Degenerate four-wave mixing diagnostics of atmospheric pressure diamond deposition

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Abstract

Optical diagnostic techniques for the study of atmospheric pressure diamond synthesis reactors are evaluated. Benefits and disadvantages of optical emission spectroscopy (OES), laser-induced fluorescence, and a promising new technique, degenerate four-wave mixing (DFWM), are discussed in terms of their applicability to the harsh environment of atmospheric pressure diamond deposition reactors. *In situ* DFWM measurements of trace radical species, CH and C_2, in an atmospheric pressure diamond synthesis reactor are reported. These measurements are believed to be the first application of this new spectroscopic technique to an atmospheric pressure plasma synthesis reactor. DFWM measurements of the CH radicals in the boundary layer of an r.f. inductively coupled plasma deposition reactor are compared with results of OES and a computational model of the deposition environment.

1. Introduction

Chemical vapor deposition of diamond films at atmospheric pressure is attractive for several reasons. The high reactant densities available at atmospheric pressure can yield large growth rates over large areas. Operation at atmospheric pressure also precludes the loading and unloading of samples to be coated from a vacuum system. From a modeling point of view, the atmospheric pressure reacting flowfield is in the continuum, rather than the molecular or transitional, flow regime and is more readily simulated. These beneficial attributes of atmospheric pressure deposition are tempered by the presence of a collision-dominated, chemically reacting boundary layer above the substrate surface in which important chemical species are both produced and destroyed. This aspect of atmospheric pressure techniques is strikingly different from low pressure deposition techniques in which production and diffusion of chemical species controls the deposition process.

In the past several years, studies of high growth rate polycrystalline diamond film synthesis at atmospheric pressure have been performed using an r.f. inductively coupled plasma torch [1–3]. An r.f. inductively coupled plasma offers the benefits of an "electrodeless" discharge for minimum film contamination, as well as the ability to produce a large-area uniform freestream to aid further both deposition and modeling. Experimental parametric investigation of substrate temperature, methane to hydrogen feed ratio, substrate location, and freestream Reynolds number have been coupled with simulations of the growth environment to define and characterize the atmospheric pressure diamond growth regime [1–7]. Comparison of experimental growth results with computational models has proven to be very useful in understanding the growth environment, but to date these comparisons have been limited to "bottom line" quantities such as growth rate. To explore further the nature of the atmospheric pressure diamond deposition environment and process, it is necessary to make accurate measurements of temperatures and species concentrations within the reacting boundary layer over the substrate, and compare these fundamental quantities with detailed simulations.

Measurement of important quantities such as temperature and radical concentrations is a challenging problem in atmospheric pressure reactors owing to the highly luminous environment, small spatial scales, and steep thermal and species gradients. Application of the most common optical diagnostic tool, optical emission spectroscopy (OES), would at first thought be quite promising owing to the high luminosity of atmospheric pressure reactors. This approach, however, has severe limitations in that only emitting species are accessible and that emission from important species within the cooler reacting gas inside the boundary layer is overwhelmed by the line-of-sight measurements of overall plasma luminosity. Although application of OES to the

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atmospheric pressure environment is thus very limited, it can be a simple and useful tool for probing regions outside the reacting boundary layer.

The application of sensitive, laser-based diagnostic techniques allows detailed measurement of temperature and trace radical concentrations to be made, and compared with models of the deposition environment. Conventional linear laser-induced fluorescence (LIF) techniques offer significant advantages over OES in that they permit the high spatial resolution required to resolve species within the thin, chemically reacting boundary layer, and they can probe species which are not naturally emitting in the region of interest. A significant remaining drawback is that the signals produced by LIF techniques are incoherent, and must be discriminated against the intense plasma luminosity. This limitation can be overcome in some situations, and LIF techniques have been used in near-atmospheric pressure arc-jet reactors [8], although these measurements were limited to the free jet plume without a growth substrate in place. The recent application of a non-linear laser spectroscopy, degenerate four-wave mixing (DFWM) as a gas-phase optical diagnostic has opened the door for significant advancement in the area of atmospheric pressure plasma chemistry. Degenerate four-wave mixing offers much promise in the area of laser-based diagnostics of hostile environments, since it can provide high sensitivity and spatial resolution with a coherent, phase conjugate signal which can be readily discriminated against the plasma luminosity.

