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AUTHOR(S) N. S. Nogar, G. L. Keaton, J. E. Anderson and M. Trkula

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Los Alamos, New Mexico 87545

OPTICAL DIAGNOSTICS FOR A HIGH POWER, RF-INDUCTIVELY COUPLED PLASMA

N. S. NOGAR†, G. L. KEATON†, J. E. ANDERSON† AND M. TRKULA*
†Chemical and Laser Sciences Division, MS G738
*Materials Science and Technology Division, MS G770
Los Alamos National Laboratory, Los Alamos, New Mexico, 87545

ABSTRACT

Emission spectroscopy and laser-induced fluorescence have been used to monitor the field and tail-flame regions of a Hull-design [1] inductively coupled plasma. This plasma is used for a variety of syntheses [2,3] including SiC, TiC, BN, AlN and diamond. Temporally- and spatially-resolved spectra of both pure Ar and Ar/gas mixtures have been studied as a function of RF power, pressure and flow rate. Preliminary data suggest that the system is far from local thermodynamic equilibrium.

INTRODUCTION

In radio-frequency plasma chemical synthesis a flowing gas passes through a super-heated plasma fireball region. Following injection into this flow, reactant species decompose into highly active atomic, ionic and molecular fragments. As these fragments leave the plasma region, they cool and produce end-products of exceptionally high purity. This process has been used to produce a number of fine and ultrafine materials and chemicals.

Many unanswered question persist concerning the processes and mechanisms involved in these syntheses. Fundamental properties of the plasma are largely unknown, including the mechanism for the formation and transport of energetic species, temperatures (energy distributions), scaling parameters, optimal gas mixtures and mixing conditions. We are involved in an experimental program to understand the chemistry and physics of plasma synthesis and rf plasmas in general. We are applying modern spectroscopic techniques including emission spectroscopy and laser-induced fluorescence (LIF). Atomic, ionic and molecular concentrations, lifetimes and internal energy distributions are mapped out as a function of position and phase with respect to the rf cycle.

EXPERIMENTAL

A schematic of the Hull-design plasma, and associated apparatus is shown in Figure 1. We use an optical fiber to collect emitted photons, thereby facilitating spatial profiling measurements. Temporally resolved emission measurements were performed by scanning the gate of the detection electronics with respect to the rf cycle. For LIF measurements, the pump-laser trigger was scanned with a digital delay generator. Typical laser characteristics were 8 nsec, ≈0.5 mJ pulses at 10 Hz, with a bandwidth ≈0.5 cm^{-1}.

The plasma was typically run at 545 kHz, with flow rates, except for diamond synthesis, of 1-10 STP LPM, and a chamber pressure between 2 and 580 torr. Rf powers for most experiments were between 5 and 15 kW.

