Plasma surface modification and plasma chemistry

Schram, D.C.; Bisschops, T.H.J.; Kroesen, G.M.W.; de Hoog, F.J.

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Technical University of Eindhoven, The Netherlands.
P.O.Box 513, 5600 MB Eindhoven, The Netherlands.

1. Introduction.
Fundamental knowledge of the dynamics and kinetics of the fourth state of matter: plasmas, have been developed in the framework of light production, of astrophysics, gas lasers and to a large extent of thermonuclear fusion. Especially in the course of large scale fusion research much attention has been paid to dynamics, instabilities and equilibria of magnetized plasmas. These were mainly hydrogenic plasmas of relatively high temperatures, which can be considered as collisionless magnetized fluids. Even so, radiation losses and wall interaction has persuaded researchers in this field to study also excitation kinetics and the influence of heavy particle interaction as non resonant charge transfer between highly charged impurity ions and neutral hydrogen particles.

In the last decade another field of interest of plasma research has become more and more important: plasma chemistry. This subdiscipline has evolved as an extrapolation from chemical techniques as volume chemistry and chemical vapour surface modification as is clear from the nomenclature. In the first approaches plasmas were seen merely as a high temperature medium with large specific reactivity. Of course, pretty soon it was realized that a plasma is rarely in, or even close to, thermal equilibrium so that it cannot be defined by one temperature. Right now, it would be better to describe the field as plasma physical chemistry, or to see it as another branch of plasma-physics. The research has also been mainly of phenomenological nature; even so plasmas have been applied successfully in many techniques in a short time as plasma enhanced chemical vapour deposition (PECVD), plasma etching, and polymerization e.g. in (sub)micron integrated circuit technology and also new materials as plasma-polymers have evolved from these studies. The importance of this branch of plasma physics has become enormous and more and more university groups and research institutes start to devote attention to it. However, the other starting point (chemistry and surface physics) has caused a late introduction of diagnostic techniques and fundamental concepts developed in other branches of plasma physics research as thermonuclear fusion. This process could be accelerated if at least on the fields of diagnostics and plasma-description contact is organized between the various subfields of our discipline as in this conference.

In this paper we will shortly review various applications, divided in three major subfields. To illustrate the physics we will concentrate on a description of plasma etching in a RF-plasma. Then we will indicate possible ways for a systematic approach based on plasmaphysical principles there with supplementing the somewhat heuristic character of the chemical kinetics approach. In doing so we will see that not the (electron) temperature, but the electron density and the ionization degree are the characteristic plasma parameters and should be used in a classification of plasmas.

2. Plasma chemistry applications.
The various applications of plasma covered by the name plasma chemistry can be subdivided in three main branches:
   a. volume chemistry
   b. surface modification
   c. spraying, welding, melting, extractive metallurgy.
We will shortly review these application fields and then concentrate on surface-modification.

2a. Volume plasma chemistry is used to convert chemical species into new gaseous products. In the discharge radicals and ions are formed which serve as intermediate for the formation of new molecules. A pertinent example of this class is the conversion of oxygen molecules into ozone in the so called ozonizer (Nagelschatz (1983)). Usually a corona type discharge (Goldman, Goldman, Sigmund (1985)) is used as discharge; also attention is paid to the silent discharge, in
which intermittent current pulses run between capacitively coupled isolated electrodes separated by a small gap. Another example of this line is the conversion of methane into acetylene and nitrogen binding in D.C. arcs.

Also plasmas used in spectrochemical analysis (Raaijmakers and co-authors (1983)) fall in this class. A very important discharge type is the so called ICP, inductively coupled plasma (Boulos, 1985) shown in Fig. 2. Here the plasma is used to dissociate, excite and ionize the chemical species of the sample introduced as an aerosol in the central gas flow which is injected in the inductively coupled plasma in the carrier gas, usually argon. The radiation is used to determine quantitatively the amount of elements present in the sample. Detection limits are in the order of 1-10 ppb for most elements.

Plasma surface modification is an assembly name for many forms of surface treatment. In the thermonuclear fusion research cleaning of tokamak walls is one example. Plastic surfaces can be made wettable by plasma wetting. Plasma etching, plasmadeposition and polymerization are widely used as process steps in e.g. (sub)micron IC technology. Still other examples are found in nitriding, boriding and carbonizing of steelsamples to improve hardness and durability of the surface. A variety of discharges are used for these techniques: capacitively or inductively coupled RF plasmas, corona discharge, silent discharge, arcs, magnetron, and microwave discharges. The latter is sometimes used with magnetic fields at electron cyclotron resonance conditions. Optimization of layer or treatment quality and efficiency and rates of the process looks still possible provided a more systematic approach would be possible.
Plasma etching is a very important item in the group as it is an essential process step in IC technology. With plasmas the etching can be anisotropic which is essential to reach the required (sub)micron lateral dimensions. The anisotropy, i.e. the lateral etching is much smaller than the perpendicular etching, is caused by the ions which are accelerated through the potentials developed across the sheath between the plasma and the substrate. In section 7 we will give a detailed description of the etching process, which at the same time serves as an example of RF plasma surface treatment.

