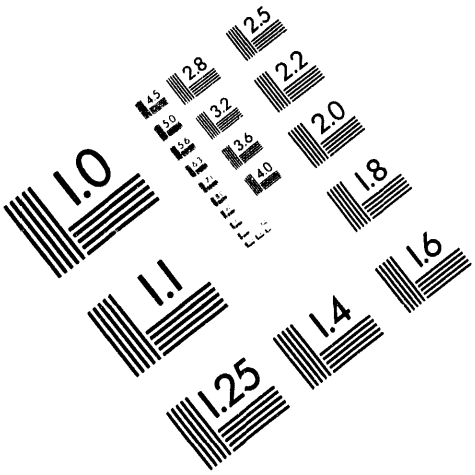
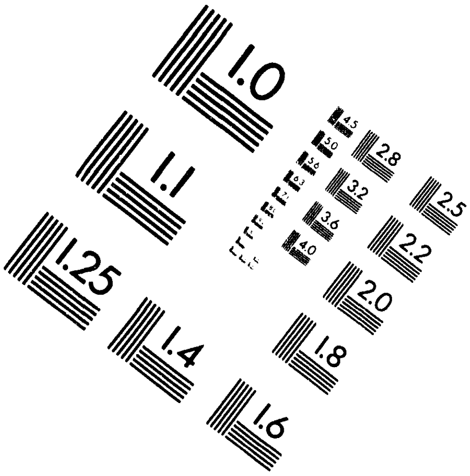
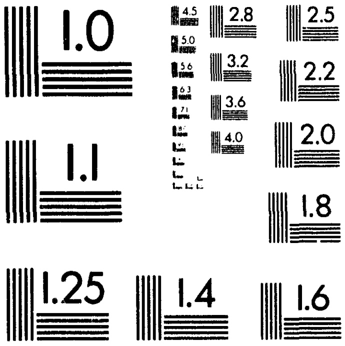


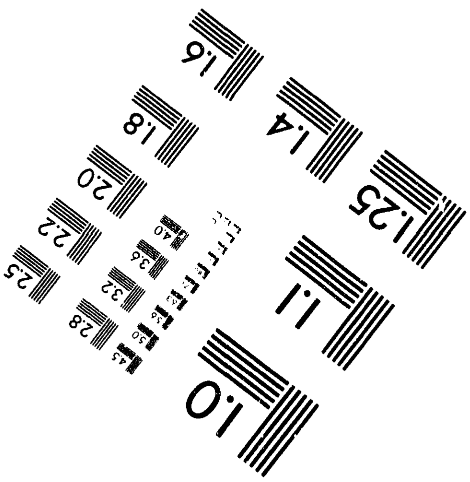
AIIM

Association for Information and Image Management

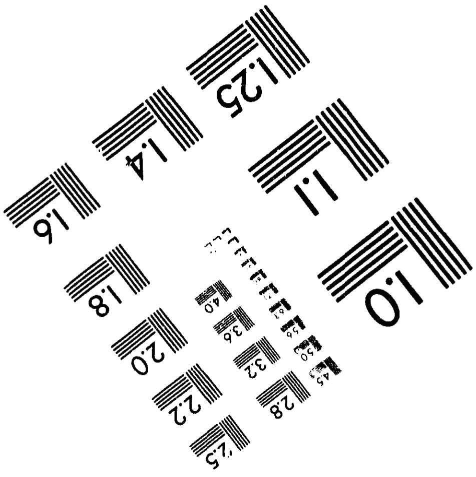
1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202







MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.



DOE/ER/13957--T1

ADVANCED DIAGNOSTICS FOR PLASMA CHEMISTRY

A Proposal Submitted to the
U.S. DEPARTMENT OF ENERGY
Office of Basic Energy Sciences

Proposal ME 26-94C

Submitted by

Professor Charles H. Kruger
Principal Investigator

Department of Mechanical Engineering
High Temperature Gasdynamics Laboratory
Stanford University
Stanford, California 94305

March 1994

MASTER

FG03-88ER13957

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

1.0 Introduction

Since July 15, 1992, the High Temperature Gasdynamics Laboratory in the Department of Mechanical Engineering at Stanford University has been engaged in a four-year research program sponsored by the Office of Basic Energy Sciences on ADVANCED DIAGNOSTICS FOR PLASMA CHEMISTRY. This work has been conducted under the direction of Principal Investigator Charles H. Kruger and Associate Investigator Thomas G. Owano. The research was initially funded for the first two years of the four-year grant, that is from July 15, 1992, until July 14, 1994.

