# Characterisation of plasmas by advanced diagnostic methods

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**Abstract** The paper discusses the problems with measuring characteristic plasma quantities under the nonideal conditions of plasma chemistry in low pressure discharges and gives an overview over ideas and methods for improving shortcomings of some principal diagnostic methods.

## 1 Introduction

A good part of low pressure plasma processing is plasma physics plus surface chemistry. For characterising surfaces and surface reactions there exist powerful tools and surface kinetics is well understood. To obtain an understanding of the interaction of plasmas and surfaces, a simultaneous understanding of plasma processes is necessary.

Plasma diagnostic methods are old and well established. Probes e.g. were introduced by I. Langmuir in 1923 and have been excessively used since that time in many different plasmas. Optical emission spectroscopy as a tool of chemistry was even earlier introduced namely by the famous work of Kirchhoff and Bunsen in 1859 and the papers on this subject are even more numerous. Plasma spectroscopy is also well established since comparable times.

Thus what means „advanced methods". My personal attitude is to translate „advanced" by „well adapted to the problems of low pressure plasma processing". I will give a rather subjective approach to this theme from the point of view of a plasmaphysicist.

Though surface processes are always involved in plasma chemistry, some of these are mainly due to radicals etc. produced in the main body of the plasma (e.g. PACVD etc.) others more influenced by processes in the plasma-surface transition region e.g. ion acceleration in the space charge sheath as important for sputtering and etching. Thus besides the bulk this transition region needs special consideration.

An obstacle immersed into a plasma is usually negatively charged and I want to restrict my considerations to this case. Low pressure plasmas usually have low degrees of ionisation ($(n_{pl}/n_{gas}) < 10^{-3}$ typically) high electron temperatures ($kT_e$ in the eV range except for negative glows and afterglows with kTe in the 0.1 eV range and below) but low ion and gas temperatures. Thus diffusion of plasma to the walls is fast as compared to neutral diffusion ($D_{plasma}/D_{gas}) \sim T_e/T_{gas}$. The walls are sinks for charged particles but not necessarily for unstable neutrals like metastables and radicals. This implies in general accumulation of such neutrals to higher densities as compared to plasma density.

Due to the high electron temperatures the bulk plasma is dominated by electron-neutral reactions and/or reaction chains starting with electron-neutral reactions. Ion reactions in the bulk are those of thermal ions with low temperature. Close to the walls a transition region develops which consists of the so called presheath and the space charge sheath [1]. These regions are dominated by electric fields accelerating the ions. In the presheath the ion distribution function changes and the average ion energy approaches $kT_e$ at the presheath/sheath transition. This may alter the character of ion chemistry as reactions occurring at higher collision energies (e.g. break-up) may become more important. Inside the sheath the plasma electrons are repelled and almost disappear and the ions are accelerated to high energy. Secondary electrons from the surface are fired back into the plasma and may undergo inelastic collisions. They are responsible for the luminous glow around obstacles introduced into plasmas.

## 2 Ion kinematics in the plasma-surface transition region

The probability of reactions in the sheath and presheath depends on the sheath thicknesses which depend on the plasma density and the sheath voltage [2]. In low density plasmas (e.g. parallel plate rf discharges) the thicknesses are high, therefore, ion reactions in the transition region may be more important than in plasmas of high density (e.g. inductively coupled discharges). In discharges having high space potential

(e.g. parallel plate discharges and glows) reactions in the sheath are more important than in those with low space potential (inductivity coupled discharges) [3]. As a simple model system we discuss the case of Ar plasmas which have been extensively studied. Here $Ar^+$ is the dominant ion (besides $Ar^{2+}$, $Ar_2^+$ and impurities) which undergoes symmetric charge exchange collisions

