

# Plasma Diagnostics

In the plasma, a large number of variables affect the balance between competing chemical and physical processes. The number of parameters is normally so big that the use of a random sampling technique to achieve optimization of reactor conditions for a given process would be extremely cumbersome. Appropriate reliable diagnostic tools are therefore necessary to provide an understanding of the plasmas and the actual phenomena taking place, which in turn will enable the control of the process.

The objective of plasma diagnostics is to obtain information about the state of the plasma by means of experimental examinations of physical processes occurring in it. Knowledge of plasma physics is required to understand fully the effects of the physical processes taking place in the plasma and to deduce from them its properties. The discussion of plasma physics is, however, beyond the purpose of the present book, and only the basic principles, those related to the specific diagnostic tools, will be presented.

The diagnostic techniques can be classified into *ex-situ* and *in-situ techniques*. The *ex-situ* techniques sample the contents of the plasma reactor and transfer a fragment of the contents outside the reactor for examination. Among *ex-situ* or *off-line* techniques that are used for plasma diagnostics are mass spectrometry and gas-phase electron paramagnetic resonance. Since the contents of a plasma reactor include many highly reactive species, such as ions, radicals, and reactive atoms, one can never be certain that species analyzed *ex-situ* have not undergone changes during their transfer from the reactor.

The *in-situ* or *on-line* techniques can be further classified into *intrusive* and *nonintrusive* methods, although this division is somewhat arbitrary. Any diagnostic

technique is to some extent intrusive and perturbs the plasma. In some cases, this perturbation may be negligible, while in others it may be quite significant. The degree to which the perturbation is significant depends on the required information.

The diagnostic methods are also sometimes classified according to the parameter of the plasma to be determined or by the experimental technique used. As the first approach has the drawback that many methods typically measure more than one parameter, the second approach will be adopted in this chapter.

The most used techniques for plasma diagnostics, namely, mass spectrometry, electric probes, and optical methods, will be explained in this chapter. More detailed discussion and analysis of the different diagnostic methods can be found in specialized treatises on plasma diagnostics, such as Huddleston and Leonard [1], Loechte-Holtgreven [2], Venugopalan [3], Heald and Wharton [4], Hutchinson [5], Auciello and Flam [6]. Applications of different plasma diagnostic tools for process characterization can be found in many papers dealing with different processes and in various reviews, such as, for example, [7, 8].

## 5.1 MASS SPECTROMETRY

Mass spectrometry is one of the most used tools for diagnostics of cold plasmas in research laboratories as well as in manufacturing plants. The mass spectrometer is a device of high detection sensitivity, which allows the identification of molecules, radicals, atoms, or ions by their molecular or atomic weight.

The mass spectra of gaseous components in cold plasmas are relatively simple. As a result, mass spectroscopy is a very useful method for quantifying the composition of the plasmas in the study of plasma chemistry or in controlling a manufacturing process.

Mass spectrometry can be used either for identification or for quantitative analysis of plasma species, and the results can be used for the determination of the kinetics of the reactions in the plasma or for controlling the process to obtain the desired results.

Several types of mass spectrometers are available: the magnetic analyzer, which selects ions of similar momentum; the time-of-flight spectrometer, which analyzes ion velocity; and the quadrupole mass spectrometer, which analyzes ions on the basis of their mass to charge,  $m/e$ , ratio (atomic mass units, amu). In recent years most mass spectrometry studies of cold plasmas have been performed using the quadrupole mass spectrometer (QMS), first described by Paul et al [9].

### 5.1.1 The Quadrupole Mass Spectrometer

A state-of-the-art discussion of the quadrupole mass spectrometer, its theory and operation, were given by Dawson [10]. Detailed descriptions of applications of mass spectrometry for plasma diagnostics can be found in reviews by Venugopalan [3], Austin et al. [11], and Vasile and Dylla [12]. The quadrupole



mass spectrometer and its application for plasma diagnostics are explained in the following sections.

### 5.1.1.1 The Quadrupole Mass Analyzer

The main part of the quadrupole mass spectrometer is the *quadrupole mass analyzer*, or *mass filter*. A quadrupole consists of four conducting rods or poles, the axes of which are placed at the corners of a square, as shown schematically in Fig. 5-1. The poles often have hyperbolic surfaces and typical dimensions of the analyzer are

$$\text{pole length} = 16 \text{ cm} \quad r = 0.3 \text{ cm}$$

Opposite poles are connected electrically together, and a potential  $\Phi(t) = U + V\cos(\omega t)$  is applied to one pair of rods, while the same potential of opposite

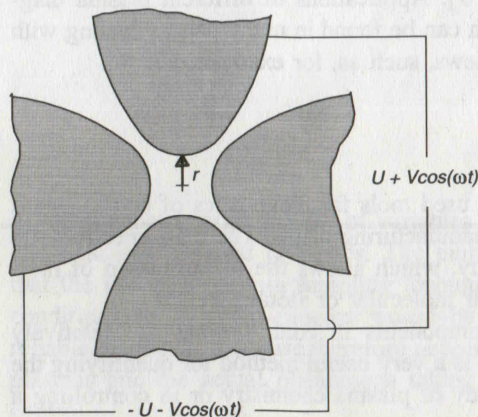
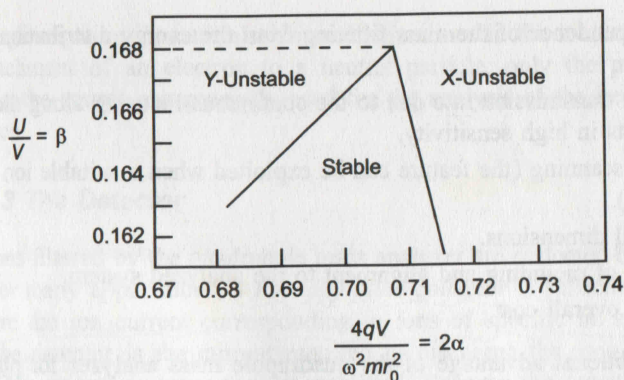


Fig. 5-1 Cross section of the quadrupole mass spectrometer rods with electrical connections.

sign,  $-\Phi(t)$ , is applied to the other pair.  $U$  is a DC voltage and  $V$  is the amplitude of a RF voltage of frequency  $\omega$ . If an ion enters the quadrupole along a direction approximately parallel to the axes of the cylinders ( $z$ -axis), the applied potentials will induce a transverse component to the motion of the ion.

The RF field removes low-mass ions from the beam entering the analyzer and focuses high-mass electrons close to the axis of the analyzer. The superimposed DC field removes ions of high mass from the beam. For a certain combination of the parameters,  $U$ ,  $V$ ,  $\omega$ , and  $m/e$ , the ion will oscillate along the  $z$ -axis and emerge at the second end of the quadrupole. For all other combinations of parameters, the ion will move away from the  $z$ -axis, ultimately strike an electrode, and be neutralized. By a suitable selection of  $V$  and  $U$  values, only ions of a given  $m/e$  range will have a stable motion and will be transmitted through the quadrupole. The quadrupole thus acts as a  $m/e$  filter that can be tuned to a chosen mass by adjusting the amplitude of the RF voltage.

For fixed  $U$  and  $V$  values and constant ion charge, there is a range  $\Delta M$  of masses for which the ions will pass through the quadrupole analyzer. This range



**Fig. 5-2** Diagram of stable solutions for the movement of ions through quadrupole mass analyzer (from [13], reprinted with permission).

of masses, having a stable motion along the quadrupole, depends on the ratio  $\beta = U/V$  and decreases with increasing  $\beta$ , as illustrated in Fig. 5-2. The ratio between the DC and RF voltages thus determines the *selectivity of the analyzer*.

For  $\beta = 0.168$ , only particles of one  $m/e$  value can pass through the analyzer. The corresponding resolution of the instrument ( $R = M/\Delta M$ ) will be infinite; however, the current of ions arriving to the detector will be infinitesimally small. Values of  $\beta < 0.168$  are therefore used to increase the value of  $\Delta M$ . The range of analyzed masses can be scanned by scanning  $U$  and  $V$  while keeping  $\beta$  fixed. As can be seen in Fig. 5-2, for fixed  $\beta$  the resolution  $R$  of the analyzer is constant. In many cases  $\beta$  is adjusted during scanning to keep  $\Delta M$  constant instead of  $R$ .

The amplitude of the RF voltage,  $V$ , and its frequency,  $\omega$ , determine the mass of the ions that are allowed to pass through the analyzer. By sweeping the RF and DC voltages from zero to their maximum value, while keeping their ratio  $\beta$  constant, ions will be transmitted sequentially in order of their  $m/e$  values. The ions, which pass through an aperture at the end of the apparatus, are detected by an ion detector, which can be either a Faraday cup, or an electron multiplier.

A quadrupole mass analyzer is characterized by a *transmission versus mass curve*. The transmission of the instrument is a function of the velocity of the ion, and at a fixed energy, ions of high mass will be transmitted less efficiently than will ions of low masses. The plasma diagnostics requires the determination of the quantitative relationship between species from different groups of masses. The decrease in *sensitivity* of the quadrupole with increasing mass must therefore be kept in mind when performing quadrupole mass spectrometry plasma diagnostics and particularly in the calibration of the instrument as described later [12].

The quadrupole mass analyzer's characteristics prove advantageous for mass spectrometry in general and plasma diagnostics in particular. Among those properties are



- Independence of the mass filtering from the energy distribution of the ion beam.
- High transmission rate due to the continuous focusing along the rods; this results in high sensitivity.
- Fast scanning (the feature can be exploited when a suitable ion detector is used).
- Small dimensions.
- Ease of mounting and alignment to the analyzed system.
- Low overall cost.

An additional advantage of the quadrupole mass analyzer for plasma diagnostics is the possibility of controlling the mass filtering characteristics, that is, resolution versus transmission, by variation of electrical parameters only.

### 5.1.1.2 The Ion Source

The quadrupole mass spectrometer can be used to analyze both ions and neutrals. To analyze neutral species, such as atoms, molecules, or radicals with the quadrupole mass analyzer, they have to be ionized first. This is achieved in a ionization source placed in front of the quadrupole analyzer. The ionization of the species extracted from the reactor is performed in the ion source by a beam of electrons passing through the vapor that flows through the source. A typical ion source is presented in Fig. 5-3.