The present submittal is a proposal for the continuation funding for the third year of this program, from July 15, 1994, until July 14, 1995. Section 2 summarizes the research accomplished during the first eighteen months of the program. Section 3 discusses the plans for continuing research activities. Publications and presentations to date resulting from this program are listed in Section 4. The proposed budget for the third year is given in Section 5.

2.0 Progress During the First Eighteen Months

Overall Objectives of the Research

The goal of this program is to develop state-of-the-art laser-based diagnostics of molecular species in harsh chemical environments, particularly those encountered in plasma synthesis of new materials. Emphasis has been placed on exploiting a new nonlinear spectroscopy, degenerate four wave mixing, as well as linear laser induced fluorescence to accomplish these goals.

Nonequilibrium behavior of thermal plasmas has emerged as an important area for the continued understanding of plasma chemistry and plasma processing. Conventional diagnostics, such as emission spectroscopy, have failed to fully characterize the nonequilibrium plasma parameters necessary to understand the reactive environments essential to plasma processing. A need exists for in-situ nonintrusive techniques for probing important properties and trace species in nonequilibrium reactive plasmas. These are harsh environments important to energy science and technology. Experimental and theoretical efforts which can increase our ability to probe gas phase and gas-surface interaction encountered under these conditions are crucial for continued progress in materials processing and plasma processing.

Although optical techniques have advanced chemical diagnostics over the past decade, few attempts have been made to bring more advanced, laser based diagnostic techniques to bear on these problems in plasmas. The future of plasma research must rely on combining the advantages of developed linear techniques with the emerging and powerful nonlinear techniques for measuring the microscopic physical and chemical parameters which are necessary to understand and develop plasma chemistry and plasma processing. Degenerate four wave mixing offers a means of measuring spatially resolved temperature and concentration information with a very high level of sensitivity. The coherent, phase conjugate nature of degenerate four wave mixing makes it ideal for application to highly luminous, difficult to probe plasma environments. The interference from intense plasma luminosity is a major reason that so few quantitative applications of conventional laser diagnostics have been reported for plasma processing. Degenerate four wave mixing is inherently advantageous in this respect because the signal beam is coherent and may thus be detected at large distances from the plasma without loss in intensity, while the interfering plasma luminosity will diminish as the distance from the plasma squared.

This four-year effort is aimed at the development of advanced diagnostics for plasma processing. This program extends our previous investigations of nonequilibrium plasma state, excitation temperatures, electron densities, radiation escape, recombination rates, and electronic quenching effects to the in-situ study of important parameters in chemically reacting plasma processing environments. This research utilizes our considerable experience with an atmospheric pressure induction plasma facility in the High Temperature Gasdynamics Laboratory and combines it with a newly developed, state-of-the-art laser facility dedicated to the induction torch facility.

In this research, the induction plasma facility will provides an operational plasma processing environment, primarily the chemical vapor deposition of diamond, for which it has proved to be exceptionally well suited for study. This reactor system provides a stable, well characterized, and realistic reacting plasma/surface environment in which advanced laser-based diagnostics can brought to bear. The dedicated Nd:YAG based nano-second laser system provides the means for investigating important parameter profiles including vibrational and rotational temperatures, and trace species concentrations. Nonlinear, degenerate four wave mixing is used in conjunction with linear laser induced fluorescence to provide complimentary information and calibration. Initial research studies have been directed towards the investigation of temperatures and concentrations of the CH, C_2, and CH_3 radicals, and important intermediates such as acetylene, C_2H_2. Compilation of an experimental database will permit comparison with developing computational models of the gas and surface chemistry. The insight provided by these measurements could greatly improve our understanding of the competing growth mechanisms, and of the importance of thermal and fluid dynamic boundary-layer effects in plasma processing.

Progress and Status of the Program

During the initial phase of this research, we have made significant progress in developing degenerate four-wave mixing (DFWM) as a viable diagnostic of atmospheric pressure plasma chemistry. We have demonstrated DFWM as a sensitive probe for measuring vibrational and rotational temperatures, as well as relative concentrations of trace (ppm level) radicals in harsh reacting environments. 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. We have found DFWM 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.

