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# Characterization of plasma processes with optical emission spectroscopy.

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## ABSTRACT

Real-time, multi-channel, Optical Emission Spectroscopy was used to record, then analyze, a color change in an argon plasma. It is shown to be an effective diagnostic tool, with value as an on-line monitor, where it can be used to call process endpoint while simultaneously testing for undesirable conditions.

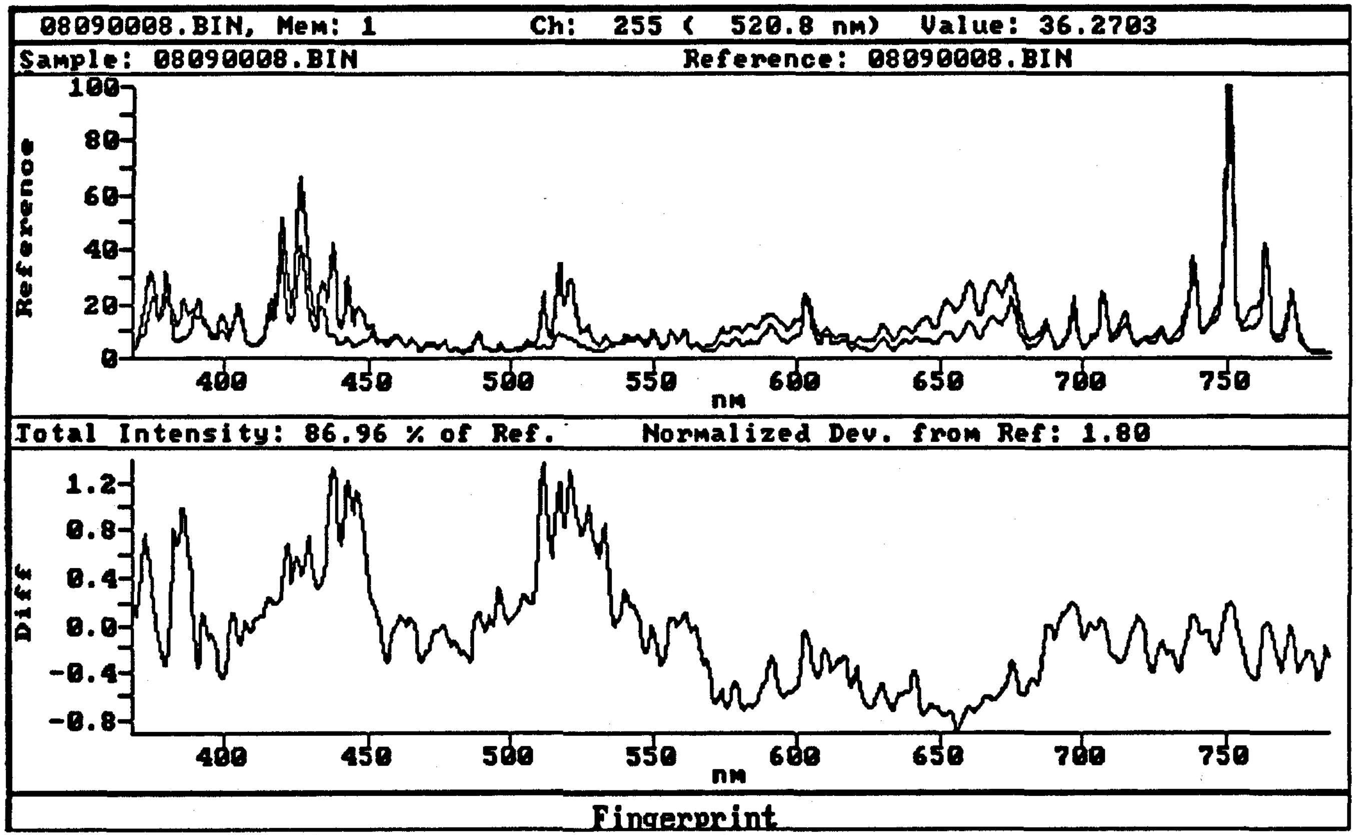
## 1. Introduction

Multi-channel Optical Emission Spectroscopy (OES) of semiconductor process plasmas can shed light on the dynamics occurring inside the chamber. Many chemical species emit light as their components relax to the ground state, each with a unique pattern of wavelengths (or colors for visible light) due to their atomic and molecular structures. Recording these light emissions, identifying the wavelengths, and tracking their behavior as a function of time or other parameters can illuminate one's understanding of the process. This knowledge can reduce process variances and improve yield.

Real-time multi-channel OES can further be used as an on-line monitor. Expensive loss of product can be prevented by signaling when the process plasma is abnormal, due to an air leak, poor cleaning practices, or gas handling mistakes.

