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Practical sensor for nitrogen in direct current glow discharges

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This paper presents a method for precise measurement of atomic and molecular nitrogen in an oxygen-nitrogen dc plasma. This is achieved by monitoring the intensities of the atomic nitrogen spectral line at 821.6 nm and the molecular nitrogen bandhead at 337.1 nm, relative to the atomic oxygen spectral line at 844.7 nm. Oxygen is one of the most frequently used gases for surface chemical treatment, including deposition and etching, therefore the ability to measure and control the process and chemical composition of the process is essential. To validate this oxygen actimetry method for N_2 - xO_2 (where x varies from 0 to 1) dc plasmas, threshold tests have been performed with Ar actinometry. The optical measurements have been performed using two methods. The first approach uses a USB2000 fiber optic spectrometer, calibrated with a Gigahertz–Optik BN-0102-1 reference standard source, to record the desired spectral lines. The second approach uses narrow bandwidth optical filters (~ 0.7 – 0.07 nm) with central wavelengths of 821.6, 337.1, and 844.69 nm and photodiodes to detect the emission intensity, also calibrated with the same standard source. Optical data are collected for a range of experimental conditions in a flowing glow discharge of N_2 - xO_2 mixture. The maximum dc voltage is 2.2 kV and maximum chamber pressure is 266 Pa. Data from both optical methods are compared and used to interpret the relative atomic and molecular nitrogen concentrations under various operating conditions. © 2007 American Institute of Physics. [DOI: 10.1063/1.2816254]

I. INTRODUCTION

The employment of high-density plasmas for the fabrication of semiconductor devices with a high throughput has required the development of sophisticated process diagnostics. The measurement of radicals in a plasma process is essential for the understanding of the complicated plasma chemistry used in such processes. Indeed, the ability to measure and control such species is seen as a possible way to improve yield in semiconductor manufacturing.

Low-pressure glow discharge nitrogen plasmas are extensively used for nitriding of various materials, especially Fe-based alloys, to improve their surface properties, including surface hardness, wear, corrosion resistance, and fatigue strength.^{1,2} The large number of treatment parameters that can be arbitrarily selected makes it attractive for the growth of specific structures and properties not manageable in conventional nitriding processes.³ As the electrons are the lightest charged particles in the discharge, they attain an energy of several electron volts from the electric field and make collisions with the other plasma species. The most important collisions are inelastic, leading to excitation, ionization, and dissociation of plasma species that eventually have an energy of several electron volts above their ground states and can affect the surface and thus deposition chemistry.⁴ Moreover,

the gas temperature in the discharge chamber is very low compared with the electron temperature, which makes this technology ecologically clean owing to the absence of chemically aggressive impurities introduced by sputtering.

Atomic N plays an important role in the synthesis of nitrides owing to its high chemical reactivity. Therefore, information regarding the concentration of active species in a nitrogen discharge is essential for better control of plasma reactions and plasma-surface interactions.

Most plasma diagnostic techniques are either electrical or optical in nature. Among the electrical techniques, the most widely used method is the Langmuir probe because of its easy implementation. However, experimental problems such as contamination of the probe tip and complexities in the theory to interpret the measurements can often lead to erroneous results. Additionally, most modern commercial reactors that use reactive plasmas as processing reagents are not amenable to probes, which are invasive by nature and risk introducing undesirable process shifts. Optical actinometry provides a nonintrusive means of studying a reactive plasma. The basic premise of this technique is that the emission intensity of the electronically excited states of plasma species is proportional to their population densities provided that the population dynamics are governed by direct electron impact excitation from the ground state without any multi-stage excitation, ionization, or self-absorption.⁵ Consequently, the intensity of the spectral line is characterized by

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both the density of the plasma species involved in optical emission and the electron energy distribution function (EEDF). Since most changes in the discharge parameters influence both the density of plasma species and the EEDF, one cannot easily use the optical emission intensity as a true monitor of the density of reactive plasma species unless considering the changes for the EEDF and excitation cross section collectively known as the excitation efficiency of the discharge.^{6,7} To circumvent these problems, trace-rare-gas optical actinometry diagnostics are employed.⁸ In this diagnostic technique, a small amount (1–2%) of a rare gas is added to the reactive plasma without disturbing the plasma properties; this serves as the actinometer. The concentration of the actinometer is kept constant and the optical emission derived from it is used to determine the excitation efficiency of the plasma when the discharge parameters are changed.^{9,10} This “actinometry” method works well when the relative energy dependence of the electron impact excitation of the rare gas matches that of the emitting species of interest.^{8,11}

