MASS SPECTROMETRIC STUDIES OF POSITIVE IONS IN rf GLOW DISCHARGES

J. W. Coburn

IBM Almaden Research Center
650 Harry Road
San Jose, California 95120-6099

ABSTRACT: Mass spectrometric analysis of positive ions extracted from glow discharges is a common experimental procedure most often motivated by basic research considerations. An exception is the fairly recent application of this technique to the elemental analysis of solids. The experimental aspects of mass spectrometric analysis of plasma ions are discussed, and it is concluded that the insertion of an electrostatic deflection energy analyzer between the sampling orifice and the quadrupole mass filter is worthy of serious consideration in many research projects of this type. Several examples of the value of energy analysis are given. A brief discussion of the use of this technique in plasma process development is presented, and it is concluded that mass spectrometric ion sampling is not an obvious first choice in an applied environment but holds considerable promise in a basic research program.

1. INTRODUCTION

Mass spectrometric sampling of glow discharges has been used by many workers with a wide range of objectives. Mass spectrometers can be used in several ways to study glow discharges: 1) direct sampling of positive ions formed in the discharge, 2) line-of-sight sampling of neutral species from the discharge most often accompanied by modulation of the beam to improve the signal-to-background ratio, and 3) analysis of the discharge gas without line-of-sight, usually through a controlled leak valve. The relative advantages and disadvantages of these three methods are listed in Table I.

TABLE I.

Mass Spectrometric Methods for Plasma Diagnostics

Method	Ion Sampling	Neutral Sampling	
		Line of Sight	Leak Valve

Advantages	- High sensitivity
	- Minimal discrimination
	  for various ionic species
		- Reactive and/or
		  condensible species
		  can be detected
			- Simple apparatus

Disadvantages	- Complex apparatus
	- Ions not representative
	  of neutral species
	  concentrations
		- Complex apparatus
		- Not very sensitive
		- Unambiguous ,
		  determination of
		  parent molecules
		  often difficult
			- No possibility
			  of detecting
			  reactive or
			  condensible species
			- Affected by
			  mass spectrometer
			  pump system

Applications	- Solids analysis
	- Ion-molecule reaction
	  studies
	- Characterization of
	  discharge
		- Basic studies
		  of plasma
		  chemistry
			- Process control
			  and process
			  characterization

It should be noted that in all these methods, an auxiliary vacuum pumping system is needed, and in the first two cases, an intimate connection to the discharge is required. In all cases, only species arriving at the plasma container wall can be detected. In this regard, optical diagnostics[1-3] of glow discharges (e.g., emission spectroscopy with and without actinometry,[4] laser-induced fluorescence) have a significant advantage over mass spectrometric methods in that the former are nonintrusive and can easily monitor species concentration profiles[5,6] well away from the plasma boundaries.

The present discussion will be limited to mass spectrometric sampling of positive ions from a glow discharge (emphasizing rf glow discharges) and will describe the experimental aspects of the method with some examples of mass and energy spectra of ions extracted from low pressure rf glow discharges.

2. EXPERIMENTAL CONSIDERATIONS

One of the first questions that must be addressed in the mass spectrometric sampling of positive ions from glow discharges concerns the type of mass spectrometer that should be used. The quadrupole mass filter is by far the most popular instrument for this application for the following reasons: 1) It accepts ions with kinetic energies in the range of a few eV to a few tens of eV. 2) The potential of the mass filter itself can be easily varied. 3) Quadrupole mass filters are compact, compatible with ultrahigh vacuum operation and are readily available from many vendors. The major disadvantages of the mass filters is their relatively low mass resolution which normally does not allow separation of several species with the same nominal mass number (e.g., CO^+, N_2^+, $C_2H_4^+$, Si^+ and Fe^{++} at mass 28) and the decreasing transmission (i.e., sensitivity) at higher mass numbers.

The experimental situation prevailing in ion extraction from glow discharges is illustrated in Fig. 1 with the geometrical aspects shown at the top and the potential distribution shown below. In this illustration, the potential of the sampling orifice is shown to be at ground potential, and the positive ions are accelerated to the orifice by the electric field in the sheath region between the bulk plasma and the grounded wall. In rf glow discharges, the plasma potential varies in time, in phase with the applied rf voltage and can have an average value as low as 10 or 20 volts or as high as several hundreds of volts depending on the plasma reactor geometry[7] and the way in which the rf voltage is coupled to the powered electrode.[8] For applied rf voltages with frequencies higher than a few MHz, the ions usually require several rf cycles to traverse the sheath thickness and consequently arrive at the grounded wall or orifice with an energy corresponding to the time average of the plasma potential. If the applied frequency is too low or if the plasma density is very large, the ions will traverse the sheath in a time comparable to or less than one rf period and consequently will arrive at the grounded orifice with a spread in energy determined by the instantaneous value of the plasma potential during the ion transit through the sheath. An example of this will be presented later (see Fig. 5).

It is preferable to operate the orifice at ground potential as this is the least perturbing situation for the plasma. The orifice can be biased negatively without grossly influencing the discharge but positive bias voltages are not acceptable. If the orifice is biased positively, large electron currents flow to the orifice, often increasing the plasma potential[9] and upsetting the charge balance to other surfaces in capacitively coupled rf systems. Thus, negative ions cannot be extracted from rf discharges without a significant perturbation of the plasma.

The two factors which determine the experimental approach needed for optimum ion sampling are the magnitude of the plasma potential and the extent to which there are ion-neutral collisions or ion formation processes in the sheath region. The latter situation is determined by the magnitude of the ion mean free path relative to the sheath thickness. The ion mean free path is very much dependent on the ionic species involved (e.g., the mean free path for Ar^+ in Ar is considerably less than the mean free path of Ar_2^+ or ArH^+ in Ar because of the large resonant charge exchange cross section between Ar^+ and Ar). The simplest possible experimental situation is a low plasma potential (e.g., 20 volts), an ion mean free path for all ions which is much larger than the sheath thickness (i.e., collisionless extraction), and an ion transit time through the sheath much longer than an rf period. Under these conditions, all ions will arrive at the sampling orifice with about 20 eV of energy, and the quadrupole mass filter can be operated at ground potential. However, this situation is not often encountered.

In most situations, there will be ion-neutral collisions and/or ion formation processes in the sheath resulting in ions arriving at the sampling orifice with a range of energies and often the plasma potential is so large that the resolution of a grounded quadrupole mass filter is badly degraded by the energetic ions. At this point, the primary interest of the investigator must be considered. If the research objective is to study ions coming from the bulk plasma only, then one can operate the quadrupole mass filter a few volts below the plasma potential, and thus electrostatically reject ions formed in the sheath or ions which have suffered energy loss during transit through the sheath. Alternatively, one could insert a retarding grid structure between the sampling orifice and the quadrupole mass filter, and accomplish the same thing. However, it will be necessary to operate the quadrupole mass filter within about 20 volts of the plasma potential to obtain optimum performance of the filter.

However, the preferred approach is to insert a deflection-type of electrostatic energy analyzer between the sampling orifice and the quadrupole mass spectrometer. Spherical[10] or cylindrical mirror analyzers[11] are preferred for this application because of their point-to-point focussing characteristics. The conventional cylindrical deflection analyzer[12] is less appropriate because of its line-to-line focussing behavior. Once the decision has been made to introduce the additional experimental complexity of an electrostatic energy analyzer, one should not hesitate to arrange to use the instrument in the best way; namely, the so-called constant ΔE mode where the voltage across the energy analyzer deflection plates is kept constant and the center-line potential of the analyzer is swept through the ion

energy distribution. The quadrupole mass filter potential should also be swept with the energy analyzer, and in general the quadrupole mass filter potential will be biased with respect to the analyzer by an amount chosen to optimize the ion energy in the filter. In order to operate the system in this way, it is necessary to insert an electrode structure between the sampling orifice and the energy analyzer which will allow retardation or acceleration of the ion beam without focussing (i.e., without a change in the ion transmission). A planar electric field is most commonly used for this purpose. When such an arrangement is used, the energy of the ions being analyzed by the energy analyzer and the quadrupole mass filter is constant, and the influence of ion energy on the transmission of these instruments is eliminated. An example of such an apparatus is shown in Fig. 2,[8] and an example of the voltages used in such a system is given in Table II.