In the experiment that is the focus of this paper, the user of a triode parallel plate etch tool noted a change in the color of an argon plasma as a function of power level (50 to 500 W applied). More curious was the change in color as a function of time while at a fixed power level of 480 watts. This paper concentrates on this latter phenomenon. As the tool is being used to study plasma impedance measurements, this color change implied that variations were taking place in the plasma. A mass spectrometer that was on the chamber indicated that the mass 28 peak went down, but this could be due to either CO or nitrogen. The user decided to try to correlate the color variations with the impedance measurements.

We found that the red component of the plasma color was due to $N_2$ while the increase in blue was due to $Ar^+$; meanwhile, copper contributed green energy at 520 nm which gave an overall white cast to the glow. Refer to the difference plot (lower graph) in Figure 1.; the 0.0 point on the Y axis marks the level on the graph where light emissions were the same at the beginning and at the end of the 3 minute process. Regions above that level increased in intensity during the run, while regions below it, decreased. The group of lines in the 425 to 450 nm region are primarily ionized argon; those at 520 are due to copper; and the two broad regions from 560 to 680 nm are due to gaseous nitrogen.



```
08090008.BIN, Mem: 1          Ch:  255 (  520.8 nm)   Value: 36.2703
Sample: 08090008.BIN                    Reference: 08090008.BIN
Total Intensity: 86.96 % of Ref.     Normalized Dev. from Ref: 1.80
```

Figure 1

Upper plot shows the last spectra of a 3 minute run overlaid on the first spectra of that run. The lower plot shows the normalized difference between the two.

## 2. Equipment

The chamber used for this experiment is a parallel plate triode, with power applied to the top electrode, and the bottom one grounded. The glow of the argon plasma in this chamber was quite readily visible to the human eye. The transition from pink to blue became noticeable two minutes after raising the power level of the chamber from below 50 watts to about 480 watts. The effective power to the plasma was estimated at about 235 W initially, but it dropped to 185 W after the glow was completely blue; the pressure also dropped from 18.3 to 16.6 mTorr. In addition, the mass spectrometer showed a significant drop in the mass 28 peak.

The chamber had been pumped down for quite a while prior to the main experiment, and had been operated for several hours during the morning while we recorded spectra at several power levels. Thus, the walls of the chamber had been heated up several times, and most residual atmospheric molecules pumped out. However, note in the difference plot the negative peak at 656 nm; this is due to the reduction in levels of atomic hydrogen during the run. The higher power level heated up the chamber walls, releasing water vapor from the aluminum, which was then disassociated by the plasma. At about 2 minutes into the run, the temperature probably reached an equilibrium, and the supply of available molecules depleted. (See Equation 3 in Figure 6.)

The OES system was an Optical Multichannel Analyzer (OMA$^{®}$) and consisted of 2 meter fiber optic cable with a slit shaped output, a .28 meter monochrometer with multiple gratings, an intensified photo-diode array with 700 channels active, and detector controller electronics packaged with a MS-DOS computer. For this experiment, a coarse 150 g/mm grating with a dispersion of 0.6 nm per channel recorded the emission from 368 to 780 nm. As the photo-diode array collects light in all channels simultaneously, complete spectra in the wavelength range of 368 to 786 nm were collected in 30 milli-second snapshots.

## 3. Test Method

To study the color change, sixty spectra were acquired over the 3 minute run, taken at an interval of 3 seconds. Each of these images was the result of averaging 55 snapshots of 0.03 seconds, greatly reducing the variations of the plasma intensity and shot noise.

### 3.1 Spectral Fingerprint

A quick idea of which wavelengths had the most change was determined via a spectral fingerprint analysis (Figure 1). This procedure first finds the area ($A_r$) under the whole spectrum of the reference curve (the first spectra acquired) and the intensity of the largest peak ($R_{max}$). It then normalizes the sample curve (spectra #60) to have the same area under the curve, and plots both on a scale of 0 to 100% of $R_{max}$ (Equation 1). A normalized difference plot was also generated, with the absolute difference divided by the average energy of both curves at each channel (Equation 3).

$$\text{Sample}_n = \text{Sample} * \frac{A_r}{A_s * R_{max}} \tag{1}$$

$$\text{Reference}_n = \frac{\text{Reference}}{R_{max}} \tag{2}$$

$$\text{Difference} = \frac{\text{Sample}_n - \text{Reference}_n}{½ * (\text{Sample}_n + \text{Reference}_n)} \tag{3a}$$

$$\text{IF} \quad \frac{½ * (\text{Sample}_n + \text{Reference}_n)}{R_{max}} < 1 \text{ then Difference} = 0 \tag{3b}$$

## 3.2 YT Analysis

With the fingerprint plot showing that the dividing line between increasing and decreasing intensities was near 540 nm, the overall intensity of each region was studied as a function of time. Figure 2 shows 4 plots, one for the blue, one for the red, one for the whole spectra, and one for the ratio of the red to blue. This plot quantifies the color change. Initially, the red region contained 2.1 times the emissions of the blue region; this ratio fell to almost unity by the end of the 3 minute run.

