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OBSERVATION OF OH RADICALS IN A FILAMENT-ASSISTED DIAMOND GROWTH ENVIRONMENT*

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The first observations of the hydroxyl radical in a hot filament assisted diamond growth environment are presented. Laser-induced fluorescence (LIF) is used to make *in situ*, nonintrusive, measurements of the spatial distribution of OH concentration near the filament as a function of feedstock composition, reactor pressure, and filament temperature. LIF measurements of the OH rotational level population distribution are used to determine spatially resolved gas temperature.

Introduction

The addition of oxygen to the feedstock gases for diamond CVD can have a profound effect on the quality of the resulting diamond film. Kawato and Kondo (1) found the deposition of graphitic or amorphous carbon could be suppressed. Several studies (2-5) of microwave diamond CVD have found that oxygen addition can extend the range of conditions which produce diamond film. For example, Liou et al. (5) found that the addition of oxygen allowed them to significantly reduce the substrate temperature. All these studies (1-5) find that the diamond growth rates can be varied and the quality of the film significantly improved by the addition of O_2.

The influence of oxygen on the gas composition of hot filament diamond CVD has been investigated using *in situ* mass spectrometry by Harris and Weiner (6). They find that oxygen addition can convert a significant fraction of the hydrocarbons to CO and H_2. They model the gas chemistry with added oxygen and find good agreement with their measurements of CO, C_2H_2, and CH_4. They postulate that the addition of oxygen produces "sufficient gas phase OH to remove the nondiamond (pyrolytic) carbon from the film (6)." Frenklach and Wang (7) have introduced oxygen into their detailed model of hot filament assisted diamond growth. They find the oxygen addition has two significant effects: 1) formation of aromatics is suppressed by the oxidation of the carbon to CO and 2) the gasification of deposited sp^2 phase carbon by OH radicals.

We have observed hydroxyl radicals in our hot filament reactor using laser-induced fluorescence (LIF). LIF has four principal advantages for the detection of chemically reactive radical species like OH. First, the LIF measurement is selective; each species has its own definitively characteristic excitation and detection spectra. Second, the measurements can be performed *in situ* without inserting physical probes into the plasma or extracting any of the plasma gases. Third, LIF is quite sensitive: ppb detection limits of OH are quite feasible. Fourth, the measurement is spatially resolved; signal is observed only from the intersection of the laser beam and fluorescence collection viewing region.

LIF measurements of the rotational population distribution in OH are used to determine gas temperatures as a function of pressure and distance from the filament. The OH concentration is measured as a function of reactor pressure, feedstock composition, and filament temperature. These measurements show that OH is indeed present in hot filament diamond CVD reactors which use H_2-CH_4-O_2 mixtures.

Experimental Method

The hot filament reactor is constructed inside a 30 cm vacuum chamber with a feedstock inlet 5 cm above the filament and gas exhaust 10 cm below. Figure 1 is a schematic drawing of the experimental arrangement showing the hot filament and the optical collection geometry. A 0.04 cm diameter, 3.3 cm long tungsten wire is mounted on molybdenum posts and is heated by direct current to temperatures 2300-2800 K as measured by an emission corrected optical pyrometer. The filament and gas inlet is mounted on a vacuum manipulator which allows us to alter the laser beam to filament distance with fixed optical collection. The laser enters the chamber through Brewster angle windows, and the fluorescence is collected f/5 at right angles to the laser beam. The excitation laser is aligned along the filament. Fluorescence from molecules excited by the laser is collected, and passes through a spatial filter which limits the field of view to a region 0.5 cm along the laser beam and 0.1 cm perpendicular to the beam. The light is then spectrally filtered with a uv pass filter (Schott UG5) and a 0.25 m monochromator, and detected on a photomultiplier, whose signal is integrated on a boxcar integrator and linearly averaged by a laboratory computer. The spatial filter eliminates much of the emission from the hot filament. At positions near the filament, significant scattered laser light is observed. To avoid much of this scattered light and improve the signal/noise ratio of the LIF measurements, the 40 ns wide boxcar gate is delayed 50 ns with respect to the laser pulse.

