

Physical aspects of plasmas for plasma-chemical applications

Citation for published version (APA):

Hoog, de, F. J., & Schram, D. C. (1986). Physical aspects of plasmas for plasma-chemical applications. In J. S. Bakos, & Z. Sörlei (Eds.), *ICPIG XVII : proceedings of the 17th international conference on phenomena of ionized gases : invited papers* (pp. 222-238). Hilger.

Document status and date:

Published: 01/01/1986

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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PHYSICAL ASPECTS OF PLASMAS FOR PLASMA-CHEMICAL APPLICATIONS

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1. Introduction

During the last ten years interest in the use of plasma for chemical applications has increased considerably. Polak gave reviews at ICPIG X (1971, Oxford) and ICPIG XIII (1977, Berlin). Suhr (1973, Prague), Fauchais and Rakowitz (1979, Grenoble), Molinari (1983, Düsseldorf) reviewed developments in the modelling of plasmas used in chemical processing based on an increasing insight in the relevant physical processes. The expansion of this field is illustrated by the ever growing attendance at the biennial International Symposium on Plasma Chemistry, the last of which took place recently in Eindhoven. The aim of this paper is to define the field of plasma chemistry and stress certain recent developments in the physical understanding of various chemical plasmas. It is impossible to be complete. For a complete survey one might consult the Proceedings of the ISPC VII [1,2].

The applications can be classified into the following three classes : volume chemistry, surface modification, heating and acceleration of (particulate) matter. The advantages of plasmas are many. In most cases use is made of the non-equilibrium character of the distribution of reactants and reaction products, which offers possibilities for unique reaction channels with large reaction rates. Especially in thermal plasmas, where the degree of ionization is high, large specific energies can be present. The heating of reactants by electric fields adds to the methods of equilibrium chemical processing in the gas phase the full spectrum of discharge modes and plasma configurations. Electron-, gas- and substrate temperatures can be different and can cause a strong difference in the vibrational temperature of participating molecules with respect to their translational temperature. Of course limitations are present. Plasma dynamics is determined by the extra constraints imposed by the Maxwell equations. Dissociative excitation and ionization require energies from 5 eV to 10 eV which may have a negative effect on overall energy efficiency. Use of low pressure discharges can lead to small gas efficiencies and may be only of interest for specific reactions. An important point is that because of the complicated physical situation in a chemical plasma modelling and interpretation of phenomena on a fundamental basis is difficult. Partly this is due to lack of data on cross sections for the relevant processes, but also, by the rapid development of the field a lot of research is concluded at an empirical level.

2. Field definition

To give an idea of the size of the field we review in table I plasma chemistry applications as they have been presented July 1985 at the VIIth ISPC. This review is certainly not exhaustive, but indicates general trends.

Product(s)	Reagents	Plasma medium	Product(s)	Reagents	Plasma medium	
<u>Pyrolysis, synthesis</u>						
H ₂ , CO	H ₂ O, carbon compounds	N ₂ arc	<u>Deposition</u> α-Si:H. α-C:H nC-Si ◇-C TiN _x α-BC SiO _x N _y TiO ₂ SiO ₂ InN <u>PA Epitaxy</u> GaAs <u>Etching</u> Si, Si ₃ N ₄ , SiO ₂ W, Mo, Ta GaAs, Al _x Ga _{1-x} As <u>Spraying</u> <u>Melting</u> <u>Evaporation</u> <u>Anodization</u> <u>Reduction</u> <u>Wetting</u>	SiH ₄ CH ₄ , C ₂ H ₆ SiH ₄ CH ₄ , H ₂ N ₂ CH ₄ , B ₂ H ₆ SiH ₄ , NO TiCl ₄ , O ₂ NO, SiH ₄ N ₂ , In(v)	glow glow glow μW, RF magn. glow RF glow glow	
C ₂ H ₂	H ₂ , coal	H ₂ arc		CF ₄ , O ₂ , H ₂ XeF ₂ NF ₃ SF ₆ , O ₂ Br ₂ , O ₂	H ₂ , Ar glow RF glow μW RIE glow	
NH ₃	H ₂ , N ₂ , catalyst	glow				
HCN	N ₂ , CH ₄					
CH ₄ , C ₂ H ₂ , C ₂ H ₆	oil	H ₂ arc				
SiC (p)	SiO, CH ₄	A arc				
Si ₃ N ₄ (p)	NH ₃ , SiCl ₄	RF arc				
<u>Oxydation</u>						
NO	N ₂ O, O ₂	RF glow				
Al ₂ O ₃ (p)	Al (p), O ₂	N ₂ -O ₂ , arc				
formaldehyd	CH ₄	RF glow				
sulfones	sulfides	O ₂ -He, glow				
ozone		corona				
<u>Decomposition, gasification of minerals</u>						
<u>Nitriding, Carburizing, Boriding</u>						
steel	steel	N ₂ , H ₂ glow				
titanium	titanium	Ar, NH ₃ glow				
iron-base alloys	iron-base alloys	Ar, CH ₄ glow				
steel	steel	Ar, B ₂ H ₆ RF glow				
<u>Polymerization</u>						
		RF, μW glow			of surfaces	

TABLE I : A choice of the various plasma chemical applications as discussed at the VIIth ISPC, Eindhoven 1985 [1].

