV resonance enhanced multi-photon ionization spectroscopy (REMPI), and laser-induced fluorescence (LIF) as the in-situ optical probes. IR diode laser spectroscopy is a highly selective and sensitive probe of small molecules at low pressures (CH$_3$, C$_2$H, CH$_2$, CH$_4$, C$_2$H$_2$, C$_2$H$_4$, etc.) while REMPI and LIF are spatially selective and highly sensitive probes of species with accessible electronic states (CH$_3$, H, CH, CH$_2$, C$_2$, C$_3$, etc.).

2. Experimental

The filament-assisted diamond deposition apparatus was contained in a stainless steel six-way cross (6 in. i.d.). The flow of reagents was controlled by mass flow controllers. Typical growth conditions were 100 sccm total flow of 0.5% CH$_4$ in H$_2$ at 25 torr. All gasses were research grade with purity in excess of 99.99%. The temperature of the filament (tungsten, GE218, 6–10 turns, 0.33 mm dia.) was monitored by a two-color optical pyrometer and that of the substrate was measured by a chromel-alumel thermocouple (and occasionally, an IR two-color pyrometer) through a fused silica window.

The IR diode laser diagnostics were performed by mounting multi-pass reflection mirrors on opposing side arms of the six-way cross and
detecting the rotational-variational spectra of the gaseous species in the optical path traversed by the laser beam. The spectrometer and optical arrangements have been reported previously.\textsuperscript{17,18} A schematic diagram of the cell is shown in Fig. 1. The laser beam was aligned to sample the volume of gas between the filament and the substrate (2 mm high, 0.5 mm above the substrate). The filament to substrate distance was typically 15 mm for the IR measurements.

The resonance enhanced multi-photon ionization spectroscopy (REMPI) measurements used a XeCl excimer laser pumping a tunable dye laser (0.25 cm\textsuperscript{-1} bandwidth, 15 ns pulse width, 20 Hz, 15 mj/pulse) as the light source, with synchronous, gated detection of the photo-electrons collected on a Pt probe wire.\textsuperscript{19,20} A bias voltage of 150 V on the surrounding surfaces increased the efficiency of photo-electron collection. The laser light was focussed 1 mm from the collection probe with a 250 mm f.l. lens. Standing wave experiments were performed to suppress interference by the third harmonic light\textsuperscript{21} by reflecting the laser light back upon itself with a spherical mirror positioned outside the exit window of the cell. The collection probe was positioned 2–4 mm above the substrate unless otherwise noted, and the filament position was variable between 6 to 20 mm above the substrate.

Laser Induced Fluorescence (LIF) measurements were attempted with the excimer pumped dye laser system mentioned above. Fluorescence was collected at right angles to the excitation laser beam with f/4 optics, filtered with appropriate color glass filters and imaged onto a photomultiplier. Gated detection of the photo-current was used to discriminate against the filament radiation.

Fig. 1. The cell used for IR diode laser diagnostics of a filament-assisted diamond deposition environment is shown schematically. The IR beam is reflected ca. 20 times across the 10 in. mirror spacing before exiting the cell.
3. Results

Material was grown on substrates of silicon (100 orientation, N-type, unpolished or polished with diamond powder), polycrystalline Ni, Ag-coated Ni, and highly ordered pyrolytic graphite (HOPG). The deposited material was characterized as diamond by X-ray diffraction (3.555(8) Å), Raman scattering (1332 cm⁻¹ phonon), X-ray photo-electron spectroscopy (only carbon, 32 eV plasmon), Auger electron spectroscopy (only carbon, with diamond lineshape), and optical and scanning electron microscopies (single and twinned cuboctahedra, polycrystalline films with well-defined 100 and 111 facets).

Selected portions of the IR spectrum between 600 and 1400 cm⁻¹ were scanned using 0.5% CH₄ in H₂, T₀=2300ºC, and T₀=900ºC. The IR absorption spectra of the methyl radical detected in this environment is shown in Fig. 2. Three lines of the ν₂ Q branch head are displayed along with absorption lines of the N₂O wavenumber calibration gas in a separate cell, and the interference pattern of an etalon used as a wavenumber marker. The “noise” in the methyl radical spectrum is due to interferences within the multi-pass cell optics. Many other individual rovibronic lines were detected, the majority of which were assigned to fundamental and hot band transitions of acetylene, C₂H₂. An example of an acetylene band head is given in reference 18). CH₄ and C₂H₄ were also detected. The following species were searched for but not detected: CH₂ (³B₁), and the stable molecules C₂H₆, C₃H₄, C₃H₆, and C₃H₅.