2. Experimental facility

The r.f. induction plasma torch has been described in previous work [1, 2]. The present experiments were conducted inside a water-cooled quartz test section which is shown in schematic cut-away along with the plasma torch head in Fig. 1. Open-ended laser access ports, approximately 6.5 cm downstream of the nozzle exit, enable the DFWM pump and probe beams to enter and exit the reactor unhindered, and to cross at a location directly below the stagnation point of the substrate.

Substrates are supported within the quartz test section in a stagnation point flow geometry by means of a water-cooled holder. The substrate is separated from the water-cooled holder by means of an adjustable thickness insulator, and is held normal to the oncoming plasma stream. The substrate can be vertically translated *in situ* to allow laser measurements to be made at various points through the boundary layer. The substrate temperature is monitored with a Pyro-Micro disappearing filament optical pyrometer. Mixture gases (hydrogen and methane) are premixed with the carrier gas (argon) before passage through the r.f. discharge.

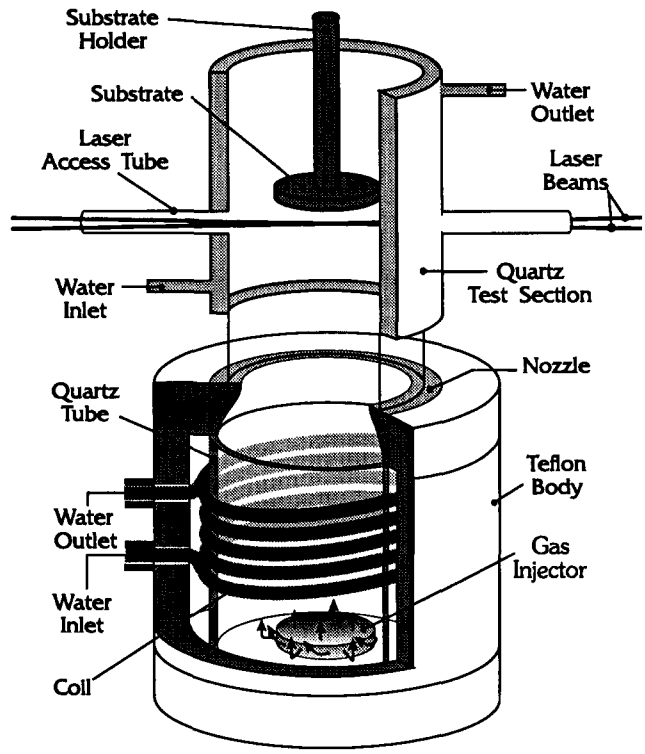

Fig. 1. Schematic cut-away of atmospheric pressure r.f. inductively coupled plasma diamond synthesis reactor.

The optical diagnostics system of this facility is shown schematically in Fig. 2. OES and LIF signals can be collected along the same optical collection train. Plasma emission measurements were made using a SPEX model 1400-II 3/4 meter scanning monochromator fitted with a Hamamatsu model R1104 photomultiplier tube. Absolute intensity calibrations were obtained by means of a tungsten strip lamp, with a calibration traceable to NIST standards. Plasma emission was monitored from the freestream, 1 cm upstream of the substrate surface.

Laser beams for LIF and DFWM experiments are produced using an Nd:YAG pumped dye laser system (Quanta-Ray model DCR-4 Nd:YAG tripled to 355 nm pumping a Lumonics model HD-500 dye laser with Bethune cell amplifier operating on coumarin 440). Dye laser output is tunable over the wavelength range 423–450 nm with a bandwidth of approximately 0.05 cm^{-1}. The output of the laser is spatially filtered to improve beam quality, and reduced in intensity with a variably rotated half-wave plate, fixed polarizer combination. The beam is then split into three beams (of approximately equal energy at the test section), the backward pump beam (denoted E_b), the probe beam (denoted E_p), and the forward pump beam (denoted E_f). Polarization of the backward pump beam is rotated