TABLE II.

Example of Ion Sampling in the Constant ΔE Mode

Energy of Ions Being Analyzed (with respect to ground)	Potential of Analyzer Center Line(a) (with respect to ground)	Potential of Quadrupole Mass Filter(b) (with respect to ground)
100	56	95
50	6	45
0	−44	−5

(a)Deflection voltage across electrostatic energy analyzer is set to transmit 44 eV ions.

(b)Quadrupole mass filter operation has been found to be optimized for 5 volt ions. Quadrupole is, therefore, biased 39 volts positive with respect to energy analyzer center-line voltage, and the potentials of both instruments are swept together through the ion energy distribution.

It should be mentioned that, in general, energy analysis by the retarding potential method is not adequate for this application. As was mentioned earlier, it is possible to use a retarding potential approach to examine the ions with the largest energy but one is forced to observe the lower energy ions in the presence of the higher energy ions, and for situations where there is a large spread in ion energies, this is not satisfactory. Furthermore, energy distributions obtained with retarding potential techniques are less precise than those obtained with deflection techniques, particularly when the retarding potential grids are followed by a detector with a small acceptance solid angle (i.e., the quadrupole mass filter). Ion which have enough energy to pass through the retarding potential grids are easily slightly deflected

by electrostatic imperfections in the retarding grid structure and thus can avoid detection by the quadrupole mass filter.

So far nothing has been said about the sampling orifice itself although this has been discussed at length in the literature.[13-15] Ideally, the length or thickness of the orifice should be much less than the orifice diameter to eliminate effects of collisions with the sides of the orifice. The orifice conductance will then be given by $U = 11.6A$ where A is the orifice area in cm^2 and U is the conductance in liters/sec. The diameter of the orifice should be much less than the sheath thickness so that the plasma will not be perturbed by the presence of the orifice. The most stringent requirement on orifice diameter usually arises from the allowable collisions between the extracted ions and neutral species downstream (i.e., analysis side) of the orifice. The attenuation of the extracted ion beam, a distance L from the orifice caused by collisions with background gas molecules, can be calculated[16] in terms of the upstream gas density n_0, the ion-neutral cross section σ, the orifice conductance U and the pumping speed in the analysis chamber S

$$I(L) = I(0) \exp[-\sigma n_0 UL/(U+S)] .$$

However, this is rarely the limiting factor on the size of the orifice. In almost all cases of practical importance, the collisional attenuation of the ion beam is not determined by collisions with the static background gas but with the neutral plume of gas streaming through the orifice with the ions. The ion speed is much greater than the neutral particle speed, and thus the neutral species streaming through the orifice behave as a local static pressure. The attenuation of an ion beam caused by collisions with this gas plume is[16]

$$I(L) = I(0) \exp[-\sigma R n_0 \tan^{-1}(L/R)]$$

where R is the orifice radius and L is the downstream distance from the orifice. For the case $L >> R$ which is always the case experimentally,

$$I(L) = I(0) \exp[\frac{-\sigma R n_0 \pi}{2}] .$$

It is this expression which poses the most stringent lower limit on orifice size during ion extraction from most rf glow discharges.

Two additional comments will be made prior to concluding this experimental section. The first relates to those situations where the research interest and the ion extraction conditions are such that a deflection energy analyzer is not deemed necessary. The analytical method, glow discharge mass spectrometry,[17] might be an example of such a situation. It is tempting in these situations to place the quadrupole mass filter on axis with the sampling orifice so there is a direct line-of-sight from the discharge through the mass filter. The effects of photons and energetic particles on the particle multipliers used to amplify the mass filter output are well known, and all modern quadrupole mass filters are constructed with the first dynode of the multiplier displaced from the axis of the mass filter so as to eliminate the possibility of spurious background signals caused by unwanted particles striking the multiplier first dynode. Although this approach eliminates most of the background signal, there is still a source of background which is not eliminated by offset particle multipliers. The energetic neutral particles (i.e., photons, metastables, fast neutrals) after traversing the quadrupole rod structure will often eject secondary electrons upon a collision with a surface (e.g., quadrupole housing, Faraday cup, etc.). These electrons can, under certain conditions, be accelerated by the various electric fields at the end of the quadrupole (e.g., rf field from the rods, dc field drawing positive ions to the first dynode of the multiplier) and can then form positive ions upon collision with background gas molecules. The ions so-formed are efficiently collected by the first dynode of the multiplier, causing an unfiltered dc background signal proportional to the discharge parameters and the background gas pressure. This entire problem can be eliminated by moving the quadrupole slightly off axis so that neutral species and photons from the discharge cannot traverse the quadrupole mass filter. The ions can be electrostatically deflected appropriately so as to be incident normally into the quadrupole. This procedure is recommended for applications such as solids analysis where sensitivity is critical.

A final comment concerns the advisability of ion-sampling through the rf-powered electrode in order to get a better understanding of cathodic processes such as reactive ion etching. This author feels that this is an ill-advised adventure. One must be concerned about issues such as whether or not the entire detection system is driven at the rf cathodic potential so that ions experience only dc fields after passing through the orifice, or whether one should try to evaluate the influence of an rf field on the ion trajectories after extraction and operate the detection system at a dc potential. If the interest is in ion energies in high-voltage sheaths, it would seem far more appropriate to use a rf hollow cathode geometry for the discharge. This causes a high-voltage sheath at the grounded electrode[8] where the

previously described approach to ion extraction can be used, provided the quadrupole mass filter can be safely operated at voltages several hundreds of volts above ground.

3. EXPERIMENTAL RESULTS – ENERGY ANALYSIS

There are no widespread technological applications of energy analysis of ions extracted from glow discharges known to this author. There are many instances in which such measurements have been made, but in each case, the motivation comes from basic science interest. One of the most well known of such studies is that of Davis and Vanderslice[18] in which the effect of resonant charge exchange reactions on the energy distribution of ions arriving at the cathode of a dc glow discharge was studied. A similar study was carried out by Houston and Uhl.[19] In this section, some results obtained with the system shown in Fig. 2 will be reviewed with the goal being to emphasize the usefulness of energy analysis in studies of positive ions extracted from rf glow discharges.

A very clear example of this is shown in Fig. 3 in which two positive ion mass spectra are shown[20] – the upper spectrum represents those ions which traversed the sheath and extraction regions essentially without collisions, whereas the lower spectra represents ions which were created (or have energies characteristic of ions created) slightly downstream of the sampling orifice as shown in the figure. Such information is very helpful in understanding the overall ion extraction situation. A second example in a similar discharge is shown in Fig. 4. This is a plot of the plasma potential as a function of time after establishing a C_2F_4 discharge in a metal container. The time dependence of the plasma potential is believed to be caused by the deposition of a dielectric fluoropolymeric thin film on the container walls which alters the electrical characteristics of the rf discharge. The effect was eliminated by lining the walls with a thick ($\sim$ 3 mm) dielectric liner which served to provide a constant impedance to the discharge. Here, the energy analysis allowed a rapid identification of a problem which might have been difficult to diagnose using mass spectrometry alone.

The influence of the ion transit time through the sheath can also be clarified using ion energy analysis methods. Figure 5 shows the energy distribution for ions traversing a low-voltage ground sheath at 100 kHz and 13.56 MHz rf excitation frequencies.[21] At 13.56 MHz, the ion requires several rf periods to traverse the sheath, and as a result, essentially all the ions arrive with an energy representative of the time-averaged plasma potential. The situation is completely different for 100 kHz rf excitation where the ion transit time is much less than one rf period. In this situation, the ion energy

distribution represents $V_p(t)$, the temporal behavior of the plasma potential as is illustrated in Fig. 6.[21] An intermediate case is shown in Fig. 7 where the 13.56 MHz rf plasma density has been increased by confining the discharge inside a small cylindrical volume.[9] As the discharge density increases, the sheath thickness decreases, and in this situation, the high mass Eu^+ ion requires several rf cycles to traverse the sheath, whereas the lighter H_3^+ ion traverses the sheath in a time comparable to or less than an rf period.