However, the use of a trace gas as an actinometer in an industrial setting can be problematic, as the requirement for an additional gas line would be outweighed by cost considerations. Also, a rare trace gas dilutes the chemically reactant gases, and for many plasma processes this is unwanted. Therefore, the ability to use nontrace gas (such as oxygen in our experiment) as the actinometric gas would negate the requirement for additional trace gases and therefore would allow this technique to be applied in a manufacturing process. It must be stated, however, that the validity of actinometry¹² is somewhat controversial, and the criteria for the utilization of the technique and its limits of validity must be verified in each case. Actinometry becomes invalid if the excited state from which emission is being detected has not been created by electron impact excitation from the ground state. The validity of actinometry using excited oxygen and argon atoms was investigated by Walkup *et al.*¹³ They found that the actinometric determination was well correlated with the variation of atom concentration up to 50 Pa in rf O₂-CF₄ plasmas, but discrepancies occurred in pure O₂ plasmas. In addition, it was shown by Booth *et al.*¹⁴ that the ratio of the intensities of the oxygen line to the argon line was poorly correlated with the oxygen atom concentration in electron cyclotron resonance (ECR) plasmas operated at ultralow pressures (0.1–0.8 Pa).

It is because of this cautionary note that extensive validation measurements have been performed on our system, which uses oxygen as the actinometry gas. The validation procedure uses the actinometric technique itself as trace amounts of Ar gas have been added to the N₂-O₂ discharge to confirm the applicability of the technique for a range of N₂-O₂ discharges. The validity of using the nontrace gas as the actinometer should be manifested as an agreement between the oxygen and argon actinometry data under a range of plasma conditions. Once this validation procedure is complete, we no longer use trace gas Ar in the process and can revert back to actinometry measurements using the buffer gas¹⁵ of the process (oxygen).

The optical measurements have been performed using an Ocean Optics USB2000[®] fiber optic spectrometer that is cali-

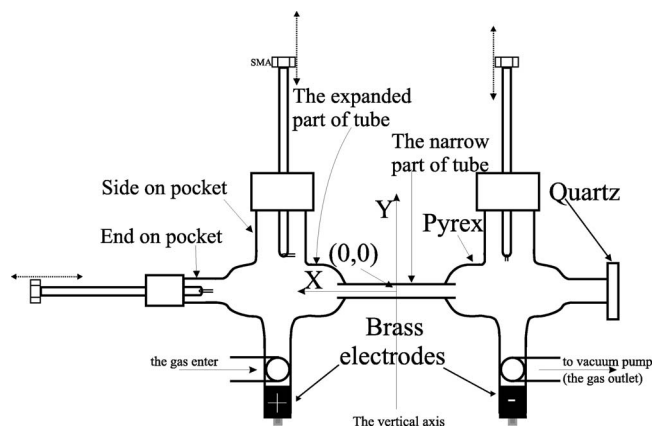


FIG. 1. Plasma source with ports for the probes.

brated with a Gigahertz-Optik BN-0102-1 reference standard source, and a customized optical sensing system consisting of three narrow bandwidth optical filters ($\sim 0.7\text{--}0.07\text{ nm}$) with the central wavelengths of 821.6, 337.1, and 844.7 nm, and their associated photodiodes, which are used to detect the emission intensity of the desired spectral line. The optical device is made to measure only the intensities of spectral lines important for determination of nitrogen density, therefore this optical device represents a practical sensor for nitrogen in a N₂-xO₂ plasma.

II. EXPERIMENT

A dc discharge is produced in a Pyrex tube of 5-mm inner diameter and an effective plasma length of 72 mm; see Fig. 1.¹⁶ The discharge tube is evacuated using a rotary vane pump that gives a base pressure of 2 Pa. The working pressures from 50 to 266 Pa are achieved using a gate valve positioned above the rotary pump. Gas flow into the chamber is controlled via mass flow controllers that precisely determine gas content in the discharge tube. The nitrogen and oxygen flow rate is varied up to 200 sccm. The power supply used was a Keithley Model 248 High Voltage Supply with a maximum voltage of 5 kV and discharge current of 5 mA. For the purposes of this experimental work, the maximum voltage is 2.2 kV. In fact, the large parameter space required of this work meant that a Design of Experiment (DOE) had to be implemented, i.e., dc voltage 700–2200 V, N₂ gas flow rate 4–200 sccm, O₂ gas flow rate 2–200 sccm, and chamber pressure 50–266 Pa. The application of this DOE reduced the number of experimental runs to 36. The creation of a DOE table is done by The Statistical Discovery software[™], JMP IN[™].