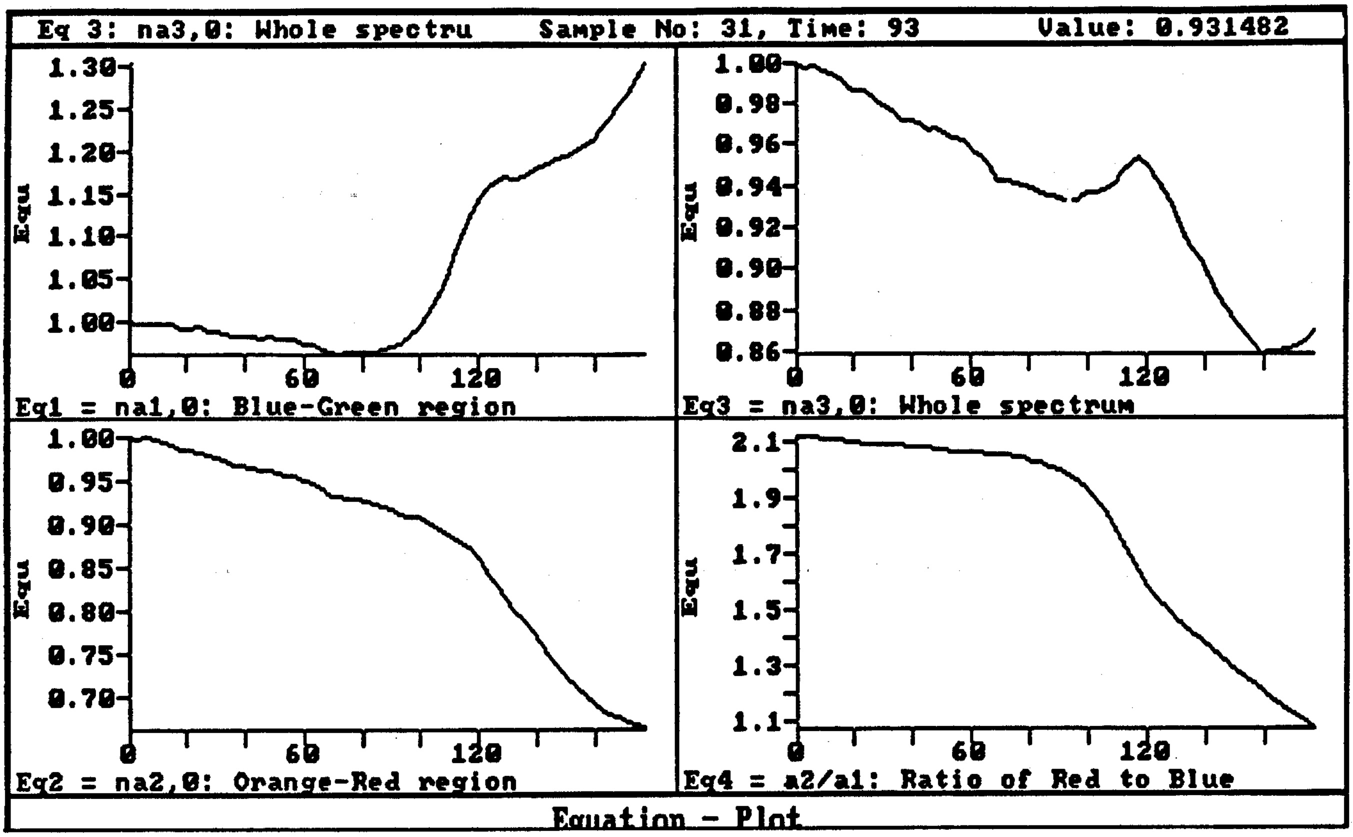


**Figure 2**

4 plots of intensity as a function of time in seconds (also referred to as YT curves). Syntax of na1,0 means the equation is equal to the value of area #1 divided by its value at 0 seconds.

As all optical components (chamber window, fiber, grating, mirrors, and photocathode) in the light path have a unique characteristic as a function of wavelength, OES measurements are made in relative, not absolute units. As this experiment, like most analyses of semiconductor process plasmas, focuses on a relative change in intensity during the run, all of the YT plots have been normalized to their initial intensities. This means that the Y axis of the YT equation plots are ratios, where a value of 1 indicates no change, a value of 1.3 indicates a 30% increase in intensity, etc.

Thus, Figure 2 shows that all intensities declined 6% in the first 90 seconds, when the blue green took off like a rocket, ultimately reaching a 30% increase. The total energy blips up as a result, but the overall trend is irresistible and it continues to decline at its previous rate to a 14% drop.