The extent to which collisions in the sheath depend upon the ion involved is shown in Fig. 8. In this figure, the energy distributions for Ar^+, ArH^+ and Al^+ extracted from the same discharge are shown. In this study, the rf electrode was aluminum and the Al^+ signal arises from neutral Al atoms which are sputtered from the electrode and ionized during their transit across the discharge to the sampling orifice. For this set of spectra, the sampling orifice was biased at -50 volts to provide an approximately 75 volt potential drop across the sheath. The peak at $+25$ volts on the right end of the spectra is due to ions formed at the plasma potential which undergo essentially collisionless extraction. The peak at -50 volts represents ions formed in the immediate region of the sampling orifice, and this peak shifts as the sampling orifice potential is varied. The reason for such a pronounced peak is not fully understood but is believed to be associated with the fact that ions formed in the vicinity of the sampling orifice are collected with a very large efficiency by the adjacent negatively biased (-100 volt) extraction electrode, whereas ions formed in the sheath region away from the sampling orifice are much less efficiently collected. However, it is easy to note the very large differences in these energy distributions where Ar^+ ions experience many charge exchange collisions leading to a large number of low energy ions, whereas Al^+ ions undergo no observable collisions.

4. EXPERIMENTAL RESULTS – MASS ANALYSIS

Although there are many wide-ranging studies involving ion extraction from glow discharges, most fall into one of three categories: 1) elemental analysis of solids, 2) mechanistic studies of processing glow discharges (e.g., sputter deposition, reactive ion etching, plasma polymerization, plasma-enhanced chemical vapor deposition, etc.), 3) basic studies of ion-molecule reactions frequently in flowing afterglow plasmas.[15] This latter area, which rarely involves rf glow discharges, is beyond the scope of this discussion.

The use of glow discharges for solids analysis has evolved significantly over the past 15 years. Three major discharge configurations have been used:

1) The low pressure electron cyclotron resonance plasma method developed by Oechsner and colleagues[22-24] (known as sputtered neutral mass spectrometry - SNMS)

2) The medium pressure 13.56 MHz rf glow discharge method developed by Coburn and colleagues[17,25,26] (known as glow discharge mass spectrometry)

3) The high pressure primarily dc plasma methods developed by Harrison and co-workers[27-29] (also known as glow discharge mass spectrometry).

Each of these approaches has advantages and disadvantages which will not be discussed here. It is sufficient to point out that these techniques can provide very sensitive elemental analysis of solids without significant matrix effects. Thus, unlike secondary ion mass spectrometry, these glow discharge methods have the potential of carrying out quantitative analyses without requiring reference standards. Furthermore, unlike Auger electron spectroscopy, X-ray photoelectron spectroscopy and other surface analysis methods, the glow discharge approach is not influenced by relative sputtering yields once a steady state condition has been achieved.[30]

An example of portions of a mass spectrum obtained with the rf medium pressure approach using a copper electrode is shown in Fig. 9.[31] The ppm level is easily observable here, and ppb concentrations have been routinely measured using higher erosion rates in the high pressure regimes.

Whereas electron impact ionization is known to be dominant in the low pressure, high electron density electron-cyclotron-resonance plasmas used by Oechsner et al.,[22-24] Penning Ionization is believed to be a dominant ionization process in the higher pressure approaches. Some evidence for this conclusion is presented in Fig. 10 which shows the ion mass spectra obtained during the analysis of a EuO:6%Fe electrode material in both argon and neon glow discharges.[32] These spectra are similar except for the oxygen signal which can be seen only in the neon glow discharge. The energy of the metastable states of argon are 11.55 and 11.72 eV, whereas for neon, these states have energies of 16.62 and 16.71 eV. Thus, O^+ with an ionization potential of 13.6 eV can be formed through Penning ionization only in the neon discharge

$$Ne^m + O \longrightarrow Ne + O^+ + e.$$

Iron and europium both have ionization potentials below the metastable levels of argon and hence can be Penning-ionized in both the argon and neon discharges.

Other secondary ionization processes, such as associative ionization,[33] produce other ion signals such as $CuAr^+$,[34] $EuAr^{++}$,[35] ArO^+,[36] etc., which can result in spectral interference during analysis. These interfering species are not observed in the low pressure electron impact ionization method.

The other major application of mass spectrometric ion sampling of glow discharges is the study of important glow discharge-based materials processing technologies. Probably the most significant results have been obtained in studies of reactive sputter deposition of thin films where correlations between the glow discharge mass spectrometric data and the thin film properties have been demonstrated.[37-39] However, the apparatus complexity associated with this technique has impeded its widespread implementation. Mass spectrometric ion analysis has been used to study the mechanistic aspects of reactive gas glow discharge methods such as plasma-assisted etching, plasma polymerization or plasma-enhanced chemical vapor deposition, but only marginal insight has resulted from most of these studies. The extreme complexity of the ion spectra coupled with the fact that neutral species play an important role in many of these processes tend to limit the mechanistic insight that can be realized from such studies. For example, in the CF_4 plasma-assisted etching of Si and SiO_2, F atoms are believed to be the most important species leading to the volatilization of Si by forming SiF_4. However, F^+ ions are a minority species in the ion spectra of such discharges,[40] as shown in Fig. 11. CF_3^+ is by far the dominant positive ion in a CF_4 glow discharge because of both the predominance of the dissociative ionization process $CF_4 + e \longrightarrow CF_3^+ + F + 2e$ and the stability of CF_3^+ in collisions with the parent CF_4 molecule. F^+ is formed only at very low concentrations because of its high ionization potential (17.4 eV). Consequently, optical studies of such discharges have proven to be far more useful in providing basic insight as to the physical and chemical mechanisms involved. This is not to say that nothing can be learned from ion extraction studies of reactive gas glow discharges. Some useful qualitative ideas have been generated, for example, the two spectra in Fig. 11 show clearly the influence of the material being etched (Si versus SiO_2) on the gas phase species. This observation, combined with others of a similar nature, led to the formulation of the fluorine/carbon ratio approach to the qualitative characterization of fluorocarbon discharge plasma-assisted etching.

5. SUMMARY

A discussion has been presented of mass spectrometric sampling of ions from glow discharges emphasizing rf glow discharges. Some of the experimental considerations are discussed in detail, and it is suggested that energy analysis prior to mass analysis with a quadrupole mass filter is highly desirable in many research applications. The most important application of this technique appears to be in the elemental analysis of solids. It is concluded that mass spectrometric ion analysis is not an approach to be seriously considered to assist in the development of glow discharge-based materials processing technologies. The optical methods are much more easily implemented and usually provide more valuable information. However, mass spectrometric ion analysis of reactive gas plasmas does seem very appropriate for basic research studies as there is a potential for new discovery and new insight.