$$Ar^+ + Ar => Ar + Ar^+ \tag{1}$$

having a cross section that only weakly depends on energy [4]. Ion kinetics can be studied by energy analysis of the ions arriving at the surface [2,5]. Fig. 1 gives ion distribution functions (IDFs) measured in the negative glow of an argon discharge with the potential of the energy analyser housing as parameter. The IDFs consist of a primary peak (the plasma peak) and a long tail whos importance increases with increasing sheath voltage, that is increasing sheath thickness. This tail is due to ions formed by charge exchange inside the sheath while the plasma peak is due to ions traversing the whole sheath without collisions. It reflects the IDF as modified inside the presheath not that in the bulk of the plasma. The latter can only under very special conditions deduced from that peak [6].
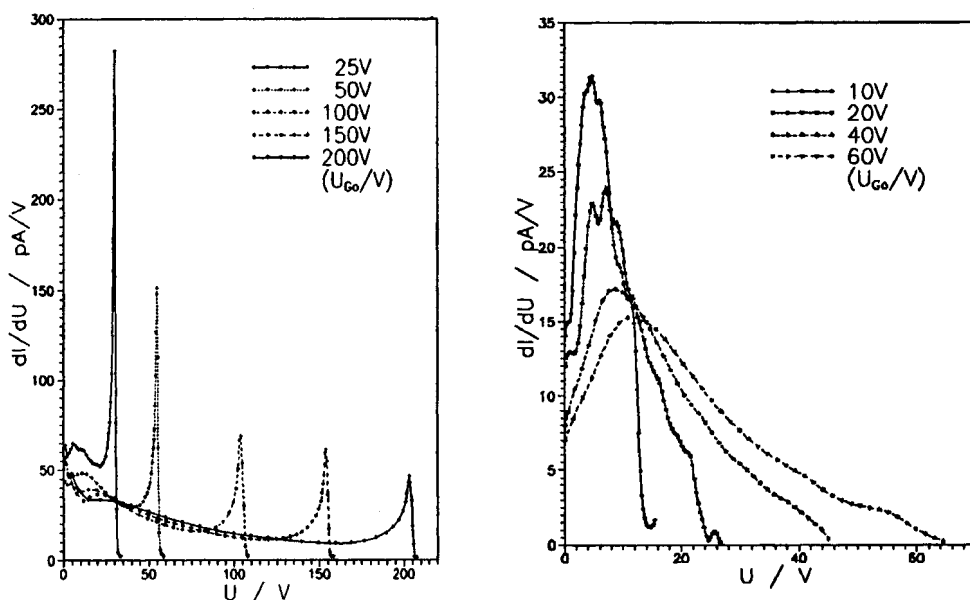


Fig. 1  IDFs at a negative surface in a glow discharge. Parameter is the surface potential.
Left: Ar, 2Pa,  $kT_e = 0.39$ eV, $n_e = 4 \cdot 10^9$ cm$^{-3}$ right: $O_2$, 4Pa, $kT_e = 0.07$ eV, $n_e = 4 \cdot 10^9$ eV.

At sufficiently low sheath voltages the tail disappears [2,3] while at higher pressure the plasma peak disappears see Fig. 1, IDFs from $O_2$ discharges. Under these conditions all ions bombarding a surface are born inside the sheath not inside the plasma.

This analysis is not only important for considering surface processes but also for critically evaluating data from mass spectrometric plasma diagnostics. Mass spectrometers analyse the particle flux to a surface. If this flux is modified inside the transition region results may be falsified and a careful discussion is necessary in order to link the measured specific currents to particle densities inside the plasma. That this is not a trivial problem is demonstrated by the differences in mass spectra taken behind the hot or grounded electrode and those taken behind the floating wall [7]. These differences may not only be due to changes in the plasma composition but also to different sheath voltages at these locations [8].
One possibility to investigate reactions in the space charge sheath is the combination of mass and energy analysis. This is also helpful to detect energy dependent transmission effects (e.g. due to surface charges influencing imaging [9,10]). An example are IDFs of $Ar^+$ and $Ar_2^+$ ions measured in the same Ar discharge that are quite different due to their different chemistry in the space charge sheath [8,11].
The other possibility is „ion sampling through a plane Langmuir probe" [12,13,11]. The entrance diaphragm of the mass spectrometer is made very small (plate 1 mm diam.) and its potential is swept as that of a Langmuir probe. When the potential is equal to the space potential there is no sheath (though some transition region) and the reactions inside the sheath disappear. This arrangement was very successfully used for studying ion neutral reactions inside (dc) hollow cathode discharges. Applying it to rf