This drop causes single channel OES systems a problem, in that they measure all of the energy passed by a bandpass filter, no matter what the source. If a peak of interest is riding on top of a continuum generated by another species, a single channel system will report the trend of the more intense emitter. With the multi-channel system, it is possible to create the equivalent of a bandpass filter by summing the counts in a group of channels under a peak. However, this suffers the same problem as single channel systems. The solution is to make note of the channel values at the edges of the area of interest. An imaginary cord is drawn across the region, and signal below the cord calculated. Subtracting this value from the total signal under the curve yields the signal from the peak above the continuum. All of the YT curves shown in this paper made use of this function to isolate one species from another.

### 3.3 Species Identification

Of course, merely confirming what was obvious to the eye would be interesting, but not particularly useful. The next step is to identify the chemical species that are causing the color change. This is mainly done by recognizing the unique patterns of wavelengths associated with most atomic and molecular species. Recognition is mainly a function of experience, but can be greatly aided by comparison with reference spectra of common semiconductor plasma species. (See Figure 3.) For this paper, reference spectra were generated from wavelength, intensity, and line shape data contained in <u>The Identification of Molecular Spectra</u> by Pearse and Gaydon[1], <u>TABLES of SPECTRAL LINES</u> by Zaidel, et al[2], and the $Ar^+$ lines from "Optical Emission from an ECR source in the 200-900 nm range", by Ronald Bell[3]. Unfortunately, the optical emission from many species overlap, and many emission lines of a species can vary or even disappear, depending on how much and by what method energy is coupled into its structure. Therefore, spectral libraries need to be used with care, even when they have been generated by RF discharge.

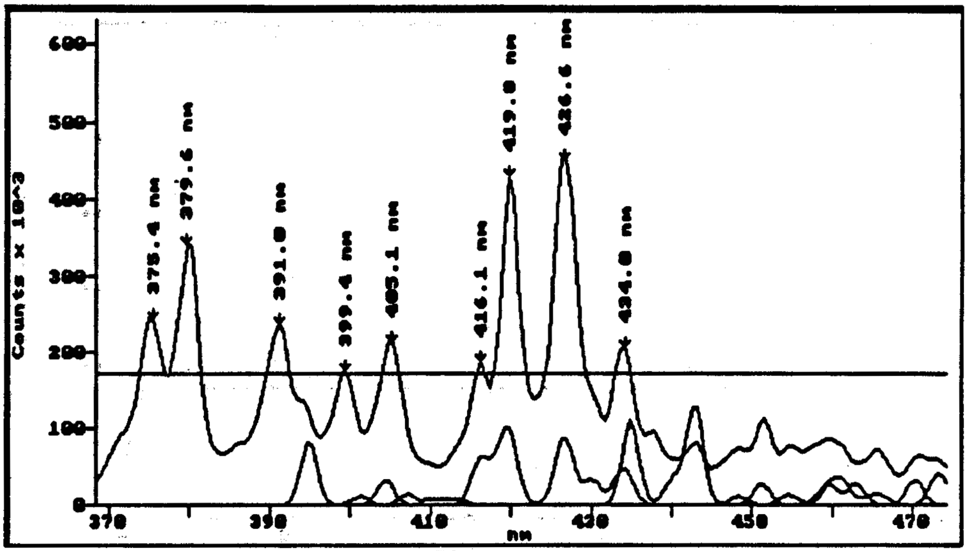


**Figure 3**
Overlay of blue region of the first, pink spectrum (upper curve) on top of both Argon (middle curve from 390 to 430 nm) and ionized Argon (larger 434 and 443 nm peaks).

Illustrations of the complexity of emission spectra appear in Figures 3 and 4. Figure 3 shows the recorded spectrum, with an overlay of both argon (Ar) and ionized argon ($Ar^+$). It is clear that the lines at 416.1, 419.8 and 426.6 are associated with atomic Ar. The line at 434 is a mixture of Ar & $Ar^+$, while the line at 443 is solely associated with $Ar^+$. This illustrates an important utility of spectral libraries: identifying regions that are reasonably isolated from other species. This is specially valuable in creating areas to follow as a function of time.