The schematic diagram of the experimental setup with associated diagnostics is shown in Fig. 2.

The measurement of electron density was performed using a hairpin probe as described in Ref. 16. To facilitate introduction of the probes into the plasma source, we have used three ports: two on the top of the expanded glass tube sections and one on the side. The quartz window, on the opposite side from the side probe, was used for the observation of spectral line shapes by the spectrometer and the cus-

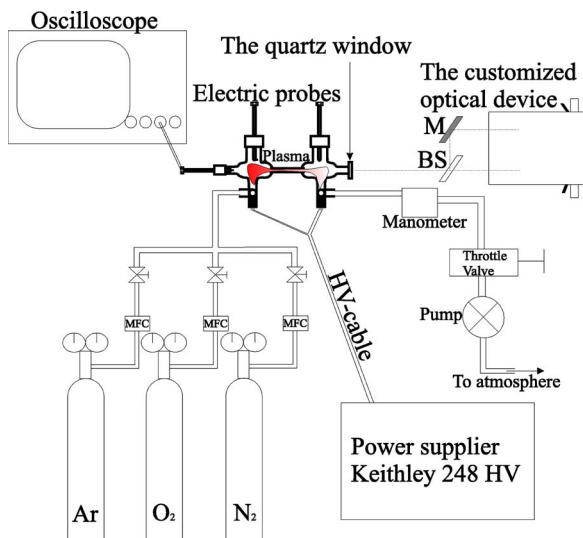


FIG. 2. (Color online) Plasma source with associated diagnostics. The BS is a 50:50 beamsplitter, and the M is a high reflectivity ($>98\%$) silvered mirror. The fiber optic $200\ \mu\text{m}$ cable could be placed on the optical axis instead of the customized optical device. Therefore, the USB2000 spectrometer could be used.

tomized optical device. At these experimental conditions, we measured electron densities from 1.7×10^{-10} to $3.7 \times 10^{-11}\ \text{cm}^{-3}$.

The light emitted by the discharge was focused into a USB2000 Ocean Optics spectrometer and the customized optical device. The USB2000 has the following characteristics: focal length 42 mm, grating with 600 lines/mm, grating could be tuned from 200 to 875 nm (controlled by computer), reciprocal dispersion from $39.61\ \text{nm/mm}@180\ \text{nm}$ to $38.29\ \text{nm/mm}@875\ \text{nm}$, and a CCD camera of 2048 pixels with a pixel size of $14\ \mu\text{m} \times 20\ \mu\text{m}$; the CCD camera was sensitive in wavelength bandwidth from 200 to 1100 nm. The resolution of the USB2000 is $0.555\ \text{nm/pixel}$ for $\lambda=200\ \text{nm}$ and $0.536\ \text{nm/pixel}$ for $\lambda=875\ \text{nm}$. We have used a multimode fiber with a core diameter of $200\ \mu\text{m}$ and a length of 2 m. The instrumental full width at half-maximum (FWHM) of $1.6 \pm 0.3\ \text{nm}$ for USB2000 was obtained by using a low-pressure mercury lamp with an external stabilized power supply. It is clear from the specifications that the USB2000 is not a high-performance spectrometer in terms of resolution, but it has the advantage that it is not too complicated to operate and lends itself to real-time measurement or plasma chemical analysis in industry.

The customized optical device used in this work is an in-house customized optical sensing system consisting of three narrow bandwidth optical filters with central wavelengths of 821.6, 337.1, and 844.69 nm and their associated photodiodes, which are used to detect the emission intensity of the desired spectral line. A schematic diagram of this device is shown in Fig. 3. It is important to point out that the optical device contains two optical filters and two photodiodes. So, for measurement of atomic nitrogen we use the optical filters with central wavelengths of 821.6 and 844.69 nm and an appropriate pair of photodiodes. For measurement of molecular nitrogen we use optical filters with central wavelengths of 337.1 and 844.69 nm and an appropriate set

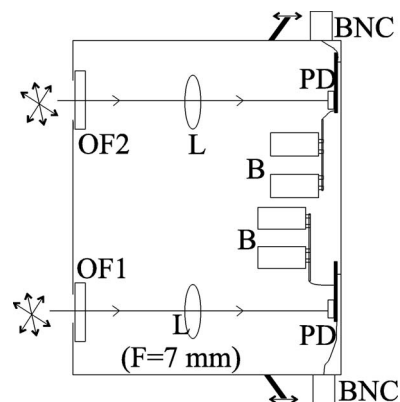


FIG. 3. Schematic diagram of the customized optical device: OF#, Optical filter (central wavelength: 821.6, 337.1, or 844.69 nm); L, Lens (focal distance); B, Batteries; PD, Photodiode.

of photodiodes. The design of the optical device makes it possible to easily replace the optical filters by switching the optical mounts.