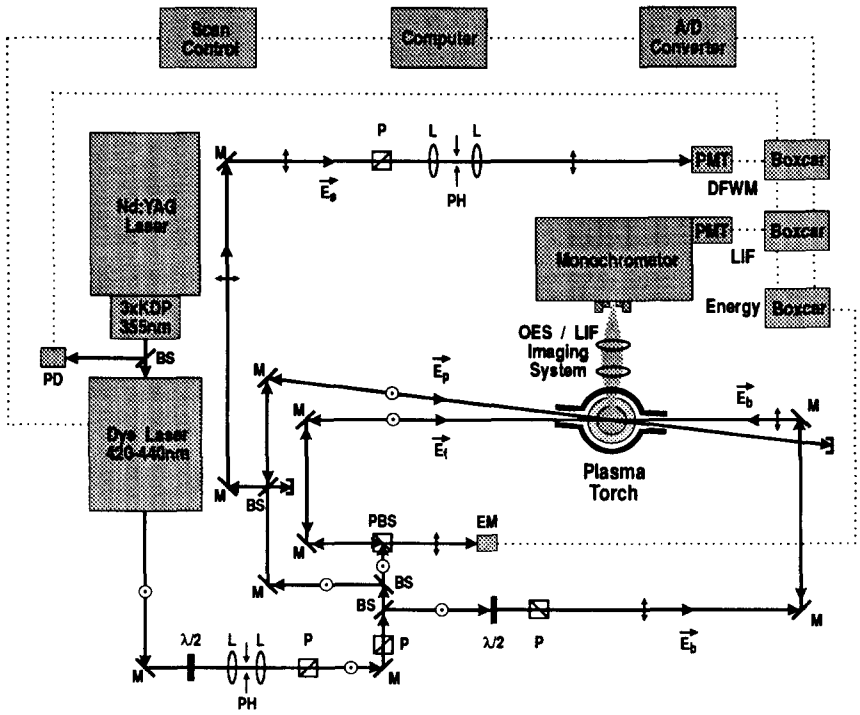

Fig. 2. Schematic diagram of DFWM, OES, LIF optical set-up. M mirror, $\lambda/2$ half-wave plate, P polarizer, L lens, PH pinhole, BS beam splitter, PBS polarizing beamsplitter cube, PD photodiode.

with a half-wave plate to be perpendicular to the polarization of the forward pump and probe beams. Convergence of the laser is adjusted to produce a mild focus at the mid-line of the test section, producing beam waists of approximately 300 μm diameter. The forward and backward pump beams are brought coaxial and counterpropagating through the test section laser ports, and the probe beam crosses the pump beams at a slight angle (approximately 2.1°) directly beneath the stagnation region of the substrate. The geometric interaction length of the pump and probe beams is approximately 16 mm (parallel to the substrate surface).

The phase-conjugate signal beam (denoted Es) is generated in the interaction region and follows the reverse path of the probe beam out of the test section. This signal beam counterpropagating along the probe beam line is separated by means of a beamsplitter, spatially filtered to reject incoherent scattering, and detected with an unfiltered photomultiplier tube (Hamamatsu model R212). Beam energy is continuously monitored by means of a joulemeter (Molectron model J4-09) which terminates the backward pump beam.

3. Computational model

To model completely this complex deposition process, one would need to consider the full two-dimensional axisymmetric reactor, including plasma energy addition from the r.f. coils, complete gas-phase and surface chemistry, and the time-dependent nucleation and growth phenomenon on the substrate. In the case of this atmospheric pressure r.f. inductively coupled plasma reactor, the problem can be cast in a much simpler form. The plasma generated by this r.f. inductively coupled plasma reactor is fairly slow moving (approximately 8 m s^{-1}) and flows approximately 10 cm from the end of the energy addition region (r.f. coils) to the region of interest in the test section (approximately 10 ms of flow time). The plasma reaching the region of interest is thus far enough downstream of the energy addition region to be free of strong electrical fields induced by the r.f. coils, and with the high collision rates at atmospheric pressure has reached a state of approximate chemical and thermal equilibrium in the freestream impinging upon the substrate [3]. Additionally, the stagnation point geometry of the reactor itself leads to a self-similar fluid dynamic solution [9], essentially a uniform boundary layer over the substrate, and leads to the reduction of a two-dimensional problem to a one-dimensional problem along the stagnation line. Full two-dimensional, simplified chemistry models of the finite extent substrate and reactor indicate that this simplification to one-dimensional flow is valid for regions inside approximately 80% of the substrate diameter [10]. Thus the deposition environment has been modeled by a one-dimensional stagnation point simulation [2, 3, 11] with coupled gas-phase and surface chemistry, utilizing an

equilibrium chemical composition at a measured free-stream temperature.