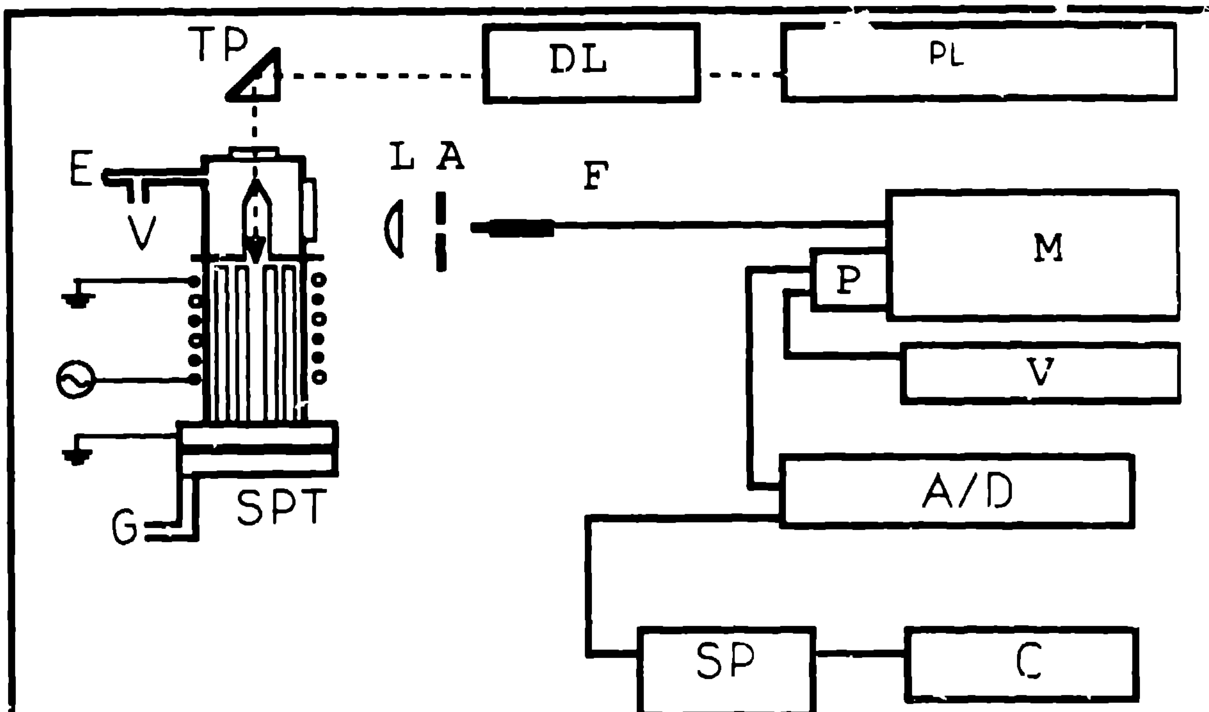


Figure 1. Schematic of the experimental apparatus. SPT is the shielded plasma tube, G is the gas inlet, E and V are the exhaust and vacuum outlets, respectively; PL is the pump (Nd^{+3}:YAG) laser, DL is the dye laser, and TP the turning prism; L is the collection lens, A an aperture, F a fiber optic, M a 1 meter monochromator, P a photomultiplier tube or photodiode array and V is a high voltage source; A/D is an analog to digital converter, SP is signal processing electronics, and C is an Apple Macintosh Plus™ computer.

RESULTS

Internal Energy Measurements.

Internal energy distributions were determined by various methods for both pure Ar and mixed gas tail flames. For pure argon measurements, the temperature was normally determined from emission intensities from selected, well-characterized, energy levels. Representative temperatures, as determined by fitting to a Boltzmann distribution, are displayed in Table I. It should be pointed out that although the electronic distribution is not well-represented by a single temperature, in many cases the relative populations within a single manifold were approximately statistical in nature. The wide diversity of results suggests that the system is not well-described by a temperature, even in a very localized regions, and that a local thermodynamic equilibrium viewpoint is inappropriate. Further, the particular distribution of internal energies seems highly dependent on the mechanism of formation.

Table I. Internal temperatures determined from electronic and rotational distributions.	
Method of Determination[1]	Temperature °K
*Ar Emission Lines, Two Line Method[2]	***
*Ar Emission Lines, Two Line Method[3]	1100< T_e <9500
*N_2 Rotational Distribution ($C^3\Pi_u$ v=0)[4]	T_r = 2090
*N_2^+ Rotational Distribution ($B^2\Sigma_u^+$ v=0)[4]	T_r = 4700
(1) Plasma conditions for these measurements were as follows. *Ar emission: pure Ar at 580 torr, 12 cm downstream, 9 kW rf; *N_2 emission: 1% N_2 in Ar at 580 torr, 12 cm downstream, and 12 kW rf power. (2) For $\Delta E < 0.05$ eV, the relative populations are approximated by their degeneracies. (3) For $\Delta E \sim 0.5$ eV, there is no simple description of relative population. (4) The temperature is manifold dependent, with an intermanifold variation of ~200 K.	

Spatial Intensity Measurements.

Time averaged LIF results were acquired on centerline of the tailflame, as a function of distance downstream from the last turn of the load coil for Ar states $^3P_2$ and $^3P_1$. The results of measurements at two pressures are shown in Figure 2.

Several points can be noted from Figure 2. First, the metastable populations extend downstream from the field region for a significant distance (~10 cm), even at relatively high pressures. This is somewhat surprising in view of the fact the electric field is well-confined to the load coil region. Secondly, as the pressure is increased, the relative populations of the metastable and short lived states tend to approach the same value.

