

## Optical diagnostics of low pressure plasmas

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**ABSTRACT:** The techniques of optical emission spectroscopy with actinometry, laser induced fluorescence spectroscopy, laser optogalvanic spectroscopy and absorption spectroscopy are discussed. Examples of the application of these techniques to probing low pressure plasmas of the type used in microelectronics materials processing are presented.

### I. INTRODUCTION

Understanding plasma behavior requires detailed knowledge of a large number of chemical and physical processes involving gas-phase and gas-surface interactions. These include knowledge of the nature, number density and kinetic lifetimes of reactive species produced in the plasma as well as the spatial distributions, velocity distributions and internal temperatures of these species. Optical measurements are particularly useful for obtaining such information, since they are species and quantum-state specific, provide good spatial and temporal resolution and are, to a good approximation, non-intrusive. This paper provides a survey of such techniques with emphasis on laser diagnostics of microelectronics processing plasmas. Techniques to be discussed are optical emission spectroscopy with actinometry, laser induced fluorescence spectroscopy (LIF), laser optogalvanic spectroscopy (LOG), and absorption spectroscopy. Laser techniques have the advantage that they can directly probe species in the ground electronic state, and they generally provide higher spatial, temporal and spectral resolution than typical optical emission studies. In addition to the determination of species concentrations and spatial distributions, laser techniques can also provide non-intrusive measurements of the physical environment, such as characterization of the spatially and temporally varying electric fields in rf plasmas.

No attempt has been made to provide a complete review of optical diagnostic techniques for plasma processes. In particular, no discussion of light scattering techniques (*e.g.* spontaneous or coherent Raman spectroscopies) or microwave techniques is included. Rather, we will discuss the four most commonly applied types of optical spectroscopy, with examples taken from the recent literature. Our goal is to provide the reader with a basic understanding of the techniques, their advantages and limitations, and the types of information obtainable from their use. For a discussion of techniques in addition to those discussed below and additional discussion of optical emission spectroscopy, the reader is referred to two reviews listed in reference (1).

### II. OPTICAL EMISSION SPECTROSCOPY AND ACTINOMETRY

Emission spectroscopy is the most widely used optical technique for glow discharge characterization. The method relies on detection of emission from plasma species in excited electronic states. The electronic excitation is imparted by some process occurring within the discharge, and is most often simply electron impact excitation. Emission spectroscopy requires relatively little sophisticated equipment and is therefore readily implemented. From optical emission spectra it is usually straightforward to identify the emitting species and to follow qualitative changes in plasma properties as a function of various external parameters (*e.g.* source gas composition and flow rates, power, rf frequency, *etc.*). However, the majority of species in a glow discharge are in the ground electronic state, and it is therefore necessary to have some measure of ground state concentrations. Unfortunately, the relationship between optical emission intensity and the concentration of ground electronic state species can be quite complicated.

Coburn and Chen (2) developed a technique known as actinometry to overcome some of these complications. Actinometry involves the use of optical emission intensity ratios to provide an estimate of ground state species concentrations. The emission intensity from the species of interest is divided by the emission intensity from an inert gas (the actinometer) which is added to the

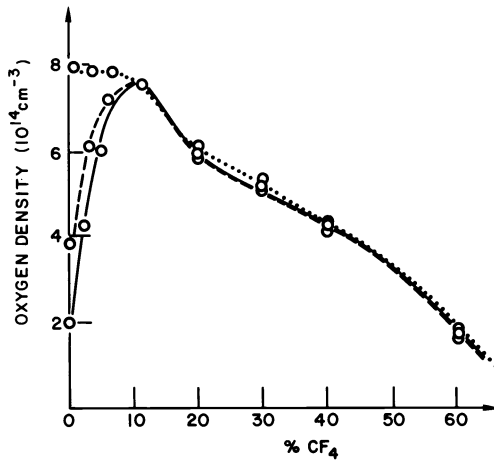
plasma in small quantities. This normalization of the emission signal can correct for the fact that a change in emission intensity may be due to a change in excitation rate, resulting, for example, from a change in the electron energy distribution in the discharge, rather than from an actual change in species concentration. The following three conditions are *sufficient* to ensure that the emission intensity ratio  $X^*/A^*$  is proportional to the concentration ratio  $X/A$ , where  $X$  is the species of interest and  $A$  is the actinometer: 1) The excited species  $X^*$  and  $A^*$  must be produced by electron impact excitation of the ground state species; 2) The excited species must decay exclusively by photon emission; and 3) The electron impact excitation cross sections for  $X$  and  $A$  must have similar thresholds and shapes as a function of electron energy. In practice, it may be possible for  $X^*/A^*$  to be proportional to  $X/A$  over some range of plasma conditions even if all three conditions are violated. However, there is no firm basis for actinometry unless the conditions listed above hold. In the case originally described by Coburn and Chen (2) a discharge in  $CF_4:O_2:Ar$  was studied, and the emission intensity ratio  $F^*(703.6\text{ nm})/Ar^*(750.4\text{ nm})$  was used to monitor the ground state F atom concentration. The  $F^*/Ar^*$  emission intensity ratio revealed an increase in F concentration as  $O_2$  was added to the plasma. This result agreed with the earlier chemical titration studies of Mogab *et al.* (3).

There have been several tests of actinometry for optical concentration measurements in a variety of plasmas. Donnelly and co-workers (4) have monitored the F atom concentration downstream from discharges by chemical titration and found that the  $F^*/Ar^*$  ratio does reflect the F atom concentration in  $CF_4:O_2:Ar$  plasmas and in  $NF_3:Ar$  plasmas. Ibbotson *et al.* (5) tested Ar actinometry of atomic Br concentrations in  $Br_2$  plasmas. In this work the  $Br_2$  concentration was measured by absorption spectroscopy, and the Br concentration was deduced from the reduction of the  $Br_2$  concentration due to dissociation in the plasma. The  $Br^*/Ar^*$  emission intensity ratio was found to follow the Br concentration.