Roughly speaking the field can be split up in several ways. Volume processes tend to be based on high density thermal plasmas, with a degree of ionization larger than 1% and large specific energy inputs of the order of 1 eV/molecule, which sets the conditions for high efficiencies and high yields. Here inductively coupled arcs, DC and AC arcs are used. Processes are mainly synthesis, pyrolysis, but these types of discharges are also used for heating, melting and acceleration of particulate matter.

Surface modification is usually based on the use of low density plasma, with a degree of ionization much smaller than 1%, but an energy input for each incoming particle in the order of 30 eV/molecule. The use of energy in this case is inefficient. Electron temperatures (≈ 1 eV) are much larger than the temperature of the ambient gas (and the substrates). When thermal loading of reagentia and products or walls and substrates should be minimized this kind of plasma mode is usually chosen. Here DC glows, capacitively coupled RF discharges and microwave discharges are utilized.

We should note here that in surface modification of substrates for IC-technology the capacitively coupled RF discharge has gained a dominant position. This is for a great part due to the specific plasma property of generating a negative potential of the substrate vs. the plasma. This bias potential causes ion enhanced surface processing at much larger rates than when no bias is present. In etching this phenomenon brings about anisotropic etching which makes it possible to prevent undercutting of micron sized structures. In the second part of this presentation we would like to focus in on these kind of discharges.

It would be worthwhile to discuss here whether the energy- and gas-efficiency of high density thermal plasmas could be utilized in surface modification at the same time maintaining low substrate temperatures. A possibility is to make use of passive plasmas. In this case the plasma production and the plasma utilization should take place separately. Provisions have to be made to expel the plasma from the plasma source and to direct it to the surface to be treated. Such a solution has two advantages: the constraints on the plasma near the surface are less stringent as there is no demand to generate plasma at that location. Secondly, only the power in the particle beam is transferred to the surface. At the Vth International Conference on Ion and Plasma Assisted Techniques (München, May 1985) a number of applications based on this principle have been presented. Here we would like to present such a plasma source base on a magnetized hollow cathode plasma [3,4].

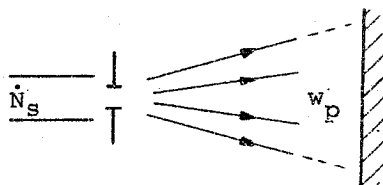


FIG.1

gas : argon
 cathode : Ta \varnothing 6 mm
 pressure : 0.27 Pa
 magn.field : 0.2 T
 arc current: 50 A
 arc length : 1.3 A

FIG.1 : Characteristics of a Magnetized Hollow Cathode Source
 (from ref. [3,4]).

In Fig.1 a schematic set-up is shown. The plasma source (index s) is fed with a total gas flow \dot{N}_s , which is ionized within the cathode tube and is propelled into a vacuum chamber which is continuously pumped. Mass conservation requires at the hollow cathode orifice

$$\dot{N}_s = \int (n_p w_p + n_n w_n) 2\pi r dr, \quad (1)$$

where w_p , w_n are transport velocities and n_p , n_n are particle densities of ions and neutrals respectively. Because the medium expands into vacuum the transport velocity and the effective area in the expanding beam increase. The power consumed is used to produce the plasma, to raise the temperature and to accelerate the resulting plasma. To analyze this process we have to consider the overall momentum balance

$$(n_p + n_n) w_p (w \cdot \nabla) w = -\nabla p - \nabla \cdot \Pi_{i,o} + \vec{j} \times \vec{B} \quad (2)$$

in which we have ignored the electron contributions to the inertia and viscosity terms. If we neglect the latter for simplicity and note that $\vec{j} \times \vec{B}$ is small compared to the pressure gradients, we can see that eq.(2) suggests acceleration to sonic velocities provided substantial pressure gradients are created.

In the hollow cathode arc, plasma is produced and heated to temperatures in the eV range. Power densities are in the range 10^{10} W/m³ which leads up to substantial ionization. Because of heating and ionization the pressure increases leading to expansion into the low pressure volume with sonic or even supersonic exit velocities.

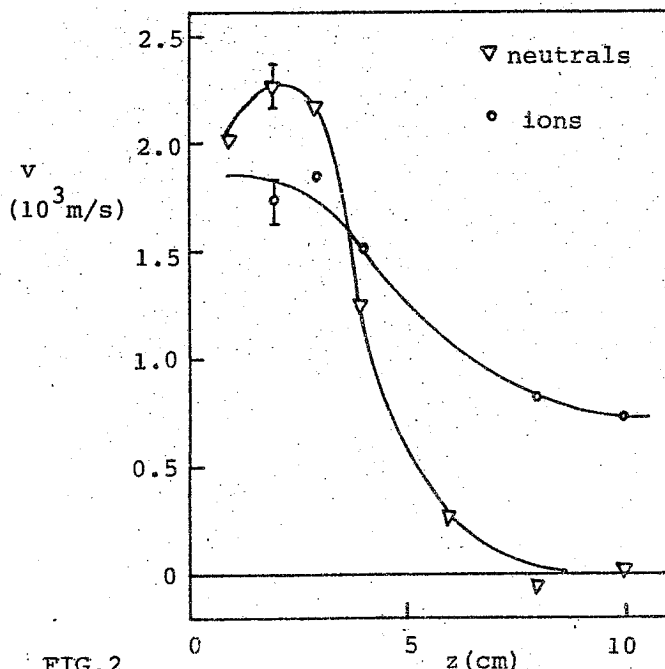


FIG. 2 :

On axis velocities of ions, and neutrals from a MHCA in argon at various distances from the cathode tip (from ref. [4]).