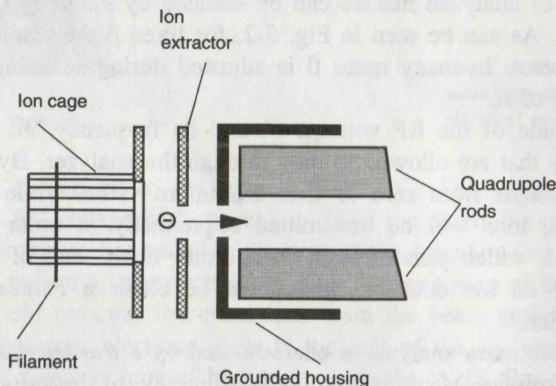


Fig. 5-3 Diagram of an ion source of a quadrupole mass spectrometer.

A heated thermionic filament, usually made of thoria-coated iridium wire, produces an electron beam that is accelerated to the ion cage, which serves as an anode at a potential of about + 70 V DC. The neutral particles, passing normal to the electron beam, are ionized by electron impact. An ion extractor, or ion focus electrode, extracts the ions from the ionization source, focuses them into a narrow beam, and projects them into the quadrupole filter, along its  $z$ -axis (parallel to the direction of the rods).

Although negative ions are also formed sometimes in the ionization process by the attachment of an electron to a neutral particle, only the positive ions generated in the source are generally used for the analysis of the beams ionized in the source.

### 5.1.1.3 The Detector

The ions filtered by the quadrupole mass analyzer are collected by a suitable detector. For many applications, a *Faraday plate collector* is sufficient to collect and measure the ion current corresponding to ions of specific  $m/e$  value. The signal of the detector is the current required to discharge the ions striking the collector. This current is consequently amplified. Because the sensitivity for nitrogen is  $2 \times 10^{-4}$  amp.torr $^{-1}$ , the current of the Faraday plate (or cup) is very low. The Faraday plate detector is very stable and does not pose a lifetime problem.

For detection limits higher than those achievable with the Faraday detector and for faster response required in rapid mass scanning, electron multipliers are used. A *secondary electron multiplier (SEM)* acts as preamplifier of the ion signal. It consists of several stages, also called *dynodes*, with surfaces characterized by a high yield of secondary electron emission. The first dynode operates at about  $-2000$  V. An energetic ion accelerated at that voltage, striking the sensitive surface (often made from CuBe alloy), causes the emission of a number of secondary electrons, which are accelerated to the next stage of the detector, where in turn they cause emission of secondary electrons. The acceleration of the electrons is performed at a voltage sufficiently high to produce a secondary electron yield much bigger than unity, so that the number of electrons is multiplied at each stage. The number of stages in the electron multiplier, about 15, is limited by the maximum current carrying capacity of the latest stage. The gain of the electron multiplier depends strongly on the operating voltage and the condition of the surfaces of the dynodes, that is, whether fresh or oxidized. Typical gain of an electron multiplier operating at  $-2000$  V is about  $10^5$ .

The sensitivity of the CuBe surface of the dynodes is affected by exposure to air or by hydrocarbon contamination. Exposure of the electron multiplier to air should therefore be avoided as much as possible. A main source of hydrocarbon contamination is the backstreaming of oil vapors from vacuum pumps. This kind of contamination can be eliminated by using turbomolecular pumps. The deterioration of the dynode surfaces can result in a reduction of the gain by 50 to 90%. To compensate for this deterioration, the electron multiplier can be operated over a range of voltages, for example, 1000 to 3000 V, to adjust its gain which generally changes with time.

The sensitivity of Faraday cup detectors is not dependent on the mass of the ion; that is, the Faraday detector has no mass discrimination. Secondary electron multipliers may have mass discrimination, depending on their design and operating voltage. At high voltages their sensitivity is higher for ions of larger mass.



The electron multiplier has the disadvantage that its gain tends to vary with time. Therefore, the electron multiplier requires regular calibration. The Faraday plate detector is more accurate and simpler to operate. The applicability of the different detectors is dependent on two characteristics, namely, the detection limit and response time to be discussed next.

Detection Limits

Ion currents as low as  $10^{-15}$  amp can be detected with a time constant of the order of 1 sec. Because the sensitivity for masses up to 200 amu is about  $10^{-4}$  amp.torr<sup>-1</sup>, partial pressures as low as  $10^{-11}$  torr can be detected at the relatively large time constant. As faster response times are normally required, the practical sensitivities are lower, decreasing with decreasing response time.

The Faraday plate detector is characterized by a detection limit as low as  $10^{-10}$  torr. Higher sensitivity can be obtained with the electron multiplier. When potentials between 2 and 4 kV are applied to the secondary electron multiplier, gains between  $10^4$  and  $10^8$  can be obtained, corresponding to a detection limit of about  $10^{-14}$  torr.

The secondary electron multiplier ion detector is, however, practically used with the quadrupole mass analyzer in the pressure range of  $10^{-11}$ – $10^{-4}$  torr. The lowest practical measurable pressure represents the detection limit defined by a signal-to-noise ratio (or noise level) of approximately unity after integration of the minimal output current ( $10^{-11}$ – $10^{-12}$  amp) of a typical 14-stage CuBe multiplier over a period of 1 sec [ 12].

The high-pressure limit of about  $10^{-4}$  torr for both types of detectors is usually defined as the pressure at which gas scattering in the ion source becomes significant and the signals become nonlinear with total pressure. Practical sensitivities achievable with a Faraday cup detector and with a secondary electron multiplier are shown in Table 5-1.

TABLE 5-1 Sensitivities of Quadrupole Mass Spectrometer for Determination of Pressure with 10% Accuracy (from [ 10], reprinted with permission from *Quadrupole Mass Spectrometry and Its Applications*, p. 138, 1976)

Pressure (torr)	$10^{-8}$	$10^{-9}$	$10^{-10}$	$10^{-11}$
Current (amp)	$10^{-12}$	$10^{-13}$	$10^{-14}$	$10^{-15}$
Time electron multiplier (sec)	$10^{-5}$	$10^{-4}$	$10^{-3}$	$10^{-2}$
Time Faraday cup (sec)	0.02	0.2	2	

Although the numbers in Table 5-1 show that the quadrupole mass spectrometer has a dynamic range of  $10^7$ , in practice, this range is rarely achieved in plasma diagnostics because of high background levels. The background is of special concern in plasmas, due to the high reactivity of the plasma species. Especially high backgrounds are often encountered in cold plasmas of practical interest at atomic mass units (amu) of 28 and 29. Possible sources of these backgrounds are

CO, C<sub>2</sub>H<sub>4</sub>, N<sub>2</sub>, <sup>28</sup>Si at  $m = 28$  amu

and

<sup>13</sup>CO, <sup>14</sup>N<sup>15</sup>N, C<sub>2</sub>H<sub>5</sub>, <sup>29</sup>Si at  $m = 29$  amu

The lower detection limit mentioned for the secondary electron multiplier refers to molecular species. For free radicals, however, the lower detection limit is higher, and the detection sensitivity is lower by several orders of magnitude due to the rapid destruction of the active species within the system and interference effects from the background. Nevertheless, the sensitivity of the quadrupole mass spectrometry technique is very high, much more than attainable by other methods.

### Response Time

The response time of the ion detector is important because rapid mass scans are frequently required. The response of the Faraday plate detector depends on the used amplification and is a function of the allowable noise level. For the lowest noise levels of about  $10^{-5}$ , the response time is several seconds, while the response can be made faster if a higher noise level is allowed. The response time can be lowered to the order of tens of milliseconds at the expense of the detection limit.

The response time of the electron multiplier, which is determined by the motion of electrons in vacuum, can be much faster, on the order of microseconds. The time resolution of the secondary electron multiplier is generally in the range of 30 to 300 kHz.

#### 5.1.1.4 Resolution of the QMS

The *resolving power* of a spectrometer is defined as its ability to separate adjacent mass peaks. The commonly accepted definition for the resolving power of the mass spectrometer is the "10% valley" definition, although a 50% valley definition is also used. According to this definition, the resolving power is the largest atomic mass number at which peaks of adjacent molecular weight have a valley between them, lower than 10% of the height of the peak.

The resolution of a peak of mass  $M$  is defined by the ratio  $M/\Delta M$ , where  $\Delta M$  is the distance between the points at 10% of the maximum height of the peak of mass  $M$ .

Operating the quadrupole mass filter in the constant resolution mode over the entire mass range will cause a decrease in sensitivity for the more massive, lower-velocity ions [11]. Operation in the constant  $\Delta M$  mode, where the resolution increases with the mass, compounds the effect of the instrument transmission. It is convenient to keep the  $\Delta M$  constant at a value that ensures adequate separation of masses that are 1 amu apart. In this scanning mode, called constant  $\Delta M$  mode, the resolution is proportional to  $M$ . If  $\Delta M = 1$ , the resolution required to separate adjacent peaks at mass 30 is 30, while at mass 250 the resolution must increase to 250 to separate the peaks. The result is a mass spectrum with sensitivity skewed toward the lower masses.



In practice, most quadrupole systems can be electrically tuned to operate either at constant resolution mode or at constant  $\Delta M$  mode. Once a mode has been selected appropriate to the experimental purpose, calibration has to be done with known compounds or standard gas mixtures. The calibration should include peak intensity measurements as well as resolution measurements over the mass range to be investigated.

When the quadrupole analyzer is tuned to detect ions of low masses, both  $U$  and  $V$  approach zero values. The ratio  $V/U$  can become very large, and the analyzer stops acting as a mass filter, letting a large number of ions of unseparated masses to pass through it. A high current called *zero blast* is detected. The zero blast interferes with the detection of ions of masses 1 and 2 by the quadrupole mass spectrometer. Hydrogen is therefore not analyzed with QMS.

### 5.1.1.5 Calibration

The basic calibration procedure is the establishment of the signal level for each particular gas in the reactor as a function of its partial pressure. This is achieved by adding each source/reactant gas of interest separately to the reactor and measuring the signal for a principal ion in the cracking pattern of this gas in the ion source. The procedure has to be repeated over a range of pressures and/or flow rates, and without a discharge in the reactor. The calibration has to be performed also as a function of the ionization potential in the ion source. The procedure should also include for reference an inert carrier gas such as argon or neon.

Once the correlation between the chosen signal and partial pressure of the gas has been established, the partial pressures of plasma species, corresponding to the precursor gases, can be deduced from the calibrated mass numbers. This is true, provided that there are no plasma species that could cause interference at the calibrated mass numbers. A self-consistency check of the analysis is possible because the measured partial pressures have to satisfy the following equation:

$$\sum_i p_i = p \quad (5.1)$$

where  $p_i$  is the partial pressure of the gas  $i$  and the summation is performed for all plasma species. The total pressure in the plasma reactor,  $p$ , has to be measured independently and compared to the sum of Eq. (5.1).