Argon actinometry for the determination of O atom concentrations in  $O_2:Ar$  and  $O_2:CF_4:Ar$  plasmas has been tested using a direct *in-situ* method by Walkup, Saenger and Selwyn (6). The O atom concentration in the plasma was monitored directly using two-photon laser induced fluorescence (7), a technique discussed more fully in the following section. The O atom concentration was monitored along with optical emission from  $O^*$ ,  $F^*$  and  $Ar^*$ . The  $O^*(844.6\text{ nm})/Ar^*(750.4\text{ nm})$  emission intensity ratio was found to follow the actual O atom concentration, approximately, over a wide range of conditions including variations in rf power and percentage  $CF_4$ . However, actinometry using a different  $O^*$  emission line at 777.4 nm failed to follow the O atom concentration for small amounts of added  $CF_4$ . The data are shown in Figure 1. The discrepancy arises because the primary source of the  $O^*(777.4\text{ nm})$  emission is dissociative excitation of molecular oxygen, whereas the primary source of the  $O^*(844.6\text{ nm})$  emission is direct electron impact excitation of O atoms. Studies of the cross sections for these processes (8-11) show that in general both excitation mechanisms must be considered. Actinometry can fail when the dissociative excitation mechanism for production of excited state atoms is important.

The excitation mechanism responsible for the production of excited state species can sometimes be inferred from measurements of optical emission lineshapes. Direct excitation of ground state atoms produces excited atoms with a narrow, thermal ( $\sim 400\text{ K}$ ) velocity distribution, and hence a narrow, Doppler-broadened, emission lineshape would be observed. In contrast, dissociative excitation often produces excited species with high kinetic energies. This results in emission profiles which are Doppler broadened substantially beyond that expected for typical thermal kinetic energies. Gottscho and Donnelly (12) have analyzed emission lineshapes from  $F^*$ ,  $Cl^*$  and  $Ar^*$ . They found that in  $CF_4:O_2:Ar$  plasmas, both  $F^*$  and  $Ar^*$  emission profiles were consistent with direct electron impact excitation of the ground state atoms. However, in  $Cl_2:Ar$  plasmas additional broadening of the  $Cl^*$  and  $Ar^*$  emission lines was observed in the sheath region. This implies additional mechanisms for excited state production. In this case actinometry cannot be expected to provide a valid measure of the ground state Cl atom concentration.

Information about electron energy distributions can be obtained by monitoring optical emission from species which have very different excitation cross sections as a function of electron energy. This application of optical emission spectroscopy has been discussed by d'Agostino and co-workers (13,14). The method is most effective when species with very different thresholds for excitation are monitored, *e.g.*  $Ar^*$  (13.7 eV) and  $He^*$  (23 eV), and it is most revealing for systems for which the excitation cross sections as a function of electron energy are well known. Understanding the electron energy distribution is central to an understanding of plasma processes, because it is the electrons which couple energy from the external circuit into the production of reactive neutrals and ions.

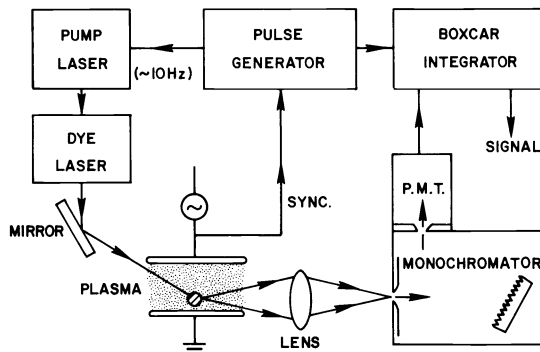


**Figure 1.** Comparison of two-photon LIF measurements of O atom concentration with emission actinometry ratios. The  $O^*(844.6 \text{ nm})/Ar^*(750.4 \text{ nm})$  ratio is shown as the dashed line and the  $O^*(777.4 \text{ nm})/Ar^*(750.4 \text{ nm})$  ratio is shown as the dotted line. The LIF measurements are shown as the solid line. Absolute number densities were obtained by calibration of the LIF apparatus using a known concentration of atomic oxygen generated by photolysis of molecular oxygen. Note that only the 844.6 nm results agree with the LIF data, because the 777.4 nm line arises primarily from  $O^*$  produced by dissociative excitation of molecular oxygen at low  $CF_4$  densities.

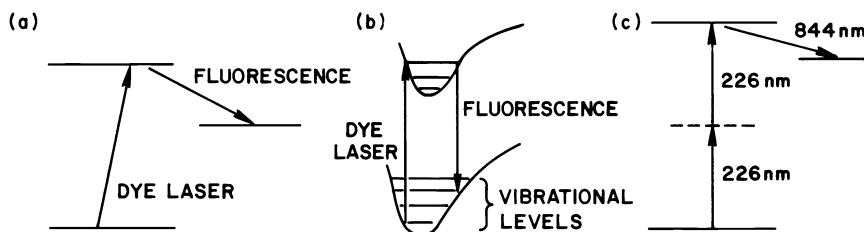
### III. LASER INDUCED FLUORESCENCE

In order to obtain detailed quantitative information about plasma processes, it is clearly desirable to use an optical probe which can directly detect atoms, molecules or ions in their electronic ground states. The most widely used technique which fulfills this requirement is Laser Induced Fluorescence (LIF). LIF combines the high spectral and spatial resolution of a laser technique with sufficient sensitivity to detect low concentrations of reactive radicals and ions. In the following section we describe a typical experimental apparatus for LIF measurements, discuss the advantages and disadvantages of the technique and present examples which illustrate the utility of LIF as a plasma diagnostic.