The in-situ measurement of temperature and species concentration within the boundary layer of a diamond growth substrate is both challenging and very informative. Previous techniques for sensitive, spatially resolved measurements of thermal plasmas have been faced with many difficulties in implementation and interpretation due to the very nature of these plasmas. The highly luminous environment, steep gradients, and nonequilibrium behavior complicate attempts to study and model these plasmas, but are also the driving forces behind the increasing usefulness and desire to learn more of these plasmas.

The most demonstrative example of this trend is in the synthesis of diamond thin films via atmospheric pressure plasmas. Here, the high density and steep gradients (producing strong nonequilibrium) are used to produce high quality diamond films at high growth rates. The very limited understanding of this process, however, has been gleaned from careful interpretation and creative theories based on many parametric studies of diamond growth. The bulk of these data comes from ex-situ study of two "bottom-line" quantities, namely growth rate and quality (with the latter being evaluated by a number of techniques ranging from Raman scattering and morphology to thermal diffusivity). The few in-situ diagnostics (e.g. residual gas analysis, emission spectroscopy, molecular beam mass spectroscopy, absorption, etc.) have been primarily directed at low pressure growth environments (which often have additional complications compared with their atmospheric pressure counterparts), and have had some limited success.

In the initial phases of this research, the applicability of in-situ DFWM to thermal plasmas has been investigated using the well controlled, atmospheric pressure inductively coupled plasma (ICP) diamond growth environment as a test case. In-situ measurements of the trace radicals CH and C_2 have been performed to determine vibrational temperatures, rotational temperatures, and relative species concentration measurements (including profiles of these quantities through the reacting boundary layer above the growth substrate), and compared with the results of emission spectroscopy. In these studies 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.

In-situ DFWM measurements of the CH $A^2\Delta \leftarrow X^2\Pi$ (0,0) system near 431 nm have been performed to determine vibrational and rotational temperature profiles through the reacting boundary layer. Figure 1 shows a DFWM spectrum of this region taken with approximately 10 μJ laser beam energies. The small groups of lines to the left side of the figure are the grouped components of individual rotational lines in the R branch, while the closely spaced lines toward the right side of the figure are individual lines comprising the Q branch (the P branch is not shown). The v″=0 and v″=1 sets of individual R 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 rotational temperature measurements to be made throughout the reacting boundary layer. An example of this rotational temperature determination is shown in Figure 2 where the intensity of measured Q branch lines (from N = 6 to 20) are plotted on a DFWM Boltzmann plot. This is shown to yield a straight line distribution (indicating rotational equilibration) whose inverse slope indicates a rotational temperature of 3135 K.

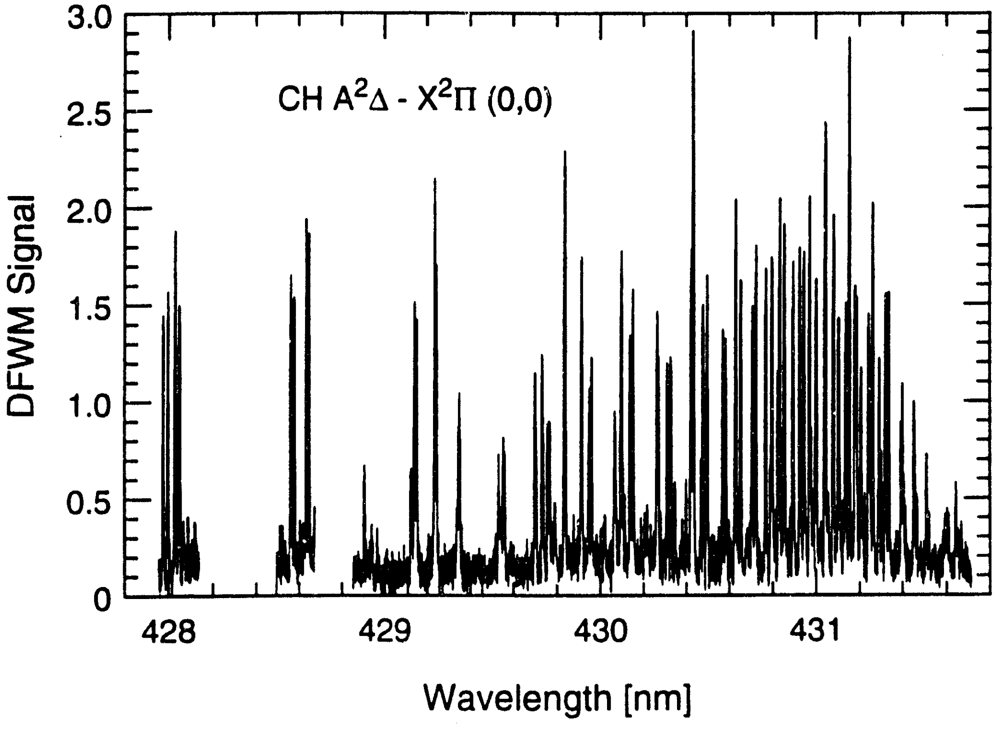


Figure 1. DFWM Spectra of CH $A^2\Delta \leftarrow X^2\Pi$(0,0).