4. Degenerate four-wave mixing

DFWM is a third-order non-linear optical process in which three laser beams of a single frequency ω overlap in a medium to produce a coherent fourth beam, also at frequency ω. A complete description of the DFWM process is too lengthy to include in this paper but appropriate references include Abrams *et al.* [12], Farrow *et al.* [13], and Williams *et al.* [14]. To overview the technique briefly, we employ a collinear phase-conjugate geometry which consists of two coaxial and counterpropagating pump beams (E_f and E_b), which are crossed at a small angle θ by a probe beam (E_p). A grating analogy for the technique involves the idea of interference between the three beams. When the frequency is tuned to an atomic or molecular resonance, the interference leads to a spatial modulation in the complex index of refraction, and hence forms a grating. Two such modulations result, one from the interference of E_f with E_p at their crossing region to form a grating that scatters E_b into E_s (the DFWM signal, phase conjugate to E_p), and the second finer spaced grating which results from the interference of E_b and E_p to scatter E_f into E_s. The depth of modulation of the gratings is minute, and their scattering efficiency is poor (approximately 10^{-8} for the present conditions), but E_f and E_b contain so many photons (around 10^{13} per pulse for typical energies) that E_s is readily detected. The coherent nature of the phase-conjugate signal beam allows the detection at large distances from the plasma (about 7 m in this case) and thus results in excellent rejection of the incoherent plasma luminosity and laser scatter from the signal beamsplitter. This phase conjugate behavior also "self-corrects" any distortions the probe laser may encounter while propagating into the plasma, and thus is an excellent candidate to probe unsteady plasma jet flows. In some ways, the DFWM process may be thought of as a resonant form of coherent anti-Stokes Raman spectroscopy (CARS), but with several advantages. Like CARS, DFWM produces a coherent signal, but the DFWM process is fully resonant with one-photon transitions of the species being probed, and thus is a much stronger non-linear effect. For this reason, CARS is typically used as a major species probe, but DFWM has excellent application to both major and minor species. Another benefit that DFWM offers over CARS is the possibility for imaging applications due to the fact that its signal is phase conjugate and automatically phase matched.

For purposes of this preliminary study into the application of DFWM to atmospheric pressure plasma processing environments, it was decided to attempt detection of CH and C_2 radicals. Previous investigations [1–3] have indicated that there is a strong role of partial equilibrium amongst the C_1 and C_2 species with atomic hydrogen. In this manner, the investigation of CH and C_2 will have consequences for the more commonly thought of radicals such as C, CH_3 and C_2H_2. In the near future we also hope to be able to probe important radicals such as C and CH_3 directly with DFWM.

Representative DFWM spectra are shown in Figs. 3 and 4 of the CH and C_2 radicals. In Fig. 3 we see the resolved components of the R(5) lines of the $A^2\Delta \leftarrow X^2\Pi$ transition of CH. Both the $v''=0$ and $v''=1$ transitions are shown in this figure, and it is from these line pairs that vibrational temperatures can be evaluated [13, 14]. In Fig. 4 we see the region near the $A^3\Pi(v=3) \leftarrow X^3\Pi(v=1)$ band head of the C_2 Swan band system.

5. Results

In this study it was desired to make *in situ* measurements during normal operation of the atmospheric pressure r.f. inductively coupled plasma diamond synthesis

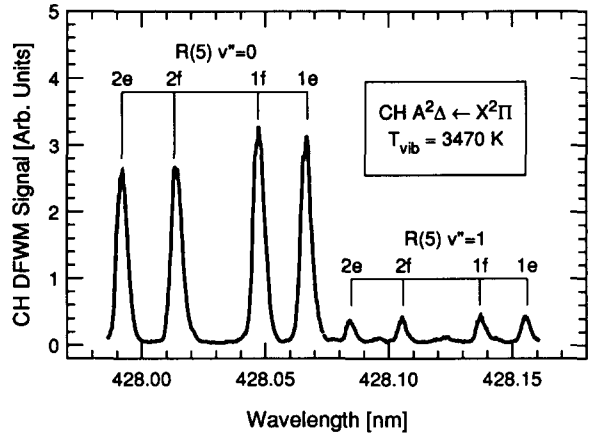

Fig. 3. DFWM spectrum of CH $A^2\Delta \leftarrow X^2\Pi$ R(5) lines.