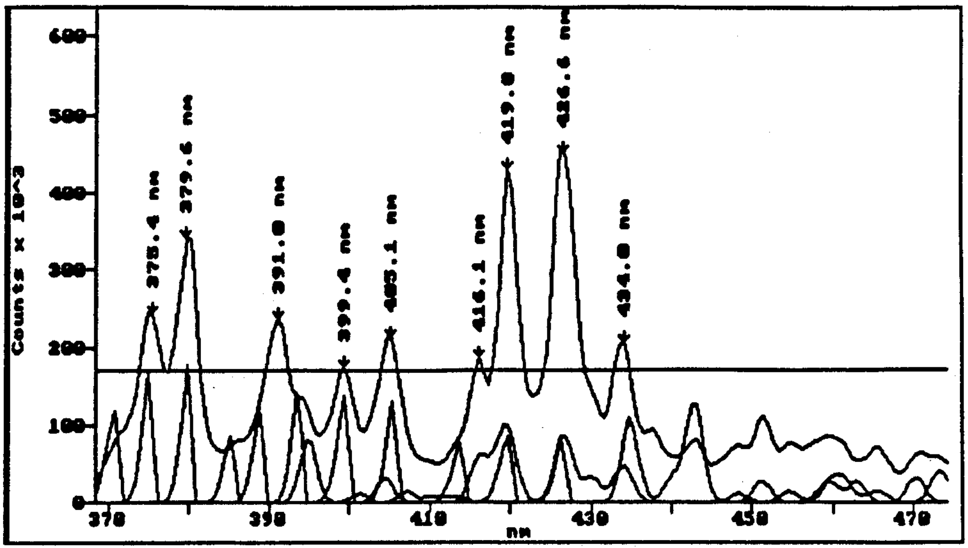


Figure 4

Nitrogen ($N_2$) reference spectrum overlaid on top of Ar, $Ar^+$, and the pink spectrum.

Figure 4 is similar to Figure 3 but with the addition of gaseous nitrogen ($N_2$). As one looks at the combination of lines at the bottom of the graph, it becomes apparent how they add together to make the recorded spectrum. One wonders, though, how to track the changes in one species independently of the others.

The solution requires choosing peaks with a minimum of overlaps with the peaks of other species, and the use of the continuum correction mode described in section 3.2. For this paper, $N_2$ was tracked via the peak at 400 nm, blue Ar via the double peaks of 416 and 420 nm, and $Ar^+$ via 443. Not shown in these graphs is the reference spectrum of $N_2^+$ which drives the peak at 391 nm. Several other peaks for $N_2$ were studied. Before activating the correction mode, they were quite dissimilar; afterwards, they were very much alike. One peak at 437 nm that grew during the run is yet to be identified.

### 3.4 Areas & Equation Tables

Using similar plots to these, the following Area and Equation Tables were developed. They show the wavelength areas and YT equations that were used to isolate and analyze the behaviors of the different process plasma species.

Note the column labeled Correction Mode shows 'Background' for all of the equations. This is the continuum correction described in Section 3.2. Also note the use of 0 or 1 second as the normalization time for all of the equations. As the

**Area - Table**

| Comment | Range | Corr-Mode |
|---|---|---|
| A1 :Ar @ 433.8 & Ar+ @ 434.9 nm | 432nm - 436nm | Background |
| A2 :Ar+ @ 442.6 | 441nm - 445nm | Background |
| A3 :H @ 656.3 | 655nm - 658nm | Background |
| A4 :Ar @ 763.5, used as red line | 762nm - 765nm | Background |
| A5 :Ar @ 415-420, blue lines | 414nm - 423nm | Background |
| A6 :N2+ @ 391.0 | 389nm - 392nm | Background |
| A7 :N2 @ 399, used as blue line | 396nm - 401nm | Background |
| A8 :N2 @ 379 | 378nm - 381nm | Background |
| A9 :N2 @ 405 | 403nm - 407nm | Background |
| A10:N2 group 627-681nm, red lines | 627nm - 681nm | Background |
| A11:Cu @ 521.8, green line | 519nm - 524nm | Background |
| A12: | *-------------* | none |

**Equation - Table**

EQU 1: na11,0: Cu @521.8 nm
EQU 2: na2,1: Ar+ @442.6 nm
EQU 3: na3,1: H @656.3 nm
EQU 4: na10,1: N2 group @627-681 nm
EQU 5: na5,1: Ar @415-420 nm
EQU 6: na6,1: N2+ @391 nm
EQU 7: na7,1: N2 @399 nm
EQU 8: na4,1: Ar @763.5 nm

Table 1

A listing of the wavelength regions and equations used for plotting changes as a function of time.

sample time per spectra was 3 seconds in this experiment, the use of 1 second here dictates the normalization to be based on the equation values for the first spectra acquired. This spectra is considered to be the time zero spectra when plotted in the YT equations.

Figure 5 illustrates the location of the areas listed in Table 1. Not all of the 11 areas listed were used for the final YT plots as overlaps with other peaks made it difficult to isolate their behavior from the others. The spectrum shown is from the end of the run; note the $Ar^+$ peaks in the 430-450 region, and the Cu family around 520 nm. They were not apparent in the first spectrum.