The 3+1 REMPI spectrum of the H atom, Fig. 3, was obtained at 364.5 nm using a three photon resonance with the 1s–2p transition, 121.57 nm, and ionization by an additional photon. Also shown are Ne optogalvanic lines which were used for wavelength calibration. This spectrum was obtained with no methane present and with traveling wave excitation. The variation of the H atom REMPI signal with filament temperature for different concentrations of methane in hydrogen is shown in Fig. 4. The filament was 8 mm above the probe position and standing wave excitation geometry was employed for these measurements. The signal was reduced when the filament-to-probe distance was increased. When the probe was placed 8 mm above the filament, similar REMPI signal intensities were observed as when it was below the filament. This was true for mass flow rates of 100 scem and 1500 scem.

The presence of the methyl radical was confirmed by the detection of its 2+1 REMPI spectrum at 333.5 nm (3p ¹A₂⁺→ X ¹Σ⁺). Detection of the transient species C₂, CH and C₃ was attempted by LIF. Only C₃ was detected with poor signal-to-noise ratio. Scattered light from the hot filament was a severe limitation with the present cell geometry.

4. Discussion

Estimation of the absolute concentrations of the various species from the observed IR absorptions requires knowledge of the optical path length, species distributions, temperature, and absorption
Fig. 3. The 3+1 REMPI spectrum of the atomic hydrogen 1s→2p resonance is shown. Neon transitions detected optogalvanically in a hollow cathode lamp were used for wavelength calibration.

Fig. 4. The logarithm of the relative H atom REMPI signal intensity is plotted as a function of the filament temperature for various mass flow percentages of CH₄ in H₂.

coefficients. For stable molecules, crude calibration was attempted by filling the chamber with a known pressure of the gas, and then assuming a uniform temperature equal to the measured rotational temperature of acetylene, 200–300°C, estimated from the relative intensities of the (ν₄+ν₅−ν₄) Q branch band head.¹⁸ This temperature is closer to that of the cold walls of the cell than either the filament or the substrate, and is due to the absorption of acetylene molecules distributed throughout the optical path. The very crude estimates of concentrations and upper limits of concentrations made by this approach are summarized in Table 1. The major uncertainties were the temperature inhomogeneities across the cell for stable molecules and the spatial distribution of methyl radicals in the optical path. The estimate of the methyl radical concentration was made using the transition moment determination of Yamada.²³ Also indicated in Table 1 are the species detected using REMPI and LIF.

It is significant that all of the observed gaseous hydrocarbon species are those which are stable at high temperatures. Figure 5 presents the results of
Table 1. Summary of observations showing molecules examined, technique employed for detection (no entry indicates the technique was not used), and estimate of the concentration for 20 torr of 1% CH₄ in H₂, 2200°C filament temperature, and ca. 900°C substrate temperature.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Detected by</th>
<th>Concentration estimate (molec./cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IR REMPI LIF</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>CH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₂ (³B₁)</td>
<td>no</td>
<td></td>
</tr>
<tr>
<td>CH₃</td>
<td>yes yes</td>
<td>2±1.5×10¹²</td>
</tr>
<tr>
<td>CH₄</td>
<td>yes</td>
<td>8±1×10¹⁴</td>
</tr>
<tr>
<td>C₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₂</td>
<td>yes no</td>
<td>2±1×10¹⁴</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>yes</td>
<td>6±2×10¹²</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>no</td>
<td></td>
</tr>
<tr>
<td>C₃</td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td>C₃H₄-allene</td>
<td>no</td>
<td>&lt;8×10¹³</td>
</tr>
<tr>
<td>C₃H₅-methyl acetylene</td>
<td>no</td>
<td>&lt;8×10¹³</td>
</tr>
<tr>
<td>C₃H₆-cyclopropane</td>
<td>no</td>
<td>&lt;6×10¹³</td>
</tr>
<tr>
<td>C₃H₆-propylene</td>
<td>no</td>
<td>&lt;2×10¹³</td>
</tr>
<tr>
<td>C₄H₆</td>
<td>no</td>
<td>&lt;3×10¹³</td>
</tr>
</tbody>
</table>