Figure 2 shows a schematic of the basic components of a LIF spectrometer. A tunable dye laser beam passes through a discharge chamber and resonantly excites atoms or molecules, which subsequently fluoresce. A representation of the absorption and fluorescence process in terms of



**Figure 2.** Schematic illustration of a typical LIF apparatus. The pump laser is usually an excimer, nitrogen or YAG laser. Alternately, an ion laser can serve as the pump for CW operation. Some variations are: a frequency doubler placed after the dye laser extends the wavelength range to 217 nm, and cut-off or interference filters can be substituted for the monochromator in some instances. For measurements as a function of position, the plasma chamber is commonly translated and the optical components remain stationary. Spatial resolution is determined by the overlap of the volume irradiated by the laser beam with the volume imaged onto the monochromator slit by the collection lens system. For time-dependent measurements in rf plasmas, the laser is triggered at some specific time during the rf cycle.



**Figure 3.** Energy level diagram for typical LIF excitation of (a) an atom, (b) a diatomic molecule, radical or ion, and (c) a multiphoton transition. The vibrational levels in (b) are typically separated by 400 to 2000  $\text{cm}^{-1}$  and are illustrated. The rotational level splittings of  $\sim 1$  to 40  $\text{cm}^{-1}$  and are too numerous to illustrate.

atomic and molecular quantum levels is shown in Figure 3. The fluorescence induced by the laser is collected by a suitable lens system, spectrally filtered with a monochromator and detected with a photomultiplier tube (PMT) and associated signal averaging electronics, such as a boxcar integrator. Excellent spatial resolution is possible, since species are detected only in the volume defined by the intersection of the laser beam and the collection optics. High spectral resolution is easily achieved since the resolution is determined by the laser linewidth or the Doppler width of the transition, whichever is larger. Excellent temporal resolution is possible because the LIF measurement is usually performed with pulsed dye lasers which have  $\sim 10$  nsec pulse lengths.

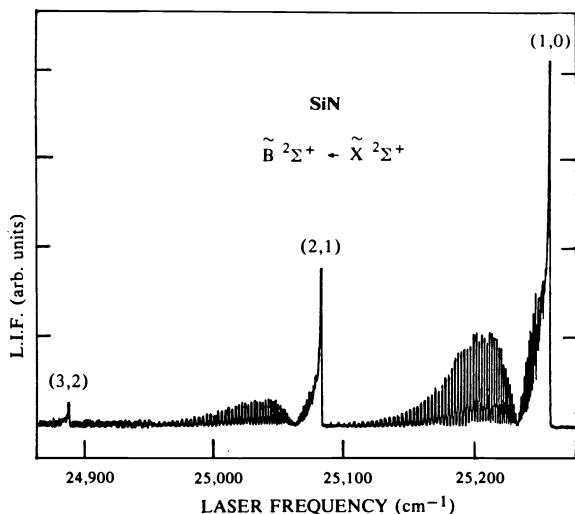
It is straightforward to estimate the sensitivity of LIF for a typical experimental arrangement. Simple geometrical, optical and spectroscopic considerations give an estimate of 1 photoelectron per laser pulse for  $\sim 10^5$  atoms in an active volume of  $\sim 0.1 \text{ cm}^3$ . This assumes that the transition is saturated and that the fluorescence quantum yield is close to one, a situation which is often attainable for atomic transitions. For diatomic and polyatomic species, the detection sensitivity is also  $\sim 10^6 \text{ cm}^{-3}$ . This value, however, is for detection of a single vibration/rotation transition. Since the ground state population is distributed over a large number of rotational states (see (15) for a discussion of diatomic spectroscopy), LIF sensitivity drops to  $\sim 10^8$  molecules  $\text{cm}^{-3}$ . These estimates are typical for many experiments; however, they do not represent fundamental limitations. Orders of magnitude improvement is possible in some cases, and orders of magnitude less sensitivity may be encountered in other cases. Nonetheless, sensitivities in the range discussed above are usually sufficient for the detection of reactive species in low pressure plasmas where total source gas densities are  $\sim 10^{15}$  molecules  $\text{cm}^{-3}$ .

While LIF is clearly a versatile and powerful technique, there are some important limitations to its applicability as a plasma diagnostic. A significant limitation is that the species to be detected must fluoresce with reasonable quantum efficiency. This is usually the case for atoms and diatomics in low pressure environments. It need not be the case for larger polyatomic molecules which can return to the electronic ground state non-radiatively or possibly photodissociate in the excited electronic state. A second limitation is that background light must be kept to a minimum in order to achieve the detection sensitivities discussed above. The two most prevalent background sources are plasma emission, possibly at the same optical frequency as the LIF signal, and scattered laser light. Both of these noise sources can usually be made insignificant by appropriate spectral filtering and temporal gating techniques, although scattered laser light has, thus far, prevented detection of  $\text{SiH}_2$  in silane glow discharges by LIF (16).

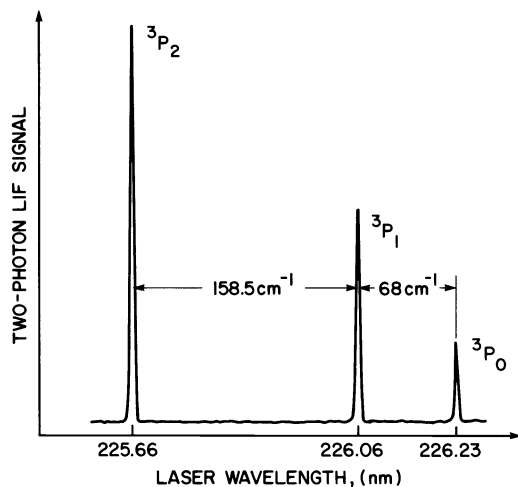
A final consideration, which applies to all the laser techniques discussed in this paper, is that a laser source of the appropriate wavelength to match a spectroscopic transition of the species to be detected is necessary. Tunable dye lasers are currently capable of producing light from the near infrared to the ultraviolet, with the short wavelength cut-off around 217 nm for commercially available systems. Unfortunately, a number of interesting plasma species, including H, O and F atoms and molecular hydrogen, have transitions from the ground electronic manifold only at shorter wavelengths. Tunable vuv radiation can be generated using non-linear optical techniques, although at present these techniques produce only relatively low light intensity. Nevertheless, LIF using tunable vuv sources has been used to detect such species as H atoms (17), B, Be, C and Si atoms (18) and CO molecules (19). An alternative to generating vuv light is to access high lying electronic states using available uv lasers and multiple-quantum transitions of the species to be detected. Examples of species which have been detected in this manner include H (20), N and O (7), S (21), and Cl (22).