The identification and measurement of plasma products are much more complicated. They have to be performed by iterative procedures, since the calibration for many of the species produced by the plasma may not be available a priori. The mass spectrum observed for the plasma products has to be interpreted first in terms of possible stable neutral products, which are able to form in the plasma from the starting gas or gas mixture. Additional calibration measurements with molecules that are deduced as products have to be then performed for determination of both the sensitivity factors and cracking pattern at the relevant electron energy in the ion source.

In some cases, the discharge products cannot be obtained as stable molecules. Indirect methods for the determination of sensitivity factors must then be used [ 14 ].

The use of this calibration procedure in the analysis of neutrals is not widespread, presumably because of the convenience of using relative methods. There are two disadvantages to adhering to the calibration procedures just outlined, which have apparently discouraged their widespread use in the past, namely, the large volume of calibration data needed for both qualitative analysis (determination of cracking patterns and appearance potentials) and for quantitative analysis (determination of absolute sensitivities, i.e., the ratio between the signal strength and partial pressure). The widespread use of computers for rapid data acquisition makes this tedious task far less forbidding than it was before.

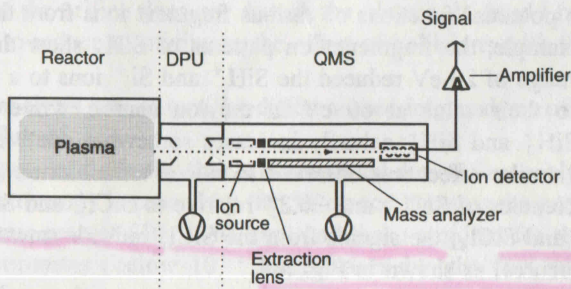
### 5.1.2 Plasma Analysis

Plasma diagnostics with the quadrupole mass spectrometer is performed by sampling plasma particles (ions and neutrals) which stream through a *sampling aperture* located at or near the wall of the plasma reactor. After extraction from the plasma, the flux of particles is mass analyzed. Analysis of the energy of the sampled particles can be added to their mass analysis. A typical experimental set up for plasma analysis with quadrupole mass spectrometry is shown in Fig. 5-4.

The system consists of three main components:

1. The particle *extraction/collimation optics* (ion source, the extraction lens, and as shown in Fig. 5-4, the differential pumping unit described in Section 5.1.2.1)
2. The mass analyzer
3. The ion detector

The most complicated component in the system, in terms of its design and effect on signal collection and interpretation, is the extraction optics.



DPU = differential pumping unit

⊙ - pumping system

Fig. 5-4 Quadrupole mass spectrometer (QMS) setup for plasma diagnostics.



In sampling neutral species one must cope with the complexity introduced by dissociative ionization that can take place in the ion source. Most molecules undergo dissociation upon ionization, and the same detected ion can be the result of several different precursors. For example, the ion  $\text{CH}_3^+$  can result from ionization of neutral species originating from methane, ethane, propane, methyl radicals, and so on.

The ion source of a quadrupole mass spectrometer is usually operated at about 70 eV. An electron energy of such magnitude is sufficient to frequently induce also *fragmentation* of the neutral molecules or radicals entering the source. In plasma diagnostics, the fragmentation in the ion source often results in the formation of fragment ions from one species, which interfere with ions from another, since many of the molecules produced by the plasma are either multimers or very simple fragments of the starting molecules. The analyzed gas may therefore not be identical to the one in the plasma. Thus one has to be careful in the interpretation of results obtained with the mass spectrometer when trying to discern between the radicals originating in the plasma and those that are the result of fragmentation in the mass spectrometer.

To reduce the fragmentation of molecules or radicals extracted from the plasma in the ionization source, it is possible sometimes to operate the source at a reduced voltage. Electron energies of the order of 20–30 eV have been found to be helpful to reduce this effect [15, 16] and simplify the mass spectra in general.

When reducing the energy of the electrons in the ion source, one must choose energies above the ionization potential of the species of interest but below the ionization potential of interfering species. Lowered ionization energies, however, result also in reduced sensitivity. The lower limit of the usable electron energy in the ion source is determined by the requirement to obtain an adequate signal-to-background ratio, since the absolute signal levels are reduced at lower electron energies due to the decrease of the ionization cross-sections.

The extent to which the electron energy should be reduced depends also upon the appearance potential functions of various fragment ions from the molecule of interest. For example, the fragmentation patterns of  $\text{SiH}_4$  show that an electron energy in the range of 20 eV reduced the  $\text{SiH}^+$  and  $\text{Si}^+$  ions to a very low level with respect to their value at 60 eV in the ion source, while the ionization efficiency of  $\text{SiH}_3^+$  and  $\text{SiH}_2^+$  actually increases somewhat relative to the 60 eV value [17]. A similar effect was observed in silicon tetrachloride ( $\text{SiCl}_4$ ) for the ionization efficiencies of  $\text{SiCl}^+$  and  $\text{SiCl}_2^+$  relative to  $\text{SiCl}_3^+$  and  $\text{SiCl}_4^+$  [16]. In plasmas of Ar and  $\text{SiCl}_4$ , the signals from the  $\text{SiCl}_x$  radicals saturate at about 30 eV in the ion source, as shown in Fig. 5-5.

### 5.1.2.1 Flux Analysis of Neutral Species

According to Vasile and Dilla [12], one can distinguish between two types of plasma diagnosis with quadrupole mass spectrometry: *flux analysis* and *partial pressure analysis*. In flux analysis, after sampling the plasma through a small

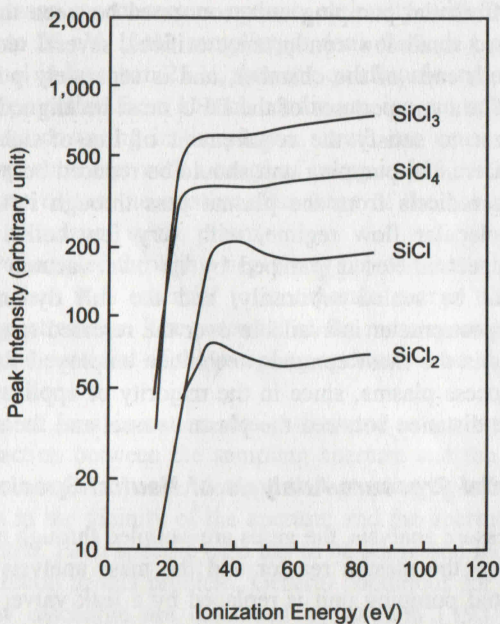


Fig. 5-5 Peak intensities versus ionization energy in ion source in an Ar + SiCl<sub>4</sub> plasma (from [16], reprinted with permission from *Plasma Chem. Plasma Process*, vol. 3, p. 235, 1983).

aperture in the plasma reactor, collisionless trajectories lead directly to the ion optics of the mass spectrometer as shown in Fig. 5-4. The analysis is therefore performed on line-of-sight particles forming a molecular beam. This method is best suited for the identification of plasma species and for the optional analysis of their energy.

The size of the sampling orifice should be less than the Debye length so that the presence of the orifice does not disturb the plasma. It should have practically "zero length" to reduce to minimum the effect of collisions with the walls of the orifice.

The flux analysis can, in turn, be differentiated into analysis of flux of neutral particles and flux of ions.

An experimental difficulty that is encountered during flux analysis of plasmas with mass spectroscopy is caused by the difference between the pressures prevailing in the plasma reactor ( $10^{-3}$ – $10$  torr) and those required for the operation of the mass spectrometer (below  $10^{-4}$  torr). To enable the flux analysis of line-of-sight particles, it is necessary to use a pressure reduction stage between the plasma sampling port and the chamber of the quadrupole mass spectrometer. The pressure reduction can be accomplished with a low-conductance connection which is pumped separately as shown in Fig. 5-4 and called a *differential pumping unit*, (DPU).



A typical differential pumping unit, connected between the plasma and the ion source, has two small low-conductance orifices, several tens of micrometers in diameter, at both ends of the chamber, and is separately pumped by its own vacuum system. The two apertures of the DPU must be aligned with the quadrupole mass analyzer to satisfy the requirement of line-of-sight extraction. The pressure in the differential pumping unit should be reduced below  $10^{-4}$  torr, such that molecules or radicals from the plasma pass through it to the mass spectrometer in a molecular flow regime, with very few collisions. Because the chamber of the spectrometer is pumped by its own vacuum pump, the upper pressure limit can be scaled arbitrarily, and the full dynamic range of the quadrupole mass spectrometer is available over the rescaled range.

Flux analysis is the most common technique employed for sampling glow-discharge-type process plasma, since in the majority of applications there are no restrictions on the distance between the plasma vessel and the spectrometer.

### **5.1.2.2 Partial Pressure Analysis of Neutral Species**

In partial pressure analysis, the gases are sampled through a low-conductance connection between the plasma reactor and the mass analysis chamber. In this case, the differential pumping unit is replaced by a leak valve, a sintered porous disk of inert material, or a capillary.

In the arrangement used for partial pressure measurement, collisions take place between the plasma particles and between the particles and the walls of the connecting unit before reaching the mass spectrometer. Condensible or reactive species, especially radicals, react by collisions in the gas phase or on the surfaces or condense on the walls and are lost during the passage to the mass spectrometer. Thus the measured partial pressures may not correspond to those prevailing in the plasma. In addition, the measured partial pressures depend on the pumping speed in the mass spectrometer region.

Partial pressure analysis does not measure line-of-sight plasma particles and hence allows simpler vacuum connections between the mass spectrometer and the plasma chamber and generally requires less stringent differential pumping than flux analysis. The instrumentation for partial pressure analysis can therefore be made simpler than the flux analysis.

### **5.1.2.3 Ion Analysis**

In most plasma diagnostic experiments only neutral species of the plasma are analyzed with the quadrupole mass spectrometer. With suitable ion optics such as special ion lenses, either positive or negative ions can also be extracted from the plasma and analyzed. In such a lens, the filament of the ion source is turned off, and suitable voltages are applied to the ion optics. Since the analyzed ions are produced at the plasma potential, the entire mass analyzer has to be electrically isolated in such a way that it could be adjusted to the potential of various plasmas.

Quadrupole mass spectrometers operate optimally with ions in the energy range of about 5 to 25 eV. If the sampling is done through a grounded wall and the plasma potential is less than 25 V, then the quadrupole mass spectrometer can operate at ground potential. Even in such conditions, ion-neutral collisions and ion formation processes occurring in the plasma sheath can cause the arrival of the ions at the mass spectrometer with a range of energies [18]. The energy distribution of the ions can distort the relative abundance of the observed ions as compared to the true abundance in the plasma.