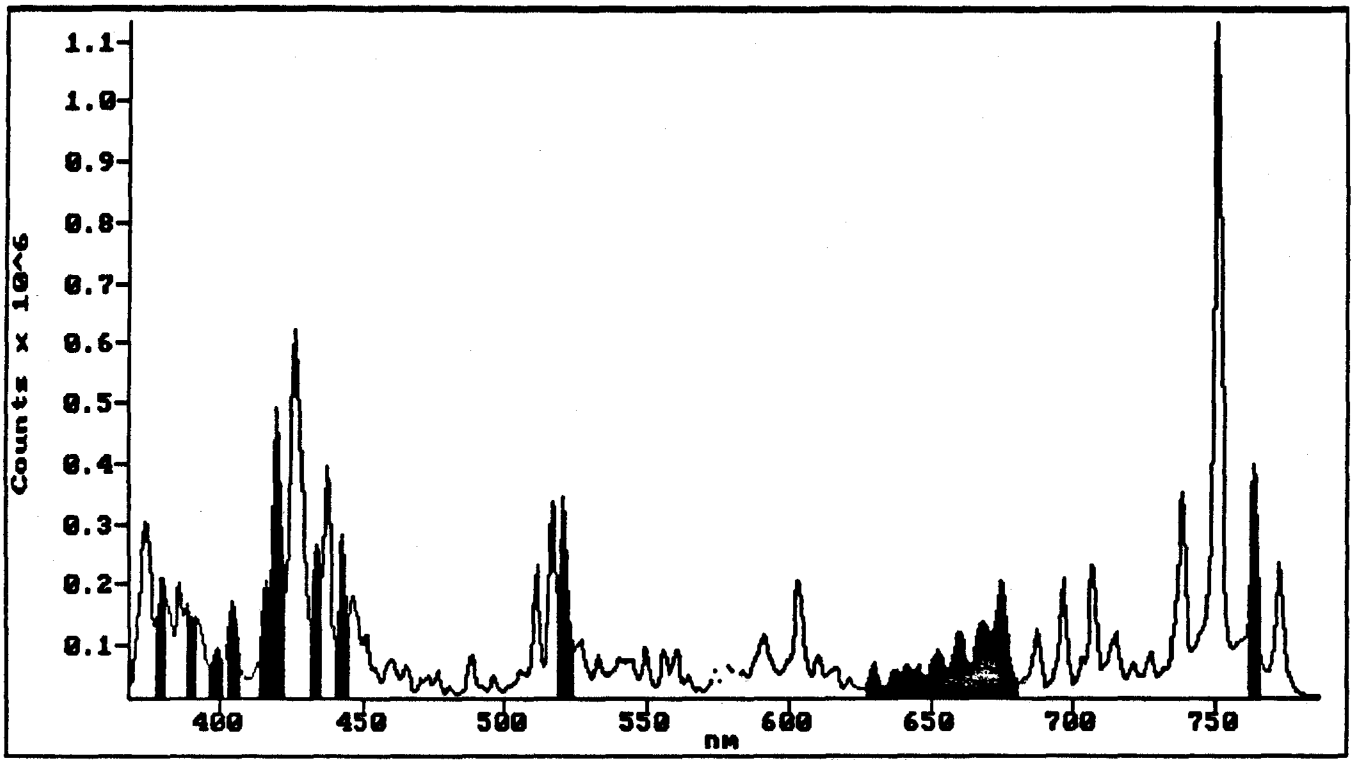


**Figure 5**
The intensified regions graphically show the location of the areas listed in Table 1.

## 4. Experimental results and discussion

In analyzing the YT plots (Figures 6 and 7) generated by the experimental technique, one is struck by the change that occurs 120 seconds after raising the power level in this chamber. Prior to that, Ar, $N_2$ and $N_2^+$ have been trending down; Cu, $Ar^+$, and H have been trending up. After that, all of the nitrogen peaks and the hydrogen peak practically disappear, and the argon peaks join copper in taking off to the sky. The color change from pink to blue is driven by the disappearance of the broad red emissions of nitrogen (down 55%), and the strong addition of the blue ionized argon peaks (up by 600% for one line of the group).

It seems significant that the Cu is the first to really change slope. However, the user reports that the Cu was probably introduced by an experiment in the chamber a month prior to our session