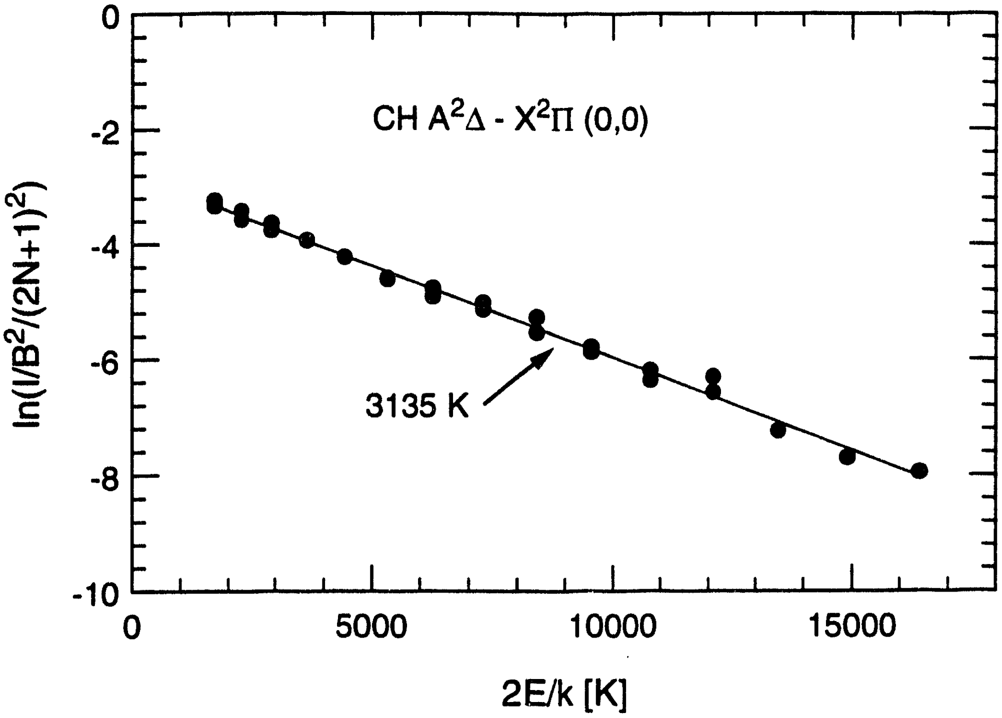


Figure 2. DFWM rotational Boltzmann plot.

A comparison of measured CH vibrational and rotational temperatures along the stagnation line of the substrate with values from a computational simulation are shown in Figure 3. Boundary conditions for the simulation are the DFWM measured freestream temperature of approximately 3900 K, an estimated freestream velocity of approximately 8 m/s, and the measured substrate temperature of 1035°C. We can see in Figure 3 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 rotational temperature measurements even closer to the substrate than shown in Figure 3, but for these particular experimental conditions the CH concentration in that region has dropped below approximately 2 ppm, which is our current detection limit.