discharges introduces some problems due to the rf modulation of the plasma potential. From the recipes developed to tackle this problem at probe measurements only the method of driving the probe with the same modulation signal promises some success. Here, however, the whole mass spectrometer head needs to be driven which is nontrivial. Nevertheless, attacking this problem seems to be worth trying.

# 3 Bulk plasma measurements

Heavy species (radicals, ions, ...) can be measured in the bulk plasma by all kinds of emission spectroscopy. However, I will not discuss these methods here, because they are well known or covered by other talks at this conference. The most important entity for characterising plasmas is the electron gas which itself is characterised by the electron density $n_e$ and the electron distribution function EDF. In low pressure plasmas Langmuir probes, i.e. small auxiliary electrodes whos current voltage characteristics are measured, are the most easiest way to measure $n_e$ and the EDF. How this is done is described in many reviews, e.g. [14-17] and will not be discussed here. Instead I want to treat some special problems.

## 3.1 RF currents in the space charge sheath of a probe

As the probe characteristics are highly non-linear any rf modulation of the sheath voltage falsifies these characteristics and thus plasma parameters deduced from them as is well known. Mainly two methods exist to overcome this problem: rf current blocking by resonant circuits [18,19,20] or driving the probe with the same modulation signal as the plasma potential [21]. All circuits for this purpose have in common that their effectivity depends on the frequency of the fluctuations. As the fluctuations are usually nonsinusoidal harmonics constitute a problem. When combining reactances with different resonance frequencies the frequency characteristic of the entire system contains resonances besides the (desired) cut-offs that may be problematic if broad band noise fluctuations are present. A broadband arrangement would be the best solution. The simplest nevertheless most efficient approach is to insert a simple ohmic resistor R into the current path. R must be large as compared to the sheath impedance, which can be described as the non-linear characteristic paralleled by the sheath capacity $C_s$. If the frequency $\omega$ of the fluctuations is large as compared to the ion plasma frequency $\omega_{pi}$, this condition can be easily fulfilled as it means $R \gg 1/\omega C_s$. To compensate for the perturbation by the dc voltage across R a simple circuit using a low pass band operational amplifier can be used. In the commonly used 13.56 MHz discharges the fundamental is of the order of $\omega_{pi}$, i.e. the resistor blocks effectively the harmonics. For blocking the fundamental it must be combined with an appropriate resonant circuit. This scheme was proven to act very effectively even under very unfavourable conditions and seems to present a unique solution for all cases where nonheated probes are used [22], see Fig. 2.