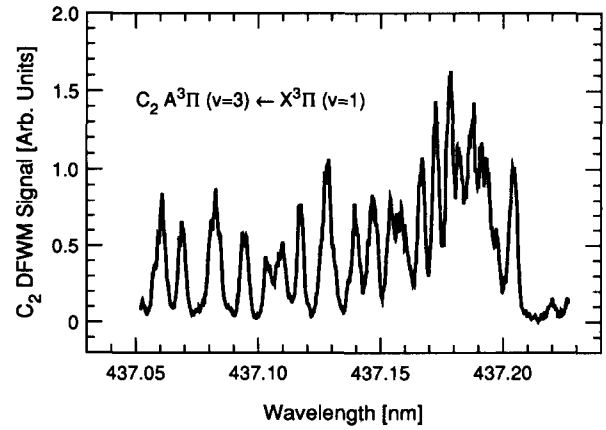

Fig. 4. DFWM spectrum of the C_2 $A^3\Pi$ $(v=3) \leftarrow X^3\Pi$ $(v=1)$ band head region.

reactor—with a substrate in place, and growing diamond. The conditions chosen for this preliminary study were indeed diamond growth conditions (although they were not optimized for best possible growth) and all measurements reported here were taken with the growing substrate in place. The reactor gas feed mixture comprised 106.5 l min^{-1} argon, 12.0 l min^{-1} H_2, and 0.55 l min^{-1} CH_4 premixed before introduction to the plasma torch. Calorimetric energy balance of the reactor indicates a net plasma enthalpy of 6 kW leaving the nozzle exit. The molybdenum substrate had a measured surface temperature of 1035 °C.

OES measurements were made on atomic hydrogen lines, continuum emission, C_2 Swan bands, and the CH $A \leftarrow X$ bands. Absolute and relative intensity measurements of the atomic hydrogen lines indicate a freestream temperature of approximately 5600 K. It is interesting to note that the line-of-sight emission of atomic hydrogen lines changes very little as a function of distance from the substrate surface. This indicates that the majority of atomic hydrogen emission is arising from regions radially outside the boundary layer in front of the substrate, and is thus not an appropriate measure of the growth environment of the substrate. Absolute continuum measurements indicate a freestream electron density of 1.4×10^{15} cm^{-3}. Vibrational temperature measurements of the C_2 $A^3\Pi(v=0,1,2,3) \leftarrow X^3\Pi(v=1,2,3,4)$ band system at near 5600 Å yield a freestream temperature of approximately 3200 K. This value is due primarily to the fact that line-of-sight radical emission measurements are dominated by the region of peak radical concentration (which for C_2 in equilibrium is approximately 3800 K), and thus temperatures derived from these measurements are biased toward that temperature. It is important to note here that unlike many flame situations, the C_2 emission and corresponding radical concentration in this experiment are not likely to be the result of chemiluminescent reaction. This is due to the high collision rates present at atmospheric pressure, combined with the fact that the reactor under study is chemically well downstream (approximately 10 ms) of the region of energy addition. Thus the C_2 radical concentration and emission are expected to be very close to those prevailing under equilibrium at the gas temperature. Both CH and C_2 line-of-sight emission are found to change very little as a function of distance from the substrate (approximately a factor of three decrease from 10 mm away to less than 1 mm away), indicating that those emissions as well are dominated by regions radially outside the boundary layer in front of the substrate.

At the time of this writing, spatially resolved LIF measurements of CH in this stagnation point boundary layer have not been completed. These measurements are performed by significantly raising the energy in the laser beams to produce LIF signals detectable against the strong plasma luminosity. Previous preliminary LIF measurements in a similar plasma flow [15] indicate that LIF measurements are possible for this flow, but only with strong laser intensity (saturated limit) and achieve poor signal-to-noise ratios.

Preliminary investigation of CH and C_2 radicals using DFWM have been made, using laser intensities of approximately 7.5 μJ in each of the three beams. Measurements of CH and C_2 features are found to be possible to within a few hundred micrometers of the substrate surface. A comparison of measured CH vibrational temperatures along the stagnation line of the substrate with values from the computational simulation are shown in Fig. 5. Boundary conditions for the simulation are the DFWM measured freestream temperature of approximately 3700 K, an estimated freestream velocity [3] of approximately 8 m s^{-1}, and the measured substrate temperature of 1035 °C. We can see in Fig. 5 the predicted thermal boundary layer (approximately 5 mm thick) with a steep fall-off in temperature very close to the substrate. The measured CH vibrational temperatures are in close agreement with the predictions, although the loss in signal of the $v=1$ transitions in the cooler region very near the substrate prevents accurate vibrational temperature measurement for distances less than 1 mm. Rotational temperature measurements from the CH $v=0$ lines, which remain strong enough for accurate measurement very near the surface but are more complex in interpretation, are currently being performed.

