Diagnostics of Boundary Layer Chemistry in Thermal Plasma CVD

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Abstract

Chemical Vapor Deposition (CVD) using thermal plasmas is attractive for diamond synthesis applications due to the inherently high reactant densities and throughput, but the associated high gas-phase collision rates in the boundary layer above the substrate produce steep thermal and species gradients which can drive the complex plasma chemistry away from optimal conditions. To understand and control these environments, accurate measurements of temperature and species concentrations within the reacting boundary layer are needed. This is challenging in atmospheric pressure reactors due to the highly luminous environment, steep thermal and species gradients, and small spatial scales. The applicability of degenerate four-wave mixing (DFWM) as a spectroscopic probe of atmospheric pressure reacting plasmas has been investigated. This powerful, nonlinear technique has been applied to the measurement of temperature and radical species concentrations in the boundary layer of a diamond growth substrate immersed in a flowing atmospheric pressure plasma. In-situ measurements of CH and C_2 radicals have been performed to determine spatially resolved profiles of vibrational temperature, rotational temperature, and species concentration. Results of these measurements are compared with the predictions of a detailed numerical simulation.

Introduction

Thermal plasma CVD of diamond thin films is an attractive synthesis technique due to several inherent attributes. The high reactant densities available at atmospheric pressure can produce high radical fluxes to the deposition surface, resulting in large growth rates. Operation at atmospheric pressure also precludes the loading and unloading of samples to be coated from a vacuum system, yielding a corresponding decrease in process cost and complexity. From a modeling standpoint, 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 rapidly 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.

Previous studies of the atmospheric pressure deposition environment have yielded important knowledge of the parameters affecting diamond formation[1-4], but have been limited to mostly post-deposition characterizations and comparisons. To further explore the nature of the atmospheric pressure diamond deposition environment and process, it is necessary to make accurate in-situ measurements of temperatures and species concentrations within the thin (< 1 cm) reacting boundary layer over the substrate, and compare these fundamental quantities with detailed simulations.

It is quite difficult, for many diagnostic techniques, to provide useful and accurate information from such a harsh and potentially nonequilibrium environment. Sensitive measurement of temperature and trace radical concentrations within a reacting boundary layer is a challenging problem in atmospheric pressure reactors due to the highly luminous environment, small spatial scales, and steep thermal and concentration gradients. It is in this environment where the application of sensitive, laser based diagnostic techniques can allow the detailed measurement of temperature and trace radical concentrations to be made, and compared to models of the deposition environment. The application of a powerful 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, since it can provide high sensitivity and spatial resolution with a coherent, phase conjugate signal which can be readily discriminated against the plasma luminosity[5-8].

The DFWM technique utilizes three laser beams of a single wavelength interacting with the plasma to produce a fourth spatially coherent, polarized signal beam that can be collected with high efficiency, and effectively filtered from the intense plasma luminosity. This feature is perhaps the greatest advantage of DFWM over other traditional diagnostic tools of atmospheric pressure plasmas which are often disabled or corrupted by the intense background luminosity. DFWM is found to be an extremely useful nonintrusive probe of the plasma, capable of providing high spectral and spatial resolution, and permitting measurements of temperature and relative species concentrations of trace radicals under conditions in which other spectroscopic techniques fail. Since DFWM can be used to probe the ground state of electronic transitions, it is much less subject to misinterpretation as a result of nonequilibrium effects[9] than conventional techniques such as optical emission spectroscopy (OES). Measurements of vibrational and rotational temperatures, as well as relative concentration profiles for CH and C_2 radicals have been measured in the thin boundary layer of a diamond-growth substrate immersed in a flowing atmospheric pressure plasma. These results are compared with the results of a detailed numerical simulation[10] of the reacting plasma, and found to be in good agreement.

Experimental Facility

The RF inductively coupled plasma (ICP) torch facility has been described in previous work.[1,4] 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 Figure 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 can be vertically translated in-situ to allow laser measurements to be made at various points through the boundary layer. Substrate temperature is monitored with a Minolta/Land Cyclops 152 infra-red optical pyrometer. Reactant gases (hydrogen and methane) are premixed with the carrier gas (argon) before passage through the RF discharge.

Laser beams for the DFWM experiments are produced using a Nd:YAG pumped dye laser system (~0.05 cm^{-1} bandwidth). 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, the probe beam, and the forward pump beam. 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 (≈2.1°) directly beneath the stagnation region of the substrate. The three beams lie in a plane parallel to the substrate surface. Geometric interaction length of the pump and probe beams is approximately 16 mm (parallel to the substrate surface). Polarization of the backward pump beam is rotated with a half-wave plate to be perpendicular to the polarization of the forward pump and probe beams, thus aiding signal isolation. Beam convergence is adjusted to produce a mild focus at the mid-line of the test section, producing beam waists of approximately 300 μm diameter.