Another approach consists in measuring probe current time resolved. To obtain the time resolved characteristics the displacement current has to be separated from the measured signal. This allows the determination of the time evolution of the EDF. Some pioneering work on time resolved EDFs has been published in the USA and Japan [23-25].
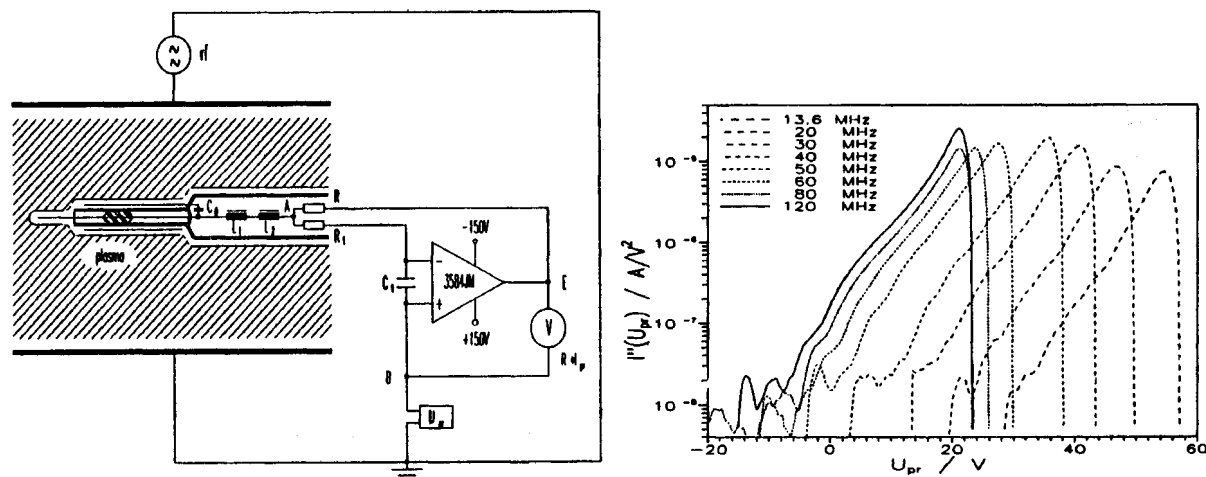


Fig. 2 Broad band blocking circuit for Langmuir probes. The chokes have resonances close to 13.6 MHz, R is 100kOhm. EDFs measured with the circuit shown in parallel plate discharges in Ar with different excitation frequencies [22].

## 3.2 Probe Measurements in the presence of different kinds of ions, negative ions and clusters

The ionic current to a probe is proportional to $1/m_i^{1/2}$ ($m_i$ ionic mass). To evaluate plasma densities from this current $m_i$ needs to be known. If several kinds of ions are present the so called Bohm current (see, e.g. [26]) is proportional to a sum of the partial densities divided by the square root of the resp. ion masses. If the ionic mass spectrum is not known, the density can not be obtained. This may be a source of error in double probe measurements. The most abundant ion may be quite different from the most abundant of the neutral parents. Thus probe measurements in such cases need to be accomplished by mass spectrometric measurementsegative ions are important constituents of many chemical plasmas (e.g. in $H_2$, $O_2$, $SF_6$, $CF_4$ and others). If negative ions or negatively charged clusters are present the probe measurements may be greatly distorted and the procedure of plasma data evaluation needs to be changed. As long as there are electrons the electron current in the electron retardation region is not disturbed. However, the positive ion current may change due to changes in the presheath electric field [27]. (There are other means of measuring negative ion densities [28]).

Under certain circumstances electrons may completely disappear. Then interpretation of probe characteristics becomes simple again and the ratio of the ion saturation current is proportional to the square root of the mass ratio. Thus a probe can be used as a simple mass spectrometer, which e.g. can be used to pursue the growing of particulates. The method is sensitive to particle sizes too small to be detected by light scattering [29]. This is a good example that the many parameters influencing probe characteristics constitute a chance of measuring very different kinds of quantities or processes.

## 3.3 Probe coating by insulating films

Coating of probes by insulating films is another example of a perturbation that can be used for measuring purposes. Such films act as a - mostly non-linear - series resistor in the probe circuit. The additional voltage drop across the film flattens the probe characteristics and naive data evaluation may introduce big errors. However, if the plasma is stable and/or the coating can be removed in order to measure the unperturbed probe characteristics, it is possible to obtain from a comparison of perturbed and unperturbed probe characteristics the current-voltage characteristic of the film [26]. The probe again is sensitive to films much thinner than those measured with the usual optical methods. Even fractions of a monolayer may have measurable effects [30]. If the probe can be kept clean or by a suitable probe temperature the conductivity of the probe coating sufficiently high to prevent distortions [31] the coating of a metallic counterelectrode used as substrate can be measured [32].