The results of Walkup *et al.* (23) illustrate the use of LIF to detect diatomic radicals formed as products of plasma-surface interactions. The species SiN and SiO were produced in low concentration as the result of plasma sputtering of Si substrates with ions, and detected using LIF. The species SiF was also detected in silicon etching plasmas, but was most probably produced by gas phase fragmentation of the etch product SiF<sub>4</sub>. Figure 4 shows the LIF spectrum of the species SiN, produced during plasma nitridation of silicon in a nitrogen glow discharge. The concentration of SiN in the plasma was estimated to be  $\sim 10^8$  molecules cm<sup>-3</sup>. The spectrum of SiN, obtained with a commercially available excimer laser pumped dye laser, illustrates the high spectral resolution of LIF. Three vibrational bands of the electronic transition are shown. Each vibrational band shows well resolved rotational structure. Analysis of the intensity of the lines in the spectrum provides information on the population of SiN molecules in different vibrational and rotational quantum levels of the ground electronic state. Thus, vibrational and rotational temperatures of the molecules can be obtained. For SiN, a rotational temperature comparable to the ambient gas temperature (400-500 K) was found, while a somewhat higher than ambient vibrational temperature (740 K) was found. The spatial distribution of SiN in the plasma, obtained by translating the discharge chamber with respect to the LIF apparatus, was found to be uniform. This indicates that SiN has a relatively long kinetic lifetime in the discharge and is consistent with equilibration of the rotational temperature. The higher vibrational temperature is attributed to unrelaxed vibrational excitation imparted by the dynamical processes which produce SiN from the nitrated silicon surface. Additional diatomic species which have recently been investigated in microelectronic materials processing environments by LIF include SiH (24), CCl (25), GaCl, InCl, P<sub>2</sub>, and As<sub>2</sub> (26).

The work of DiMauro *et al.* (27) and Selwyn *et al.* (6,28) illustrates a more demanding application of LIF. The absolute concentration of ground state oxygen atoms in a reactive ion etching discharge was measured with submillimeter spatial resolution using a two-photon excitation scheme (7). The energy required for the electronic transition is  $\sim 11$  eV. This energy is acquired by the

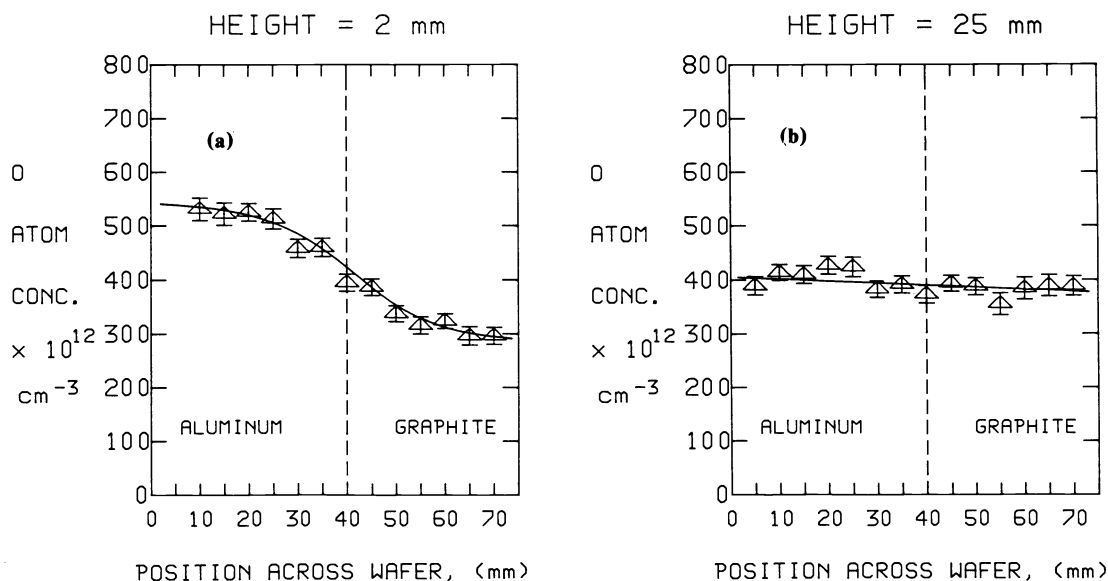


**Figure 4.** The LIF spectrum of SiN in a N<sub>2</sub> plasma with a silicon cathode. Transitions from 3 different vibrational levels of the ground electronic state are observed.