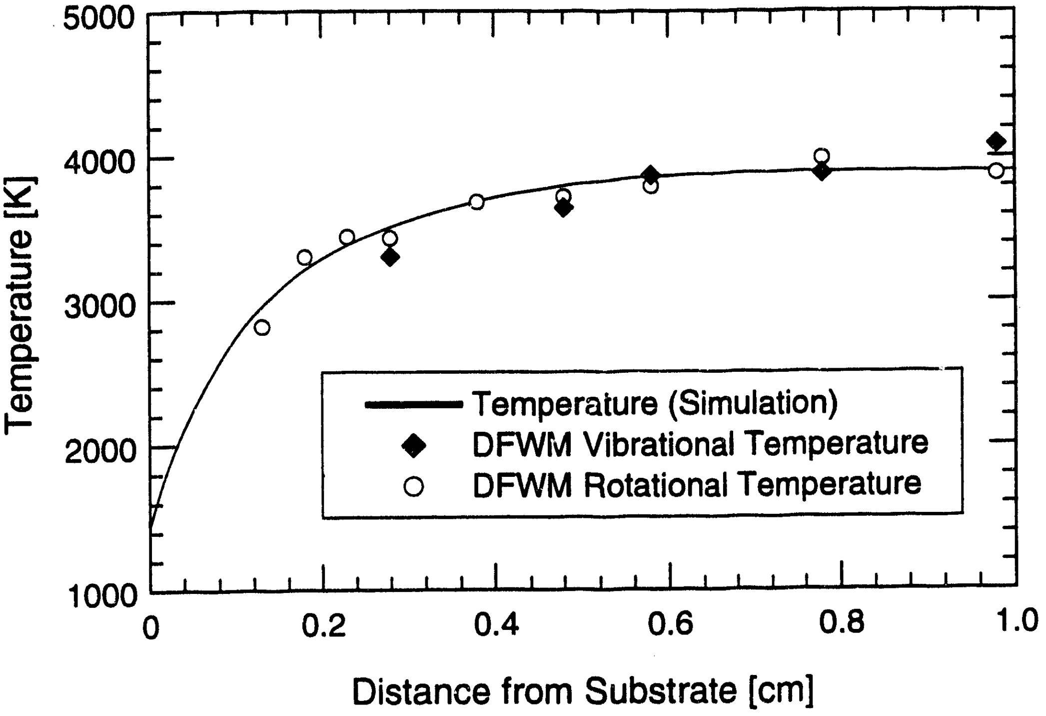


Figure 3. Measured and predicted temperature profiles.

A stoichiometric study of the freestream concentrations of CH and C_2 radicals as a function of methane to hydrogen feed gas ratio was undertaken to achieve several goals. First, since the methane to hydrogen feed gas ratio is an important process parameter in controlling diamond synthesis, it was necessary to judge the sensitivity of DFWM measurements of CH and C_2 radicals to this parameter. Secondly, an important assumption in modeling this environment is that the freestream be a known input condition, namely that the freestream outside the boundary layer is in chemical equilibrium at the measured freestream temperature. Although this a priori assumption is a good one since the flowtime of the plasma from the region of excitation is chemically very long (10 ms compared to a chemical relaxation time of approximately 1 ms), it is nonetheless a prudent idea to attempt its verification for these trace radicals of interest.

In Figure 4, the results of this stoichiometric study are shown for methane to hydrogen feed gas ratios ranging from approximately 0.8% to 10%. The measured freestream temperature for this study was constant at 3500 K, with the argon and hydrogen flowrates held constant at 113 l/min and 12 l/min respectively. The closed and open circles correspond to the CH and C_2 relative mole fractions measured using DFWM, and the solid lines represent equilibrium chemical composition for the plasma mixture at 3500 K. The agreement between the equilibrium calculation and the measured relative mole fractions of CH and C_2 as a function of methane to hydrogen feed gas ratio is a very good indication that the freestream is indeed in chemical equilibrium (although not positive proof since the DFWM measurement is not a measurement of absolute concentration).