The operating principle of this device is that the polychromatic light that enters the device can be separated such that only the emission at the two wavelengths of interest falls with equal intensity onto the associated optical filters (OF) and from there onto their associated photodiode detector. The emitted light from the plasma enters the device and falls onto the beamsplitter (BS), which is a 50:50 beamsplitter. 50% of this light passes through this beamsplitter and falls onto the first optical filter with a central transmission wavelength of 821.6 nm (the bandwidth is 0.71 nm and peak transmission is 72%), thereby ensuring that only monochromatic light falls onto the first photodiode. In the case of measurement of molecular nitrogen, the first optical filter with a central transmission wavelength is 337.1 nm with the bandwidth of 0.73 nm and a peak transmission of 70%. The remaining 50% of the light is reflected through 90° and is directed onto the second optical filter by reflection off a high reflectivity ($>98\%$) silvered mirror (M). This light then passes through the second optical filter, which has a central transmission wavelength of 844.69 nm (the bandwidth is 0.07 nm and peak transmission is 66%), which results in monochromatic light falling onto the last photodiode.

It is important to note that this device is somewhat similar to an optical spectrometer and is of high resolution, although only at the three specified wavelengths. The analog voltage from each photodiode is proportional to the emitted intensity at each wavelength and this signal can be amplified via the photodiode's amplifier circuitry. To enable direct comparison between dc signals from different photodiodes and optical filters, a calibration procedure is performed on this optical system. The calibration¹⁷ has been carried out using a Gigahertz-Optik BN-0102-1 Reference Standard source. This source is a spectral radiance standard. Its tungsten halogen lamp is current controlled by an LCRT-2000 Power Supply. The spectral radiance calibration is supplied by Gigahertz-Optik's calibration laboratory for the wavelength range from 380 to 1100 nm, in 10-nm increments. After this calibration procedure, it is possible to compare the

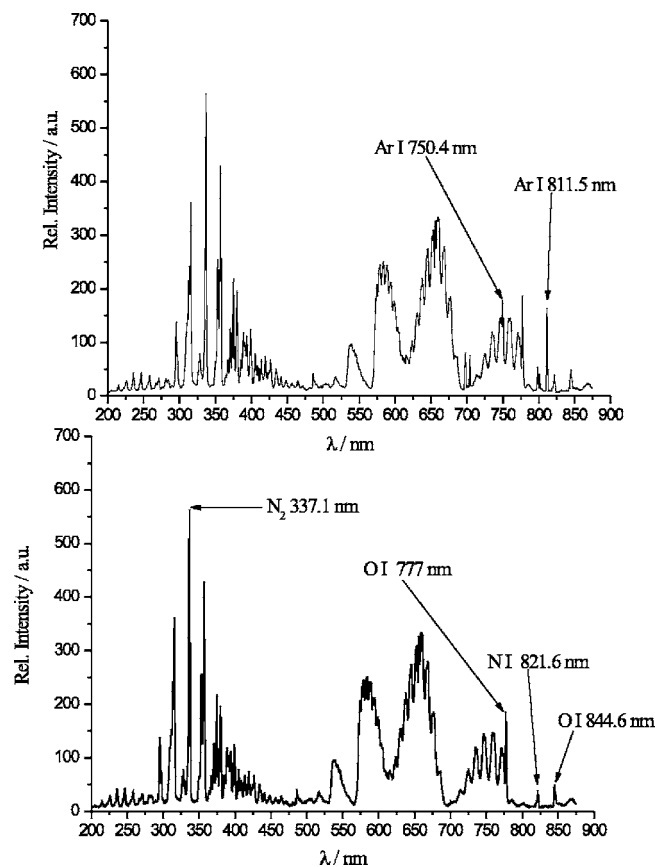


FIG. 4. Optical emission spectrum from a nitrogen-oxygen plasma (bottom). Optical emission spectrum from a nitrogen-oxygen plasma with argon as a trace gas (top). The relevant actinometry lines are indicated for clarity in each panel.

photodiode signals against each other and/or to calculate the ratio of these signals, as is required for actinometry.