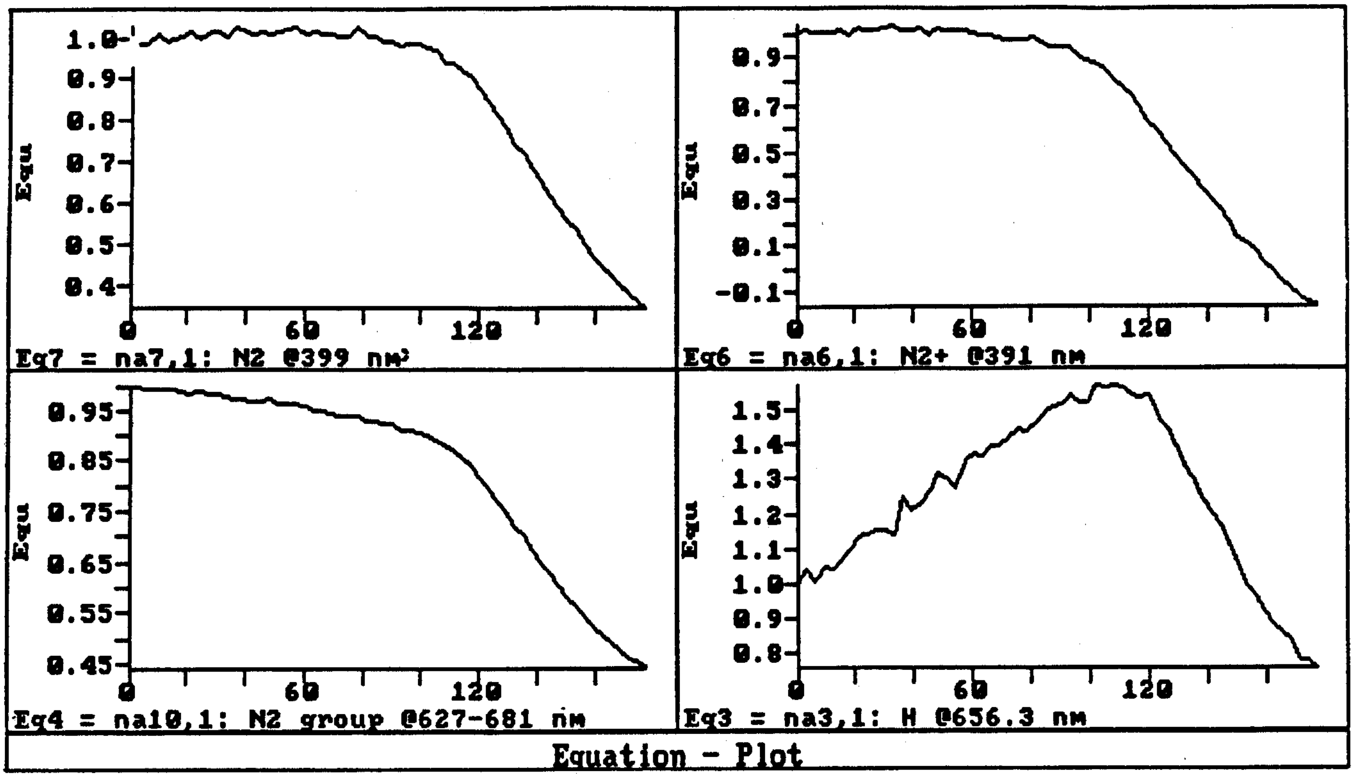


**Figure 6**
**YT Plots of a blue $N_2$ line, a red group of $N_2$ lines, a $N_2^+$line, and a Hydrogen line.**

while the color change phenomenon has been observed for several years. Nevertheless, very interesting things are happening with the Cu emissions from 93 to 137 seconds. The increase in its green emissions is enough to really impact the decline in the total emission of the plasma (see Figure 2, Equation 3).

The reasons for the changes are not clearly understood. Certainly, the nitrogen is an unwelcome presence, implying a leak that will have to be sealed before other processes can be trusted to give repeatable results. (In fact, a leak has since been found in the gas manifold leading to the chamber.) But why does the nitrogen level drop so much and only after a period of time at a higher power level? The mass spectrometer confirms that $N_2$ has gone away, but doesn't show it reappearing as N or as another molecule. Where did the nitrogen go? Did it disassociate? There was no peak at 410 nm, a prominent line for atomic nitrogen, nor was there a change in intensity at that wavelength. Nor does it seem that a different electron temperature caused some of the lines to lessen in intensity. They all seem to drop at the same rate, whether they were in the red, orange, or blue, or even if they were lines from the ion. It would seem that the source of the nitrogen was reduced as a result of the higher power.

Some of the changes, as already mentioned, are due to the increased power which would significantly heat up the chamber. An observed hysteresis effect in the color transition tends to confirm this assumption. Once the change has occurred, it will reoccur more readily if the experiment is repeated (in less time or at a lower power level). Therefore, if the chamber has already warmed, less power is needed to reach the transition conditions. It's possible that wall heating releases water vapor from the chamber walls, which in turn, dampens the argon plasma. When the ready supply of water vapor is exhausted, atomic argon more readily emits again. The