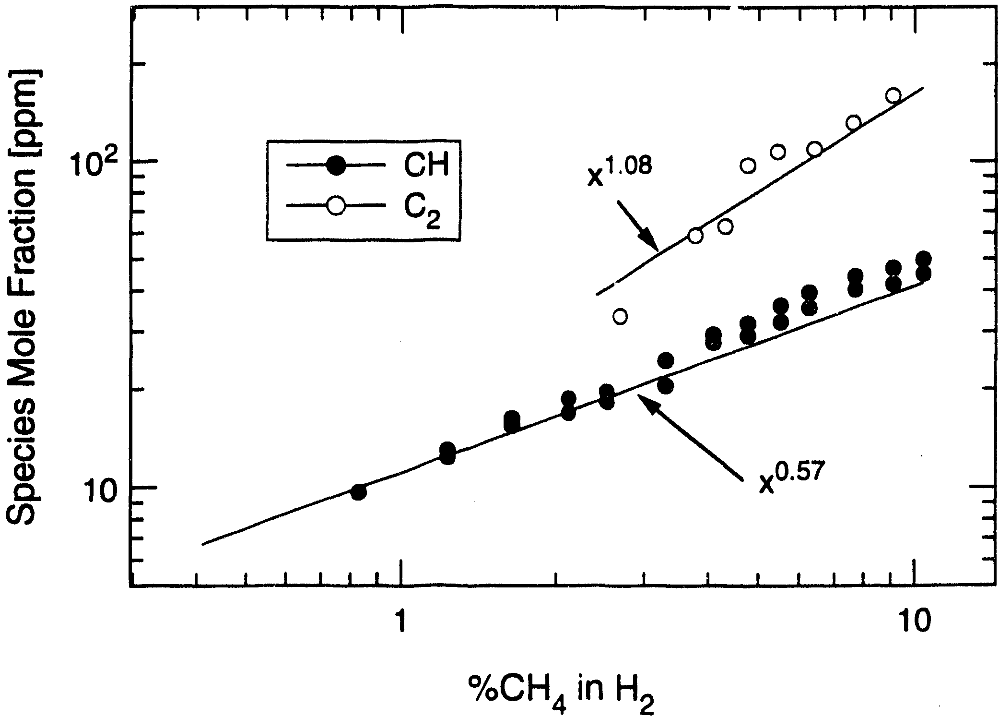


Figure 4. Freestream stoichiometric study of CH and C_2 radical concentration.

Measurement of relative radical concentration is also possible within the reacting boundary layer itself, as evidenced by the results shown in Figure 5. Here, measurements of the relative CH mole fraction and vibrational temperature are compared to the results of a one-dimensional simulation of the reacting boundary layer. In this case, at the freestream temperature of 4100 K, the CH mole fraction is approximately 20 ppm in the freestream 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. We can see that the DFWM measurements of relative CH mole fraction (scaled to the peak of the predicted curve, and in agreement with the calibrated equilibrium freestream) correspond closely to the predicted curve in both trend and magnitude, accurately reflecting the production and destruction of CH within the boundary layer and demonstrating the ability of DFWM to probe this small, harsh reaction zone.

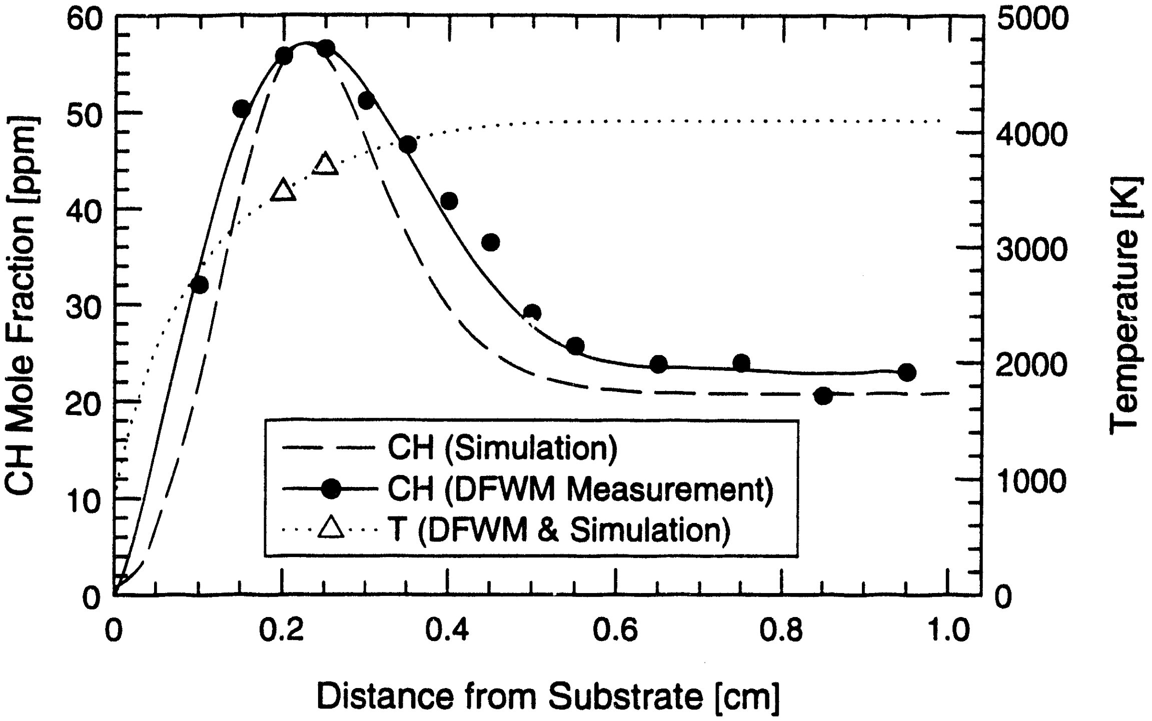


Figure 5. Measured and Predicted CH concentrations.

