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Title: Diagnostic Enhancements for Plasma Processing

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Diagnostic Enhancements for Plasma Processing

Gary S. Selwyn* and Ivars Henins

Abstract

This is the final report of a one-year, Laboratory Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). Funds obtained under this project were used to enhance the diagnostic capabilities of the plasma-processing program in the Physics Division at LANL and include successful development and implementation of in-situ Raman spectroscopy and infrared emission spectroscopy. These methods were used to detect the presence and nature of ground-state and electronically excited molecular oxygen formed in an atmospheric-pressure, nonthermal plasma source used for environmental, industrial and decontamination applications.

Background and Research Objectives

We have recently developed a novel, atmospheric-pressure plasma jet (APPJ) that produces a reactive stream of excited-state neutral metastables, radicals and atoms. Quantitative in-situ detection of plasma-generated species is needed for further development and understanding of this source, experimental verification of plasma models, and experimental evaluation of chemical reaction mechanisms, both within the source and in the downstream effluent. Because of the novel design and high operating pressure of this discharge, traditional diagnostic methods for chemical analysis of the source are either unsuitable or are limited in capability. Our goal in this one year project was to develop diagnostic methods that may be used in the operating conditions of the high pressure plasma jet and to provide enhanced measurement capability required for this new plasma domain.

The diagnostic methods intended for development include laser-based Raman spectroscopy, a very weak inelastic light scattering process, which provides insight into the electronic formation of both homonuclear and heternuclear diatomic species (note that infrared absorption spectroscopy is inactive for homonuclear diatomics, such as O_2), and infrared emission spectroscopy, which detects the relaxation of electronically-excited species, such as O_2 metastables.

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Importance to LANL's Science and Technology Base and National R&D Needs

Plasma physics is a core competency and capability at Los Alamos National Laboratory. This program improves our diagnostic capabilities in this core competency area. Within both DOE and LANL, plasmas are used for cleaning of sensitive surfaces, decontamination, thin film processing and silicon-based applications. Nationally, plasma processing is a vital industrial process used for the production of semiconductors, magnetic storage media, flat panel displays and thin film coatings. Our goal is to improve our ability to develop new methods, understanding and diagnostics in this important plasma-based technology.

Scientific Approach and Accomplishments

Work was done to develop the laser-based Raman spectroscopy method and near-infrared emission detection of reactive metastables in the plasma effluent. These two methods are described below.

Laser-Based Raman Spectroscopy

Proper use of laser Raman spectroscopy requires a single-wavelength laser. The laser available for this project was a multiline Ar^+/Kr^+ gas laser with a broad band mirror reflector. To make this laser operate at a single wavelength, it was necessary to replace the broad-band high reflector with a dielectric, single-wavelength reflector and then to tune the laser cavity for optimized operation at the 488.2 nm wavelength. With this done, we were able to achieve approximately 1 watt of cw laser power at 488 nm. Outside the laser, low-loss beam delivery was achieved using dielectric, 90^0 high reflectors. The beam was directed into the glove box housing the atmospheric-pressure plasma jet (APPJ) through holes cut into the plexiglass housing, and then was focussed to a point directly in front of the APPJ with a 20 cm glass lens. The diverging beam was allowed to exit the glove box through a second hole and was terminated with a beam stop.

Inelastically scattered light was collected at 90^0 from the laser beam using an f/2, 10 cm lens that collimated the scattered light. This light was turned using a coated Al mirror to direct it into an 0.64 m monochromator. A second lens, having a 20 cm focal length, was used to focus the light onto the entrance slit of the monochromator. This resulted in image magnification, which limited the minimum practical entrance slitwidth, typically to around 500 microns.

A multiple-layer dielectric filter was used to attenuate the resonant, elastic scattering of the laser beam and to reduce stray light inside the monochromator. Attempts to detect the Raman signal from room air using a photomultiplier and a lock-in amplifier or dc signal processing were generally unsuccessful or had low signal/noise. We were able, however to detect the Raman signal of both N_2 and O_2 in room air using a cyrogenically-cooled charge-coupled detector (CCD) attached to the monochromator. Figure 1 shows the Raman signal obtained for oxygen in room air. The very high signal/noise obtained for this condition is evident.

Oxygen content in the feed gas of the APPJ is about 10% of the concentration in room air, but as seen in Figure 1, sufficient signal/noise exists to easily detect and quantify the level of O_2 present in the APPJ feed gas. Then, by comparing the O_2 Raman signal for the ground state when the plasma is off and on, we can quantify the percent of O_2 conversion to other electronic states. Results showed about 30% conversion to electronic states other than the ground state of O_2.

