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**DEGENERATE FOUR-WAVE MIXING
AS A DIAGNOSTIC OF PLASMA CHEMISTRY**

Progress Report

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We have made considerable progress in the development of degenerate four-wave mixing (DFWM) as a new diagnostic for species' concentration and temperature in processing plasmas. DFWM has been found to be particularly well suited to industrial-scale reactors for *in situ* monitoring during plasma-enhanced chemical vapor deposition. In this environment steep gradients in species' concentration, density, velocity, and temperature are encountered through the boundary layer near the gas-surface interface. Since DFWM is generated from the interaction of three laser beams we have a unique diagnostic technique capable of probing inside a highly luminous plasma with spatial resolution on the scale of 100 microns. As the laser is tuned in wavelength the DFWM signal is resonantly enhanced and the high spectral sensitivity has permitted the identification of molecular species in response to changes in processing parameters. In particular, DFWM has been used to monitor CH and C₂ during the synthesis of diamond thin films. Spectra have been analyzed to obtain both vibrational and rotational temperature profiles. The results have been used to test a one-dimensional diamond deposition model. Our preliminary findings are being published in *Science*,* and a copy of the paper is appended to this report.

Consistent with our DOE proposal, we have confirmed that DFWM is a valuable diagnostic tool for plasma chemistry. Using DFWM spectroscopy we have investigated the presence of CH and C₂ that are present in the stagnation flow of a large-scale thermal processing plasma. This is an rf, inductively-coupled, atmospheric-pressure plasma reactor that operates with a complex mixture of Ar, H₂, and CH₄. Over the current range of operating conditions, the temperature profile of the stagnation flow is predicted to be nearly constant in the free-stream and decrease monotonically within 6 mm of the substrate surface. By translating the substrate relative to the intersection volume of the lasers our studies have permitted the first measurement of species and temperature profiles across this boundary layer. The analysis of CH rotational and vibrational spectra indicates that the temperature trend predicted by the one-dimensional model is observed. Two boundary conditions have been investigated: substrate temperature of about 1200 K and free-stream temperatures of (i) 3500 K and (ii) 4300 K. In both cases the one-dimensional simulations predict a boundary layer thickness consistent with our observations. Preliminary studies have revealed better agreement between the model and the measured temperature profile for case (ii) and suggests the need to consider radial temperature gradients below the substrate. Present studies are concentrating on the analysis of rotational lines to confirm the temperature profiles closer to the substrate surface.

Although temperature profiles do not vary dramatically between cases (i) and (ii), the change of the species concentration across the boundary layer is quite dramatic. Whereas in case (i) the CH and C₂ concentrations are predicted and observed to decline monotonically

toward the substrate, in case (ii) the species rise and fall in concentration well within the boundary layer. We have found that at a distance of about 2 mm from the surface both CH and C₂ reach a maximum concentration. Such behavior might be indicative of the formation of molecules that can be active in gas-surface reactions and are subsequently consumed during deposition.

DFWM diagnostics can be used to detect trace species (at parts-per-million levels) that may be important to sensor development and intelligent processing. For example, by studying CH and C₂, which are representative of all C₁- and C₂-hydrocarbons, as a function of mixing gas ratios we are learning about the equilibrium between hydrogen and the hydrocarbons. As we change the ratio of CH₄ to H₂ in the mixing gas we have been able to follow the relative CH and C₂ concentration profiles through the boundary layer. Previous experiments by the group of Professor Charles Kruger have demonstrated that diamond growth rates are a sensitive function of CH₄/H₂ stoichiometry. We are encouraged that these combined studies will provide information to help identify deposition precursors, to verify reaction mechanisms, and to parametrize the nonequilibrium chemistry that permits diamond thin-film synthesis at rapid growth rates and of desired quality, thickness, and morphology.

To date, we have demonstrated that using a conventional laser system, operating at visible wavelengths and with very low energies, that DFWM is nonintrusive and can generate signals that are easily monitored with standard photodetectors and processing electronics. The species of interest have been detected at levels of less than < 10 ppm and used to obtain high-resolution absorption data. These measurements have provided information that has been unavailable or incorrectly interpreted from emission and laser induced fluorescence. The most significant result from our preliminary studies is the success of DFWM diagnostics to track the spatial distribution and temperature of reactive intermediates under harsh plasma conditions. In coming months we plan to initiate our studies of CH₃, C, and C₂H₂ that are considered possible precursors to diamond growth. Research thrusts in our second year include improving the spatial resolution and signal-to-noise ratio in order to investigate a broader range of diamond synthesis conditions at elevated temperatures and higher gas velocities.

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* David S. Green, Thomas G. Owano, Skip Williams, David G. Goodwin, Richard N. Zare, Charles H. Kruger, "Boundary Layer Profiles in Plasma Chemical Vapor Deposition," *Science*, in press (1993).

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