6. ACKNOWLEDGMENTS

7. REFERENCES

1. Gottscho, R.A. and Miller, T.A., *Pure and Appl. Chem.* 56 (1984) 189.

2. Dreyfus, R.W., Jasinski, J.M., Walkup, R.E. and Selwyn, G.S., *Pure and Appl. Chem.* 57 (1985) 1265.

3. Miller, T.A., *J. Vac. Sci. Technol. A* 4 (1986) 1768.

4. Coburn, J. W. and Chen, M., *J. Appl. Phys.* 51 (1980) 3134.

5. Gottscho, R.A., Davis, G.P. and Burton, R.H., *Plasma Chem. Plasma Process* 3 (1983) 193.

6. Selwyn, G.S., *J. Appl. Phys.* 60 (1986) 2771.

7. Koenig, H.R. and Maissel, L.I., *IBM J. Res. Dev.* 14 (1970) 168.

8. Köhler, K., Coburn, J.W., Horne, D.E., Kay, E. and Keller, J.H., *J. Appl. Phys.* 57 (1985) 59.

9. Coburn, J.W. and Kay, E., *J. Appl. Phys.* 43 (1972) 4965.

10. Purcell, E.M., *Phys. Rev.* 54 (1938) 818

11. Sar-El, H.Z., *Rev. Sci. Instr.* 38 (1967) 1210.

12. Hughes, A.L. and Rojansky, V., *Phys. Rev.* 34 (1929) 284.

13. Drawin, H.W., in "Plasma Diagnostics," W. Lochte-Holgrevin, ed. (North-Holland, Amsterdam, 1968), pp. 777-841.

14. Hasted, J.B., *Intern. J. Mass Spectrom. Ion Phys.* 16 (1975) 3.

15. Smith, D. and Plumb, I.C., *J. Phys. D* 6 (1973) 1431.

16. Coburn, J.W. and Kay, E., *J. Vac. Sci. Technol.* 8 (1971) 738.

17. Coburn, J.W., Taglauer, E. and Kay, E., *J. Appl. Phys.* 45, (1974) 1779.

18. Davis, W.D. and Vanderslice, T.A., *Phys. Rev.* 131 (1963) 219

19. Houston, J.E. and Uhl, J.E., *Sandia Laboratories Research Report* SC-RR-71-0122 (1971).

20. Kay, E., Coburn, J.W. and Kruppa, G., *Le Vide* 183 (1976) 89.

21. Köhler, K., Horne, D.E. and Coburn, J.W., *J. Appl. Phys.* 58 (1985) 3350.

22. Oechsner, H. and Gerhard, W., *Phys. Lett. A* 40 (1972) 211.

23. Oechsner, H. and Gerhard, W., *Surf. Sci.* 44 (1974) 480.

24. Oechsner, H. and Wucher, A., *Appl. Surf. Sci.* 10 (1982) 342.

25. Coburn, J.W. and Kay, E., *Appl. Phys. Lett.* 19 (1971) 350.

26. Coburn, J.W., Eckstein, E.W. and Kay, E., *J. Appl. Phys.* 46 (1975) 2828.

27. Harrison, W.W. and Magee, C.W., *Anal. Chem.* 46 (1974) 461.

28. Mattson, W.A., Bentz, B.L. and Harrison, W.W., *Anal. Chem.* 48 (1976) 489.

14

29. Bruhn, C.G., Bentz, B.L. and Harrison, W.W., *Anal. Chem.* 51 (1979) 673.

30. Coburn, J.W., *J. Vac. Sci. Technol.* 13 (1976) 1037.

31. Coburn, J.W. and Harrison, W.W., *Appl. Spectrosc. Rev.* 17 (1981) 95.

32. Coburn, J.W. and Kay, E., *Appl. Phys. Lett.* 18 (1971) 435.

33. Lampe, F.W., in "Ion-Molecule Reactions," J.L. Franklin, ed. (Plenum, New York, 1972), p. 601.

34. Coburn, J.W., Eckstein, E.W. and Kay E., *J. Vac. Sci. Technol.* 12 (1975) 151.

35. Coburn, J.W. and Kay, E., *J. Chem. Phys.* 64 (1976) 907.

36. Aita, C.R. and Lad, R.J., *J. Appl. Phys.* 60 (1986) 837.

37. Purdes, A.J., Bolker, B.F.T., Bucci, J.D. and Tisone, T.C., *J. Vac. Sci. Technol.* 14 (1977) 98.

38. Hecq, M. and Hecq. A., *Thin Solid Films* 76 (1981) 35.

39. Aita, C.R., Lad, R.J. and Tisone, T.C., *J. Appl. Phys.* 51 (1980) 6405.

40. Coburn, J.W. and Winters, H.F., *J. Vac. Sci. Technol.* 16, (1979) 391.
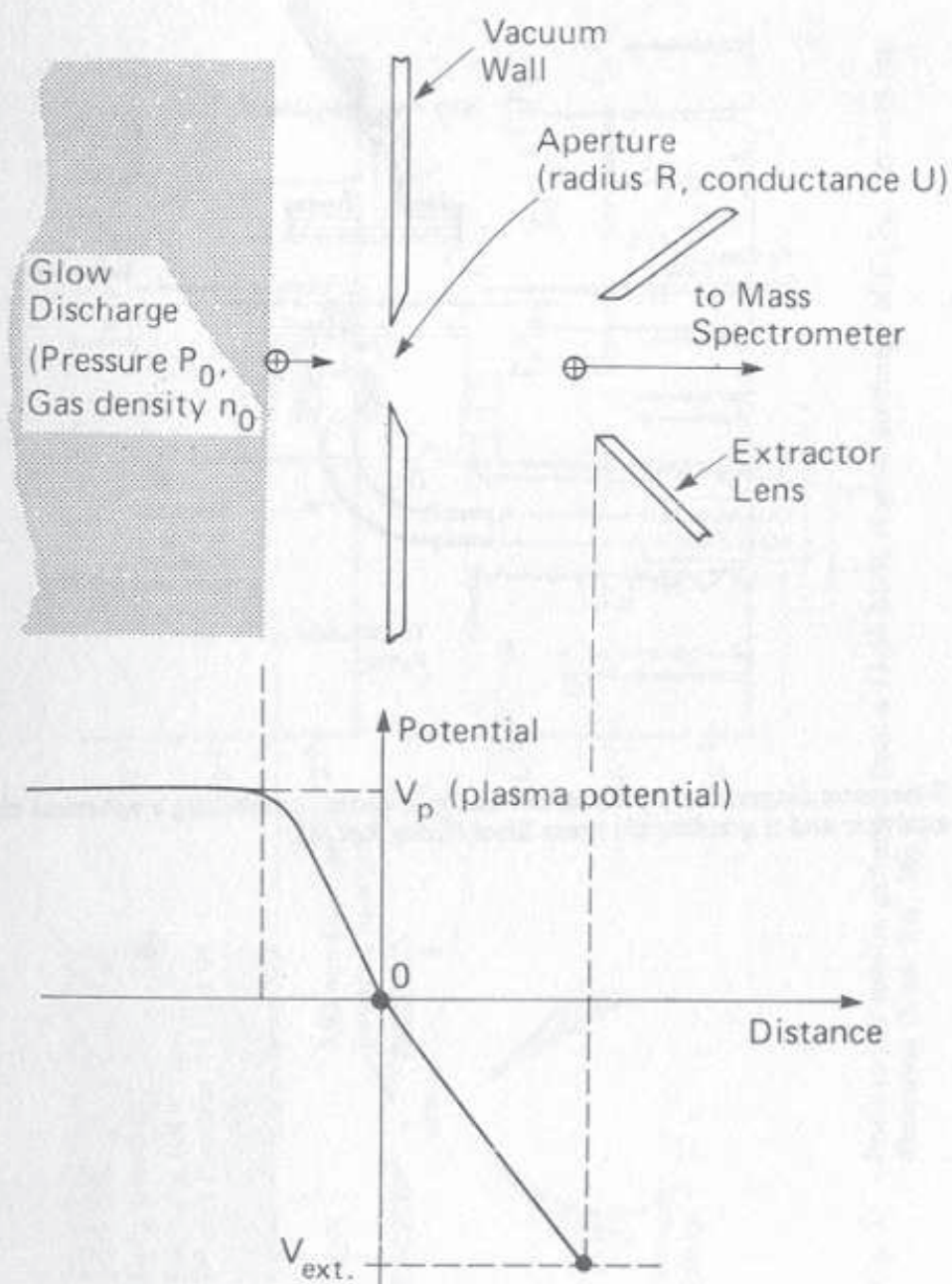
Fig. 1. Illustrative figure showing the typical geometrical and electrical aspects of ion sampling from glow discharges.