Near-Infrared Detection of O_2 ($a\ ^1\Delta_g$)

Detection of this low-lying metastable state of O_2 is difficult because of the spin *and* angular momentum forbidden nature of the relaxation to ground state, which results in a 45 minute radiative lifetime, and the low energy content of the metastable, which results in emission at 1.27 microns, beyond the productive range of most photomultlipliers and CCDs. However, by using a cryogenically cooled, indium-antinomide detector, we can detect emission in the wavelength range.

To do this work, the indium-antimonide detector was used along with a dielectric bandpass filter tuned to a 4-nm wavelength range centered at 1.267 microns. The atmospheric-pressure plasma jet was pulsed using the gating feature of the 13.56 MHz rf oscillator, which fed an rf linear amplifier attached to the center electrode of the APPJ. The infrared detector was connected to a lock-in amplifier, synchronized to the pulsed plasma. This provided sensitive detection of the phased-locked signal. Measurement of the metastable O_2 signal was then done as a function of distance from the nozzle outlet and as a function of rf power and O_2 feed gas content. This was compared with other species detected in the APPJ effluent and the results are shown below in Figure 2.

Publications

1. J. Y. Jeong, I. Henins, J. Velarde, G. S. Selwyn and R. F. Hicks, "The Evolution of the Chemical Species in a Parallel-Plate Plasma with Pressure," *J. Vac. Sci. Technol.,* submitted September 15, 1997.

2. J. Y. Jeong, S. E. Babayan, V. J. Tu, I. Henins, J. Velarde, G. S. Selwyn and R. F. Hicks, "Etching of Materials with an Atmospheric-Pressure Plasma Jet," *Appl. Phys. Lett.,* submitted September 26, 1997.

3. S.E. Babayan, J. Y. Jeong, V. J. Tu, G. S. Selwyn and R. F. Hicks, "Deposition of Glass with an Atmospheric-Pressure Plasma Jet," *Appl. Phys. Lett.,* submitted September 26, 1997.

4. S.E. Babayan, J. Y. Jeong, V. J. Tu, G. S. Selwyn and R. F. Hicks, "Plasma-Assisted Chemical Vapor Deposition of Silicon Dioxide at Atmospheric Pressure ," *J. Vac. Sci. Technol.,* submitted September 30, 1997.