To obtain an LIF signal, the laser wavelength is tuned to a hydroxyl absorption in the 0-0 band of the $A^2\Sigma^+$-$X^2\Pi_i$ electronic transition near 308 nm. When the laser wavelength coincides with a specific rotational transition, OH radicals absorb a laser photon and are excited to the A state. These excited molecules can radiate, undergo energy transfer collisions to other rotational levels which subsequently radiate, or be collisionally quenched. The fraction that radiate is called the quantum yield, and this fluorescence is the LIF signal. An example of the OH LIF signal in the hot filament

reactor is shown in the upper panel of Figure 2. The laser wavelength is scanned through a series of transitions; the wavelength of the observed features and their identification (8) shown above the upper panel unambiguously identify the LIF signal as originating from OH radicals.

Quantitative relative OH concentrations can be inferred from the signal intensity, gas temperature, density, and composition. The LIF signal is the product of the excited state number density N_e and the quantum yield Φ. The laser excites molecules with a rate $dN_e/dt = BI_L N_g f$, where N_g is the ground state concentration, f the Boltzmann fraction of population in the absorbing rotational level, B the Einstein absorption coefficient, and I_L the laser intensity. The quantum yield for the LIF is $\Phi = A/(A+Q)$, where A is the Einstein A coefficient and Q is the collisional quenching rate. $Q = \Sigma k_{Qi} n_i$ where the sum is over all the species in the gas, k_{Qi} is the quenching rate constant for the ith species, and n_i the species concentration. Rate constants for OH quenching as a function of temperature for a variety of colliders including atomic hydrogen have been measured in our laboratories (9-12). The quenching rate constants for O_2, CH_4, and H_2 differ less than a factor of two and that for atomic hydrogen is at most a factor of five larger at 1200 K. Harris and Weiner (13) find that less than 1% of the gas in the hot filament reactor is atomic hydrogen. Thus, to calculate Q we use k_Q for H_2 and n equal to the total density.

Gas temperature is an important parameter in the conversion of the LIF signal to OH concentration. Both the excitation rate dN_e/dt and the quantum yield Φ are temperature dependent. The laser excites molecules from a single rotation level from the Boltzmann population distribution over all the rotational levels. Thus, dN_e/dt depends directly on f(T). The quantum yield has temperature dependence in both k_Q and n. The pressure is constant in the hot-filament reactor, so n is simply proportional to 1/T. k_Q for hydrogen declines ~25% over the temperature range in the hot filament reactor; we calculate the quenching corrected relative concentrations from high temperature quenching measurements (11).

The gas temperature is deduced from LIF measurements of the rotational distribution; this distribution is deduced from a laser excitation spectrum like that shown in Figure 2. The signal intensity for each transition is divided by the degeneracy and rotational line strength, and ln(I/Bg) is plotted versus the rotational energy of the ground state rotational level. The lower panel of Figure 2 shows such a Boltzmann plot for the spectrum in the upper panel. The straight line indicates that the distribution is well described by a temperature, and the slope of the line is proportional to 1/T. The 0-0 band of OH extends over a broad spectral range near 308 nm. This broad bandwidth requires the photo detector to have a uniform response over the 306-321 nm to avoid spectral bias errors in the temperature. We construct a spectral filter with a trapezoidal bandpass from a small (0.25 m f.l.) monochromator by setting a narrow (0.05 cm) front slit and the broad (0.5 cm) exit slit. Systematic errors in OH LIF temperature determination from spectral bias are discussed in detail in Ref. 14.