In Fig.2 one can see for plasma and neutral densities at the orifice of about $5 \cdot 10^{20} \text{ m}^{-3}$, the particle velocities along the direction of the flow. When using the ion-momentum balance a consistent picture of the measured values of ion forward velocity, rotational velocity, electron temperatures and particle densities can be built up [4]. Close to the cathode we can compare the outcoming ion flux with the

incident gas flux. The results are depicted in Fig.3, where we see that at sufficiently low gas fluxes and sufficiently high currents gas efficiencies close to 1 are reached.

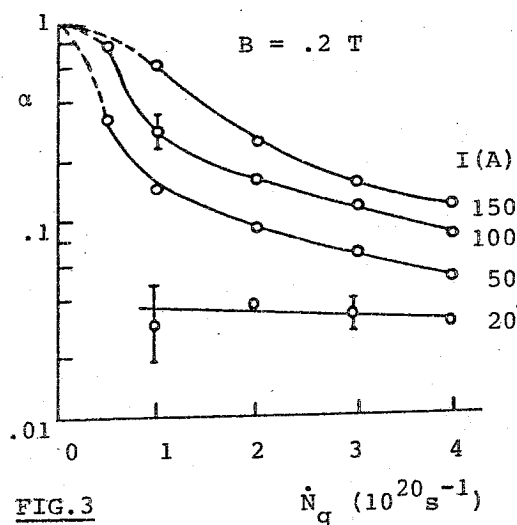


FIG.3 :
Ionized fraction (α) of mass effusing at 10 mm from cathode tip as a function of mass throughput at various currents (from ref. [4]).

This transformation of an ingoing gas flow into a high velocity, hot ion flux with excellent gas efficiency could be used in surface processing and has in fact been applied to the deposition of titanium oxide [5].

Another example of the above principle is the use of a cascade-arc to generate the effluent plasma beam. The pressure in the cathode arc is higher than in the hollow cathode and an even more intense particle beam is observed. Measurements of the temperature and of the velocity of disturbances indicate that again the plasma dynamics can be described by the conservation laws. Sonic velocities are predicted and observed [6]. Plasma ion density is estimated to be 10^{20} m^{-3} and exit velocities have been found to be $10^4/\sqrt{A} \text{ m/s}$ in which A is the mass number. High gas efficiencies can be obtained. Certainly in the field of highly efficient, high yield application more developments are to be expected. Rusanov [7] mentioned in a review paper the possibilities of electron beam generated plasma. Generally speaking he pointed out the similarity between laser plasmas and chemical plasmas. The development and modeling of the latter can benefit largely from the laser field. Also the use of intense short wave radiation for the generation of chemical plasmas is being considered [8].

3.1. Aspects of the R.F. glow discharge

In the remaining part of the paper we will focus on the R.F. glow discharge which has gained such a prominent role in surface modification, both for deposition and etching. It will be impossible to give a complete overview of the development of this field. Within this short presentation we will discuss recent developments along lines laid out by the formulation of a number of topical problems :

- 1) The biasing of electrodes and/or substrates.
- 2) The energy distribution of electrons.
- 3) Surface chemistry.
- 4) Discharge modelling.

3.2. Electrode biasing

In etch and deposition plasmas in most cases use is made of plasmas between two planar and parallel electrodes. In a D.C. coupled case the electrodes have the same negative bias with respect to the plasma. It can be noticed that either through A.C. coupling of the R.F. voltage or by the use of an isolated substrate attached to one of the electrodes it is possible to disturb this balance and to control the D.C. bias by a proper choice of the area of the plasma-electrode interfaces and the voltage of the R.F. source. In this way it is possible to control sputtering rates [9] and to bring about anisotropic etching of substrates and prevent undercutting, as it is experienced in anisotropic wet etching. Etching of micron-sized structures in this way became possible with etch rates up to $10^4 \text{ \AA}/\text{min}$ [10] in $\text{SF}_6\text{-O}_2$ on silicon. Of course one should take care that the ion bombardment does not affect the selectivity of the etch process and that thermal loading of the wafer is limited. Therefore the physical mechanisms underlying this bias-phenomenon will be discussed here. Godyak [11] discussed an equivalent circuit which makes it possible to describe the electric behaviour of the R.F. discharge in a simple way. This has been elaborated upon by Keller et al. [12].