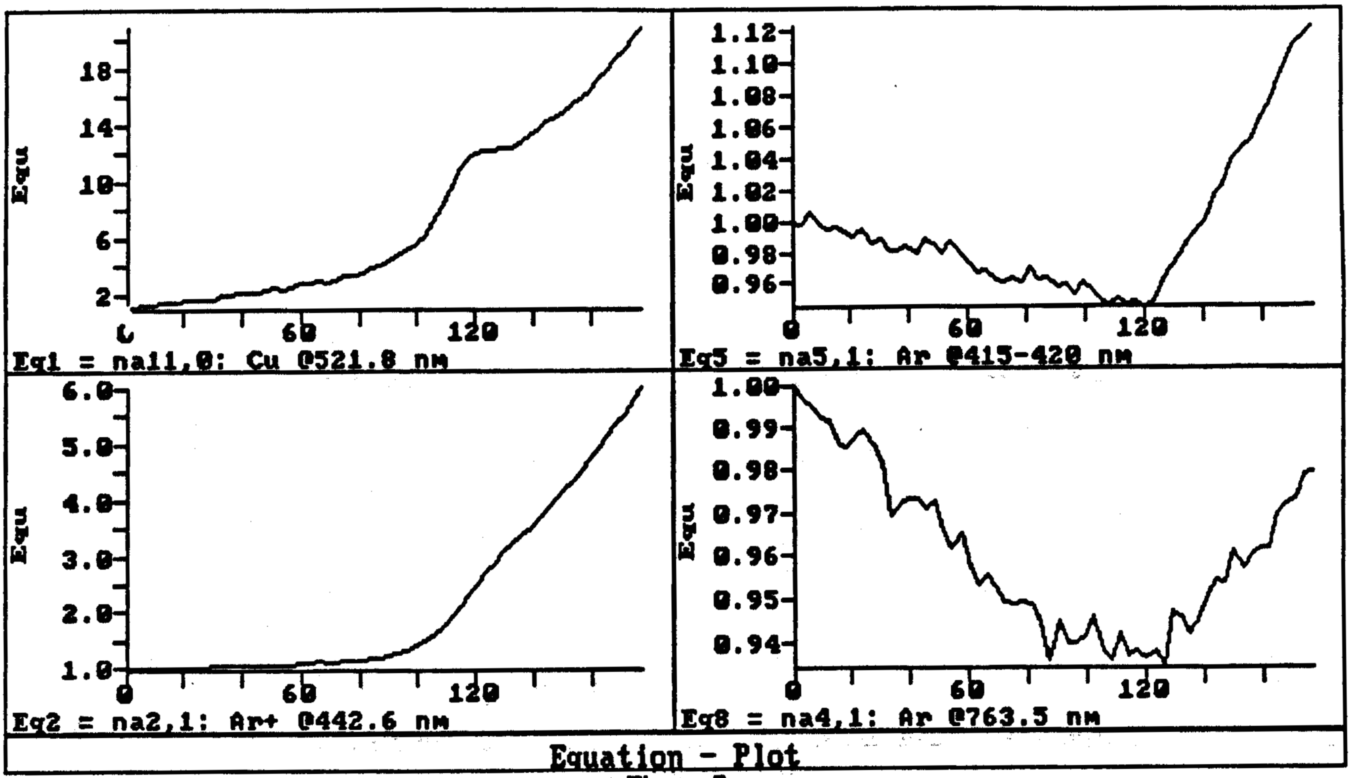


**Figure 7**
**YT Plots of atomic Cu, Ar$^+$, a blue Ar line and a red Ar line.**

hydrogen Equation 3 of Figure 6 does seem to be the inverse of the argon Equations 5 and 8 of Figure 7, indicating a linkage.

The plots of nitrogen, copper, and Ar$^+$ seem to lead the change in H and Ar by a significant amount, implying that they are driven by different effects. The Ar$^+$ could reflect an increase in electron density, for instance. The copper emission might indicate that the plasma has changed position and is sputtering some leftover piece of copper. Whatever the causes, it is clear that two common contaminants, water and air, are seriously affecting the repeatability of plasma processes in this chamber.

## 5. Conclusions

We have shown how multichannel Optical Emission Spectroscopy can be used to make a movie of changing chemistry of a process plasma, isolate the behaviors of different chemical species in the plasma, and track those behaviors as a function of time or other parameters. The sensitivity of OES to low levels of contamination has also been established. It is clear that these capabilities provide the user with a wide range of diagnostic functions. These functions complement rather than eliminate other diagnostic tools such as RGAs, but they often provide the missing piece of the puzzle necessary to solve a yield problem.

As demonstrated in an earlier paper presented by Mr. George Gifford of IBM, the multichannel OES is also a valuable on-line monitor on the manufacturing line. It is in active use, calling end point and flagging undesirable conditions BEFORE they ruin product.

## 6. Acknowledgements

I wish to thank the Princeton University Sematech Center of Excellence for Plasma Etching for the use of their chamber, Joe Cecchi, Ron Bell, and C.W. Cheah of Princeton for their assistance and discussions, EG&G-Princeton Applied Research for the OES equipment, and to my family for their patience and editing assistance.

## 7. References

1. R.W.B. Pearse and A.G. Gaydon, The Identification of Molecular Spectra, Fourth Edition, Chapman and Hall, London, 1976

2. A.N. Zaidel, et al, Tables of Spectral Lines, IFI/Plenum, New York, 1970.

3. R.E. Bell, et al, "Optical Emission from an ECR source in the 200-900 nm range", a poster paper given at the August 7, 1990 Annual Contract Review for the New Jersey Sematech Center of Excellence, unpublished, 1990. Copies can be obtained by writing Mr. Bell at the Princeton Plasma Physics Laboratory, Princeton, NJ 08540.