Results and Discussion

The gas temperature measured by LIF is significantly lower than the temperature of the hot filament. The data in Figure 2 are taken at 30.9 Torr, 1.1 mm from a filament at 2750 K. The slope of the Boltzmann plot in the bottom of Figure 2 gives a best fit of 1541 ± 88 K. The feedstock gas is H_2 with 0.5% CH_4 and 0.5% O_2. This temperature difference is slightly greater than observed with thermocouple measurements by Harris et al. (15). They measured 1800 K in the gas 1 mm from a 2600 K filament. The thermocouple measurements were not corrected for radiation. One would expect radiative heating of a thermocouple in close proximity to the brightly glowing hot filament, and thus a lower actual gas temperature.

The gas temperature depends on the reactor pressure. Figure 3 shows the OH LIF temperature as a function of distance from a 2600 K filament at hydrogen pressures of 4.4, 10.4, and 30.9 Torr. Again the added methane and oxygen are 0.5% each. The temperature gradient is in good agreement with Harris et al. (15). Both of these experiments measured the gas temperature without a substrate. With a substrate at 800-1200 K temperature and a distance from the filament of 0.5-2 cm we would expect an even steeper temperature gradient than shown in Figure 3. A temperature gradient which depends on substrate distance has been observed (16).

The relative OH concentration versus distance from the filament is shown in Figure 4. These data at 30.9 Torr are representative of the data over the entire range 4-30 Torr. The OH falls rapidly for 4-6 mm to 10-20% of the peak OH observed. The lower concentration is then nearly constant to distances of 1 cm. Note that the data in Figure 4 have been corrected for temperature dependent quenching of H_2 and the variation in Boltzman fraction, using the temperature gradient in Figure 3.

The OH concentration is strongly dependent on reactor pressure. The OH intensity exciting the $R_1(3)$ line falls by a factor of 40 from 4-25 Torr. The LIF signal depends on the product of OH number density and quantum yield. In the limit $Q>>A$, $\Phi \sim 1/Q$ and Q is proportional to gas pressure. Thus, for a constant mole fraction of OH in the limit where most of the excited molecules are collisionally quenched, the OH LIF signal is independent of pressure. Thus, the rapid drop in OH intensity is surprising and indicates that the mole fraction of OH declines with reactor pressure. Using the data in Figure 3 to predict the gas temperature as a function of pressure and correcting for quenching by H_2, the we find the OH mole fraction declines by a factor of 30 as the reactor pressure rises from 4 to 25 Torr.

Figure 5 shows the variation in the relative OH concentration as a function of added CH_4 and O_2. The OH concentration does not depend on the amount of added CH_4, as shown by the triangles in the figure for 0.7% of added O_2. However, the OH is quite dependent on the amount of added O_2; increasing the O_2 by a factor of four increased the OH by a factor of 14. This large variation is expected; Harris and Weiner (6) predict a factor of 6 increase in the OH at 7% CH_4 when the O_2 is increased from 1-3%.

Summary

We have observed LIF from OH radicals in a hot filament diamond CVD reactor in a mixture of H_2, CH_4, and O_2. We find the gas temperature is significantly cooler than the filament temperature. The gas temperature increases with increasing pressure. The OH mole fraction declines significantly with increasing reactor pressure. The OH concentration does not depend on the amount of added methane, but is strongly dependent on added oxygen.

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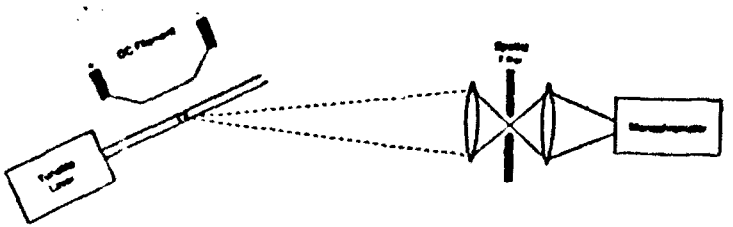

Fig. 1. Schematic diagram showing the orientation of the laser beam, hot filament, and optical collection.