If the ions are sampled through a negatively biased electrode, or if the plasma potential is large, then it is essential to incorporate energy filtering of the ions before the mass spectrometer. The potential of the mass spectrometer must be at, or slightly below the potential of the sampling aperture to be able to observe ions formed near the orifice.

Flux analysis of ions is not as straightforward as for neutrals, due to the electrostatic interaction between the sampling aperture and the plasma. The flux of the charged particles that passes through the sampling aperture depends on the plasma conditions in the vicinity of the aperture and the aperture's geometry and electrostatic potential. Each specific case has to be addressed individually as there is no common solution to this problem. General conditions for extracting plasma ions from a glow discharge are discussed by Drawin [19] as a function of magnitude of the ion mean free path,  $\lambda_i$ , the Debye shielding length,  $\lambda_D$ , and the diameter of the extraction aperture.

Ion optical lens components (cylindrical lenses in particular) have large apertures and confining surfaces that admit and scatter a solid angle of the neutral flux that is larger than optimal for ideal molecular beam formation [12]. In systems intended for flux analysis of both ionic and neutral species, collimation of incoming neutral flux is difficult to achieve. Ionization of the neutral flux before significant scattering occurs is therefore essential in such systems.

When the experimental arrangements are correctly tuned, the analyzed fluxes of positive ions can be representative of the ion fluxes arriving at the surface exposed to the plasma. However, the measured ion fluxes do not necessarily reflect the fluxes of neutral species in the plasma. Because the large fraction of low-energy electrons in the plasma favors ionization of species with low ionization potentials, relatively higher fluxes of such species will be measured.

### 5.1.3 Summary

Mass spectroscopy is an excellent technique for detecting neutral particles as well as positive and negative ions from the plasma. Mass spectrometric sampling of a plasma is an intrusive technique because the sampling port has to be in contact with the plasma. The analyzed particle fluxes depend upon the sampling sheath thickness and voltage. Ion-molecule collisions in the sheath region of the sampling orifice and downstream from it may affect the measurement accuracy of densities, especially those of ions.



Disturbances caused to the plasma by the apparatus can be minimized by choosing the right geometry for the orifice and the correct extraction voltage in relation to plasma parameters.

When setting up a quadrupole mass spectrometer for plasma diagnostics, the characteristics of the QMS must be optimized for each of the three possible applications [12]:

1. Flux analysis of neutral particles
2. Flux analysis of charged particles
3. Partial pressure analysis of equilibrated gases

When the sampling aperture and extraction optics are designed correctly, both neutrals and ions representative of the plasma composition near the aperture can be sampled in such a way that the extracted species are not affected by subsequent gas-phase and surface collisions. Plasma diagnostics with mass spectrometry can be used to study the chemical reactions occurring in the plasma and their kinetics and plasma-surface interactions (see, for example, [16, 17, 20–23]). There are examples where the flux analysis of ions and neutrals has provided the most detailed description of material production or modification by plasmas [12].

By changing the position of the sampling aperture, it is possible to perform the plasma diagnostics at different positions in the plasma [24]. The reaction rate constants can be calculated from these measurements, while local rate constants can be derived from the analysis of plasma chemistry as a function of pressure [22].

Mass spectrometry of plasmas can also be used as a tool for end-point detection in plasma etching as, for example, in RIE of silicon nitride, silicon oxide, or titanium tungsten layers over silicon [25]. The detection is based on the occurrence of a very strong change in the signal from specific species at the end-point of the etching, that is, when the surface film has been etched to a depth that exposed the substrate. A 13 times decrease in the signal from CN was observed in  $\text{Si}_3\text{N}_4/\text{Si}$ , a 5 times decrease in the signal from  $\text{Cl}_2$  was observed in  $\text{SiO}_2/\text{Si}$ , and a 23 times increase in the signal from SiCl was observed in TiW/Si etching. The response time for each mass was a few tenths of a second or less, making the technique suitable for controlling the process [25].

The main disadvantages of the quadrupole mass spectrometry analyses are

1. Requirement of careful design of the sampling and extraction optics, which cannot always be made nonperturbing to the plasma
2. Need of differential pumping requirements for maintaining collision-free conditions

The pumping speed of the chamber of the mass spectrometer is also a significant factor to be taken in to consideration since the time required for a complete set of measurements is usually quite long. The pumping speed should

be high enough to avoid the buildup of background gas over the duration of the experiment.

## 5.2 ELECTROSTATIC PROBES

*Electrostatic or Langmuir probes* are another tool for plasma diagnostics suitable for measuring parameters of cold plasmas. This technique allows the determination of plasma density,  $n$ , electron temperature,  $T_e$ , plasma potential,  $V_p$ , and floating potential,  $V_{fl}$ . The probes do not provide information on the chemistry of the plasma, but serve well in complementing the mass spectroscopy diagnostics.

A Langmuir probe is a metallic insulated electrode, except at the tip, which is exposed to the plasma. The probe is made of a high-melting-point metal such as tungsten, molybdenum, or platinum. Tungsten wire is commonly used. The probe is inserted into the plasma reactor through an electrically insulated seal. The insulator of the probe should be chemically inert at high temperatures. It can be either quartz or a vacuum-compatible ceramic, such as high-purity alumina. The tip of a cylindrical probe exposed to the plasma, as illustrated in Fig. 5-6, is several millimeters long and less than 1 mm in diameter. The vacuum seal can be fixed or can permit changes in the position of the probe.

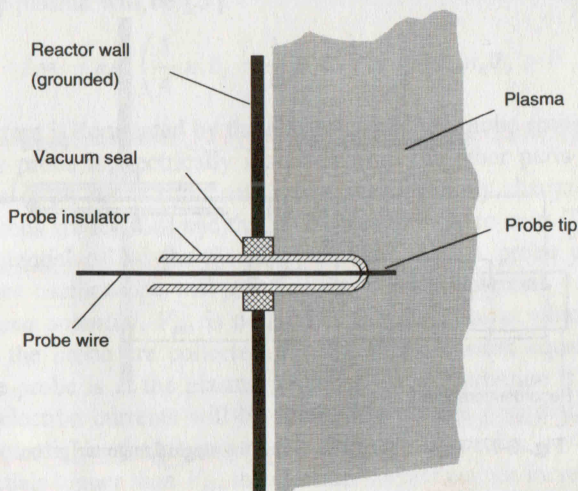


Fig. 5-6 Diagram of single Langmuir probe.

Details on the use of electrostatic probes for plasma diagnostics can be found in monographs dealing with plasma diagnostics in general and probes in particular [4, 26–29]. Due to the fact that the measurements are made by inserting a probe in the plasma, this technique is an in-situ intrusive diagnostic method that locally perturbs the plasma.



An electrode inserted in the plasma changes the physical conditions in its vicinity, which means that the measurement is done in a plasma disturbed by the probe itself. The probe affects the plasma mainly by changing the electric field, thereby the particle distribution and energy. The magnitude of this disturbance depends on the dimensions of the probe and the properties of the plasma. Probes that satisfy the relation  $r > \lambda_D$ , where  $r$  is the radius of the probe, are called *thin sheath probes*. These are conventional type probes used in diagnostics of cold plasmas.

Most used are *single* and *double Langmuir probes*. These are operated by applying an external variable potential,  $V$ , and by measuring the current through the probe as a function of the external potential; the  $I$ - $V$  characteristic of the probe is thus obtained. The applied potential is usually swept along a sawtooth-shaped time dependence. For a single Langmuir probe, the voltage  $V$  is referenced to a large metal surface in the plasma chamber or to the walls of the chamber itself. For the double Langmuir probe, also called *double floating electrostatic probe*, (DFEP), the voltage is applied between the two electrodes, both insulated from the reactor.

The experimental arrangement is simple, requiring in addition to the probe, a scanning DC power supply (usually  $\pm 100$  V) and an X-Y recorder. A typical circuit diagram for the probe is shown in Fig. 5-7.

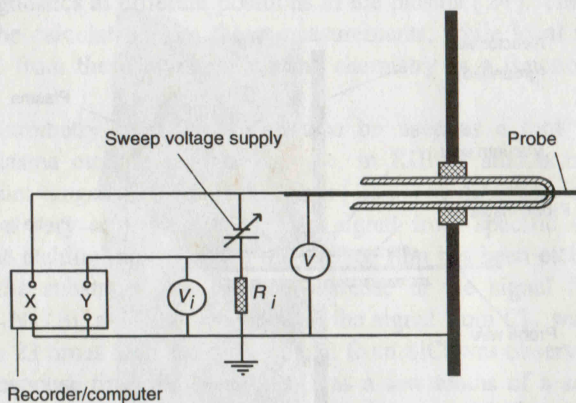
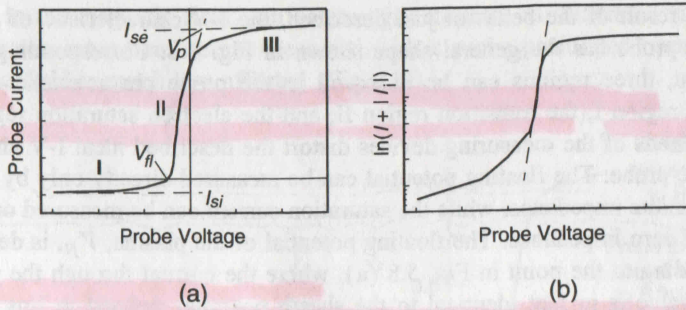


Fig. 5-7 Typical electrical circuit for single Langmuir probe.

The X-Y recorder traces the  $I$ - $V$  characteristic of the probe similar to the one illustrated in Fig. 5-8. The voltage on the probe is recorded on the  $x$ -axis, while the current through the probe is recorded on the  $y$ -axis, as the voltage drop across a reference resistor  $R_i$ . The X-Y recorder can obviously be replaced by a micro-computer to log the data and perform its analysis.