The chosen central wavelengths for the optical filters (821.6, 337.1, and 844.7 nm) correspond to the actinometry spectral lines of the nitrogen atom (821.6 nm), the oxygen atom (844.7 nm), and the nitrogen molecule via the nitrogen bandhead ($C^3\Pi_u \rightarrow B^3\Pi_g$, 337.1 nm).¹⁸ We use actinometry with oxygen as the actinometer to determine relative atomic and molecular nitrogen concentration, i.e., to “create” a practical sensor for atomic and molecular nitrogen.

The validation procedure uses the actinometric technique itself as trace amounts of Ar gas have been added to the N_2 - xO_2 discharge to confirm the applicability of the technique for a range of N_2 - xO_2 discharges. The broadband spectral sensitivity of the USB2000 spectrometer meant that it could very easily be used to test for any disturbance in the nitrogen-oxygen optical spectrum under all of the 36 plasma conditions required as part of our original DOE. Two sets of optical data were then recorded for each of the 36 experimental runs. The first set was in N_2 - xO_2 plasma only and the second set had argon added to the N_2 - xO_2 plasma. The argon flow is maintained at 5 sccm. Figure 4 shows the recorded spectra for one such nitrogen-oxygen and argon-nitrogen-oxygen plasma and reveals how similar the two spectra are, with the only apparent difference being the Ar I line at 811.5 nm. Hence we can be assured that argon can reliably be used

as our actinometer reference for the threshold tests required for oxygen actinometry in oxygen-rich plasmas.

The intensity of the signals measured with our optical sensor is compared with the USB2000 spectrometer.

III. RESULTS AND DISCUSSION

There are two well known actinometry atomic oxygen spectral lines: the 777-nm spectral line from the $3s$ - $3p$ transition originating from the $^5S^o$ - 5P multiplet and the 845-nm spectral line from the $3s$ - $3p$ transition originating from the $^3S^o$ - 3P multiplet. It is important to point out that the “777-nm spectral line” is not just one line but is actually a triplet: 777.194-nm multiplet $^5S^o_2$ - 5P_3 , 777.417-nm multiplet $^5S^o_2$ - 5P_2 , and 777.539-nm multiplet $^5S^o_2$ - 5P_1 . Similarly, the “845-nm spectral line” is also a triplet of lines: 844.625-nm multiplet $^3S^o_1$ - $^3P^0$, 844.636-nm multiplet $^3S^o_1$ - $^3P^2$, and 844.676-nm multiplet $^3S^o_1$ - $^3P^1$. The low-resolution USB2000 spectrometer will not resolve these lines and thus we need to know how each individual line behaves in comparison to the actinometric lines of 777.417 and 844.676 nm. The intensity of each spectral line is not simply its height but is the area under the line as summed from -2.5 FWHM steps on the low-wavelength side of the line peak to $+2.5$ FWHM steps on the high-wavelength side of the line peak. This investigation is described in Ref. 15 and we have determined that the unresolved triplet peak at 777 nm, as recorded by the low-resolution spectrometer, has to be multiplied by a factor of 0.31 to represent more exactly the intensity of the atomic oxygen actinometry spectral line at 777.417 nm. Similarly, the total intensity of the unresolved triplet peak at 845 nm, as recorded by the low-resolution spectrometer, must also be multiplied by a factor (0.33) in order to indicate properly the intensity of the oxygen actinometry spectral line at 844.676 nm. No such factor is required for the customized optical sensor as its signal is a direct measurement of the line intensity at each specific wavelength to be recorded. The aim of the investigation with the low-resolution USB2000 spectrometer was to understand the behavior of each O I spectral line in the triplet around 777 and 845 nm, and later on to use it as an actinometry line. In the N_2 - O_2 mixture, only the 845-nm line was used for actinometry since the 777-nm line is embedded in the first positive system of nitrogen molecules. The O I 844.476 nm is also a good choice, since the electron excitation of the ground state of O atoms is a dominant process.¹⁹

In order to check if our customized optical device can be used for actinometry work, a comparison of the data from this device and the low-resolution optical spectrometer was required. This comparison is most easily represented by a plot of the ratio of the intensities of the actinometric lines and the low-resolution spectrometer, i.e., $I_{\text{Optical sensor}}/I_{\text{USB2000}}$ for both the oxygen 844.676 atomic line.