In Fig.4a this circuit, which clearly shows the rectifying properties of the discharge, is depicted. The sheaths developed between plasma and electrode are represented by capacities. The continuous ion current leaving the plasma leaks through

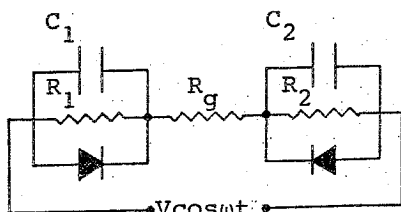


FIG. 4a

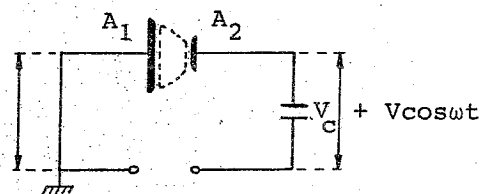


FIG. 4b

FIG. 4 : R.F. glow discharge circuits :
 a. Equivalent circuit,
 b. A.C. coupled circuit.

the resistances and the fact that the wall potential can not be larger than the plasma potential is taken care of by the diodes. If one assumes that $C_2 > C_1$ the average D.C. bias across each of the sheaths is

$$\overline{V_g - V_1} = \overline{V_g - V_2} = C_2 / (C_1 + C_2) v,$$

where v is the R.F. amplitude.

If one puts a large blocking capacitor C in series next to C_2 , then the charging of the plasma should take place through both diodes (Fig.4b) and

$$\overline{V_g - V_1} = \frac{C_2}{C_1 + C_2} v, \quad \overline{V_g - V_2} = \frac{C_1}{C_1 + C_2} v.$$

The conclusion is that the larger drop develops in front of the sheath with the

smaller capacity. In fact

$$\frac{\overline{V_g - V_1}}{\overline{V_g - V_2}} = \frac{C_2}{C_1}.$$

In practice the capacities are non-linear circuit elements. They can be calculated using Langmuir sheath theory and it is clear that not only the electrode area but also the sheath current density plays an important role. Based hereupon Koenig and Maissel [13] found

$$\frac{V_g - V_1}{V_g - V_2} = \left(\frac{A_2}{A_1}\right)^4,$$

where A_1 , A_2 are the interface areas. The large power dependency suggests that to change the sheath potentials only a minor unbalance in the electrode area is necessary. This point which is very essential in the design and control of etch and deposition systems has been checked experimentally by several authors. Coburn and Kay [14] showed that the power law tends to follow (A_2/A_1) . Horwitz [15] following Godyak pointed to the various discharge modes possible in the domain studied. It is possible to have discharges where the capacitive impedance plays a dominant role (e.g. Ar, 13.5 Mhz) and those where the resistive currents are dominating. In the first case charge can be stored in the discharge and only the current averaged over one period should be zero. In the second case instantaneous charge conservation is required. From Horwitz interpretation of Coburn's results it can be seen that the Koenig and Maissel law does not hold for both cases considered. Coburn's results are sustained by recent data by Köhler et al [16] who measured the energies of ions coming out of an argon plasma (Ar, 13.5 Mhz, 20 mTorr) having crossed the sheath. They concluded that in a D.C. coupled case the voltage drop ratio scales with the inverse of the area ratio, but that in an A.C. coupled case a larger power (≈ 2) is observed. Recently we developed an expression, based on a Langmuir sheath model and instantaneous charge conservation which explains the results of Köhler for the measured bias voltage v_c . From this model it appears that

$$v_c = V \cos\left(\frac{A_1}{A_1 + A_2} \pi\right) + \ln \frac{A_1}{A_2}.$$

From the same model it is found that

$$\frac{\overline{(V_g - V_1)}}{\overline{(V_g - V_2)}} \sim (A_2/A_1)^3,$$

which is in view of the data by Horwitz [15] and Köhler [16] a satisfactory result. To solve this problem in a more satisfactory manner a combination of both approaches should be followed. Both the conduction currents and the dielectric currents should be taken into account at the same time and results should be checked in a standard experimental situation.

3.3. Electron energy distribution

The basis for all modelling of discharges with low electron densities as they are

encountered in plasma surface processing is the electron energy distribution. They define both the transport properties of the plasma and the production rates of ions and excited particles. In molecular plasmas where chemical reactions occur with large rates the determination of this distribution is much more complicated than in monoatomic classical discharges. As Polak [17] already pointed out the superelastic vibrational deexcitation of molecules can be a very effective source of electron heating in the lower energy range. Therefore the distribution of vibrational states of the dominant molecule plays an important role. More general this implies that the solution of the Boltzmann equation for the electrons is embedded in the solution of a system of master equations of the relevant reaction products in their various states. The presence of a flowing gas complicates the problem even further. It is worthwhile to mention the work by the Bari-group which made a concentrated effort in modelling the decomposition of carbonmonoxide and the development of the EED in CO_2 and N_2 discharges [18,19]. Since these approaches are very complicated the programme sketched above has been hardly executed. Only isolated aspects have been subject of study. Margenau [20] was the first to show that in a homogeneous plasma without electron-electron interaction and inelastic collisions the EED can be written as

$$f(v) \sim \exp - \int_0^v \frac{mv \, dv}{kT_g + e^2 E_o^2 M / 3 m^2 v_m^2},$$

where v is electron velocity, T_g gas temperature, M and m are heavy particle and electron mass, v_m is the momentum transfer rate and

$$E_e = E_o \sqrt{v_m^2 / 2 (v_m^2 + \omega^2)},$$

where E_o is the amplitude of the R.F. field with circular frequency ω .

When $\omega < v_m$ and $v_m \sim v$ the Davydov-Drujvesteijn distribution evolves but for v_m constant a quasi-Maxwellian is found. The average energies are

$$\begin{aligned} \langle \epsilon_{DD} \rangle &\approx \sqrt{\frac{M}{m}} e E_o \lambda, \\ \langle \epsilon_{QM} \rangle &\approx \frac{e^2 E_o^2 M}{6m^2 v_m^2}. \end{aligned}$$

Here λ is the mean free path.