**Fig. 5-8** I-V characteristic of a single Langmuir probe: (a) linear display; (b) semilogarithmic display.

### 5.2.1 Probe Characteristics

Consider a plasma containing only two species: electrons and ions of equal and opposite charge. In an unperturbed plasma, according to Eqs. (1.32) and (1.34) of Sec. 1.3, the mean ion speed,  $\bar{v}_i$ , is much smaller than the mean electron speed,  $\bar{v}_e$ , by the ratio  $(m_i/m_e)^{1/2}$ . Therefore, the flow of electrons to the tip of the probe is higher than the flow of ions and the total current from a probe of area  $A_p$  inserted in the plasma will be [5]

$$I = -eA_p \left( \frac{1}{4} n_i \bar{v}_i - \frac{1}{4} n_e \bar{v}_e \right) \approx \frac{1}{4} eA_p n_e \bar{v}_e > 0 \quad (5.2)$$

The probe current is dominated by the electrons, and the probe emits a net positive current. If the probe is electrically insulated from the other parts of the plasma reactor, that is, if the probe is a floating one, it will rapidly charge up negatively, until the electrons are repelled and the net current brought to zero. The tip assumes a negative potential called the *floating potential*,  $V_{fi}$ . A probe connected to a high-impedance oscilloscope will measure the floating potential.

The *plasma potential*,  $V_{pl}$ , is defined as the potential at which all electrons arriving near the probe are collected and the probe current equals the electron current. If the probe is at the plasma potential, the perturbation it induces to the free ion and electron currents will be small. The plasma potential,  $V_{pl}$ , is in fact the electric potential in the plasma in the absence of a probe.

At potentials higher than  $V_{pl}$ , the electron current cannot increase any further and the *electron saturation current*,  $I_{se}$ , is measured; see Fig. 5-8(a). When the probe potential decreases to values below  $V_{pl}$ , it becomes negative relative to the plasma, and an increasing number of electrons are repelled from the probe. At sufficiently low potentials, the electron and ion current densities to the probe are equal,  $J_e = J_i$ , and the total probe current is zero. The probe potential at this point is, as mentioned before, the *floating potential*,  $V_{fi}$ . At potentials lower than  $V_{fi}$ , only ions are collected from the plasma, and the *ion saturation current*,  $I_{si}$ , is measured; see Fig. 5-8(a).



As a result of the behavior just described, the I-V characteristic of a single Langmuir probe has the general shape shown in Fig. 5-8. Corresponding to this description, three regions can be observed in the probe characteristic: the ion saturation region I, the transition region II, and the electron saturation region III.

The loads of the measuring devices distort the described ideal I-V characteristic of the probe. The floating potential can be measured directly only by a probe with an infinite impedance, while the saturation current can be measured only with a probe of zero impedance. The floating potential of the plasma,  $V_{fl}$ , is defined as corresponding to the point in Fig. 5.8 (a), where the current through the probe is zero. Its value is in fact identical to the sheath potential defined in Eqs. (1.28a) and (1.28b) in Sec. 1.3.4, which for a spherical surface is given by [27]

$$V_{fl} = -\frac{kT_e}{2e} \ln\left(\frac{\pi m_e}{2m_i}\right) \quad (5.3)$$

The plasma potential,  $V_{pl}$ , is determined from the intersection between the extrapolations of the sections of the curve in the transition region II and the electron saturation region III. Its value can be estimated from

$$V_p = kT_i \frac{\ln 2}{q_i} \quad (5.4)$$

where  $T_i$  = temperature of ions involved  
 $q_i$  = charge of ions

Consistent with the higher mobility of electrons, the electron saturation current is about two orders of magnitude higher than the ion saturation current.

### 5.2.1.1 Effect of Magnetic Field

So far, the description of the probe behavior has assumed that no magnetic field is present and that the motion of the charged particles in the plasma is controlled only by the electric field. If, however, a magnetic field is present in the plasma, the electrons and ions will no longer move in straight lines, following the electric field lines, but will orbit instead around the magnetic field lines, in circular orbits with a radius equal to the *Larmor radius*, defined by Eq. (2.13) in Sec. 2.4:

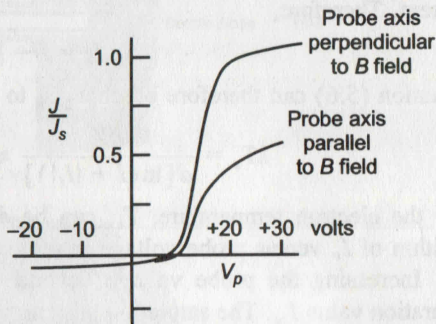
$$r_L = \frac{mv_{\perp}}{eB} \quad (5.5)$$

As a result, the motion of the particles across the magnetic field is strongly restricted, while the motion along the magnetic field line is almost unaffected. The effect of the magnetic field can be neglected only if  $r_L \gg a$ , where  $a$  is the typical dimension of the probe ( $a = r$  for cylindrical probes).

According to Eq. (5.5), the Larmor radius of the electron,  $r_{Le}$ , is smaller than that of the ion,  $r_{Li}$ , by the factor  $m_e/m_i$ ; hence the electrons are much more affected than the ions by the presence of the magnetic field. Because normally  $r_{Li} > a$ , the ion saturation current is almost not affected by the magnetic field. On the other hand, the electron saturation current measured by a circular probe, which is

parallel to the magnetic field, can be strongly reduced, as illustrated in Fig. 5-9. The electron saturation current measured with a probe positioned normal to the magnetic field is much less affected (Fig. 5-9).

**Fig. 5-9** Effect of magnetic field on probe characteristic (from [4], reprinted by permission of John Wiley & Sons, Inc.).



## 5.2.2 Probe Analysis

Although the experimental arrangement for probe measurements is relatively simple, one has to be careful when analyzing the experimental data.

The only probe regime that can be reasonably understood is the pressure region  $p \leq 0.1$  torr, in which the mean free path  $\lambda$  is much greater than the probe size, which in turn is much greater than the Debye length,  $\lambda \gg r > \lambda_D$  [30]. However, for phenomenological estimations, or for the determination of the functional relationship between the parameters of the plasma and the discharge conditions (i.e., power, pressure etc.), the Langmuir probe is a relatively simple, valuable diagnostic tool.

An exact interpretation of the results of the probe measurements for absolute determination of the plasma parameters may be more complicated than described here. The following presents only a simplified description of the evaluation of the measurements by single and double Langmuir probe diagnostics.

### 5.2.2.1 Single Langmuir Probes

As illustrated in Fig. 5-8, increasing the probe voltage,  $V$ , beyond  $V_{fl}$  results in a steep rise in the electron current in region II of the I-V characteristic. In this region, the electron current of the probe follows the relation [4]

$$\ln I_e = \frac{V}{kT_e} + \ln A_s J_o \quad (5.6)$$

where  $A_s$  = the area of the probe sheath

$J_o$  = the random electron current density

and  $kT_e$  is expressed in electron volts and  $V$  in volts.

For a typical cold plasma with  $T_e = 1$  eV and  $n_e = 10^{11} \text{ cm}^{-3}$ , the Debye length is  $\lambda_D = 20 \mu\text{m}$ , so that the Debye length is usually much smaller than typical



probe dimension of millimeters ( $\lambda_D \ll a$ ). As the thickness of the plasma sheath is commonly much smaller than the radius of the probe, one can assume that  $A_s = A_p$ ,  $A_p$  being the area of the probe.

The total probe current,  $I$ , is the difference between the electron and ion current. Therefore,

$$I_e = I + |I_i| \quad (5.7)$$

Equation (5.6) can therefore be changed to

$$kT_e = \frac{dV}{d[\ln(I + |I_i|)]} \approx \frac{\Delta V}{\Delta[\ln(I + |I_i|)]} \quad (5.8)$$

and the electron temperature,  $T_e$ , can be determined from the slope of the logarithm of  $I_e$  versus probe voltage in region II (Fig. 5-8 (b)).

Increasing the probe voltage beyond  $V_{pl}$ , the electron current reaches the saturation value  $I_{se}$ . The saturation current, according to Eq. (5.2) is given by [4]

$$I_{se} = \frac{1}{4} eA_p n_e \left( \frac{2kT_e}{m_e} \right)^{1/2} \quad (5.9)$$

and with  $T_e$  determined from Eq. (5.8), the electron density  $n_e$  can be calculated from  $I_{se}$ .

For  $T_i \ll T_e$ , which is characteristic of cold plasmas, the saturation ion current,  $I_{si}$ , is nearly independent of the ion temperature and is given by [4]

$$I_{si} = 0.4n_i eA_p \left( \frac{2kT_e}{m_i} \right)^{1/2} \quad (5.10)$$

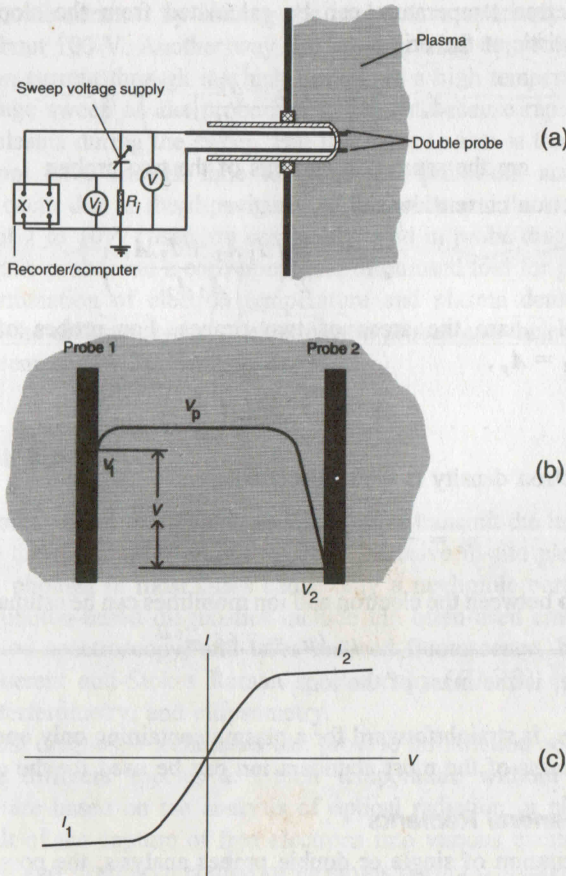
With  $T_e$  established from Eq. (5.8), the ion density  $n_i$  can be evaluated from Eq. (5.10).

The calculation of particle densities from Eq. (5.9) and Eq. (5.10) assumes that the area through which the probe collects the ions is known. However, the ion collecting area may be sometimes significantly different from the geometrical area of the probe, and the estimate of the ion density may be inaccurate. The problem is aggravated in the presence of a magnetic field, especially for the ions.

One has to remember that secondary electrons emitted from the probe by the collected ions also contribute a positive current that is indistinguishable from the ion current. This addition to the current is another source of error in the calculation of  $n_i$ .

### 5.2.2.2 Double Floating Probes

Double probes are used for diagnostics of RF and MW discharges when a reference electrode is not available, as in the case of inductively coupled RF systems. The double probe technique is also useful in a magnetized plasma. A double probe is composed of two, usually identically tipped, probes separated by a fixed distance, as illustrated in Fig. 5-10. Figure 5-10 also shows the electrical circuit, the momentary potential distribution between probes and an ideal I-V characteristic for double probes of identical areas.