## 3.4 Limits of the probe method

If not special efforts are undertaken [33,34] probe characteristics yield EDFs over 3 to 4 decades. This is in general not sufficient to measure the active electrons needed to characterise the reactivity of a plasma, see Fig. 3. In the presence of strong magnetic fields or with increasing pressure EDFs can not be measured at all. (Probe measurement at elevated pressure may yield information on the plasma conductivity [35,36]). However, for plasma modelling the EDF is needed and some experimental control of EDFs calculated by solving the Boltzmann equation is highly desirable.

## 3.5 Determination of EDFs by emission spectroscopy

From absolutely measured line intensities or band intensities the population densities of excited states can be directly measured. Ground state densities can be evaluated by using a collisional radiative model appropriate for the plasma under investigation [37]. To do so the EDF needs to be known. This is the usual use of emission spectroscopy. If the EDF is not known a priori its influence on the population of excited states can be used to get at least an educated guess of the EDF. In principle actinometry is such a method. Here the excitation of similar lines from different elements is used as a sensor (the actinometer). When measuring different lines of the same species one should obtain from them the same ground state density. Assuming a functional form of the EDF (Druijvesteijnian, power law) the structural parameters of the EDF can be varied till one gets optimum agreement between the groundstate densities evaluated from intensities of different lines. This yields a good estimate of the EDF above excitation threshold, i.e. in a range where probe measurements are difficult [38]. For overcoming the limitation to high energies it is necessary to consider the influence of inelastic processes having low threshold energies.

Such processes are e.g. vibrational excitations of molecules which in case of $N_2$ occur most efficiently via the unstable $N_2^-$ ion. Considering the excitation balance and comparing calculated with spectroscopically measured vibrational populations of the $N_2(X)$ state yields the low energy EDF - at least at low pressure.
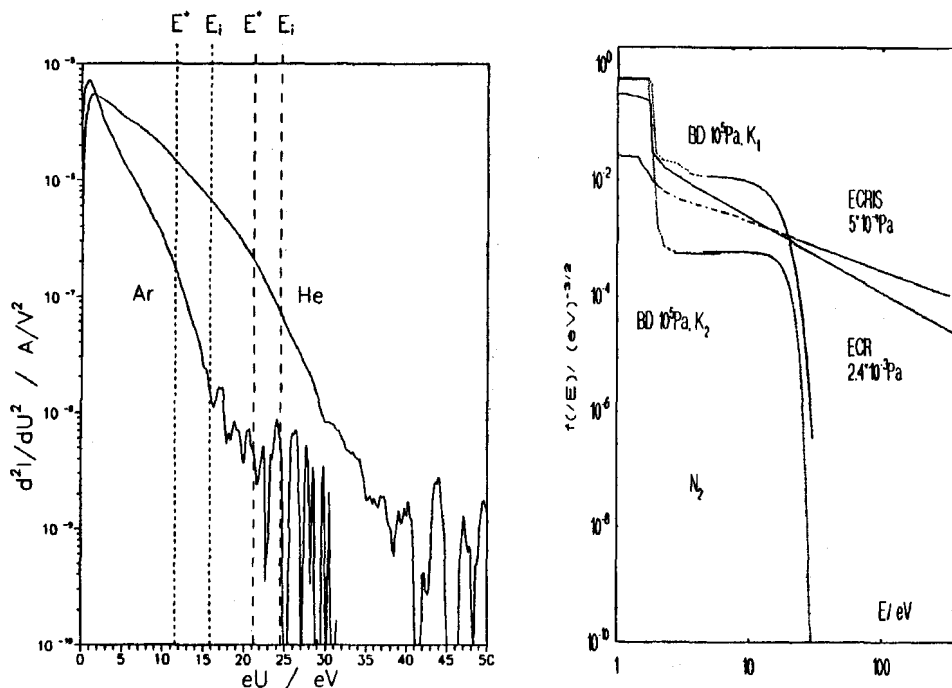
Fig. 3 (left) EDFs measured by probes in parallel plate discharges in Ar and He, vertical lines indicate threshold energies for excitation (E*) and ionisation ($E_i$)

Fig. 4 (right) EDFs determined by optical emission spectroscopy in nitrogen discharges at very low pressure (ECR, ECRIS) and at very high pressure (BD dielectric barrier discharge). $K_{1,2}$ are the assumed collisional relaxation coefficients: $K_1 = 8 \cdot 10^{-13}$ cm$^3$ s$^{-1}$; $K_2 = 5 \cdot 10^{-13}$ cm$^3$ s$^{-1}$.