3.0 Emphasis of Continuing Research

The experiments conducted in the initial phase of the research have been successful in demonstrating DFWM as a very promising diagnostic technique for plasma chemistry. We have applied DFWM, for the first time, as a sensitive and spatially resolved diagnostic for plasma temperature and trace species concentration in a realistic plasma processing environment. In fact, the progress and successful results have exceeded our initial expectations. It is now our intention to further extend the DFWM technique as a sensitive plasma diagnostic, as well as to investigate other options for probing nonequilibrium behavior in thermal plasma chemistry.

The initial phase of this research has concentrated on investigations of CH and C_2 radicals within the reacting boundary layer of a diamond synthesis environment. Because these molecules exist in only trace amounts and can provide vibrational and rotational temperature measurements, they have provided a excellent testbed for demonstrating the applicability of DFWM to plasma chemistry environments. Having used these molecules to establish a solid basis for DFWM, we would like to extend DFWM to other species such as CH_3 and C_2H_2, which are even more central to issues regarding diamond synthesis environments. Along these lines, exploratory experiments to investigate ultra-violet DFWM of CH_3 and C_2H_2 within simplified test cell environments have been started in the collaborating chemistry labs of Prof. Zare. These efforts to probe CH_3 and C_2H_2 in the ultra-violet represent significantly more complicated experiments due to the generation and handling of the short wavelengths involved and the more complex, predissociated ultra-violet systems of these trace polyatomic species.

Several alternative techniques for probing CH_3 and C_2H_2 are also possible and are being considered. One such technique is the use of DFWM in the infra-red "fingerprint" region. The recent award of an DOE University Research Instrumentation Program (URIP) grant has provided us with the opportunity to purchase and use an infra-red laser system capable of producing laser beams in the 1.5 to 10 μm range. Extending DFWM to the infrared will make the technique almost universally applicable in the sense that nearly all stable molecular species exhibit discrete vibrational transitions within their ground electronic states. This is an important distinction with regard to visible and ultraviolet excitation, because not all molecular species possess bound excited electronic states which give rise to visible and ultra-violet transitions. Furthermore, the vibrational transitions of hydrocarbon species such as CH_3 and C_2H_2 have strong transition dipole moments. For example the transition moment of the ν_2 band of the CH_3 radical is 0.280 D which can be compared to 0.376 D for the CH R(8) fine-structure components of the (0,0) and (1,1) bands of the $A^2\Delta$–$X^2\Pi$ transition shown in Figure 1. This suggests that these species can be detected with high sensitivity by infrared DFWM

Another possible technique involves use of the newly developed "cavity ring-down" spectroscopy which enables highly sensitive, quantitative measurement of trace radicals. In this technique, a resonant cavity is constructed around the medium of interest, and a laser pulse is injected into the cavity. As the laser pulse circulates in the cavity, it will be attenuated by the absorbing medium (if the laser is properly tuned to the absorption feature of interest) and the output of the cavity will decay at an accelerated rate. By measuring the time constant of this accelerated decay, the absolute concentration of the absorbing species may be determined. Although this technique produces a line of sight averaged quantity, it can provide high spatial resolution in one spatial dimension and more importantly provide absolute concentration measurements at single pass absorbances as low as 1×10^{-5}. Exploratory experiments involving this technique in a low-pressure test reactor are currently being designed.

Besides the need for interrogating various C_nH_m species, it is also of great interest to be able to probe important atomic species such as H and C. Atomic hydrogen is thought to be an extremely important radical in the diamond synthesis environment, both in gas phase and surface reactions. In the past, however, it has proven difficult to probe ground state atomic hydrogen in plasma chemistry environments. An extension of DFWM as a two-photon probe of the strong Lyman series of atomic hydrogen provides the exciting possibility of a very sensitive, spatially resolved measurement of ground state atomic hydrogen in harsh thermal plasma environments. Two-photon DFWM, possibly in conjunction with two-photon LIF, could allow the interrogation of atomic hydrogen and atomic carbon very close to a diamond growth substrate, and provide much needed insight into the nonequilibrium plasma chemistry of the near surface environment.