$$V(t) = V_{dc} + V_{rf} \sin \omega t$$

To Gas
Source

To
Turbopump

Quadrupole
Mass Filter

Spherical
Energy
Analyzer

←—15cm—→

To Diffusion
Pump
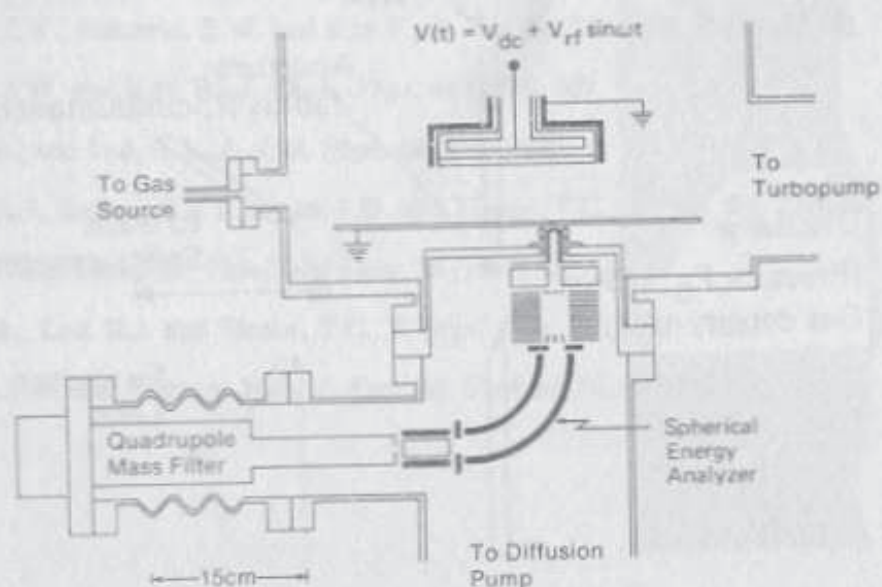
Fig. 2. Schematic diagram of a plasma ion analysis system combining a spherical electrostatic energy analyzer and a quadrupole mass filter (from Ref. 8).
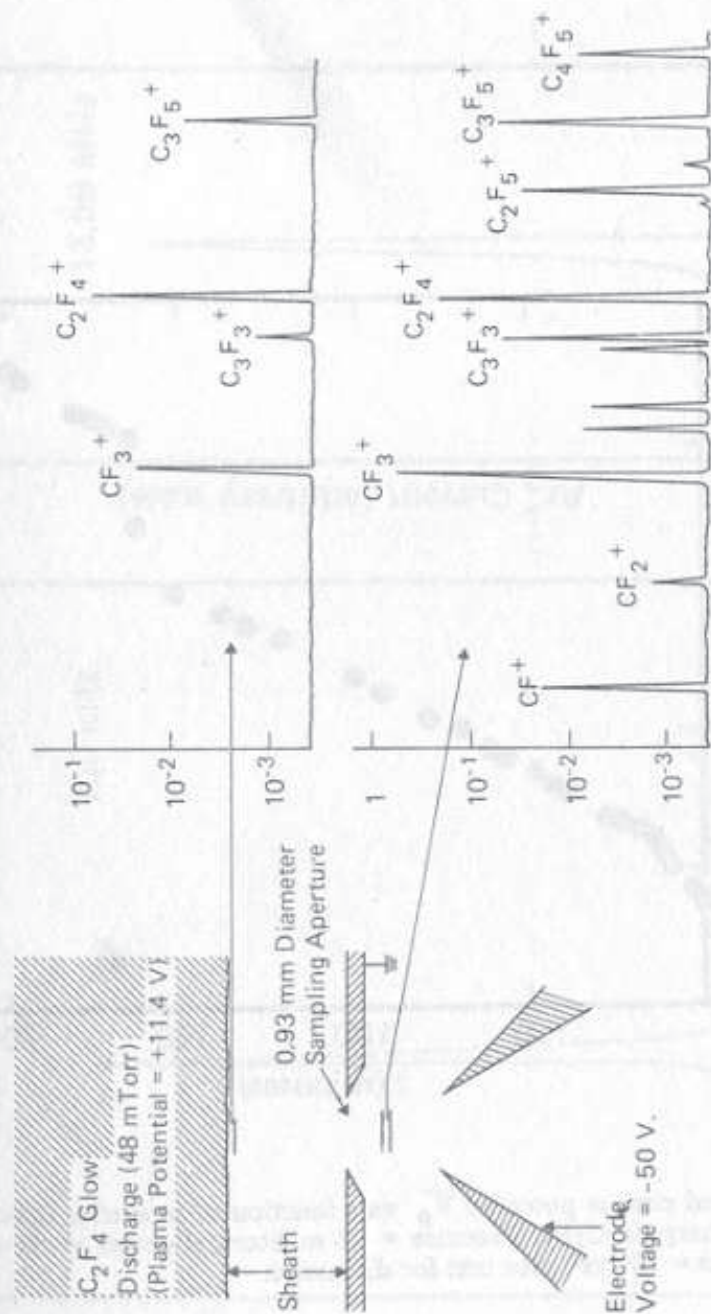
Fig. 3. Positive ion spectra extracted from a 13.56 MHz rf glow discharge of C_2F_4. See text for discussion (from Ref. 20).
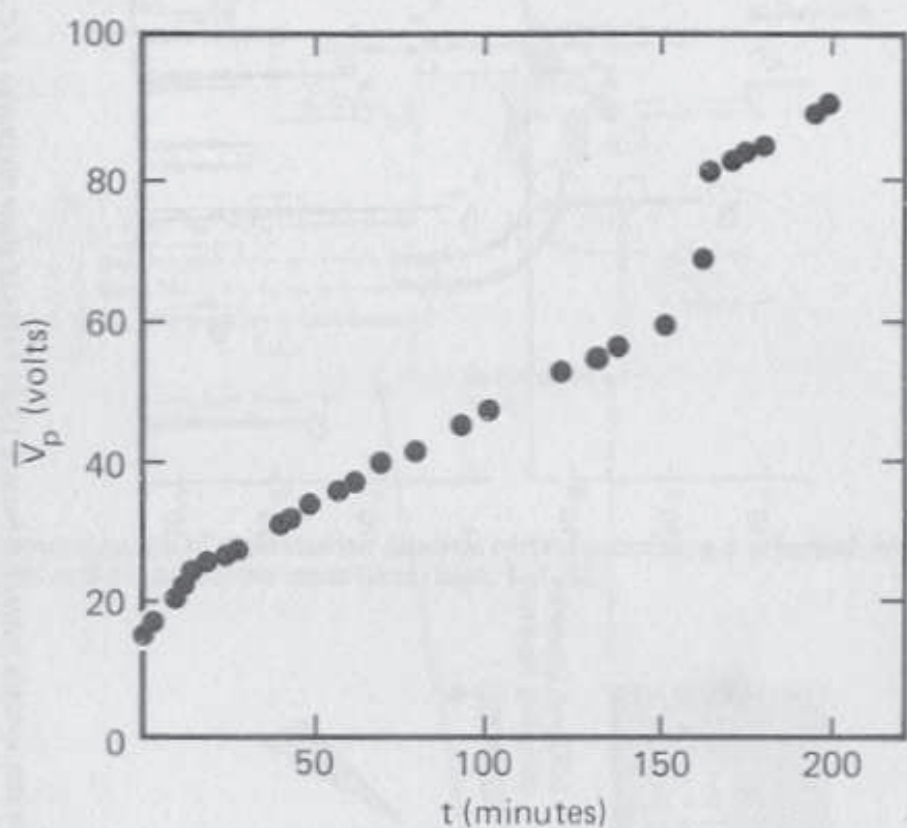
Fig. 4.   Time-averaged plasma potential $\overline{V}_p$ as a function of time after ignition of a 13.56 MHz rf glow discharge