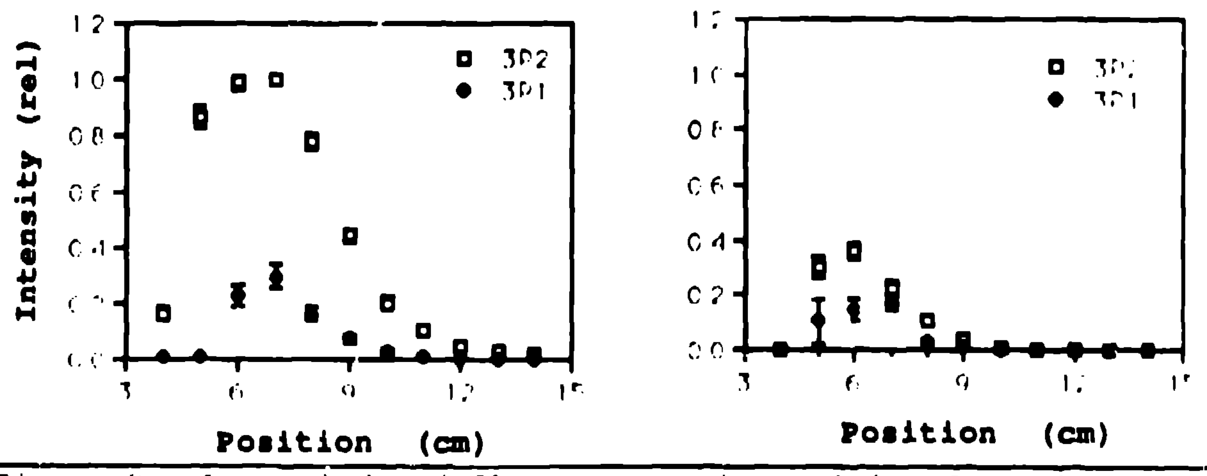


Figure 2. Laser induced fluorescence intensities from the Ar states $^3P_2$ (93751 cm^{-1}) and $^3P_1$ (94144 cm^{-1}) as a function of distance downstream from the last load coil (the quench chamber design did not allow measurements closer than 3 cm). The plot at left is for 2.5 torr total pressure, while the plot at right is for 250 torr.

Time Resolved Measurements.

Time-resolved emission spectroscopy was particularly revealing. It is well known [4] that an alternating electric field can induced a modulation in the population of certain states. This modulation normally occurs at twice the rf frequency, and is the result of electron-atom or electron-molecule collisions induced by electron migration as the electric field oscillates.

For emission near the center of field region of the plasma, a d.c. population was observed, and in addition, modulation at both the fundamental and second-harmonic of the rf frequency. In order to quantify this, the observed signals, S(t), were fit to the expansion:

$$S(t) = a_0 + a_1 \sin(ft) + a_2 \sin(2ft) \qquad (1)$$

where f is the rf radial frequency. The results of this fitting procedure are shown in Figure 3 for measurements within the fireball region.

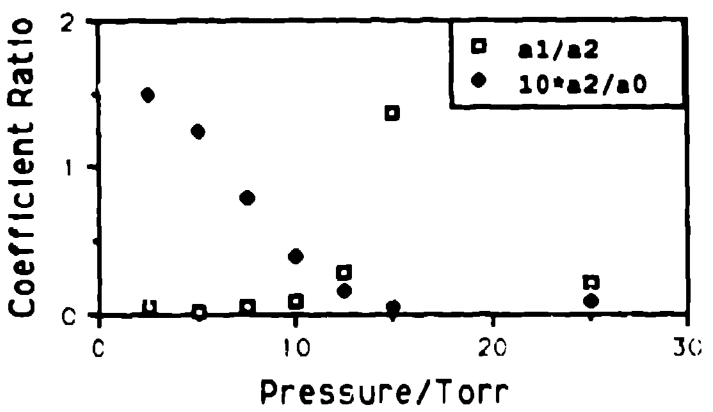


Figure 3. Expansion coefficients for emission as a function of pressure. The triangular points show (ten times) the coefficient of the second harmonic vs. the d.c. level, while the squares show the relative values for the fundamental and second harmonic. Note that at 580 torr (not shown), $10a_2/a_0=0.01$ and $a_1/a_2=10$.

Emission upstream and downstream of the field region was also time resolved. In these regions only the d.c. term and the fundamental were observed; no second harmonic was detected. Average emission intensities decreased as the distance from the field region was increased, however the depth of modulation was relatively independent of both pressure and position, with $0.4 \leq a_1/a_0 \leq 0.5$. Modulation was observed as far as 10 cm downstream. Finally, the emission waveforms are qualitatively symmetric and in-phase on either side of the plasma field region.

Discussion

The shielded plasma device exhibits a number of properties that are not reproduced in other plasma devices. In developing a coherent picture of the operation of this device, it is useful, first of all, to develop a qualitative model of the plasma structure in the load-coil region. In order to rationalize these results, one must consider the nature of the electric fields to which the electrons are exposed. The potential exerted on the plasma may be pictured in two steps, as shown in Figure 4.