When $\omega > v_m$ because of the stochastic heating mechanism also a quasi-Maxwellian is found with average energy

$$\langle \epsilon \rangle_{SH} \approx \frac{e^2 E_o^2 M}{3m^2 \omega^2}.$$

Eletskii and coworkers [21] pointed out that in R.F. discharges where $\omega \geq v_m$, assuming constant v_m , the average gain between collisions amounts to $e^2 E_o^2 / m \omega^2$ and it takes M/m collisions before a new electron fits into the EED. When loss processes like diffusion and/or inelastic collisions dominate the average energy of the distribution should scale like

$$\langle \epsilon \rangle \approx \frac{e^2 E_0^2}{m\omega^2} \frac{\nu_m}{\nu_D},$$

where ν_D is the electronic diffusive loss rate. This occurs when $\nu_m/\nu_D < M/m$. Note that in this case $\langle \epsilon \rangle$ scales proportional with the square of the gas density. This reasoning can be extended to the lumped inelastic loss rate ν_{in} . It is clear that both diffusive and inelastic losses processes tend to decrease the average energy. To maintain a discharge the value of E_0 should be adapted. Calculations on R.F. discharge EED-s in a spatial homogeneous case solving the time dependent B.E. including inelastic processes have been published recently by Winkler et al [22], albeit only in the monoatomic gas neon. Their results show clearly under what conditions in the EED modulation effects appear. For electrons with energy below the excitation threshold in that part of the EED modulation effects appear when

$$\omega < \frac{m}{M} \nu_m.$$

In the high energy part where the energy loss rate is simply ν_{in} the EED will not follow the modulation for

$$\omega > \nu_{in}.$$

In a standard situation for planar R.F. glow discharges at 13.5 Mhz at low pressures

$$\omega \approx \nu_m \quad \text{and} \quad \nu_m \approx 10 \nu_{in},$$

one may expect to be at the edge of the on-set of field modulation.

Two recent interesting approaches should be mentioned here. Starting from the idea that the electrodes in a planar reactor are bombarded by ions of 100 eV or more. Garscadden [23] assumed that secondary electrons with a very high energy should be added to the B.E. as a source term at high energies. These electrons are very effective in carrying out inelastic collisions because of their energy but also because of confinement and multipactor effects. In this respect the influence of these electrons is similar to fast electrons in a hollow cathode glow discharge. This idea has been checked in a mixture of silan and hydrogen. Numerical calculations showed that the number of fast vs. slow electrons could be 10^{-4} .

Kushner used a Monte Carlo method in calculating the EED in a planar R.F. glow discharge [24]. He also included secondary electrons emitted from the electrodes acting as an e-beam and found a solution in both energy and space in one dimension; in Fig.5 one can see some of his results for CF_4 , the electrode spacing is 3 cm, the gas pressure 50 mTorr and the R.F. frequency 13.56 Mhz. It can be seen that the electron energies in CF_4 are fairly high compared with common knowledge about electron energies in glow discharges of 1-3 eV. However, the same author states that his data are backed up by experiments [25]. Also in the fairly shallow planar geometry and at the relatively low pressures used, diffusion effects may have a large influence on the plasma balance, necessitating a higher electron temperature. That those effects may be strong has been shown by Vallinga et al [26]. He solved the B.E. in the standard situation in a CF_4 etching plasma (13.5 Mhz; 50 mTorr, electrode spacing $\sim 10^{-2}$ m). Here again $\omega\tau_m \leq 1$. Instead of a Fourier expansion in time, a multiple

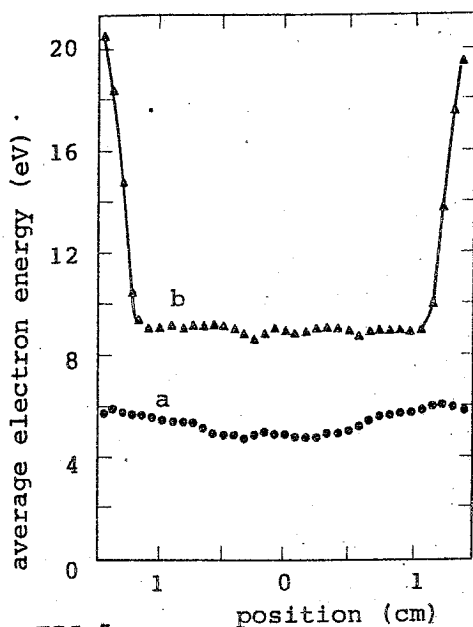


FIG.5 :

Typical computed result for the average electron energy in CF_4 in a planar discharge. Electrode spacing is 3 cm, gas pressure 50 mTorr (at 500 K), R.F. frequency is 13.6 Mhz. Curve a is without, curve b with secondary electron emission (from ref. [24]).

FIG.5

time scale formalism was used. The approach included elastic collisions and excitation, ionization, dissociative attachment and vibrational excitation. The spatial dependency was also taken into account. From the particle balance it was possible to obtain expressions for the breakdown and steady state values of the effective field strength E_e . In Fig.6 calculated values of E_e/p are shown as a function of the CF_4 -pressure.