**Fig. 5-10** Double Langmuir probe: (a) probe and electrical circuit; (b) momentary potential distribution between probes; (c) I-V characteristic of identical probes.

The tips of the probes have to be far enough from each other so that the plasma sheaths of the probes would not overlap, but close enough to sample the same region of the plasma. Both probes are insulated from the ground, float with the plasma, and are unaffected by changes in  $V_{pl}$ . The circuit is equilibrated when the electron current flowing to one probe is balanced by the ion current flowing to the other. The currents are therefore limited by the ion saturation currents for each probe, and because the ion current is much less affected by a magnetic field, the double probes are preferred when magnetic fields are present.

In an experimental arrangement, a sawtoothed time variable voltage is applied to the probe, as shown in Fig. 5-10. From the I-V characteristic, plasma parameters can be calculated as follows [23, 27]:



- The electron temperature can be calculated from the slope of the I-V characteristic at the origin,

$$T_e = \frac{e}{k} \left( \frac{I_1 I_2}{I_1 + I_2} \frac{dV}{dI} \Big|_{I=0} \right) \quad (5.11)$$

where  $I_{1,2}$  are the saturation currents of the two probes.

- The electron current density,  $J_e$ , is given by

$$J_e = -\frac{1}{2} \left( \frac{I_1 A_2 + I_2 A_1}{A_1 A_2} \right) \quad (5.12)$$

where  $A_{1,2}$  are the areas of two probes. For probes of equal areas  $A_1 = A_2 = A_p$ ,

$$J_e = -\frac{1}{2} \left( \frac{I_1}{A_p} \right) \quad (5.13)$$

- The electron density is then calculated from

$$n_e = -1.22 \frac{J_e}{e(8kT_e/\pi m_e)^{1/2} (\mu_e/\mu_i)^{1.08}} \quad (5.14)$$

The ratio between the electron and ion mobilities can be estimated from [27]

$$\mu_e/\mu_i = 7.64 m_i^{0.46} \quad (5.15)$$

where  $m_i$  is the mass of the ion.

The choice of  $m_i$  is straightforward for a plasma containing only one type of ions; otherwise, the mass of the most abundant ion can be used for the calculation.

### 5.2.2.3 General Remarks

In the discussion of single or double probes analysis, the possible existence of negative ions in the plasma has been neglected. Plasmas of halogen-bearing gases or oxygen have significant concentrations of negative ions, and in such cases the contribution of the negative ions has to be considered in the analysis.

When using Langmuir probes to evaluate the plasma parameters, certain experimental considerations should be kept in mind:

1. Insulating layers may form on the probe in a plasma used for deposition of insulators or due to contamination.
2. The probe may become short circuited or its effective area may increase if a conductive material coats the insulation of the probe in a plasma used for deposition of conductive films.
3. The collected data may be influenced by thermal effects.

The distortion of probe characteristics by contaminated probes is particularly strong in the region close to the plasma potential. The ion current at highly negative probe potentials is less sensitive to probe contamination. Some of these problems may be reduced by cleaning the surface of the probe. This can be done

through ion bombardment, by biasing the probe to a relatively large negative potential of about 100 V. Another way used for cleaning the probe is by passing a high-electron current through it which heats it to a high temperature.

The voltage sweep on the probe has to be fast because rapid changes may occur in the plasma during the sweep. But if the sweep rate is too fast, the probe sheath may not have enough time to come to equilibrium and displacement currents may occur due to the capacitance of the probe and the connecting leads. Sweep rates of 1 to 10 V/ $\mu$ sec are commonly used in probe diagnostics.

Electrostatic probes are a convenient and often-used tool for plasma diagnostics, for determination of electron temperature and plasma density. A detailed description of the different types of electrostatic probes and their analysis can be found in a recent review by Hershkowitz [29].

### 5.3 OPTICAL METHODS

Optical diagnostic techniques, which use photons to transmit the information from the plasma to the detection tool, are the least intrusive in-situ plasma diagnostic methods. The photons in most cases cause only a negligible perturbation to the process. The photon-based diagnostics include the often-used emission spectroscopy, absorption spectroscopy, and laser induced fluorescence, but also Raman scattering, coherent anti-Stokes Raman spectroscopy (CARS), optogalvanic effects, laser interferometry, and ellipsometry.

The optical diagnostic techniques can provide information about the concentration of the different species and their temperature without perturbing the plasma. They are based on the analysis of optical radiation in plasma, which is mostly a result of the capture of free electrons into various excited states of the atoms and ions and from acceleration of electrons during collisions with ions and atoms (*bremsstrahlung*).

The different types of optical spectra observed in cold plasmas and their sources are summarized in Table 5-2. It can be seen that the spectra can contain

**TABLE 5-2** Spectra Observed in a Plasma (from [31], reprinted by permission of John Wiley & Sons, Inc.)

Particle	Degree of Freedom	Type of Spectrum	Spectral Region
Atom or ion	Electronic excitation	Line	UV-visible-IR
	Ionization	Continuum	UV-visible-IR
	Translation	Line profiles	
Electrons	Recombination	Continuum	UV-visible
	Free-free transitions	Continuum	IR
Molecules	Rotation	Line	Far infrared
	Vibration-rotation	Band	IR
	Electronic excitation	Band systems	UV-visible-IR



individual spectral lines, band, or continuum radiation and span the range from the far infrared (IR) to ultraviolet (UV). Soft X rays are also existent to some extent in cold plasmas characterized by high  $T_e$ . Radiations in the visible and IR spectra can be used to identify excited plasma species. Absorption measurements with a suitable radiation source can be used to evaluate the population of non-radiating metastable levels of first excited states that radiate in vacuum UV.

Laser interferometry does not provide chemical information, but it does give an extremely accurate measurement of material deposition or etching rates. In-situ ellipsometry can be used for measuring small thickness changes or to characterize very thin layers ( $< 30 \text{ \AA}$ ).

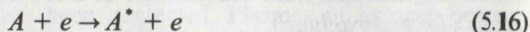
Several optical diagnostic methods are discussed in more detail next.

### 5.3.1 Optical Emission Spectrometry

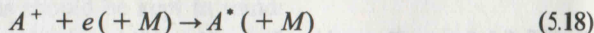
Optical emission spectrometry (OES), which is the spectral analysis of the light emanating from a plasma, is probably the most widely used method for monitoring and diagnosis of plasma processes. By measuring the wavelengths and intensities of the emitted spectral lines, one can identify the neutral particles and ions present in the plasma. The method is implemented both in research laboratories and in manufacturing for production control.

The spectral fingerprint of optical plasma emission provides information about the chemical and physical processes that occur in the plasma. This technique has the advantage of being external to the reactor and vacuum system and provides besides spatial and temporal resolution also high reliability. However, the OES technique is limited to the monitoring of light-emitting species, and the emission intensity is not always directly related to the concentration of the species in the plasma.

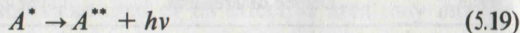
Optical emission can be produced in a plasma as a result of electron impact excitation or dissociation



or by an ion impact process,



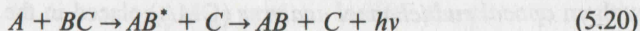
which create an excited species  $A^*$ , followed by the release of energy of the excited species  $A^*$ :



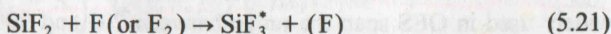
In the foregoing equations, the sign \* indicates the excited, emitting species;  $e(+M)$  designates a neutral species, a negative ion, an electron plus a third body, or a surface in contact with the plasma [32]; and  $A^{**}$  is either the ground state of the atom or another excited state at an energy level lower than  $A^*$ . For example, the reaction described by Eq. (5.16) is responsible for radiation emission from excited fluorine atoms in  $\text{CF}_4 + \text{O}_2$  discharges or from Cl in  $\text{Cl}_2$  discharges, while the process described by Eq. (5.17) has been observed by time-resolved emission

in the momentary cathode sheath of a radio frequency  $\text{Cl}_2$  discharge [32]. Excitation of hydrogen atoms in a DC discharge of hydrogen has been ascribed in part to the reaction described by Eq. (5.18).

Molecular species can also be excited by chemiluminescent recombination reactions:



Such processes occur in  $\text{Cl}_2$  discharges due to recombination of Cl atoms. In discharges containing fluorine atoms in the presence of silicon, optical emission results from the reaction



Metastable species can also excite emission in plasmas as is the case, for example, in the enhancement of H-Balmer- $\alpha$  emission caused by addition of Ar to  $\text{H}_2$  discharges observed by Krogh et al [33].

Usually, the most intense radiation emitted from the plasma originates in the transition from the first excited state,  $W_1$ , to the ground state,  $W_0$ , of the particle. As every particle (atom, molecule, ion, radical) has precisely defined energy levels, each emits a characteristic spectral line of frequency:

$$\nu_{10} = \frac{W_1 - W_0}{h} \quad (5.22)$$

and wavelength

$$\lambda_{10} = \frac{hc}{W_1 - W_0} \quad (5.23)$$

where  $c$  is the velocity of light.

The apparatus required for OES is one of the least complicated. It necessitates a monochromator to disperse the light emitted from the plasma, a set of optics to image the light into the detector, and a photodetector to measure the dispersed light. A typical experimental arrangement is presented in Fig. 5-11.

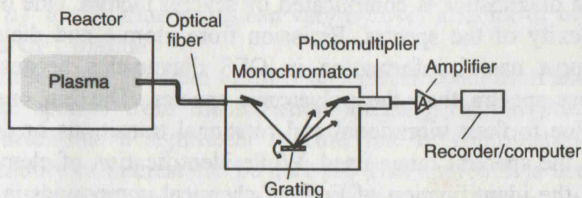


Fig. 5-11 Experimental setup for optical emission spectroscopy of plasmas.

The light emitted by the plasma is conveyed to the monochromator either directly or via a fiber optic cable. Diffraction at the grating of the monochromator disperses the light into its spectral components. Only the light of a selected wavelength passes through the exit slit of the monochromator and strikes a photomultiplier detector where it produces a photocurrent proportional to the



intensity of the incident light. The spectrum of the plasma emission is obtained by rotating the grating of the monochromator with a motor.