If the two optical systems behave in a similar manner, then the ratio of the intensities recorded by each should be constant. Therefore, over a range of operating conditions, as plotted in Fig. 5, the ratio should be a flat line. While noting the error bars in this figure, for some experimental runs there is significant deviation in the ratio from a flat line. Since the

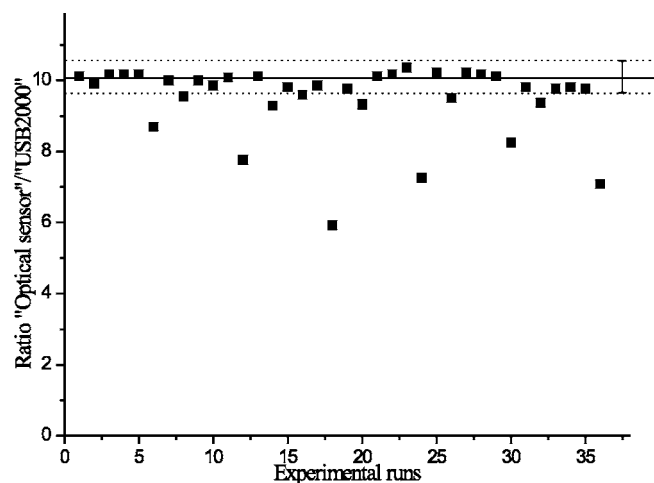


FIG. 5. The full squares represent the ratio of oxygen line measured by two different optical systems. The straight lines represent the mean value of the majority experimental ratio between USB2000 and the optical sensor. The error bar is determinate taking into account the reproducibility of measured values at the same experimental condition.

spectral characteristics of the optical filters (± 0.035 nm around 844.69 nm) is better than the spectrometer, we believe that measurement by the customized optical device is more accurate for that experimental run. The reason that multiplication by a factor 0.33 for some experimental runs does not give a good result is related to the resolution of the spectrometer. Namely, increased power and pressure should increase the intensity of a particular line, but in addition there is an increase in the recorded continuum across the spectral region. Furthermore, there is an increase in the contribution of unwanted spectral lines that leads to significant deviation from this flat line. These unwanted lines are the cluster of lines close to 845 nm. As stated previously, the resolution of the USB2000 does not allow the possibility to distinguish the oxygen lines from the $3p-3s$ transition and multiplet $^3S^o-^3P$. This leads to an error in the calculation of the ratio and subsequently in the calculation of the concentration by actinometry.

Significantly, our customized optical device delivers a signal that is directly proportional to the intensity (area) of the spectral line. Furthermore, this customized optical device requires no additional recording software, spectral “line” deconvolution procedures, or theoretical line profile fitting techniques applied to the measured experimental data points. Another advantage associated with using the customized optical device over a low-resolution spectrometer is that it can be used to record spectral lines of low intensity since it is more sensitive than the spectrometer. Spectrometers can record low-intensity spectral lines by increasing integration time, but this will also lead to an increase in the continuum measured, which would also contribute substantially to the unresolved peak profile.

The density of atomic nitrogen is determined by measuring the emission of the spectral line at 821.634 nm from the $3s-3p$ transition and the $^4P_{5/2}-^4P_{5/2}^o$ multiplet, while the density of molecular nitrogen is determined by the measurement of emission from a second positive system, i.e., the 337.1-nm transition $C^3\Pi_u, v'=0 \rightarrow B^3\Pi_g, v''=0$. Transitions from the

second positive system are usually used for this purpose because they are mainly populated by direct electronic excitation from the ground state of N_2 , and the excitation energy is close to that of the excited nitrogen atom.

We use actinometry with oxygen as the actinometer to determine the relative nitrogen concentration, i.e., to establish a practical sensor for nitrogen. The actinometer should not disturb the discharge, but oxygen is, in fact, part of the plasma chemistry used in these experiments. Therefore, argon was required to be employed as an actinometer in trace amounts (about 4% of the total pressure) in order to determine the threshold for actinometry by oxygen in these plasmas.

It is essential that as little argon as possible be introduced into the nitrogen-oxygen plasma, only enough to be able to record the argon actinometry line. Argon is commonly chosen as an actinometer, and the 750-nm Ar I spectral line from the $4s-4p$ transition originating from the $^2[1/2, 3/2]^o-^2[1/2]$ multiplet is very popular because it is not sensitive to two-step excitation. However, there is a problem with this argon line. Namely, a low-resolution spectrometer, like USB2000, will not resolve two Ar I spectral lines: 750.387-nm multiplet $^2[1/2]^o-^2[1/2]_0$ and 751.465-nm multiplet $^2[3/2]^o-^2[1/2]_0$.¹⁵ Therefore, in the spectrum only one can be observed, namely the “750-nm Ar I spectral line.” The total intensity of the unresolved “doublet” peak at 750 nm, as recorded by the low-resolution spectrometer, must also be multiplied by a factor in order to indicate properly the intensity of the argon actinometry spectral line at 750.387 nm. The factor can be recovered by similar analysis to that used in the case of the oxygen triplets.