**Figure 5.** Two photon LIF spectrum of O atoms in a 92% O<sub>2</sub> : 5% CF<sub>4</sub> : 3% Ar plasma.

absorption of two 226 nm laser photons by an oxygen atom. Fluorescence from the electronic state populated by the laser to a lower lying excited electronic state was detected at 845 nm (Figure 3(c)). A two-photon LIF spectrum of the atomic oxygen transition from (6) is shown in Figure 5. The three lines arise from the three spin-orbit levels of the <sup>3</sup>P ground electronic state. The concentration of atomic oxygen was  $\sim 10^{14}$  cm<sup>-3</sup> and the signal-to-noise ratio was  $\sim 200$ . Thus, the achieved detection sensitivity was  $\sim 5 \times 10^{11}$  atoms cm<sup>-3</sup>. In order to determine the absolute concentration of atoms, the detection efficiency of the LIF apparatus was calibrated by detecting a known concentration of oxygen atoms produced by photolysis of molecular oxygen. Figure 6 shows the spatial distribution of atomic oxygen across an aluminum cathode half covered with graphite (28). At a height of 25 mm above the cathode, no concentration gradient is evident. At a height of 2 mm above the cathode a clear concentration gradient is seen. This gradient is due to the rapid consumption of atomic oxygen by reaction with the graphite substrate.



**Figure 6. (a).** Spatial dependence of O atom density measured by two-photon LIF at a position 2 mm above a cathode which was half graphite and half aluminum. The cathode-anode spacing was 55 mm and the sheath thickness was  $\sim 12$  mm. The feed gas densities were 27 mTorr  $O_2$  : 80 mTorr Ar. The depletion of atomic oxygen over the graphite surface is due to rapid chemical reaction of the oxygen atoms with the graphite.

**Figure 6. (b).** Same conditions as (a), except the measurement position is 25 mm above the cathode, well into the negative glow region. The surface induced O atom depletion is no longer evident.

There are a number of important polyatomic species in microelectronics processing plasmas. However, only a few of these species have been monitored in discharge environments by LIF. These species include  $CF_2$  (29) and  $HSiF$  (30). Spectra for many polyatomic radicals and ions of interest are not well established, and radiative properties of the excited states are often not known. Recently radiative lifetimes for excited  $CF_3$  have been measured (31,32), however detection of ground state  $CF_3$  by LIF has not been successful (33).

Laser induced fluorescence can also be used to measure time resolved local electric field strengths in rf discharges. Moore *et al.* (34) have used LIF of the diatomic radical BCl, produced in a  $BCl_3$  discharge, as a probe of the electric field distribution. The method is based upon analysis of the rotationally resolved fluorescence from BCl following laser excitation of a specific rotational transition. In the presence of an electric field, Stark mixing of the lambda-doubled rotational levels in the excited electronic state of the molecule occurs. The magnitude of the field determines the relative intensities of the transitions observed in fluorescence. For example, excitation of an R-branch transition of BCl in the absence of an electric field results in only two fluorescence transitions to the ground state, one R-branch transition and one P-branch transition. In the presence of an external electric field, a third, Q-branch, transition becomes allowed and its intensity grows as the electric field strength increases. Thus, a measurement of the ratio of intensities of the parity forbidden (Q) to the allowed transitions (P,R) provides a measurement of the local electric field strength. Different ranges of electric field strength can be measured by choosing appropriate rotational lines of BCl. By taking advantage of the fact that the LIF measurement time is short compared to the rf period, field strengths have been measured as a function of time during the rf cycle. While this technique requires a relatively sophisticated understanding of molecular spectroscopy and careful calibration, it provides a sensitive, non-intrusive, time-resolved measurement of electric field strength at any point in a discharge. Knowledge of the time-dependent and spatially varying electric fields is crucial to the development of accurate theoretical models of rf discharges.

The time-varying electric fields have a major effect on the motion of ions. Gottscho and co-workers (35) have investigated the motion of  $N_2^+$  and  $Cl_2^+$  in rf discharges. The development of sheath regions near the electrode surfaces results in large gradients in the ion concentration at the plasma-sheath boundary. The plasma region toward the center of the discharge is characterized by weak electric fields and high ion and electron densities, with the number density of ions approximately equal to the number density of electrons. In the sheath region the electric fields are strong, and the ions are rapidly swept across the sheath, resulting in low ion density. The ion concentration profiles obtained with LIF directly show the response of ions to the time-dependent fields in the discharge (35). However, the low concentration of ions in the sheath region has thus far prohibited LIF measurements of ion motion within the sheath.

#### IV. OPTOGALVANIC SPECTROSCOPY

Optogalvanic spectroscopy encompasses a wide range of optical methods which are of increasing importance as plasma diagnostic techniques. In optogalvanic spectroscopy, one monitors changes in discharge characteristics (i.e. current, voltage, electron density) induced by the absorption of light. Spectroscopic information is gained by tuning the light source through atomic or molecular resonances. There are a host of mechanisms which can give rise to optogalvanic signals. We will illustrate some of these mechanisms and examine the information that can be obtained by considering recent examples of optogalvanic studies of glow discharges.

The most straightforward mechanisms for generating light-induced changes in discharge characteristics are photoionization and photodetachment. Photoionization of neutrals generates additional charge carriers, and photodetachment of negative ions generates free electrons, carriers which have a much higher mobility than the parent negative ions. The increase in charge carrier density is readily detected by monitoring the discharge current, voltage, impedance, *etc.*, or by more direct probes of electron density.

In an interesting set of experiments, Greenberg *et al.* (36) measured the negative ion density in  $NF_3$  discharges via the photodetachment process  $F^- + h\nu \rightarrow F + e^-$ . The increase in free electron density following pulsed laser photodetachment of  $F^-$  was measured by conventional microwave techniques. By monitoring the increase in free electron density as a function of laser fluence, an absolute measurement of the negative ion density was made. These measurements indicated that the principal negative charge carriers in  $NF_3$  discharges are negative ions, not free electrons. The photodetaching species in this work was sensibly assumed to be  $F^-$ . Spectroscopic identification of the detaching species could have been made using tunable lasers to probe the frequency region near the photodetachment threshold. A partial list of negative ions detected by optogalvanic techniques includes  $H^-$  and  $O^-$  (37),  $I^-$  and  $Cl^-$  (38), and  $CN^-$  (39).