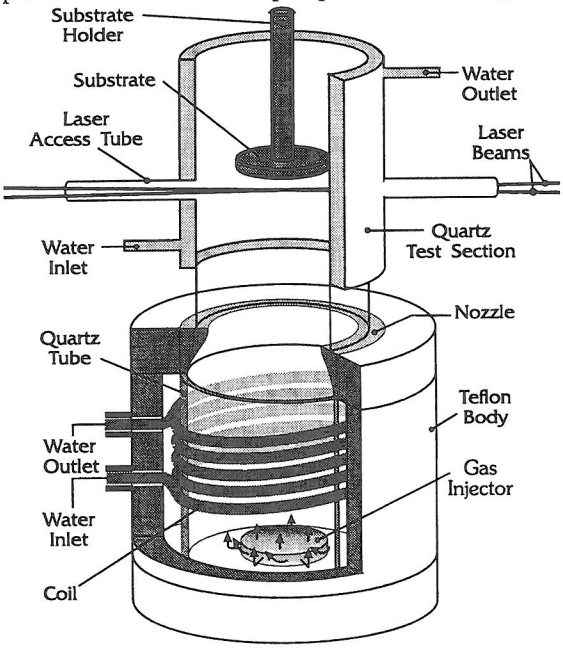

Figure 1. Schematic of RF-ICP reactor.

The phase-conjugate signal beam is generated within 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 two joulemeters (Molectron J4-09) which terminate the probe and backward pump beams.

Results

The applicability of in-situ DFWM to the atmospheric pressure diamond synthesis environment has been investigated using the well controlled, atmospheric pressure ICP reactor (Figure 1). It was desired to make in-situ measurements during normal operation of the atmospheric pressure RF-ICP diamond synthesis reactor - with a substrate in place, and growing diamond. The conditions chosen for these studies 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 was comprised of 106.5 l/min Ar, 12.0 l/min H_2, and 0.8% to 10% CH_4 (in H_2) 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.

The CH radical was probed with in-situ DFWM measurements of the CH $A^2\Delta \leftarrow X^2\Pi$ (0,0) system near 431 nm. Figure 2 shows a DFWM spectrum of one R branch group taken with approximately 10 μJ laser beam energies.. The v″=0 and v″=1 sets of the individual R(5) branch lines are closely grouped and permit determination of vibrational temperatures. The Q branch region allows fairly rapid measurements of several v=0 lines, thus permitting measurements of rotational temperature. The C_2 radical was probed with in situ DFWM measurements of the C_2 $d^3\Pi_g \leftarrow a^3\Pi_u$ (3,1) system near 437 nm.

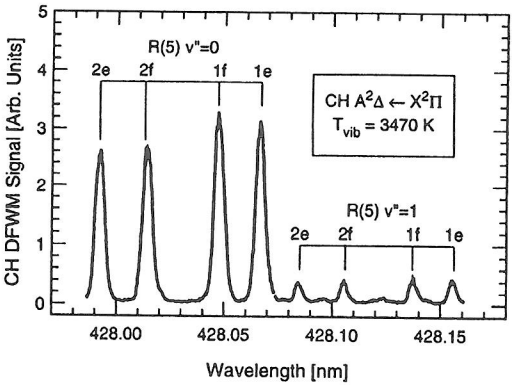

Figure 2. CH R(5) v″=0 and v″=1 components.

Temperature and concentration profiles within the reacting boundary layer were probed using DFWM. A comparison of measured CH vibrational and rotational temperatures along the stagnation line of the substrate with values from the computational simulation is shown in Figure 3. Boundary conditions for the simulation are the measured freestream temperature of 3900 K, an estimated freestream velocity of 8 m/s, and the measured substrate temperature of 1035°C. We can see the predicted thermal boundary layer (≈6mm 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 < 2mm. Rotational temperatures measurements from the CH v=0 lines, which remain strong enough for accurate measurement closer to the substrate, are in good agreement with both the measured vibrational temperatures and the computational simulation. It is possible to make measurements even closer to the substrate, but for these experimental conditions the CH concentration in that region has dropped below approximately 2 ppm, which is our current detection limit.

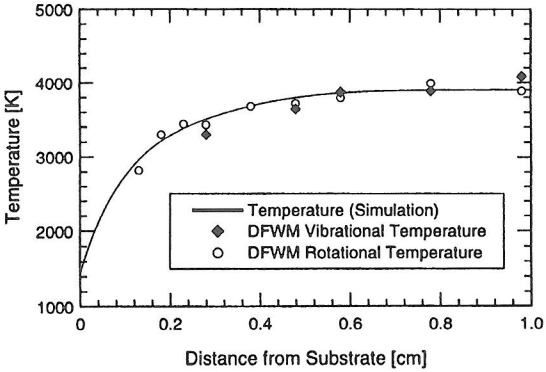

Figure 3. Boundary layer temperature profiles.