However, for the same reasons as in the case of the oxygen actinometry line 777.4 nm, the emission of the argon 750.4-nm spectral line is disturbed by the emission of nitrogen. However, this problem can be overcome by using another atomic argon actinometry line 811.531 nm. This line belongs to the $4s-4p$ transition and the $^2[3/2]^o-^2[5/2]_3$ multiplet.

Before coming to the experimental actinometry signal itself, preliminary results have been evidenced: First of all, it has been confirmed that introducing a few percent argon in the nitrogen-oxygen plasma changed neither the electron density profile nor the intensities of the nitrogen lines (337.1 and 821.6 nm) and the oxygen lines (777 and 844 nm); secondly, it has been established that the intensities of argon lines (750 and 811.5 nm) were proportional to the argon percentage and to the electron density and were perfectly superimposed.

The USB2000 spectrometer was used to test for any disturbance in the nitrogen-oxygen optical spectrum under all of the 36 plasma conditions required as part of the Design of Experiment. A contribution of about 4% argon to the total chamber pressure was used for all plasma experimental set points. Two sets of optical data were recorded for each of the 36 experimental runs, the first set to include only nitrogen and oxygen and the second set operating under the same nitrogen/oxygen set points but with 4% of argon added (with respect to chamber pressure and N_2-xO_2 flows).

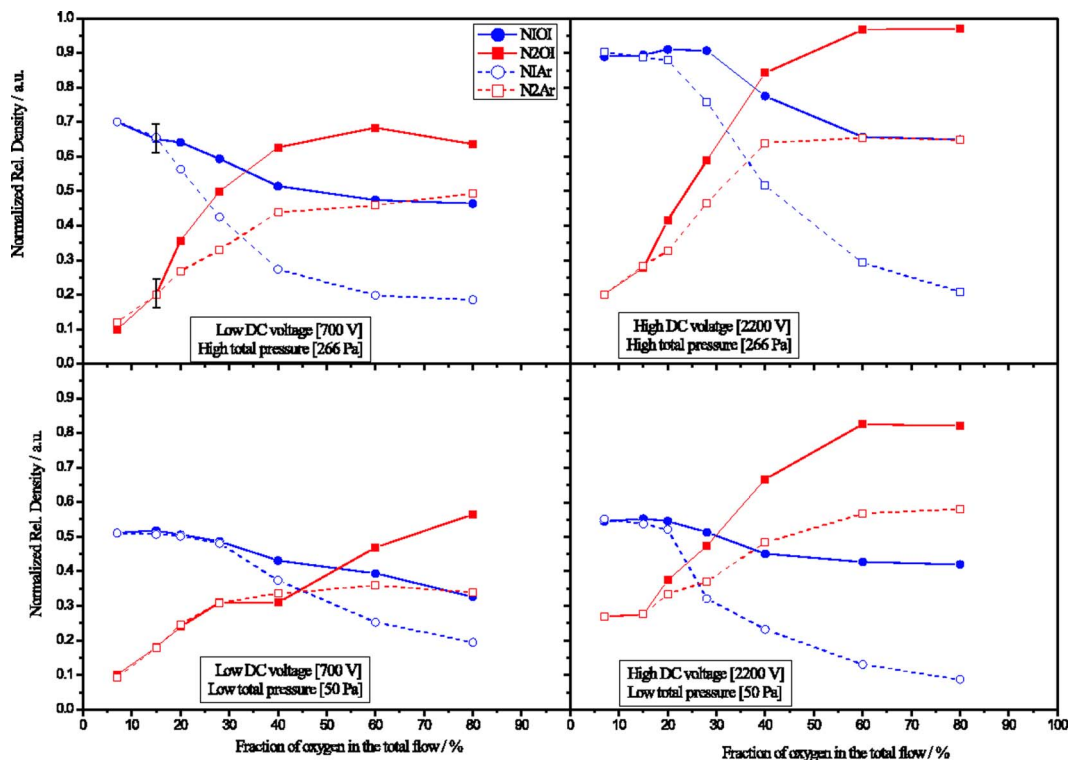


FIG. 6. (Color online) Actinometry results by oxygen (full lines) and by argon (broken line). NIOI and N2OI represent the densities of atomic nitrogen and molecular nitrogen, respectively, determined by oxygen as actinometer. NIAr and N2Ar represent the densities of atomic nitrogen and molecular nitrogen, respectively, determined by argon as actinometer. The error bar includes the reproducibility of the measurement.