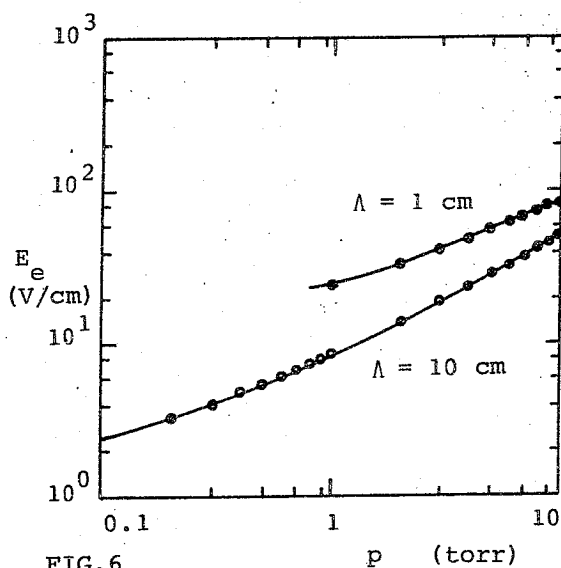


FIG.6 :

Breakdown ($\Lambda = 1$ cm) and maintenance ($\Lambda = 10$ cm) values of the reduced effective field in a R.F. plasma in CF_4 (13.6 Mhz) as a function of pressure (from ref. [26]).

FIG.6

In Fig.7 the EED at E/p of 12 V/cmTorr is shown. From the calculations it was also possible to explain some features in the experimental data of the average electron density in a planar R.F. plasma in CF_4 taken by Bisschops et al [27] (see Fig.8). One can see that at pressures in the order of 20 Pa the electron density per unit of input power displays a clear maximum. It is however not possible to ascribe this maximum to the transition pressure where $\omega = \nu_m$ and where the electron heating

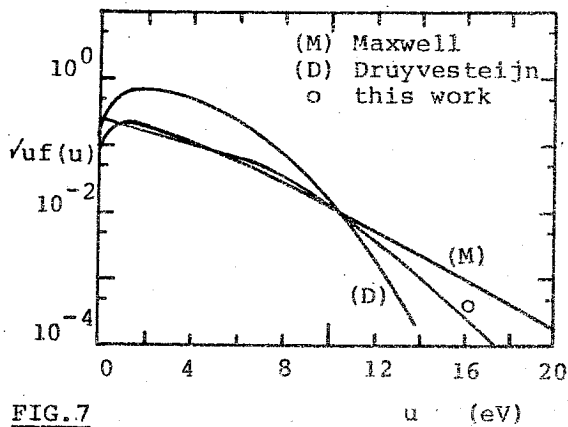


FIG.7

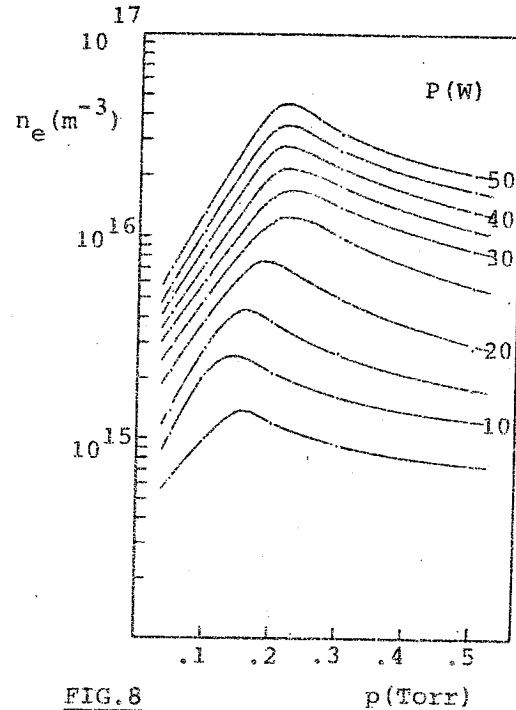


FIG.8

FIG.7 :

Calculated electron energy distribution compared with standard distributions of the same average energy (from ref. [26]).

FIG.8 :

Experimental values of electron density in quasi-planar R.F. discharge in CF_4 as a function of pressure at various input powers (from ref. [27]).

mechanism is changing character. For CF_4 this point should be at a pressure of 0.02 Torr. We noticed however that at the experimental value of 0.2 Torr the mean free path of an electron becomes of the order of the thickness of the glow; lowering the pressure will certainly have effects on the electron heating mechanism. This point is sustained by experiments in argon where no such effect has been found within the experimental range of pressures. This may be explained by the fact that momentum transfer cross sections are one order of magnitude higher in Ar than in CF_4 . Conclusively we may say that the work on electron energy distributions in low pressure etching plasmas is proceeding slowly. Possibly only the implementation of large scale computer efforts, on a scale as in laser or fusion plasma modelling will generate real breakthroughs.

3.4. Surface processes

In low pressure plasma etching the main point is the removal of surface material with good anisotropy and selectivity. Here we will sketch the viewpoints presently discussed on the various surface mechanisms. We will focus in on the controversy about physical sputtering and chemical sputtering discussing the results of some experiments. The spontaneous etch rate of a substrate can be drastically increased when exposed to fluxes of energetic particles. Ion bombardment appears to be the most important process, although electron beams and lasers are also used. Usually the

process is subdivided into three steps [28].