in C_2F_4. Pressure = 15 millitorr, rf power = 50 watts, electrode area = 20 cm^2. See text for discussion.
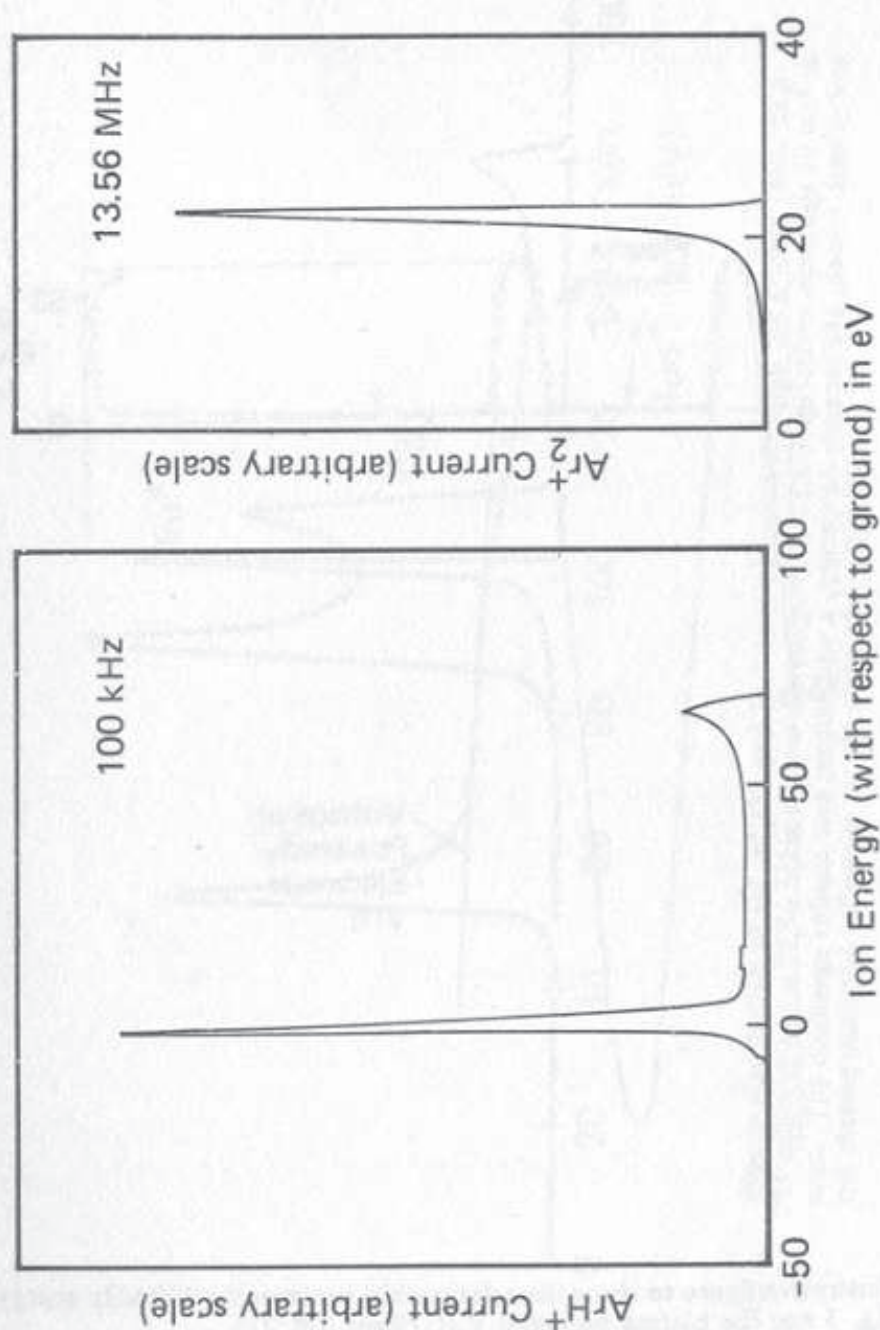
Fig. 5.   Energy distributions of ions extracted through the ground plane of a planar diode rf glow discharge system with 100 kHz and 13.56 MHz excitation frequencies. Argon pressure = 50 millitorr (from Ref. 21).
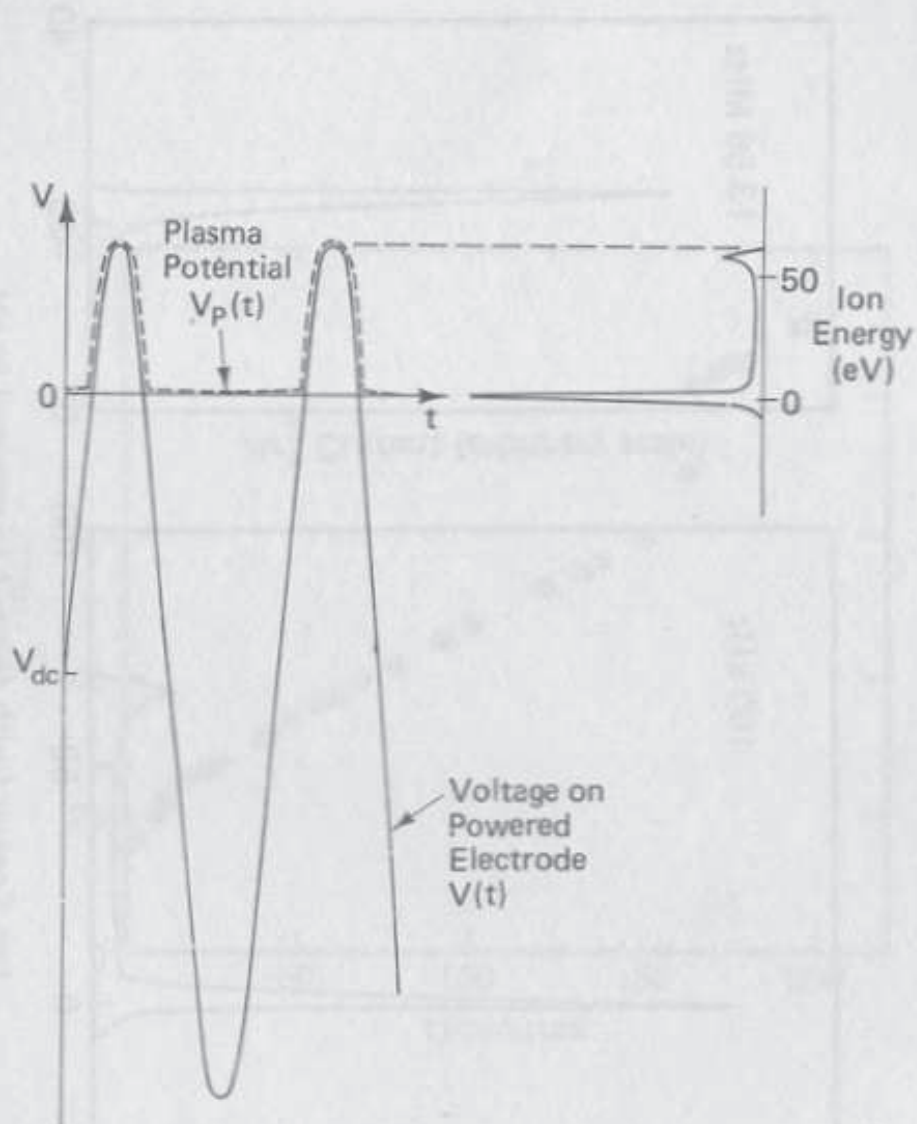
Fig. 6. Illustrative figure to show the relationship between the 100 kHz energy distribution in Fig. 5 and the plasma potential $V_p(t)$ (from Ref. 21).
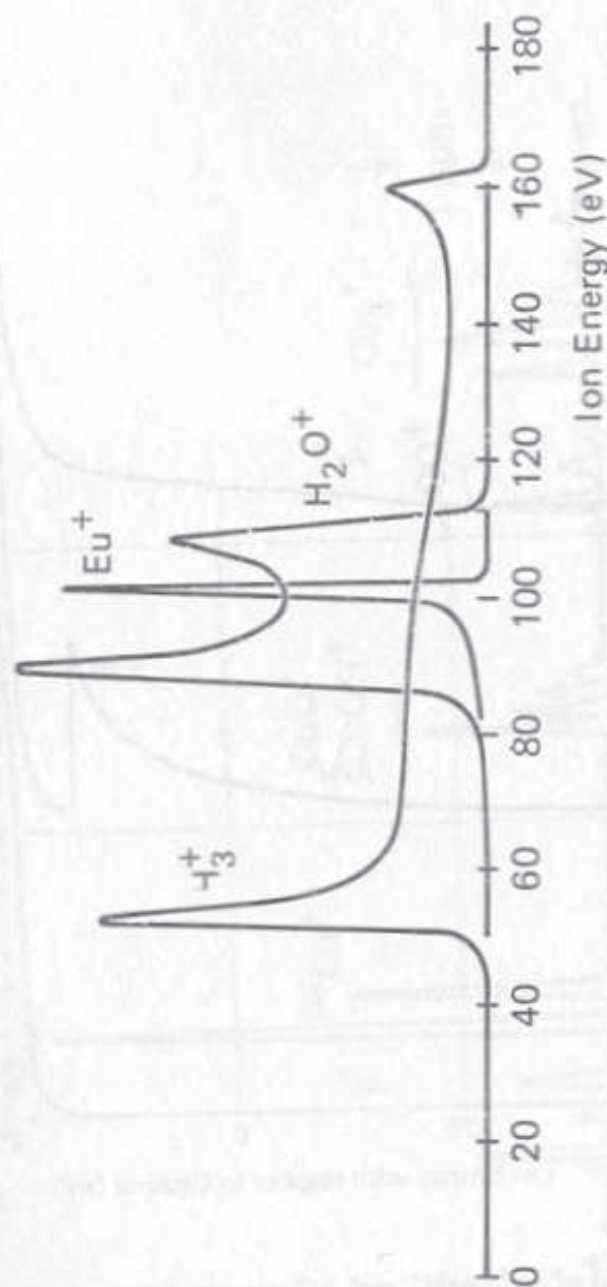