Excitation of atoms or molecules to high Rydberg states will result in subsequent collisional ionization with high probability. Thus, resonant transitions to Rydberg states produce easily detected changes in discharge impedance. Since high Rydberg atoms are particularly sensitive to electric fields (40), optogalvanic spectroscopy can provide Stark-based measurements of E-fields in plasmas. This has been demonstrated by Nakajima *et al.* (41), Doughty *et al.* (42,43) and Ganguly and Garscadden (44). The measurements of Ganguly (44) show that sensitivity to fields as low as  $\sim 1 \text{ V cm}^{-1}$  can be achieved with good spatial resolution. Ordinarily, optogalvanic measurements probe the plasma along a column, in a way analogous to absorption spectroscopy; thus spatial resolution is somewhat limited. Full three dimensional spatial resolution can be achieved, however, by using a two-step excitation scheme, where the effect of interest occurs in a region where two laser beams intersect. This has been demonstrated by Doughty *et al.* (43).

In the cathode sheath region of the plasma, positive ions are the principal charge carriers. Optogalvanic spectroscopy can provide a sensitive probe of ion motion in the sheath (45). When ion motion is limited by collisions, a change in discharge current will occur if the ions excited by the laser have a different effective mobility than ground state ions. This effect has been used to obtain column integrated measurements of ion velocities in the cathode sheath region of dc discharges (45).

Species specific optogalvanic detection has been demonstrated for a wide variety of neutral atoms and molecules as well as positive and negative atomic and molecular ions. In addition, a number of basic discharge studies can be made using light as a means of generating charge carriers. For example, ambipolar diffusion rates can be measured by generating a local excess of electron-ion pairs by photoionization and then monitoring the time dependent change in plasma density. The role of secondary electrons can be investigated by generating secondary electrons at an electrode surface with a pulsed laser, and then monitoring the subsequent change in discharge current. In a number of cases, a detailed understanding of the time dependent change in discharge characteristics following excitation of a plasma species is quite difficult, owing to the large number of processes which can alter the delicate balance of steady state discharge operation. However, even in these cases, the *spectroscopic* information obtainable from optogalvanic measurements can be quite useful. A more complete survey of optogalvanic spectroscopy can be found in reference (46) and references therein.

## V. ABSORPTION SPECTROSCOPY

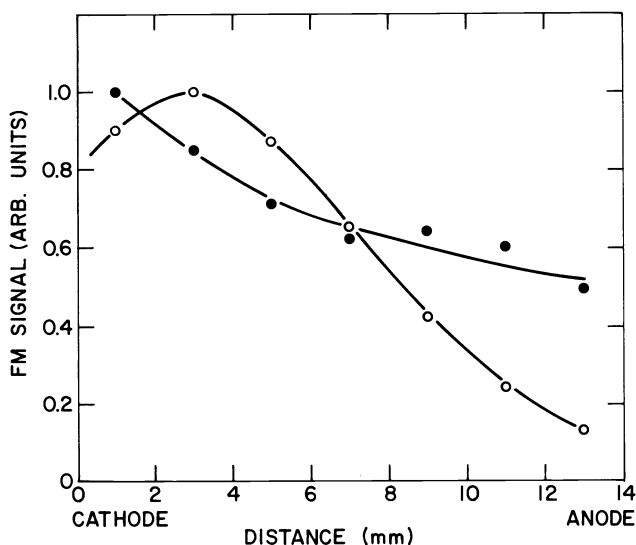
Absorption spectroscopy in the infrared, visible or ultraviolet is, in principle, the most straightforward optical technique for the detection of ground state atoms, molecules or ions in a glow discharge. Absorption techniques can provide line-of-sight spatial resolution, and they readily provide quantitative values for absorbance, from which absolute absorber number densities can be calculated. The latter feature is not as readily attained in optical emission, LIF or LOG spectroscopies. Furthermore, the detection schemes for absorption do not, in general, depend on the radiative properties or transport properties of the upper state. Thus, species which do not fluoresce or do not give rise to an optogalvanic effect can still be detected.

A major drawback of absorption techniques is that they are typically much less sensitive than the other methods discussed in this paper. This lack of sensitivity comes from the fact that, with the simplest detection schemes, the absorption signal is detected as a small difference between the incident and transmitted photon fluxes. Therefore, the signal-to-noise ratio in an absorption experiment is usually determined by the stability of the light source and can be orders of magnitude less than the theoretical (shot noise) limit. For this reason direct absorption techniques require either long optical path lengths or high densities of absorbing species. Consequently, direct absorption spectroscopy has most frequently been used to monitor abundant chemical species in processing discharges, such as the source gas or stable reaction products, rather than chemically transient species such as ions or free radicals, which occur in much lower concentrations. Exceptions to this are the use of atomic resonance lamps to monitor ground state atom concentrations and the use of fairly sophisticated modulated laser absorption techniques to detect ions and radicals.

Detection of stable species in processing discharges using direct absorption techniques has been carried out at varying levels of instrumental sophistication and spectral resolution. As discussed above, Ibbotson *et al.* (5) have used absorption in the visible to monitor the concentration of Br<sub>2</sub> in GaAs etching discharges via an electronic transition. Nishizawa and Hayasaka (47) have used a standard infrared spectrometer to detect stable molecules in reactive ion etching (RIE) discharges via vibrational transitions. Knights *et al.* (48) have used an extremely high resolution Fourier transform infrared instrument to observe silane in deposition discharges and have extracted rotational and vibrational temperatures from analysis of the spectra.