![MODEL OF FILAMENT-ASSISTED DIAMOND DEPOSITION](image)

Fig. 5. A simple model of the gaseous chemistry occurring in the filament-assisted deposition of diamond is presented. On the right is a plot of the log of the mole fraction of the gaseous constituents of a 25 torr gas mixture (initial composition 0.5% CH₄ in H₂) at equilibrium versus the equilibrium gas temperature.
an equilibrium calculation of the gaseous component concentrations vs. temperature for an initial gas mix of 0.5% CH₄ in H₂. Comparison of the crude concentration determinations reported in Table 1 with this equilibrium calculation indicates that the chemical composition of the gaseous environment between the hot (2300 to 2600 K) filament and deposition surface is similar to that of the thermodynamic equilibrium composition of a 0.5% CH₄ in H₂ gas mix at 1500 to 2300 K. The most glaring exception in this comparison is that of the initial hydrocarbon reactant, CH₄, whose concentration is higher than expected for the equilibrium model. This may indicate that the residence time of the gas near the hot filament is insufficient for complete equilibrium to be established. As the species generated at/near the filament diffuse or flow to the colder deposition surface, it is likely that the most reactive species, (e.g., C, CH, CH₂, etc.) will be depleted and the "chemical" temperature of the gas will be lowered. Since the growth surface temperature is significantly lower than the "chemical" temperature of the gas (1200 K versus 1500 to 2300 K), condensation of carbon from this "super-equilibrium" gas is likely. This simple model also suggests an explanation for the observed lack of dependence on the nature of the hydrocarbon reactant in that the thermodynamic equilibrium concentration of chemical species is independent of the nature of the initial reactants.

What is the role of atomic hydrogen in this deposition environment? This question will be very difficult to answer without detailed surface studies of the growing surface. The REMPI measurements indicate the presence of atomic hydrogen (Fig. 3) with increasing concentration as the filament temperature (Fig. 4) is raised, in agreement with the thermodynamic calculation presented above. The data for 3% CH₄ in H₂, Fig. 4, suggest a poisoning of the filament surface or suppression of the gaseous H atom concentrations at temperatures lower than 2250°C, as compared with reactant gas mixes with lower CH₄ concentrations. This correlates with the evidence for higher concentrations of graphitic/amorphous carbon deposits reported for the higher CH₄ concentration gas mixes. Thus, one of the roles of the atomic hydrogen may be the preferential etching of non-diamond forms of carbon simultaneous with the deposition of all forms of carbon. Other functions, such as surface stabilization, shifting of gas phase equilibria, etc. are also possible.

H atom transport within ca. 15 mm of the filament is predominantly by diffusion. This is shown by the similarity of the H atom REMPI signals detected above and below the filament and by the lack of mass flow rate dependence when the probe is between the H₂ inlet and the filament. This observation is consistent with estimates of the H atom diffusion velocities of ca. 10⁴ cm/sec. The transport of heavier species and gases in regions away from the immediate vicinity of the filament is probably driven by buoyancy (convection) and inlet/pumping effects (forced flow) in this hot filament-cold wall cell.

5. Conclusions

This work has demonstrated the utility of in-situ optical diagnostics in understanding the gaseous chemistry of the filament-assisted diamond CVD environment. The radical (H, CH₃) and stable (CH₄, C₂H₂, C₂H₄) species detected indicate that a simple thermodynamic equilibrium calculation is very instructive about the gaseous chemical composition above the diamond deposition surface, while the need for more refined modeling calculations is evident. Diffusion was shown to be the main transport mechanism for H atoms near the filament, and a suppression of H atoms was observed for filament temperatures below 2200°C with methane concentration greater than 3.0%.

Acknowledgements. We thank Dr. Earl Skelton for performing the X-ray diffraction measurements and Drs. John Reintjes, Steve Harris, and H. Doug Ladouceur for helpful and insightful discussions. This work was supported in part by the Office of Naval Research.

REFERENCES