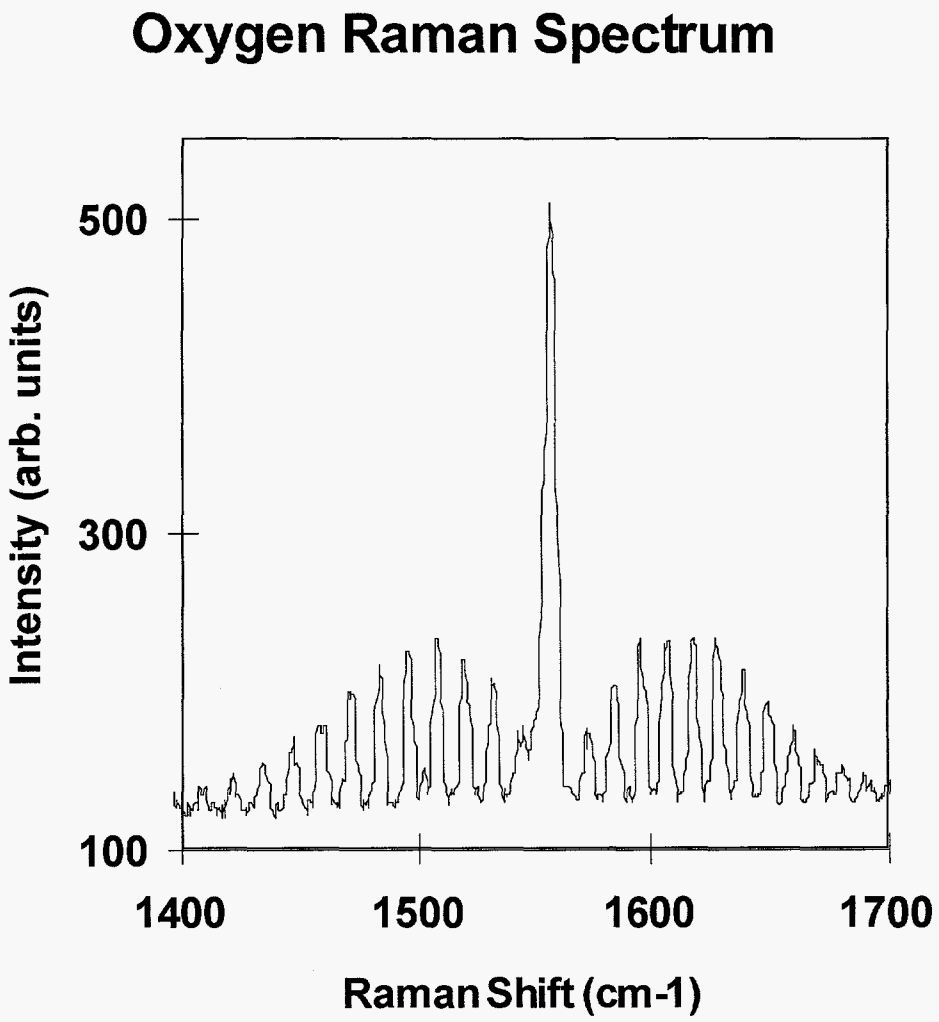

Figure 1. Molecular oxygen Raman signal.

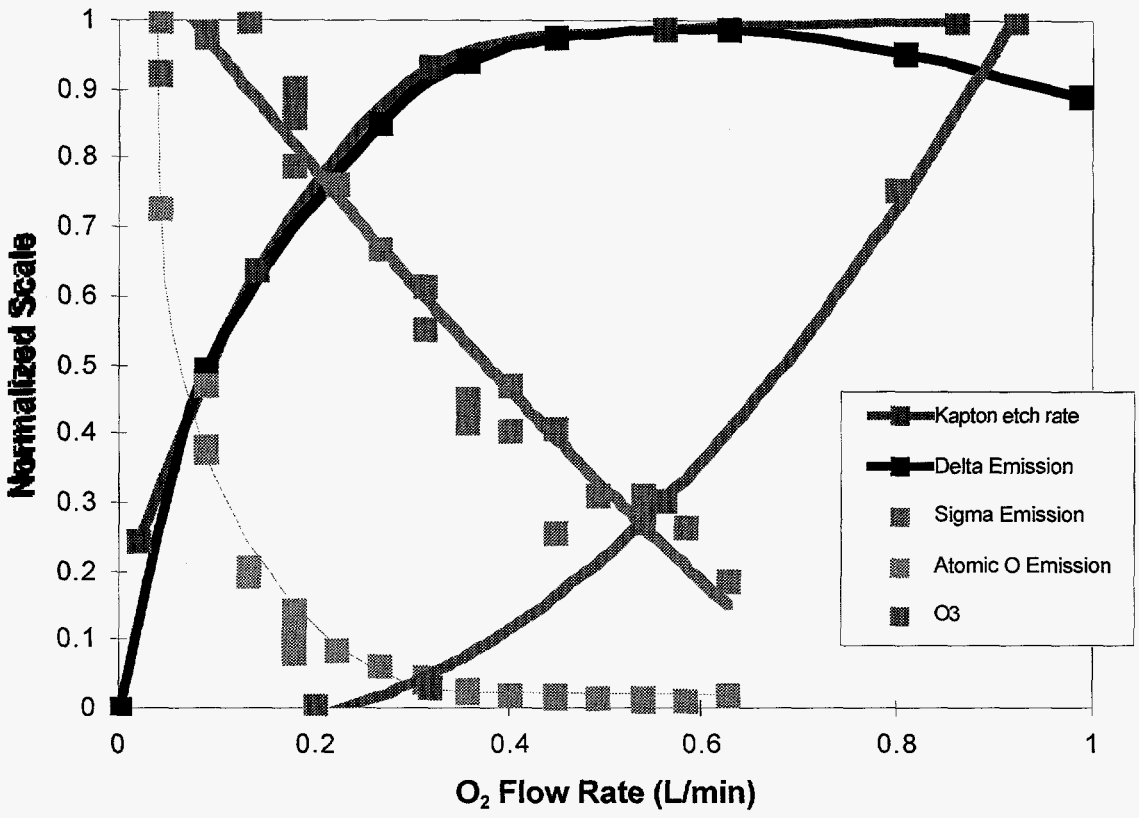

Figure 2. Spatially resolved O_2 (a $^1\Delta_g$) signal as a function of distance from the nozzle.