Figure 4 shows the recorded spectra for one such nitrogen-oxygen and nitrogen-oxygen-argon plasma. This figure shows how similar the two spectra are, therefore we can be assured that we can reliably use argon as our actinometer reference. This gives us the basis to compare argon and oxygen actinometry so that we can identify where oxygen actinometry is valid and where it is no longer valid.

The actinometry results with oxygen as the actinometer are now compared with those with argon as the actinometer. In this method, we monitor the nitrogen density value as determined by oxygen and by argon as the actinometer. Since the contribution of oxygen in the plasma is varied from the extremes of an oxygen-rich plasma to a nitrogen-rich plasma as part of the 36 experimental set points required of the DOE, it is not surprising that there is a significant deviation in the nitrogen density results as determined by oxygen and by argon actinometry. The contribution of argon is a constant for all 36 experimental runs. Therefore, it is possible to determine the threshold for actinometry by oxygen by monitoring the moment when the concentration of oxygen becomes too high as evidenced by a disagreement between oxygen and argon actinometry data.

Figure 6 shows a selection of the actinometry results obtained from oxygen and argon as the percentage of oxygen in the nitrogen-oxygen plasma is increased from 0% to 100%.

This plot reveals that in the plasma operating conditions used here, oxygen can be used as an actinometer when the concentration of oxygen in the plasma is not higher than

28%, the dc voltage is less than 1.1 kV, and the total pressure is less than 120 Pa. To operate successfully over the full range of dc voltage, pressure, and flows, oxygen can only be used as the actinometer if its concentration in the nitrogen-oxygen plasma is less than 15%.

As we have determined the threshold for actinometry by oxygen, the customized optical device can therefore be used for actinometry purposes up to the threshold limit. This means that we can measure the intensities of the oxygen line, the nitrogen line, and the nitrogen band and use these data to determine the relative atomic and molecular nitrogen concentration, thereby creating a practical sensor for nitrogen in this regime. The actinometry data show that the atomic nitrogen and molecular nitrogen densities are in the range of 10^{20} – 10^{21} m^{-3} . These densities are calculated using all the relevant actinometry data^{20–23} and assume a gas temperature, according to our previous investigations, that changes linearly with dc voltage from 450 K (the discharge tube-wall temperature) at 700 V up to 600 K at 2.2 kV.

The calculated value for densities of atomic and molecular nitrogen are within the expected limits for the dc voltage and pressures used in the plasma chamber and are typical for many similar dc plasmas.²⁴ Hence it has been demonstrated that the customized optical device is a good replacement for a spectrometer and could be very useful for the measurement of the density of a species in the plasma. This could then be used for real-time measurement of species density, which is a requirement for active species control in a plasma-processing environment.

IV. CONCLUSION

We have presented a technique using optical emission spectroscopy for the measurement of nitrogen density in a nitrogen-oxygen dc glow discharge.

The validity of using the nontrace gas (oxygen) as the actinometer was determined by a set of actinometric measurements with argon gas used in trace amounts.

It has been shown that oxygen could be used as the actinometer when the concentration of argon in the plasma is less than 28%, the dc voltage is less than 1100 V, and the total pressure is less than 120 Pa. To operate successfully over the full range of dc voltage, pressure, and flows, oxygen can only be used as the actinometer if its concentration in the nitrogen-oxygen plasma is less than 15%. The calculated value for densities of atomic and molecular nitrogen is within the expected limits for the dc voltage and the pressures used in the discharge tube, and is typical for many similar dc glow discharge plasmas.

For many low-resolution spectrometers, the recorded oxygen 845-nm triplet is a single line. We investigated the possibility of using a low-resolution spectrometer for actinometry purposes. The measured intensity of the atomic oxygen peak obtained by the low-resolution spectrometer, i.e., the “triplet spectral line,” needed to be multiplied by a factor 0.33 to ensure the correct intensity associated with the one relevant spectral line contained in this triplet that can be used for atomic oxygen actinometry purposes. It should be stressed that these particular factors are only applicable in instances in which the contribution to the summed intensity by the background continuum and/or unwanted spectral lines in the region is low.

We believe that the customized optical device described in the paper is a good replacement for a broadband spectrometer and could be very useful for measurement of the density of a species in the plasma. This could be used for real-time measurement of species density, which is a requirement for active species control in a plasma-processing environment.

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