Monochromatic light emerging from the exit slit of the monochromator can be detected with a photomultiplier tube used in analog mode (current measuring) or digital mode (photon counting). As an alternative, the exit slit can be replaced with an *optical multichannel analyzer* (OMA) placed in the plane of the exit slit. The advantage of an OMA is that a portion of the emission spectrum can be recorded simultaneously without scanning the monochromator, thus providing much faster data collection. Although the emissions from the plasma span a very large range of frequencies, from the infrared to the soft X ray, the spectra most widely used in OES span the range between 200 and 900 nm.

Identification of ions in the plasma by optical emission spectroscopy requires a detector able to monitor lines with wavelength  $\lambda < 200$  nm, because ion transitions occur at these shorter wavelengths. For ion identification, the monochromator must be maintained under vacuum to avoid absorption of radiation at these short wavelengths. Fiber optics are not available at these wavelengths. For observation of lines with  $\lambda < 110$   $\mu\text{m}$ , the monochromator must be connected directly to the plasma chamber through a hole, because there are no materials with sufficient optical transmission at these wavelengths from which to fabricate the lenses. Even mirrors cannot be used due to reflectances lower than 10% at these wavelengths. Instead, a concave grating, which performs both the task of diffraction and optical imaging, is used.

A spectrometer resolution of 0.1 to 1 nm is required for identification of species. A monochromator of 0.25-m focal length can provide  $\sim 0.05$ -nm resolution, sufficient for most studies. When higher resolution is required to detect atomic fine structure or molecular rotational levels, a monochromator of long focal length (e.g., 1-m focal length with 0.01-nm resolution) or a Fabre-Perot interferometer ( $\sim 0.0005$ -nm resolution) can be used.

The species emitting a certain radiation can be identified from the specific frequency of the radiation, using tables of emission spectra. However, the use of OES for plasma diagnostics is complicated by several factors. One of them is the extreme complexity of the spectra. Emission from atomic and diatomic species provides the most useful information in OES diagnostics because they have simpler narrower spectra than the polyatomic species. The last ones have very broad spectra due to their vibrational and rotational transitions or do not radiate significantly in the spectral range used. While identification of elemental lines is relatively easy, the identification of lines of chemical compounds is difficult due to the large number of emission lines produced by each element in the compound. Identification of weaker lines, or identification of plasma species of low density, is complicated because the main components of the plasma possess many spectral transitions. The optical signals from the main components may thus obscure those from less abundant species.

Another difficulty in the use of OES in plasma diagnostics for quantitative analysis is the dependence of the optical emission intensity on the ability of the

plasma to excite the ground state species into electronically excited emitting species  $A^*$ .

For quantitative evaluation of the emission spectra a first assumption will be that the *emission intensity*,  $In_s$ , from a specific species is proportional to its concentration,  $[F]$ :

$$In_s = a_s^e [F] \quad (5.24)$$

where the proportionality factor  $a_s^e$  is constant. The proportionality constant  $a_s^e$  is given by [34]

$$a_s^e = K \int_0^\infty Q(p, n_e) \sigma_s^e(\varepsilon) N_e(\varepsilon) d\varepsilon \quad (5.25)$$

where  $K$  = a constant depending on the sensitivity of the detector  
 $\sigma_s^e(\varepsilon)$  = cross section for excitation of the emitting species to a given excited state caused by the impact of an electron of energy  $\varepsilon$   
 $N_e(\varepsilon)$  = number of electrons in the energy range  $d\varepsilon$  present in the volume of the reactor viewed by the detector  
 $Q(p, n_e)$  = quantum yield for emission from the given excited state as a function of discharge pressure and electron density

In principle,  $Q$  varies between 0 and 1.

According to Eq. (5.24) and (5.25) the factor  $a_s^e$  is obviously not a constant. Because  $N_e(\varepsilon)$  depends on the applied RF power and gas mixture and  $Q$  depends on the total pressure and gas mixture,  $a_s^e$  will never be exactly a constant.

If no significant changes are made in the plasma parameters, it can be still assumed that the excitation efficiency of the plasma is constant. If any modifications are made in the plasma parameters such as power, pressure, or gas composition, this assumption is no longer valid, and the intensity of the emitted light cannot be assumed to be proportional to the density of ground state species.

Furthermore, the foregoing equations assume that all the emissions stem from excitation of the ground state of the species. Whenever other processes contribute to  $In_s$ , then Eq. (5.24) is completely invalid. Measurements by Mogab et al. [35] showed that  $a_F^e$  for fluorine atoms can vary by over a factor of two when oxygen is added to a  $CF_4$  plasma.

It is therefore not possible to draw any direct conclusion about the concentration of the species from the emission intensity  $In_s$ . In practice, one must empirically determine a significant spectral line or combination of lines from which the quantity of interest can be derived. This approach is used for end-point detection in plasma etching. At the end point, when the upper film is etched through, pronounced changes occur in the emission lines of the plasma. These changes serve as a stop signal for the etching process. Optical detection of In emission provided, for example, excellent end-point detection during etching of  $/In/GaAsInP/InP$  with  $CH_4-H_2$  plasma [36].

However, in some cases of practical interest, the situation may be somewhat simpler than indicated above. In plasma etching applications, the pressure and electron density are relatively low; thus  $Q(p, N_e)$  may be close to unity over a



range of operating conditions, especially for short-lived excited states [34]. Similarly  $\sigma_s^e(\varepsilon)$  may be a relatively "slow" function of electrons energy,  $\varepsilon$ , and  $N_e(\varepsilon)$  may not depend strongly on gas composition. Under such conditions  $a_s^e$  may be almost constant. A narrow Doppler width (Fig. 5-12(a)), which corresponds to the measured gas temperature, is evidence for emission caused by the reaction described by Eq. (5.16). A broadened emission (Fig. 5-12(b)) corresponds to other pathways similar to those described by Eqs. (5.17)–(5.20).

Optical emission can also provide information on electron energy distributions in RF discharges. More detailed description of OES and other optical plasma diagnostic methods is given by Donnelly [32].

### 5.3.1.1 Actinometry

To overcome the problem of nonconstancy of the proportionality coefficient  $a_s^e$  in Eq. (5.24), actinometry diagnostics has been developed by Coburn and Chen [37]. This is a relatively simple procedure designed to remove the effect of plasma excitation efficiency from the OES data. A recent review of actinometry and its application for plasma polymerization studies was published by d'Agostino and Illuzi [38]. In this technique, a small quantity (1–2%) of an inert gas, which serves as *actinometer*, is mixed into the gas fed to the plasma. It is assumed that the actinometer does not change the characteristics of the plasma to which it is added. The concentration of the actinometer gas is kept constant and the optical emission derived from it is used as a measure of the excitation efficiency of the plasma when the plasma parameters are changed.

In actinometry, one monitors in the same plasma both the emission  $In_r$  from the reactive species and the emission  $In_i$  of the inert actinometer gas. If the quantum yield and the cross sections of the reactive and inert species have the same energy dependence, the following relation exists:

$$\frac{In_r}{In_i} = C \frac{[F]_r}{[F]_i} \quad (5.26)$$

where  $C$  is a constant not affected by plasma parameters.

Equation (5.26) assumes that the cross sections for excitation of the actinometer and the active species are equal. Although there might be differences between the values of the cross sections, the error introduced is not large [38]. A larger error can be introduced if the excitation threshold of the actinometer is significantly different from that of the active species. Actinometry can therefore be used only for emissions from species that have excitation thresholds close to that of the actinometer, a condition, for example, satisfied for Ar and F [37]. The excited state of argon lies at  $\sim 13.5$  eV compared to  $\sim 14.5$  eV for the corresponding fluorine state, and the excitation efficiency is approximately equal for the two atoms. Different actinometers have to be used to study different active species. Coburn and Chen [37] first studied F atoms with Ar as actinometer, while d'Agostino et al. [39] used actinometry for studies of F and O atoms and CO and CO<sub>2</sub> molecules using Ar and N<sub>2</sub> as actinometers.

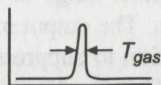
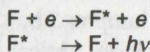
Although actinometry is not an accurate technique, it can provide a good approximation for the evaluation of densities of species. Actinometry does not, however, solve the problem associated with emissions originating from dissociative processes. The spatially resolved quantity  $In_{Ar}$  can provide information about the uniformity of plasma density. In an RF plasma, concentrations and energies of electrons and ions change dramatically during an RF cycle, leading to a high degree of modulation in emissions excited by ion and electron impact. Ion modulation becomes limited at  $\approx 3$  MHz for typical ions ( $Cl_2^+$ ,  $CF_3^+$ , etc.), while electron energy can be modulated up to  $\approx 100$  MHz. As a result, time-resolved emission spectroscopy can distinguish between emissions caused by electron impact (Eq. (5.16)) and those caused by impact of heavy particles such as described by Eq. (5.20).

The process described by Eq. (5.16) can also be distinguished from other emission processes by measurement of line shapes.

The light-emitting particles possess translational velocities that cause a Doppler shift to the frequency of the radiation. Since the electron mass is very small compared to atomic or molecular masses, the velocity distribution of the emitting species formed by the reaction described by Eq. (5.16) is the same as for species in the ground state. The velocity distribution of the particles in the ground state is, in turn, determined by the gas temperature. Excited species formed by other impact processes will be created with significantly different translational energy as illustrated schematically in Fig. 5-12.

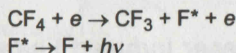
### Mechanism of F-atom Emission in Plasmas and Resultant Line Widths

#### 1. Electron Impact Excitation

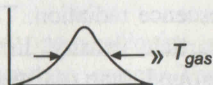
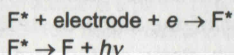


Doppler Width Determined by  $T_{gas}$

#### 2A. Dissociative Excitation, for example,



#### 2B. Electrode Bombardment, for example,



Doppler Width Determined by Translational Energy in Recoiling F-Atom.  $T_F \gg T_{gas}$ .

**Fig. 5-12** Effect of collision type on Doppler widening of emitted lines (from [32], reprinted with permission from *Plasma Diagnostics*, vol. 1, 1989).



### 5.3.2 Absorption Spectroscopy

The major drawback of the emission spectroscopy is that it can only provide information about species that are already excited and that may form only a small fraction of the total number of species in question. Absorption spectroscopy, on the contrary, provides for this deficiency and can supplement the optical emission diagnostics. Absorption spectroscopy, however, requires higher resolution because otherwise sharp absorption lines may be lost in the background. Cold plasmas are quite amenable to absorption spectroscopy diagnostics, yet relatively few plasma diagnostic studies have been performed with this technique.