Fig. 7. Energy distribution of H_3^+, H_2O^+ and Eu^+ ions extracted through the ground plane of a 75 millitorr argon 13.56 MHz rf glow discharge with a EuO excitation electrode 20 cm² in area. The discharge volume was confined by a cylinder to increase the plasma density and the plasma potential. rf power = 100 watts (from Ref. 9).
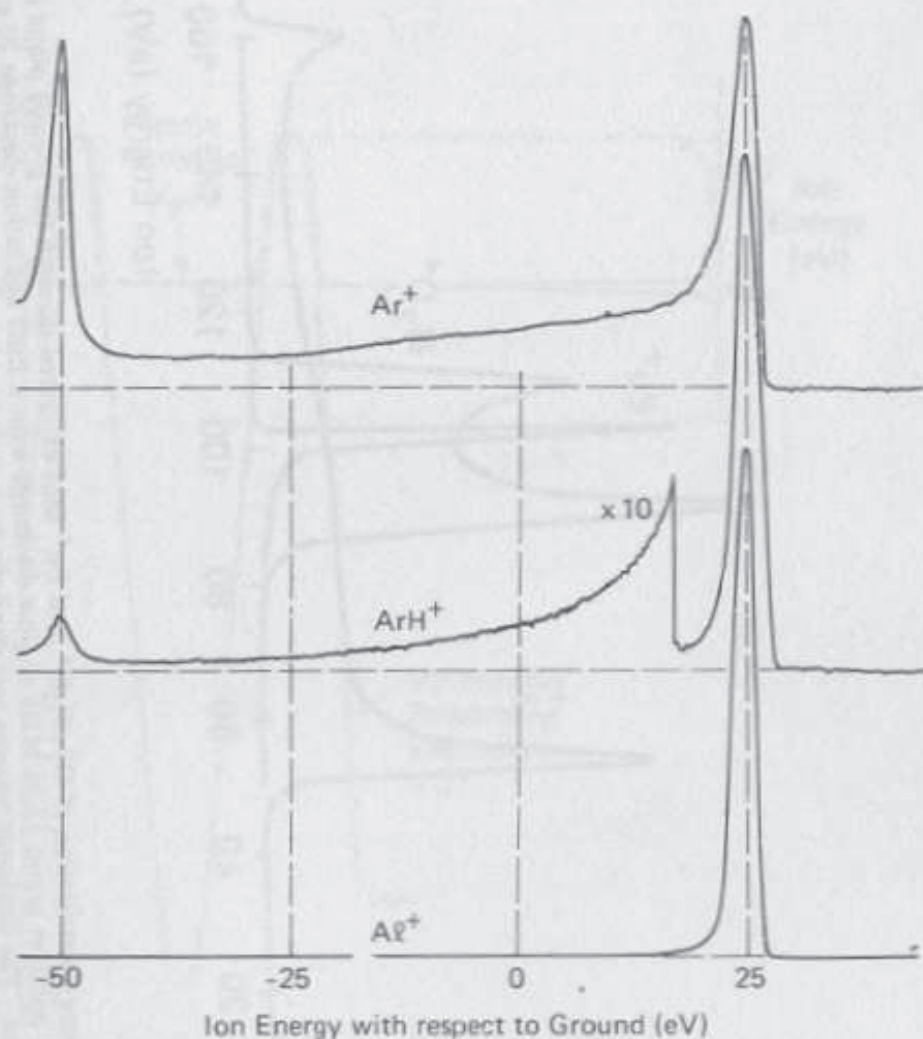
Fig. 8. Energy distributions of Ar+, ArH+ and Al+ extracted through an aperture, de-biased at − 50 volts, from a 100 millitorr argon glow discharge. 100 watts of 13.56 MHz rf power were applied to an aluminum electrode 182 cm² in area to establish the discharge. See text for discussion.
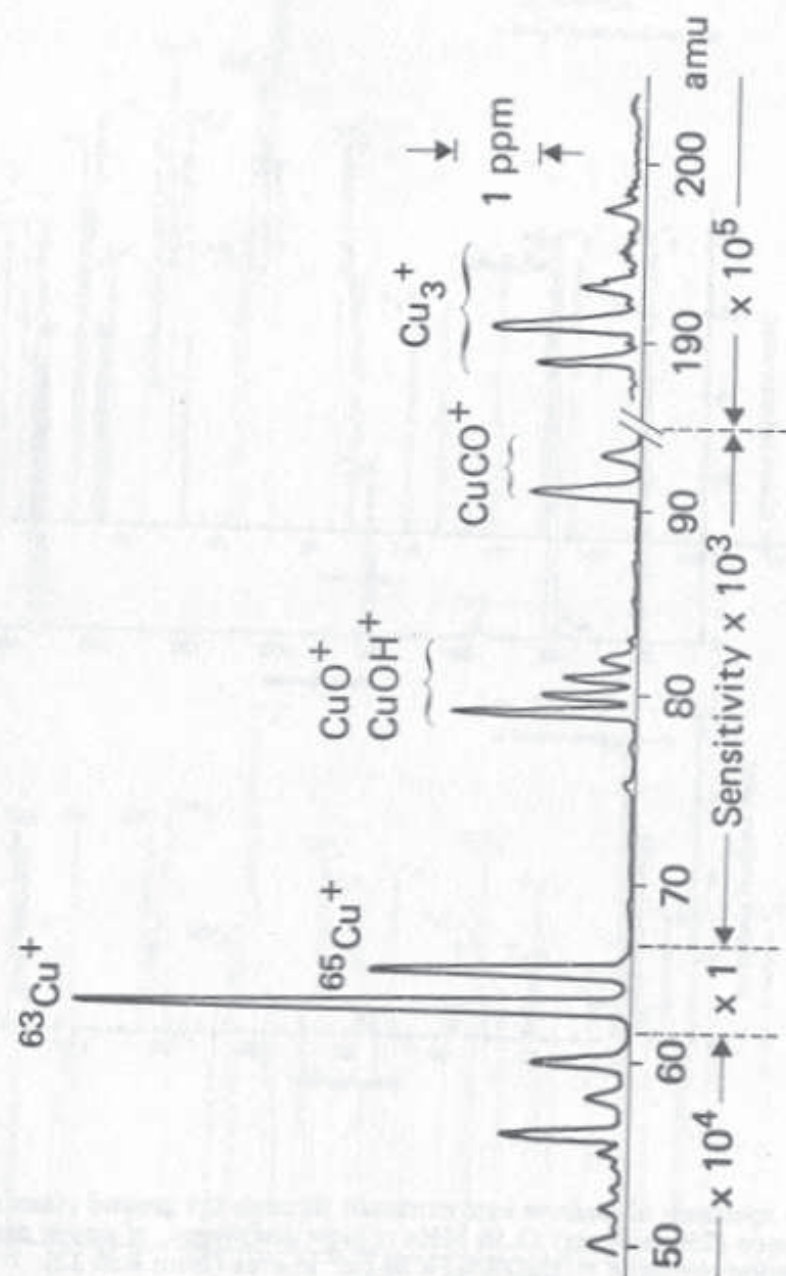