Atomic absorption spectroscopy using either continuum lamps or atomic resonance lamps (typically hollow cathode discharge lamps) is an old and well documented technique (49). Since incoherent light sources can be extremely stable and since atomic peak absorption cross sections for fully allowed electronic transitions are extremely large,  $\sim 10^{-11}$  cm<sup>2</sup>, excellent sensitivity can be achieved. Sensitivity is further improved when atomic resonance lamps are used, since the absorption and emission lineshapes can be closely matched. Atomic absorption spectroscopy has been used as a diagnostic in processing glow discharges to detect species such as Cu atoms in a sputtering system (50), and Si atoms in a pulsed silane discharge (51).





**Figure 7.** Spatial dependence of  $\text{SiH}_2$  concentration for (●) silane and (○) argon: silane discharges. Data are normalized to the maximum signal for each gas mixture. For pure silane, the cathode dark space extends 7 mm. For argon:silane, the cathode dark space extends for 2-3 mm. Spatial resolution is  $\pm 1$  mm.

Lasers are desirable as light sources in absorption experiments because of their high spectral brightness, narrow linewidth and low divergence. However, they also have some undesirable features. Compared to incoherent sources, lasers have large amounts of amplitude noise at frequencies well into the MHz range. Several high frequency modulation schemes have been developed to alleviate this difficulty, and some have demonstrated nearly shot noise limited sensitivity. The basic approach in most such schemes is to amplitude or frequency modulate the light source at high frequencies where the laser is nearly shot noise limited and to detect the effects of optical absorption in this high frequency regime. A combination of frequency modulation of a cw dye laser at 800 MHz with low frequency modulation of a DC discharge has recently been used to detect the important radical species  $\text{SiH}_2$  in silane glow discharges with excellent signal to noise (52). Absorption due to an electronic transition of  $\text{SiH}_2$  in the visible was measured. Spatial distributions of  $\text{SiH}_2$  in the discharge and relative concentrations of  $\text{SiH}_2$  under different discharge conditions were obtained. Examples of spatial distribution data for  $\text{SiH}_2$  in silane and argon:silane discharges are shown in Figure 7.

A limitation of all laser techniques in probing complicated, chemically interesting glow discharges is that they are frequently capable of detecting only one transient species while being completely insensitive to any other species present. This is because electronic transitions in the visible and ultraviolet are most often used for detection. Electronic transitions for different species occurring in the same discharge are often found in very different spectral regions, all of which may not be easily accessible with the same laser system. In principle, a more informative spectral region is the infrared, where vibrational transitions of molecules occur. Since molecules with the same types of chemical bonds tend to have vibrational frequencies in the same wavelength range, infrared laser absorption techniques might prove very useful as processing discharge diagnostics. While these techniques have not yet been extensively applied to the detection of transient species in processing discharges, a substantial amount of work has been published on the detection of a number of simple molecular ions. Velocity modulation of the ions with dual beam detection using a difference frequency infrared laser (53) has approached the shot noise limit in detecting the species  $\text{DNN}^+$ , while modulation of a DC discharge in combination with a long optical path length has been used to detect simple molecular ions with excellent signal to noise (54).

## VI. SUMMARY

We have discussed four optical techniques which are proving increasingly useful for plasma diagnostics. Of the techniques considered, it should be evident that optical emission spectroscopy

with actinometry is the easiest to apply, but the least quantitative. Of the more powerful, direct techniques for detecting ground state chemical species, LIF has been used most widely. Direct absorption measurements and LOG measurements have been made more sparingly. In certain cases, however, these techniques may be methods of choice. In all cases, it is important to realize that the most appropriate technique depends crucially on the species to be detected and the information desired. As optical techniques continue to be developed and applied to plasma diagnostics, increasingly detailed information will become available. This should facilitate the development of comprehensive models for plasma processes which have considerable predictive power.

#### REFERENCES

1. R.A. Gottscho and T.A. Miller, *Pure and Appl. Chem.* 56, 189 (1984); D.M. Benenson and H.S. Kwok, *Pure and Appl. Chem.* 54, 1157 (1982).
2. J.W. Coburn and M. Chen, *J. Appl. Phys.* 51, 3134 (1980).
3. C.J. Mogab, A.C. Adams and D.L. Flamm, *J. Appl. Phys.* 49, 3796 (1978).
4. V.M. Donnelly, D.L. Flamm, W.C. Dautremont-Smith and D.J. Werder, *J. Appl. Phys.* 55, 242 (1984).
5. D.E. Ibbotson, D.L. Flamm and V.M. Donnelly, *J. Appl. Phys.* 54, 5974 (1983).
6. R. Walkup, K. Saenger and G.S. Selwyn, to be published, *Materials Research Society Symposium Proceedings 30*, Boston, MA. (1984).
7. W.K. Bischel, B.E. Perry and D.R. Crosley, *Chem. Phys. Lett.* 82, 85 (1981); W.K. Bischel, B.E. Perry and D.R. Crosley, *Appl. Opt.* 21, 1419 (1982).
8. G.M. Lawrence, *Phys. Rev. A* 2, 397 (1970).
9. E.C. Zipf, *Electron-Molecule Interactions and Their Applications*, ed. L.G. Christophorou, Academic Press (New York, 1984), Vol.1, Chapter 4.
10. T. Sawada and P.S. Ganas, *Phys. Rev. A* 7, 617 (1973).
11. P.S. Julienne and J. Davis, *J. Geophys. Res.* 81, 1397 (1976).
12. R.A. Gottscho and V.M. Donnelly, *J. Appl. Phys.* 56, 245 (1984).
13. R. d'Agostino, F. Cramarossa, S. De Benedictis and G. Ferraro, *J. Appl. Phys.* 52, 1259 (1981).
14. R. D'Agostino, F. Cramarossa, S. De Benedictis and F. Fracassi, *Plasma Chem. and Plasma Proc.* 4, 163 (1984).
15. G. Herzberg, *Molecular Spectra and Molecular Structure I: Spectra of Diatomic Molecules*, Van Nostrand (New York, 1950). Useful compilations of spectroscopic data are: K.P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV: Constants of Diatomic Molecules*, Van Nostrand, (New York, 1979); R.W.B. Pearse and A.G. Gaydon, *The Identification of Molecular Spectra*, Chapman and Hall, (New York, 1976).
16. G. Inoue and M. Suzuki, *Chem. Phys. Lett.* 105, 641 (1984).
17. P. Bogen, R.W. Dreyfus, Y.T. Lie and H. Langer, *J. Nucl. Materials* 111, 75 (1982).
18. H.F. Dobeles and B. Ruckle, *J. Nucl. Materials* 111, 102 (1982).