At high pressure the collisional relaxation has to be taken into account. Estimating the high energy part of the EDF from the population of the electronically excited $N_2$ states (a, C, $N_2^+$(B)) yields the EDF over a wide energy range. Some very preliminary results of this method are shown in Fig. 4 spanning a very wide pressure range [39]. Some improvements especially of the data base have to be made in order to obtain a reliable method.

## 4 Conclusions and Acknowledgements

I hope that these examples have demonstrated: plasma diagnostic methods are well established. If problems exist they can - at least in principle - be overcome. However, the necessary effort grows the more refined knowledge one wants to attain. One could pose the question for „advanced methods" in another way: is it possible to define and to measure a minimum number of parameters which are sufficient to characterise a plasma. Not in the way that knowledge of these parameters implies a complete knowledge of the whole plasma but thus that reproducing the values of these parameters under well-defined conditions reproduces the characteristic features of the plasma.

Such parameters if easily measured may constitute candidates for parameters for process control. I think it is worth to invest some effort to make those methods applicable in plasma chemistry. Among the well-established methods I want to mention the microwave resonator and the microwave interferometer which yield electron density and electron collision frequency (which is a measure of the average electron kinetic energy) [40,41].

The same type of information can be obtained by using the „self excited electron resonance" method, which determines the geometric sheath resonance inside a parallel plate rf discharge by a Fourier analysis of the nonsinusoidal rf discharge current [42].

Last not least I want to mention the „floating triple probe" initially proposed by Chen and Sekiguchi [43-45] which replaces measurement of probe characteristics by measuring two voltages and a current by the help of three probes (one floating, two constituting a double probe with fixed bias). This probe has found recently application in fusion research but may be also helpful in plasma chemistry in the sense defined above.

Coming to an end I am tempted to turn my initial statement into the following form: We have powerful tools for diagnosing plasmas and we know what happens inside the plasma. However, what does this do to

the surface? This question, I think, must be answered by a combination of plasma and surface diagnostics. Work in this direction is proceeding well and perhaps at the next ISPC a review on such synergetic studies should be given.