Measurements of the relative CH and C_2 mole fractions within the substrate boundary layer are compared to results of the computational simulation in Figures 4 and 5. In Figure 4, the CH mole fraction is approximately 20 ppm in the freestream (4100 K) and is predicted to first rise within the approximately 6 mm thick boundary layer (due to production) as the plasma cools toward approximately 3700 K, reaching a peak of approximately 55 ppm at 2 mm from the substrate surface, then to be destroyed as the plasma cools further on its approach to the substrate surface. In Figure 5, we see a similar behavior for the C_2 concentration profile with a much higher peak concentration (~300 ppm). We can see that the DFWM

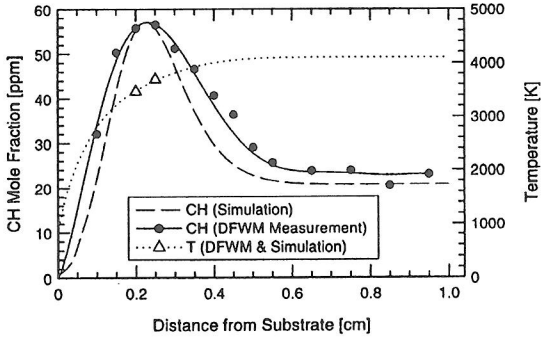

Figure 4. CH concentration profile.

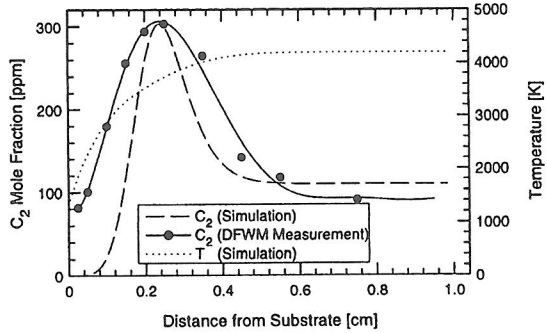

Figure 5. C_2 concentration profile.

measurements of relative CH and C_2 mole fraction (which have been scaled to the peak of the predicted curve) correspond closely to the predicted concentration in both trend and magnitude, accurately reflecting the production and destruction of the radicals within the boundary layer and demonstrating the ability of DFWM to probe this small, harsh reaction zone.

Conclusions

Degenerate four-wave mixing has been demonstrated as a sensitive, spatially resolved diagnostic of boundary layer chemistry in thermal plasma CVD of diamond. The coherent, phase-conjugate signal produced in this technique enables the rejection of intense plasma luminosity, and allows the accurate interrogation of temperature and trace (ppm level) radical concentrations within the reacting plasma. In-situ measurements of vibrational and rotational temperatures, as well as relative CH and C_2 radical concentrations in the reacting boundary layer of a diamond growth substrate are found to be in good agreement with model predictions.

Acknowledgments

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References

1. T.G. Owano and C.H. Kruger, *P. Chem. and P. Proc.* **13**, 433 (1993).
2. B.W. Wu and S.L. Girshick, *J. of Appl. Phys.* **75**, 3914 (1993).
3. R. Hernberg, T. Lepisto, T. Mantyla, T. Stenberg, and J. Vattulainen, *Diamond and Related Materials* **1** (1992) 255
4. S.K. Baldwin, T.G. Owano, and C.H. Kruger, *P. Chem. and P. Proc.* **14**, 383 (1994).
5. T.G. Owano, C.H. Kruger, D.S. Green, S. Williams, and R.N. Zare, *Diamond and Related Materials* **2**, 661 (1993).
6. D.S. Green, T.G. Owano, S. Williams, D.G. Goodwin, R.N. Zare, and C.H. Kruger, *Science* **259**, 1726 (1993).
7. T.G. Owano, E.H. Wahl, C.H. Kruger, D.S. Green, and R.N. Zare, *Proceedings of the 11th International Symposium on Plasma Chemistry* **1**, 416 (1993).
8. S. Williams, D.S. Green, S. Sethuraman, and R.N. Zare, *J. Am. Chem. Soc.* **114**, 9122 (1992).
9. C.H. Kruger, M.H. Gordon, and T.G. Owano, *J. of Pure and Appl. Chem.* **64**, 637 (1992).
10) D.G. Goodwin, and G.G. Gavillet, *J. Appl. Phys.* **68**, 6393 (1990).