The first step is chemisorption of the particles taking part in the etching process. The next step is the formation of the reaction product. The third step is the desorption of the reaction product. E. g. first in a F-Si system F_2 is chemisorbed (when F-containing molecules are used this chemisorption has to be dissociative). After formation of the saturated product (SiF_4) desorption of the molecule follows, although it is known that SiF_2 is also a reaction product [29]. The presence of a discharge may influence all three steps.

- I. - The formation of radicals from the plasma increases the chemisorption on surfaces which appear inert to the parent molecule.
 - The ion bombardment may enhance the access to the surface of etchant species by preventing the blockage of the surface by deposition of unsaturated species and polymerization.
- II. The formation of reaction products is a complex phenomenon.
 - Winters [28] considers this step to be similar to the oxidation of a surface. The difference is that halogen compounds usually are volatile. Anion and cation formation generate electric activity which assist the kinetics of the reactants in the surface layer. Ion bombardment may supply energy for the activation of those reactions producing weakly bound molecules desorbing into the gas (chemical sputtering).
 - Flamm et al [30] stress the possibility of damage induced by the ion bombardment resulting in active sites at the surface and several monolayers below where the product formation can take place at higher rates (damage induced chemical reaction, RIE).
- III. - Ion bombardment may assist the desorption rate of adsorbed reaction products by sputtering. This process is known as chemically enhanced physical sputtering.

It is clear that in any etching process, depending on the composition of the etching gas and the character of the substrate one or more of the mechanism indicated above may dominate. It is in this specific field that only slow headway is being made and that controversial interpretations of the scarce experiments is evident. An interesting example of this phenomenon will be discussed here.

In order to find definite answers to questions in this field experiments should be well defined. The etching of silicon by chlorine under simultaneous bombardment of argon ions has been investigated recently in beam experiments by several groups. Recently Sanders et al [31] and McNevin et al [32] addressed the question whether physical sputtering or chemical sputtering is the dominant mechanism in the etching of silicon. Both experiments were similar albeit that in one of the experiments the substrate temperature could be varied. A new feature in both these experiments was the use of ion beam modulation techniques in order to analyze the time dependency of the etching process. Sanders found that the dominant product was $SiCl_2$ and $SiCl$. Interesting is that the products show an energy distribution which is definitely super-thermal (Fig.9) and the authors drew the conclusion that physical sputtering plays a dominant role in the $Si(Cl, Ar^+)$ process. On the other hand McNevin found the

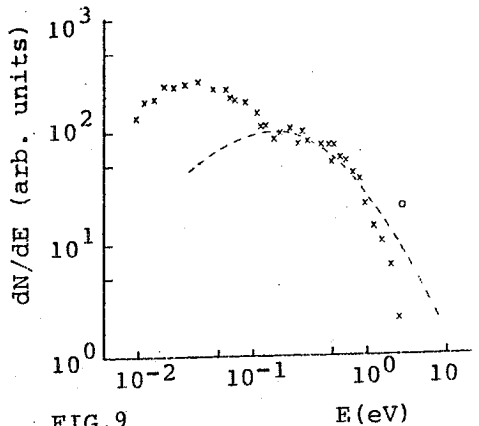


FIG.9

Kinetic energy distribution of SiCl₂ from Si surface under Ar⁺ and Cl₂⁻ bombardment (ion energy 1 keV, substrate temperature 300 K) (from ref. [31]).

FIG.9

dominant product to be SiCl₄ and observed a definite time delay for the reaction to get started after the ion beam has been switched on. Thus suggest an ion-enhanced chemical reaction, where the incident ion provides energy to the surface and this energetically excited surface then has an enhanced reaction rate to form the SiCl_x products. These experiments using quite sophisticated techniques give a good idea what the state of the art is in discriminating the various surface reactions. A lot of progress has been made in the experimental approach, but controversies still flare.

3.5. Etch plasma modelling

In the last couple of years several groups have tried to set up plasma models of R.F. discharges at conditions comparable to etch- and deposition conditions.

A number of studies have concentrated specifically on discharge dynamics. From these the recent work Tachibana et al [33] should be mentioned. They studied a discharge in methane, compounded a complicated discharge model based on a manifold of coupled rate equations and checked their model by measuring the EED, the dissociation of CH₄ by an absorption technique and the deposition rate of carbon films.

In Fig.10 the concentrations of the various reactants vs. power input as they emerge from the model is shown. From the deposition rate it was concluded that the active species for the deposition should have a density of 10¹¹ - 10¹² cm⁻³. When the sticking probability of CH₃ is close to unity this radical certainly is the one responsible for the deposition. If however the sticking probability of CH₃ is lower, it was concluded that CH₂ is the molecule responsible for the deposition. From a study like this it can be seen how complicated it is to model a plasma which is really etching. Apart from the homogeneous reaction also heterogeneous processes should be taken into account and problems like reactor loading and flow dependency should be faced.

Recently Edelson and Flamm published a one dimensional plug flow reactor model of flowing CF₄ etching Si. They did not calculate the electron energy distribution in a self consistent approach but instead plugged in a plasma density and an electron energy from experiment.