Fig. 9.   Section of a plasma ion mass spectrum recorded with a 5 cm diameter copper electrode in a 13.56 MHz rf neon glow discharge (from Ref. 31).
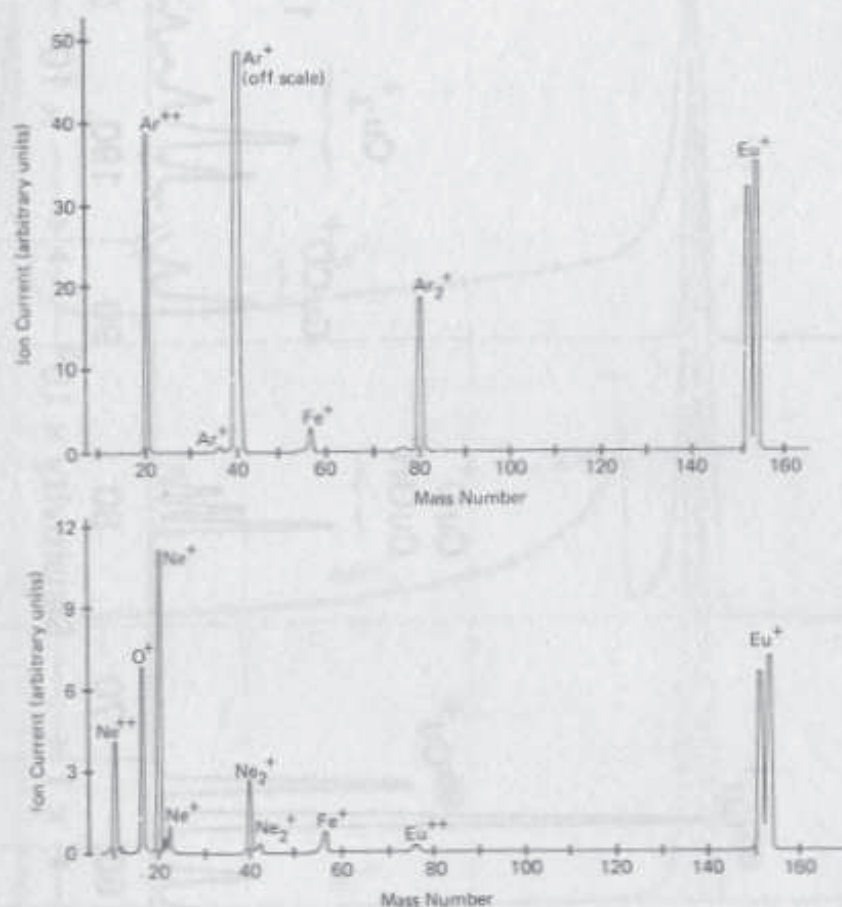
Fig. 10.   Mass spectrum of positive ions extracted through the ground plane of argon (102 millitorr) and neon (250 millitorr) 13.56 MHz rf glow discharges.   rf power density = 10.5 W/cm^2; excitation electrode = EuO:6%Fe 20 cm^2 in area (from Ref. 32).
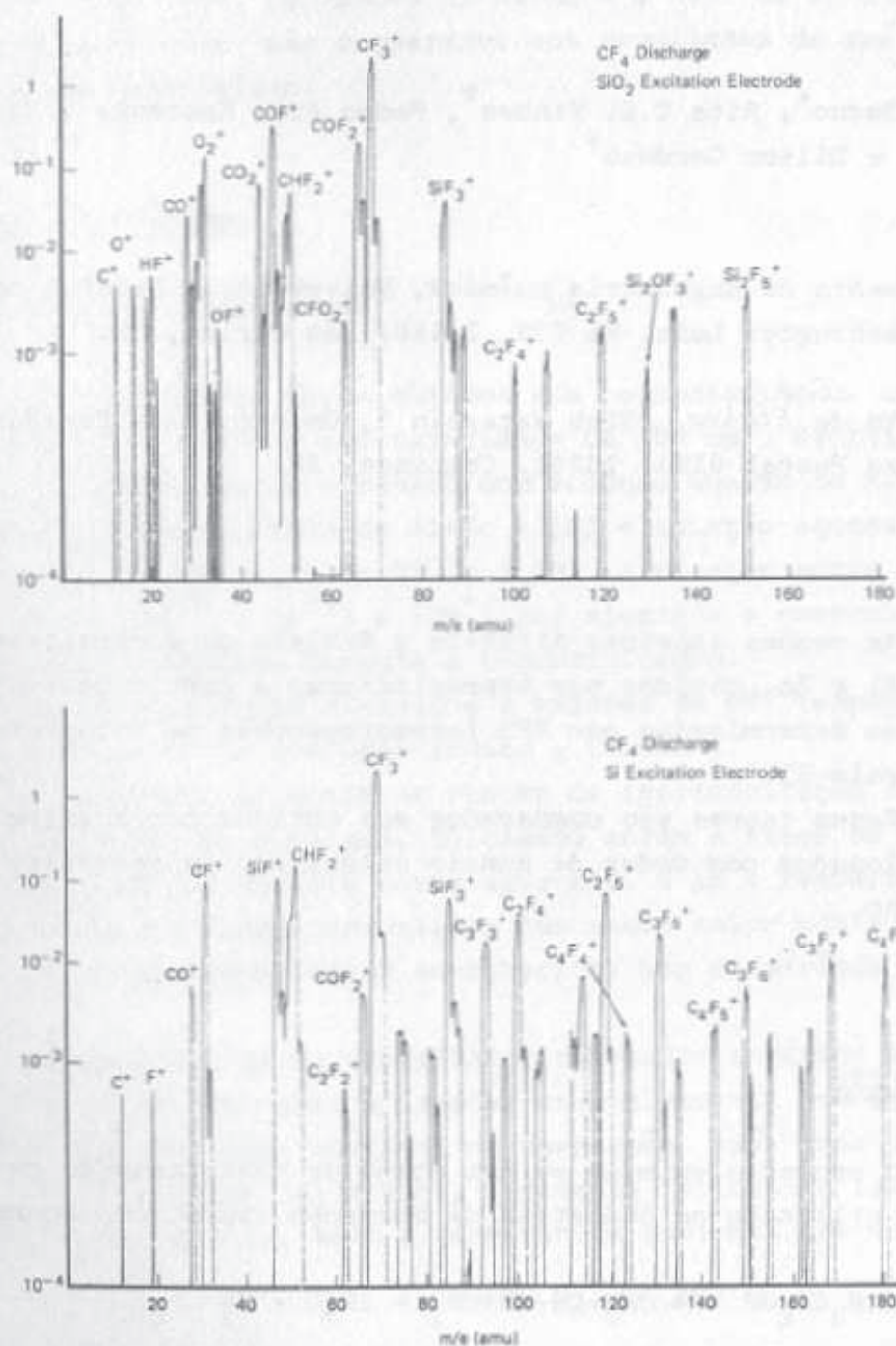
Fig. 11. Mass spectra of positive ions extracted from a 13.56 MHz rf CF_4 glow discharge during the etching of Si and SiO_2. CF_4 pressure = 20 millitorr; CF_4 flow rate = 1.3 sccm; rf power = 100 watts; electrode area = 100 cm^2 (from Ref. 40).