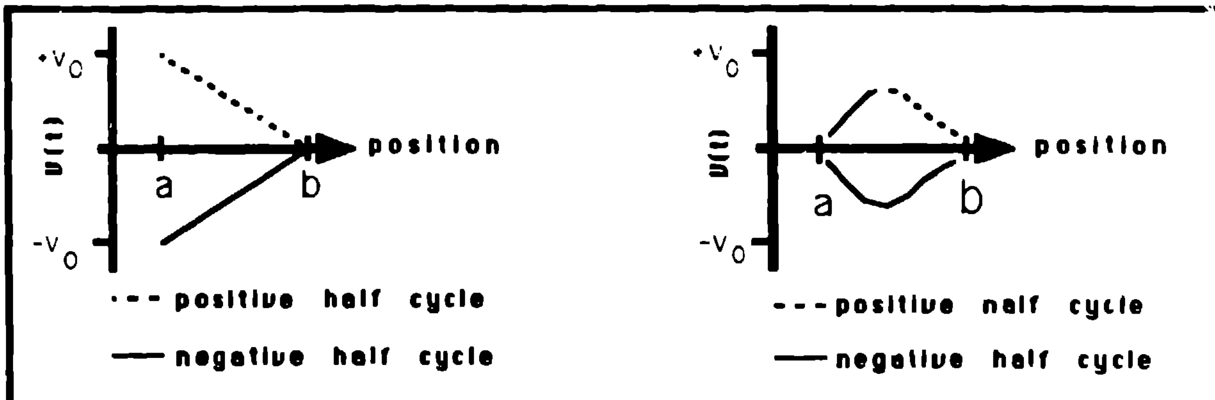
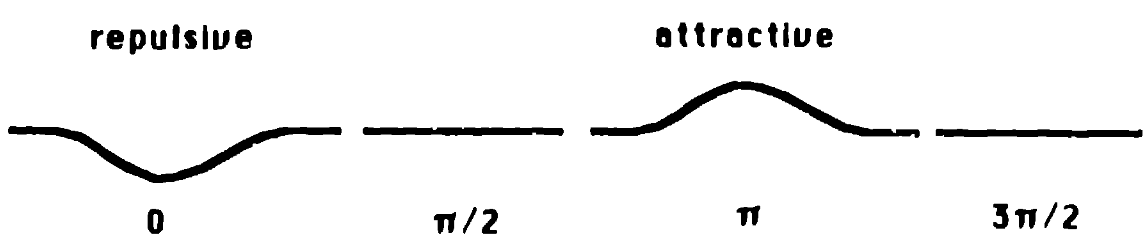


Figure 4. Schematic of the potential within the plasma load coil region: (left) potential due to an rf load coil, (right) modified potential due to the addition of the shield rods, where 'a' is the high voltage end of the coil and 'b' is the rf ground end of the coil.

The effective potential seen by electrons in the plasma will be qualitatively similar to that shown in the right half of Figure 4. Thus, the electrons in the field region will experience a potential which is alternately attractive during one half of the rf cycle, and repulsive during the other half. The electrons will thus have their <u>velocity modulated at the second harmonic</u>, due to changes in the field direction within the load coil region, and their <u>population modulated at the rf frequency</u> by the field gradient during the negative half of the cycle. The population modulation is due to the periodic ejection of electrons and is the direct result of the shield modified potential as shown below.



From the preceding diagram, it is clear that electrons will be ejected from the load coil region during one half of each rf cycle. Thus, one expects that time resolved spectra in the load coil region will be composed of dc and 2f components, typical of previous rf plasma results and an f component from the modification of the potential by the plasma shield. In addition, time-dependent components outside the load coil region will be due only to ejected electrons, so that only dc and f components should be observed. These predictions are consistent with the experimental observations on temporal dependence discussed above, suggesting that this model is at least qualitatively correct.

This description is also consistent with other observations noted above. In particular, the observation of metastable and highly excited atoms far downstream from the high-field region. Since Ar metastable states are typically produced in collisions with electrons [5], the ejection of a "jet" of electrons from the fireball during one half of each rf cycle will tend to generate metastables outside of the load-coil region, in contrast to most plasma reactors, where metastables are produced almost exclusively within the fireball region. The evolution of our metastable signal as a function of distance from the high field region can be explained qualitatively in terms of a competition between production, as a result of the ejected electrons, and quenching by the cooling tail flame. Close to the high-field region, production dominates, and the signal rises as the electron energy distribution cools to the optimal range for excitation. Further downstream, the electrons have cooled sufficiently that metastable production is no longer possible, and quenching dominates, leading to a reduction in the Ar metastable number density.

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