On the basis of our successful measurements using visible DFWM as a probe of nonequilibrium plasma chemistry environments, we believe that we are well poised to make further significant contributions to the advanced diagnostics of thermal plasmas.

4.0 Publications and Presentations
(7/15/92 - 7/14/94)

Owano, T.G., Goodwin, D.G., and Kruger, C.H., "Boundary Layer Effects in RF Plasma Synthesis of Diamond Thin Films at Atmospheric Pressure," submitted to *Journal of Applied Physics.*

Owano, T.G., and Kruger, C.H., "Parametric Study of Atmospheric Pressure Diamond Synthesis with an Inductively Coupled Plasma Torch," *Plasma Chemistry and Plasma Processing*, Vol. 13, No. 3, pp. 433-446, September, 1993.

Owano, T.G., Green, D.S., Wahl, E.H., Kruger, C.H., and Zare, R.N., "Degenerate Four-Wave Mixing as a Spectroscopic Probe of Atmospheric Pressure Reacting Plasmas," 11th International Symposium on Plasma Chemistry, Loughborough, Leicestershire, England, August 22-27, 1993.

Baldwin, S.K., Owano, T.G., Kruger, C.H., Wahl, E.H., Green, D.S., and Zare, R.N., "Growth Rate Studies and Gas-Phase Diagnostics in Atmospheric Pressure RF Diamond Synthesis," American Chemical Society Annual Meeting, Symposium on Plasma-Aided Materials Processing and Manufacturing, Chicago, Illinois, August 22-27, 1993.

Owano, T.G., Kruger, C.H., Green, D.S., and Zare, R.N., "DFWM Measurements of Boundary Layer Radical Profiles in Atmospheric Pressure Diamond Deposition," Third International Symposium on Diamond Materials, Honolulu, Hawaii, May 16-21, 1993.

Baldwin. S.K., Owano, T.G., and Kruger, C.H., "The Effects of Substrate Temperature and Methane-to-Hydrogen Ratio on Diamond Growth Rate," Third International Symposium on Diamond Materials, Honolulu, Hawaii, May 16-21, 1993.

Owano, T.G., Kruger, C.H., Green, D.S., Williams, S., and Zare, R.N., "DFWM Diagnostics of Atmospheric Pressure Diamond Deposition," *Diamond and Related Materials*, Vol. 2, pp. 661-666, April, 1993.

Owano, T.G., Kruger, C.H., Green, D.S., and Zare, R.N., "Degenerate Four-Wave Mixing Diagnostics of Plasma Boundary Layers in Atmospheric Pressure Diamond Deposition," Department of Mechanical Engineering (Invited Seminar), California Institute of Technology, Pasadena, California, April 6, 1993.

Green, D.S., Owano, T.G., Williams, S., Goodwin, D.G., Zare, R.N., and Kruger, C.H., "Boundary Layer Profiles in Plasma Chemical Vapor Deposition," *Science*, Vol. 259, pp. 1726-1729, March 19, 1993.

Owano, T.G., Kruger, C.H., Green, D.S., and Zare, R.N., "DFWM Measurements of CH and C_2 in Thermal Plasma Diamond Deposition," Engineering Research Center for Plasma-Aided Manufacturing - Diagnostic Workshop, Minneapolis, Minnesota, March 8, 1993.

Owano, T.G., Kruger, C.H., and Beddini, R.A., "Electron-Ion Three Body Recombination Coefficient of Argon," *AIAA Journal*, Vol. 31, No. 1, pp. 75-82, January 1993.

Owano, T.G., Kruger, C.H., Green, D.S., and Zare, R.N., "Boundary Layer Profiles in an Atmospheric Pressure Diamond Synthesis Plasma," Fifth Annual Meeting of the

Engineering Research Center for Plasma Aided Manufacturing, Madison, Wisconsin, December 9-10, 1992.

Green, D.S., Williams, S., Zare, R.N., Owano, T.G., and Kruger, C.H., "Degenerate Four-Wave Mixing as a Diagnostic of Species Temperature and Concentration in a Reactive Plasma," 8th Interdisciplinary Laser Science Conference, Albuquerque, New Mexico, September 20-25, 1992.

Owano, T.G., Kruger, C.H., Green, D.S., Williams, S., and Zare, R.N., "DFWM Diagnostics of Atmospheric Pressure Diamond Deposition," Diamond 1992, Heidelberg, Germany, August 31 - September 4, 1992.

DATE
FILMED
11 / 1 / 94

END