A cylindrical packet of gas is flowing in the downstream direction entering and passing the active plasma region and an afterglow region. The corresponding one-dimensional equations for the production and loss of the various species can be

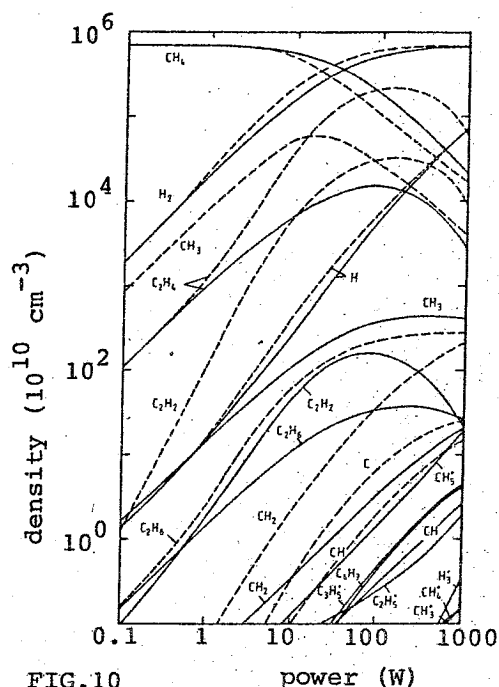


FIG.10

Calculated densities of CH_4 and other species produced in a planar R.F. discharge (13.6 Mhz, 0.22 Torr) vs. input power. (Solid lines : CH_3 sticking probability 1, dashed lines : CH_3 sticking probability 10^{-3}) (from ref. [33]).

FIG.10

treated as an initial value problem. The authors took into account 16 gas phase reactions, 11 surface reactions, ambipolar diffusion of electrons, positive and negative ions, surface recombination and polymerization. Rate constants were put in that were known from literature, although measuring conditions may not be matching. In some cases rates from homolog reaction or only order of magnitude estimates have been put in. In Fig.11 we can see the development of the various concentrations along the distance coordinate for a CF_4 plasma containing Si. (Fig.11a Charged species, Fig.11b Neutral species). It is noteworthy to stress the important role

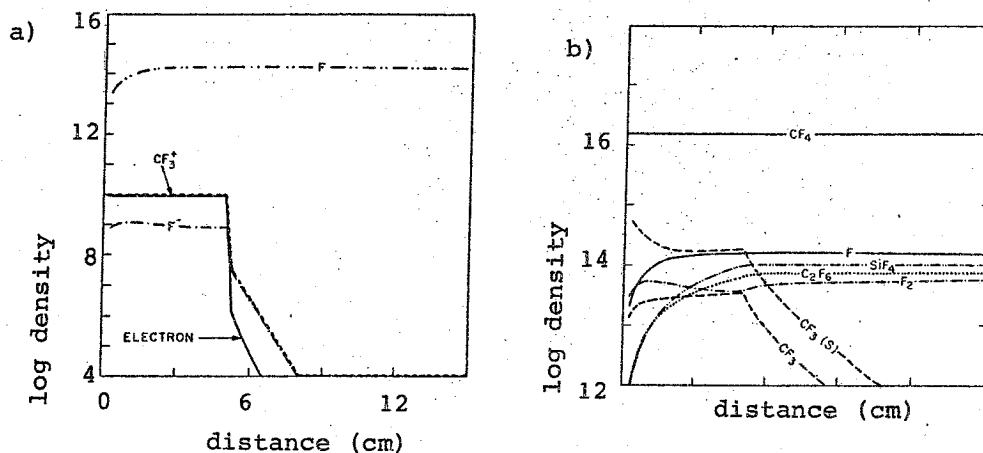


FIG.11 : Model calculations of density of species in and downstream of active CF_4 plasma zone etching Si. a) Ionic densities vs. distance, b) Neutral species vs. density (from ref. [34]).

C_2F_6 which is being formed from CF_3 . The comparison with an experiment consisting of downstream sampling of neutral species with a mass spectrometer was only partly satisfactory [35]. A full quotation from the paper by Edelson and Flamm may sum up properly the present state of modelling of plasmas used for plasma chemical applications.

"The results show that many key processes are very poorly known from a quantitative standpoint. Major uncertainties arise from the transport of radicals and ions, which has been included in the mechanism in an approximate manner, with rate coefficients which are only crude estimates. Improvements to the model will most certainly require a more detailed representation of transport in what is essentially a three dimensional problem, - - - - -

Expansion of the gas phase chemistry model does not seem to be warranted, however the surface chemistry needs better quantifications".

4. Final remarks

In this presentation we only were able to give a glancing survey of the physical problems encountered in the applications of plasma to chemical processing. Here in this field of exploding size so many disciplines meet that one can hardly speak of a cross- or interdisciplinary science, but of a discipline in itself. Workers have to be able to understand if not to speak the language of physical chemistry including surface physics, surface chemistry, atomic and molecular physics but also that of plasma and discharge physics.

A noteworthy trend is that applications seem to be running ahead of more fundamental studies. This certainly does not contribute to the scientific status of the field. In this respect plasma physicists have an obligation of staying in touch with the applications, their main task being the improvement of diagnostic methods and the design and use of numerical codes.

5. Acknowledgements

The authors would like to express their gratitude for the support by their colleagues from the group Plasma- and Atomic Physics (EUT) in the preparation of this contribution.

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