Shown in Fig. 6 is a comparison of predicted CH mole fraction through the reacting boundary layer with relative values calculated from the measured DFWM signals (through the simplified relation $I_{DFWM} \approx (N_{CH})^2$ [13]). (Similar measurements of C_2 DFWM signal variation through the boundary layer have been performed, but not completed at the time of this writing.) The DFWM

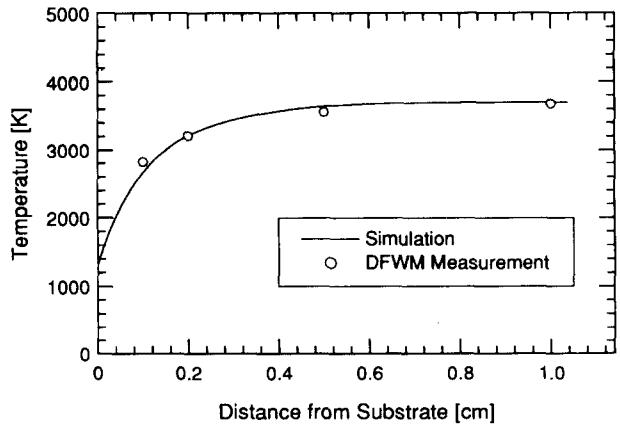

Fig. 5. Comparison of calculated temperature profile with experimentally measured CH DFWM vibrational temperatures.

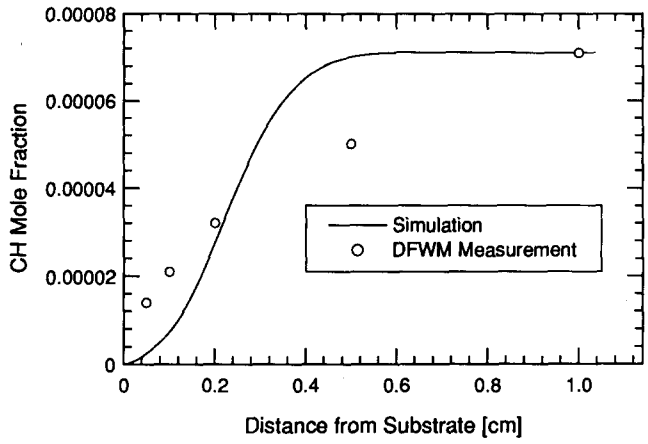

Fig. 6. Comparison of predicted CH concentration profile with values obtained from DFWM measurements.

measurements have been set equal to the predicted concentrations at 10 mm for comparison. It should be made clear that the purpose of Fig. 6 is not to make an absolute comparison with model predictions, but rather to demonstrate at this preliminary stage, that *in situ* DFWM measurements can be made in this environment and can probe regions very close to the substrate surface. The application of non-linear spectroscopic techniques to plasma processing environments offers great promise for the investigation of trace species, but is not without a price. The interpretation of DFWM signals to make quantitative measurements in these harsh environments is only in its infancy, and will require further study, characterization, and comparison with linear spectroscopic techniques, such as LIF, where possible to become a useful quantitative tool. These preliminary studies clearly demonstrate the possibilities of DFWM diagnostics in an actual atmospheric pressure synthesis reactor, and are continuing to be developed [16].

6. Conclusions

Atmospheric pressure plasma synthesis of diamond is an attractive and productive method for producing diamond thin films. The ability to understand and model this complex deposition environment is currently limited by the availability of detailed information on the chemistry within the reacting boundary layer above the substrate. A new non-linear spectroscopic technique, DFWM, has been applied for the first time to an atmospheric pressure synthesis reactor to fill this need. Preliminary measurements of CH and C_2 radicals have been made within the reacting boundary layer of a growing substrate placed in a flowing plasma. Vibrational temperature and preliminary concentration measurements made using DFWM are compared with a computational model of the growth environment, with vibrational temperatures found to be in good agreement with predictions. Work remains to be done making DFWM a viable, quantitative technique for probing atmospheric pressure plasma synthesis reactors, but these initial studies have shown DFWM to be a unique and promising spectroscopic tool.

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