The main advantage of the absorption spectroscopy technique is its ease of implementation in most cases. If light is transmitted through a plasma, its intensity,  $I_n$ , at a given wavelength, is given by Beer's law,

$$I_n = I_{n_0} e^{-\sigma n l} \quad (5.27)$$

where  $I_{n_0}$  = intensity of incident light at the considered wavelength

$\sigma$  = cross section for absorption

$n$  = density of absorbing species

$l$  = optical path length

If the absorption cross sections of the different species are known, the absolute concentrations can be calculated from the intensity of the transmitted light.

The experimental setup used for optical emission measurements can easily be adapted for absorption measurements by adding an external light source. Light from the source, which can be a lamp or a laser, is directed through the discharge onto the entrance slit of the monochromator. The optimum light source depends on the species that have to be detected. For diatomic and polyatomic species, a continuum light source is best suited. A deuterium lamp can be used in the ultraviolet range of 160–350 nm, while a tungsten lamp is suitable in the visible region. The output of the lamp can be chopped and combined with phase-sensitive detection to suppress the large optical background from the plasma.

The disadvantages of absorption spectroscopy are that it requires vacuum ultraviolet sources for many elements of interest, it has a low sensitivity in the infrared region of the spectrum, and spectrums of multicomponent mixtures can overlap.

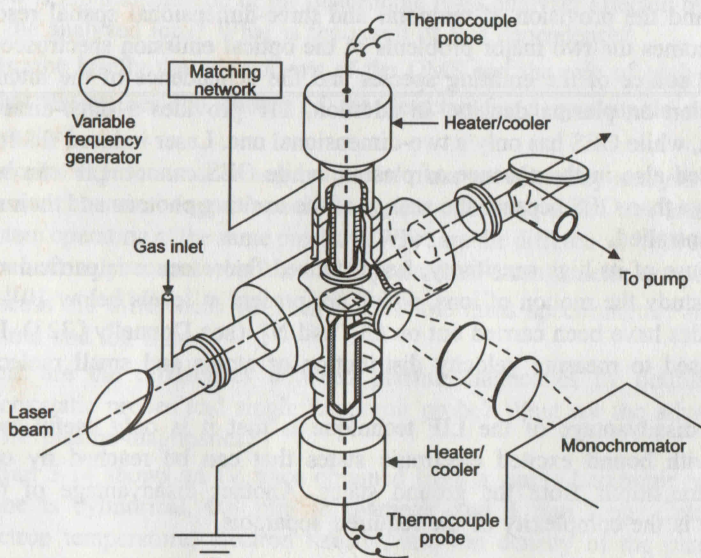
### 5.3.3 Laser Induced Fluorescence

Particles excited by absorption of radiation may undergo radiative transition in which light of the same or different frequency is emitted. When the transition occurs between states of the same multiplicity, the particle is said to emit fluorescence radiation. The intensity of the fluorescent radiation is proportional to the particle density. In principle, the density of molecules, atoms, and ions in the ground state, as well as in metastable or unstable, excited states, can be determined by measuring the intensity of the fluorescence. Due to the fact that fluorescence times are much shorter than a microsecond, it is necessary to use laser

pulses with a width of the order of nanoseconds for the excitation of the fluorescence. This diagnostic technique is called *laser induced fluorescence (LIF)*. Laser induced fluorescence is the most used diagnostic tool of the laser-based techniques; further discussions on LIF can be found in review papers such as [32, 34, 40].

The LIF technique employs a laser whose frequency is tuned to excite a resonance between a lower electronic state and an excited electronic state of a chosen species. A tunable dye laser is generally used to tune the frequency of the exciting light. Continuous tunable dye lasers are pumped by  $N_2$  lasers, Nd-YAG lasers, excimer lasers, or flash lamps for pulsed output or by  $Ar^+$  and  $Kr^+$  lasers for CW radiation. Dye lasers, pumped by either an excimer laser or a Nd-YAG laser are highest in peak power and are the most common tunable pulsed sources. Excimer laser pumped dye lasers provide output from 330–900 nm, while frequency doubled and tripled Nd-YAG lasers can be used to pump dye lasers between  $\sim 380$  and 900 nm.

The experimental setup is illustrated in Fig. 5-13. The laser is usually placed in a horizontal position, parallel to the surface of the discharge electrode. By



**Fig. 5-13** Experimental setup for laser induced fluorescence in a parallel plate plasma reactor (from [32], reprinted with permission from *Plasma Diagnostics*, vol. 1, 1989).

such an arrangement the discharge can be probed in a direction perpendicular to the electrode surface by translating the laser beam and detection optics. The fluorescence is detected at right angles with a monochromator or a filter in front of a photomultiplier tube or by an optical multichannel analyzer. To discern



between the fluorescence emission and the plasma background, the spectrally resolved emission is detected and amplified using a boxcar integrator with gated detection. In this arrangement, the signal is recorded only during a very narrow time gate, which is selected to coincide with the timing of the laser pulse, thus identifying only the LIF emissions.

To use the LIF technique, the investigated species must fluoresce with a reasonable quantum efficiency, and the tunable laser must be able to match a transition for the investigated species. The last requirement is impeding the application of LIF for studies of atomic species such as F, O, H, and Cl. The lowest energy of electronic transition of these species is in the vacuum ultraviolet, beyond the reach of commercially available tunable lasers.

Laser induced fluorescence measurements are characterized by very high sensitivities. Molecular species at a density as low as  $10^6$ – $10^7$   $\text{cm}^{-3}$  can be detected by LIF. The detection sensitivity decreases to a minimum of  $10^{13}$   $\text{cm}^{-3}$  for atomic species whose excitation usually requires simultaneous absorption of two photons.

The advantages of laser induced fluorescence include, in addition to the high sensitivities, selectivity (there is usually no detectable interference from other species) and the provision of temporal and three-dimensional spatial resolution. LIF overcomes the two major problems of the optical emission spectroscopy: the undefined source of the emitting species and the dependence of the intensity of the emission on plasma density. In addition, LIF provides a three-dimensional resolution, while OES has only a two-dimensional one. Laser induced fluorescence can be used also in the absence of plasma, while OES cannot. LIF can be more quantitative than OES because the energy of the exciting photons and their number can be controlled.

Because of its high sensitivity, laser induced fluorescence is particularly well suited to study the motion of ions, which are present at levels below  $10^{11}$   $\text{cm}^{-3}$ . Such studies have been carried out on  $\text{Cl}_2^+$  and  $\text{N}_2^+$  (see Donnelly [32]). LIF can also be used to measure velocity distribution of atoms and small molecules in plasma.

The disadvantage of the LIF technique is that it is only useful for those species with bound excited electronic states that can be reached by optically allowed transitions from the ground states. Another disadvantage of the LIF technique is the complexity of the required apparatus.

### 5.3.4 Summary

Optical plasma diagnostic methods are widely used for investigation of chemical processes in cold plasmas and plasma-surface interactions. Optical methods are used both for studying basic plasma phenomena and for analysis of processing plasmas. No single optical method can be regarded as a universal plasma diagnostic tool. Several complimentary techniques are required to provide detailed information on a variety of processing plasmas.

Of all optical techniques, optical emission is the easiest to implement and can provide qualitative data on concentrations of species. OES provides real time information that can be used to improve control of plasma processing techniques such as etching and deposition. It can also provide quantitative information on relative number densities as well as discharge kinetics and dynamics.

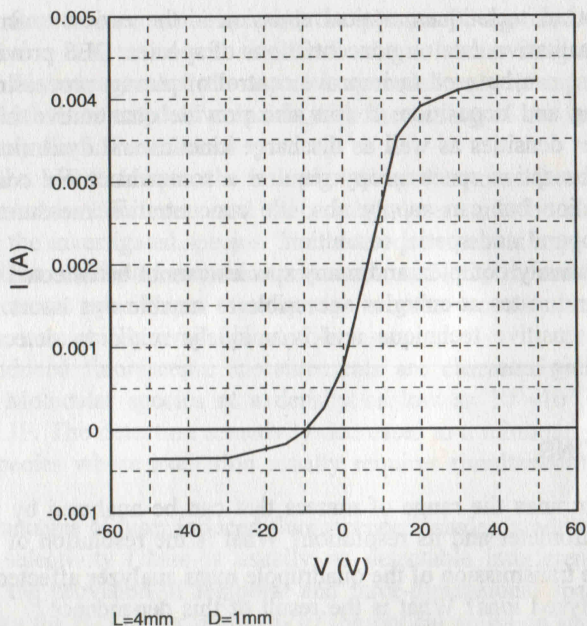
Optical absorption spectroscopy requires a somewhat more complex degree of instrumentation but can supply absolute concentration measurements and is capable of temporal and spatial resolution.

LIF is relatively complex and many species cannot be detected due to a lack of excited bound states at energies accessible to tunable dye lasers. Yet, it is by far the most sensitive technique and is uniquely suited to detection of trace species, including ions.

## 5.4 QUESTIONS

1. What determines the range of masses that can be analyzed by a quadrupole mass spectrometer and its resolution? What is the resolution of the QMS?
2. How is the transmission of the quadrupole mass analyzer affected by the mass of the analyzed ions? What is the result of this dependence?
3. Describe briefly the components of the QMS and the role of each of them.
4. What determines the choice of the detector for a quadrupole mass spectrometer?
5. Describe experimental arrangements for mass spectrometry analysis of a low-pressure chemical vapor deposition system operating at 0.1 torr and a plasma system operating at the same pressure. What are the differences between the two types of analyses and what kind of experimental arrangements are possible?
- ✓ 6. Discuss the differences between quadrupole mass spectrometric analyses of neutral and ion fluxes.
- ✓ 7. What are the differences between plasma diagnostics by double floating electrostatic probes and single Langmuir probe? What are the advantages of DFEP plasma diagnostics?
- ✓ 8. Figure 5-14 shows an IV trace obtained from a single Langmuir probe. The probe is cylindrical, 0.8 mm in diameter and 3 mm long. Calculate the electron temperature, electron density, and ion density of the plasma from which this probe characteristic was obtained.
- ✓ 9. a. What affects the accuracy of evaluation of plasma properties by electrostatic probe measurements?  
b. What can preclude the use of electrostatic probes for plasma diagnostics?
- ✓ 10. a. What are the differences between the experimental setups for optical emission spectroscopy and absorption spectroscopy?  
b. Which plasma species can be analyzed by each method?
11. a. What is actinometry and how can it be used for plasma analyses?





**Fig. 5-14** I-V trace of single Langmuir probe for question 8.

- b. What types of gases can be used for actinometry and what conditions do they have to satisfy?
12. What are the principles of LIF and what are its advantages and disadvantages for plasma diagnostics?

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