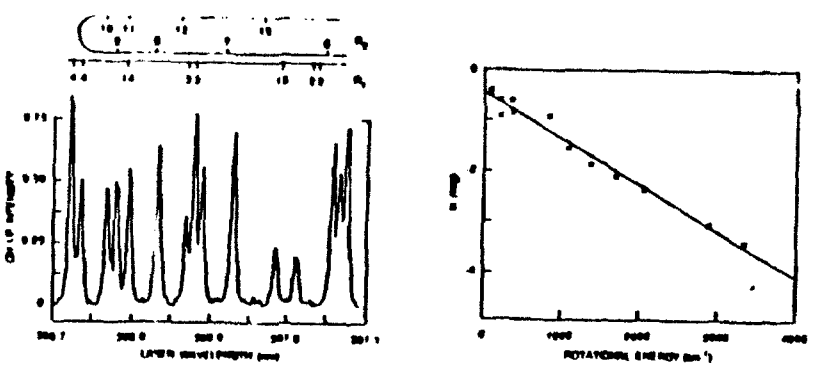

Fig. 2. Left: OH LIF rotational excitation spectrum taken 1.1 mm from a 2750 K filament in 30.9 Torr H_2 with 0.5% CH_4 and 0.5% O_2.

Right: Boltzmann plot of the relative rotational level populations determined from peak height analysis of the spectrum in the top panel. The best fit slope gives T = 1541 ± 88 K.

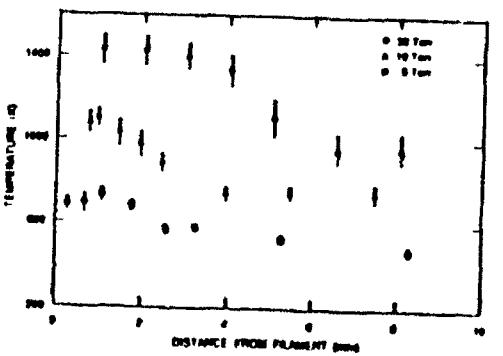

Fig. 3. Gas temperature determined from OH rotational excitation spectra versus distance from the filament for 30.9, 10.4, and 4.3 Torr pressure of H_2 with 0.5% CH_4 and 0.5% O_2 with a 2600 K filament temperature.

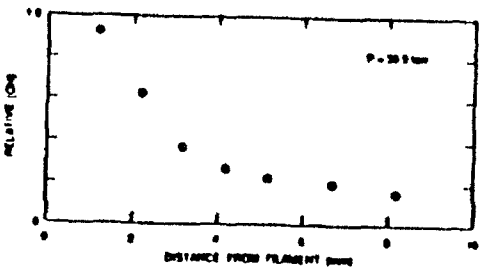

Fig. 4. Relative OH concentration versus distance from a 2600 K filament at 30.9 Torr from quenching corrected LIF measurements.

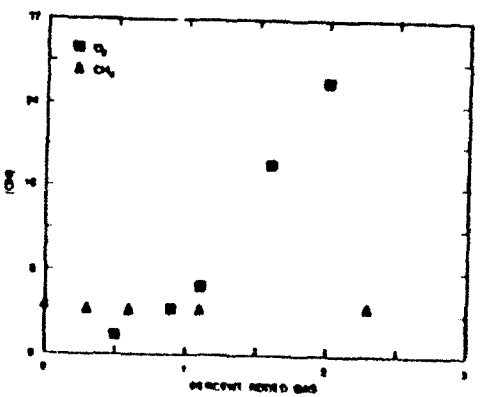

Fig. 5. Relative OH concentration from quenching corrected LIF measurements versus added CH_4 and O_2 at 4.4 Torr of H_2 1.0 mm from a 2700 K filament. CH_4 variation (triangles) at 0.7% added O_2 and O_2 variation (squares) at 0.6% added CH_4.