19. R. Hilbig and R. Wallenstein, *IEEE J. Quantum Electronics QE-17*, 1566 (1981).
20. J. Bokor, R.R. Freeman, J.C. White, and R.H. Storz, *Phys. Rev. A* **24**, 612 (1981).
21. P. Brewer, N. VanVeen and R. Bersohn, *Chem. Phys. Lett.* **91**, 126 (1982).
22. M. Heaven, T.A. Miller, R.R. Freeman, J.C. White and J. Bokor, *Chem. Phys. Lett.* **86**, 458 (1982).
23. R. Walkup, Ph. Avouris, R.W. Dreyfus, J.M. Jasinski and G.S. Selwyn, *Appl. Phys. Lett.* **45**, 372 (1984).
24. J.P.M. Schmitt, P. Gressier, M. Krishnan, G. De Rosny and J. Perrin, *Chem. Phys.* **84**, 281 (1984).
25. R.A. Gottscho, G.P. Davis and R.H. Burton, *Plasma Chem. and Plasma Proc.* **3**, 193 (1983).
26. V.M. Donnelly and R.F. Karlicek, *J. Appl. Phys.* **53**, 6399 (1982).
27. L.F. DiMauro, R.A. Gottscho and T.A. Miller, *J. Appl. Phys.* **56**, 2007 (1984).
28. G.S. Selwyn, to be published.
29. P.J. Hargis, Jr. and M.J. Kushner, *Appl. Phys. Lett.* **40**, 779 (1982).
30. H.U. Lee and J.P. de Neufville, *J. Non-Cryst. Solids* **66**, 39 (1984); H.U. Lee and J.P. de Neufville, *Chem. Phys. Lett.* **99**, 394 (1983).
31. C.R. Quick, Jr., J.J. Tiee, J. Preses and R.E. Weston, Jr., *Chem. Phys. Lett.* **114**, 371 (1985).
32. R.W. Dreyfus and L. Urbach, *Chem. Phys. Lett.* **114**, 376 (1985).
33. R.W. Dreyfus, unpublished.
34. C.A. Moore, G.P. Davis and R.A. Gottscho, *Phys. Rev. Lett.* **52**, 538 (1984).
35. R.A. Gottscho, R.H. Burton, D.L. Flamm, V.M. Donnelly and G.P. Davis, *J. Appl. Phys.* **55**, 2707 (1984).
36. K.E. Greenberg, G.A. Hebner and J.T. Verdeyen, *Appl. Phys. Lett.* **44**, 299 (1984).
37. M. Bacal, G.W. Hamilton, A.M. Bruneteau, H.J. Doucet and J. Taillet, *J. de Physique Colloque C7* **40**, C7-791 (1979).
38. C.R. Webster, I.S. McDermid, C.T. Rettner, *J. Chem. Phys.* **78**, 646 (1983); I.S. McDermid and C.R. Webster, *J. de Physique Colloque C7* **44**, C7-461 (1983).
39. R. Klein, R.P. McGinnis and S.R. Leone, *Chem. Phys. Lett.* **100**, 475 (1983).
40. M.L. Zimmerman, M.G. Littman, M.M. Kash and D. Kleppner, *Phys. Rev. A* **20**, 2251 (1979).
41. T. Nakajima, N. Uchitomi, Y. Adachi, S. Maeda and C. Hirose, *J. de Physique Colloque C7* **44**, C7-497 (1983).
42. D.K. Doughty and J.E. Lawler, *Appl. Phys. Lett.* **45**, 611 (1984).
43. D.K. Doughty, S. Salih and J.E. Lawler, *Phys. Lett.* **103A**, 41 (1984).

44. B.N. Ganguly and A. Garscadden, *Appl. Phys. Lett.* **46**, 540 (1985).
45. R. Walkup, R.W. Dreyfus and Ph. Avouris, *Phys. Rev. Lett.* **50**, 1846 (1983).
46. "International Colloquium on Optogalvanic Spectroscopy and Its Applications," *J. de Physique Colloque C7 44* (1983).
47. J. Nishizawa and N. Hayasaka, *Thin Solid Films* **92**, 189 (1982).
48. J.C. Knights, J.P.M. Schmitt, J. Perrin and G. Guelachvili, *J. Chem. Phys.* **76**, 3414 (1982).
49. See, for example, M.A.A. Clyne and W.S. Nip, "Generation and Measurement of Atom and Radical Concentrations in Flow Systems," in *Reactive Intermediates in the Gas Phase*, ed. D.W. Setser, Academic Press (New York, 1979).
50. J.E. Greene, *J. Vac. Sci. Technol.* **15**, 1718 (1978).
51. K. Tachibana, H. Tadokoro, H. Harima and Y. Urano, *J. Phys. D* **15**, 177 (1982).
52. J.M. Jasinski, E.A. Whittaker, G.C. Bjorklund, R.W. Dreyfus, R.D. Estes and R.E. Walkup, *Appl. Phys. Lett.* **44**, 1155 (1984).
53. D.J. Nesbitt, H. Petek, C.S. Gudeman, C.B. Moore and R.J. Saykallay, *J. Chem. Phys.* **81**, 5281 (1984).
54. T. Amano and J.K.G. Watson, *J. Chem. Phys.* **81**, 2869 (1984).