## 5 References

1. KU Riemann 1991, J. Phys. D: Appl. Phys. 24, 493-518
2. KU Riemann, U. Ehlemann, K. Wiesemann 1992, J. Phys. D: Appl. Phys. 25, 620-633
3. U Kortshagen 1995, Plasma Sources Sci. Technol. 4, 172-182
4. EW McDaniel, E Mason 1973, The mobility and diffusion of ions in gases (New York: Wiley)
5. U Flender, K Wiesemann 1994, J. Phys. D: Appl. Phys. 27, 509-521
6. H Köhler, M Frank, BA Huber, K Wiesemann 1987, Nuclear Instrum. Methods B23, 186-189
7. J. Vasile, G. Smolinsky 1975, Int. J. Mass Spectrom. Ion Phys. 18, 179-192
8. JK Olthoff, RJ Van Brunt, SB Radovanov 1992, J. Appl. Phys. 72, 4566-4576
9. JK Olthoff, RJ Van Brunt, SB Radovanov 1995, Appl. Phys. Lett. 67, 473-475
10. J Vasile, HF Dylla 1989, in Plasma Diagnostics Vol. I, O. Auciello, DL Flamm (Eds.) (Boston: Academic Press)
11. H Helm, TD Märk, W Lindinger 1980, Pure Appl. Chem. 52, 1739-1757
12. M Pahl, W Lindinger, F Howorka 1972, Z. Naturf. 27a, 678-692 (in German)
13. W Lindinger 1973, Phys. Rev. 7A, 328-333
14. N Hershkowitz 1989 in Plasma Diagnostics Vol. 1, O. Auciello, DL Flamm (Eds.) (Boston: Academic Press)
15. BE Cherrington 1982, Plasma Chem. Plasma Proc. 2, 113-140
16. G Dilecce 1992 in Plasma Technology, M. Capitelli, C. Gorse (Eds.) (New York: Plenum Press)
17. K Wiesemann 1995 in Kohlrausch, Praktische Physik 24. Edition V. Kose, S. Wagner (Eds.) (Stuttgart: Teubner) (in German)
18. F Schneider 1954, Z. Angew. Physik 6, 456-462 (in German)
19. RRJ Gagné, A Cantin 1972, J. Appl. Phys. 43, 2639-2647
20. M Hirayama, W Shindo, T Ohmi 1994, Jpn. J. Appl. Phys. 33, 2272-2275
21. NSJ Braithwaite, NPM Benjamin, JE Allen 1987, J. Phys. E: Sci. Instrum. 20, 1046-1049
22. U Flender, BH Nguyen Thi, K Wiesemann, NB Kolokolov 1994, RF-harmonic suppression in Langmuir probe measurements in rf discharges, Report 39-A7-94, Arbeitsgemeinschaft Plasmaphysik Bochum/Jülich, submitted to Plasma Sources Sci. Tech.
23. M Mizumura, S Uotsu, S Matsumura, S Teii 1992, J. Phys. D: Appl. Phys. 25, 1744-1748
24. RB Turkot, DN Ruzic 1993, J. Appl. Phys. 73, 2173-2179
25. T Tatsuno, T Taniguchi, S Matsumura 1994, Japn. J. Appl. Phys. 33, 4344-4347
26. U Flender, K Wiesemann 1995, Plasma Chem. Plasma Proc. 15, 123-157
27. H Amemiya 1990, J. Phys. D: Appl. Phys. 23, 999-1014
28. M Bacal 1993, Plasma Sources Sci. Techn. 2, 190-197
29. T Fukuzawa, M Shiratani, Y Watanabe 1994, Appl. Phys. Lett. 64, 3098-3100
30. GV Jørgensen, GK Wehner 1965, J. Appl. Phys. 36, 2672-2674
31. Z Xi, G Zhang, F Yong, F Xu 1993, Chin. Phys. Lett. 10, 100-102
32. U Flender, S Rudakowski, K. Wiesemann 1995, Proc. XII. ISPC, Minnesota
33. MB Hopkins, WG Graham 1986, Rev. Sci. Instrum. 57, 2210-2217
34. G Dilecce, M Capitelli, S De Benedictis 1991, J. Appl. Phys. 69, 121-128
35. MS Benilov, BV Rogov 1991, J. Appl. Phys. 70, 6726-6731
36. RM Clements, SAH Rizvi, PR Smy 1994, IEEE Trans. Plasma Sci. 22, 435-441
37. IP Vinogradov, B Jettkant, D Meyer, K Wiesemann 1994, J. Phys. D: Appl. Phys. 27, 1207-1213
38. IP Vinogradov, D Bolshukhin, D Meyer, K. Wiesemann, to be published
39. N Bibinov, D Kokh, IP Vinogradov, K. Wiesemann, to be published
40. H Meuth, E Sevillano 1989 in Plasma Diagnostics Vol. 1, O. Auciello, DL Flamm (Eds.) (Boston: Academic Press)
41. KJ Overzet, MB Hopkins 1993, J. Appl. Phys. 74, 4323-4330
42. M Klick, W Rehak 1995, Proc. XII. ISPC, Minnesota
43. S Chen, T Sekiguchi 1965, J. Appl. Phys. 36, 2363-2675
44. JS Chang, GL Ogram, RM Hobson, S Teii 1980, J Phys. D: Appl. Phys. 13, 1083-1092
45. S Matsumura, AA Berezin, JS Chang 1992, Rev. Sci. Instrum. 63, 1783-1787