Plasmadeposition is the second major application area. The discharge is used to produce radicals, which with ions lead to deposition of amorphous layers at the surface of the substrate. One can start from gaseous species as methane for amorphous carbon layers and silane (SiH₄) for amorphous hydrogenated silicon layers.

2c. Surface covering, joining, cutting, wetting. In this third subclass of plasma processing the plasma is primarily used to provide heat and momentum: the reactive properties are of less importance. Plasmaspraying (Fauchais (1985)) is one of the major applications here.

In the plasmagun, gas (argon with hydrogen, nitrogen) is ionized, heated and accelerated. In the resulting plasmajet with temperatures in excess of 10,000 K and velocities of 400 m/sec, spray particles are introduced. These particles are accelerated and heated to the melting temperature during the distance to the substrate. They are finally splashed onto the surface and adhere by subsequent processes in the droplet and substrate. At first sight this process resembles plasma deposition, but it is quite different in procedure, process and result. In plasma deposition the layer is deposited atom by atom, whereas in plasmaspraying particulate matter of typically 50µm size is sprayed as a whole on the surface.

Plasmamelting is another important example. Here plasmaguns are used which are similar in principle to the one described above. Again heat is used to melt the material and momentum is used to transport the energy away from the source. Other examples are plasma cutting, welding. Inductively coupled plasmas mentioned already under 2a. for spectrochemical analysis are also used in this application area, e.g. for plasma spraying or the production and sintering of ceramic powders (Akashi (1985)). Because of its advantage of clean operation it is also potentially a useful candidate for other preparational techniques as plasma deposition and plasma polymerization.

3. Why the use of plasmas
From the quoted examples of plasma treatment it is evident that the primary reason of the use of plasmas is the provision of a high temperature. Since the plasma is conducting it can be heated electrically (D.C. or RF) and plasma processing can be done in relatively small units without increasing the price significantly.

The high temperature leads to a large specific reactivity: this relates as well to reactivity per unit volume as per particle (atom or molecule). The reactivity is usually determined by the electron temperature, Tₑ, which does not need to be in equilibrium with the heavy particle temperature. In most discharges Tₑ is in the range of a few eV, whereas, at low pressure, the heavy particle, or gas temperature is close to ambient temperature. So, even though at low pressure the reactivity is lower than the one in chemical equilibrium at the electron temperature, the reactivity is very large since Tₑ is high, and is appreciably higher than the one of a gas at the gas temperature. This is probably the most pertinent advantage of the use of a plasma.
This feature enables one to have a high reactivity without the associated bulk heat content of a system in chemical equilibrium. The background gas may have a low temperature and also the density of the background gas can be low. The latter has a definite side advantage for e.g. deposition where the ambient pressure may be an important parameter. Also the temperature of the substrate to be treated or covered can be low. An independent variation and control of the substrate temperature is of importance to improve the quality of the product, e.g. the adhesion of deposited layers.

A definite advantage of plasmas is the large freedom of choice of materials. The easiest form of introduction of the desired materials is in gaseous form and though there are limitations here still a large variety is possible. But the material can also be introduced as a liquid in droplets of aerosols, or as a solid by sputtering or vaporization.

In many cases hazardous or environmentally problematic materials and/or products have to be dealt with. Then the high reactivity per particle (atom or molecule) is an advantage as this tends to improve the material efficiency and to reduce environmental waste production. However, as the plasma is a nonequilibrium system careful modelling and testing is required to optimize the system also for these aspects.

Because of several reasons it is advantageous to optimize with respect to material efficiency in the various processes. Larger rates would be possible with equal pumping speed; waste removal limits are less severe, and wall loading can be less. It is with respect to such optimization that a systematic plasma physical approach supported with modelling and experimental verification is desired.

Finally the achievable quality of the product is one of the major reasons to use plasma assisted technologies. Several plasmaproducts have unique properties which can only be achieved by these techniques. Again, to optimize, skillful handling and careful treatment on the basis of models and diagnosis helps to obtain the best achievable quality.

4. Plasma appearances

Depending on the power density absorbed by the plasma, on the type gas used and on the discharge geometry the plasma appearance shows a wide variety. The type of gas is of great influence as the atomic and molecular processes depend on it. As electrons and ions must be produced by ionization it is evident that ionization potential, and the reaction rates for these processes determine partly the plasma parameters and the plasma composition. As loss of electrons has to be compensated for by sufficiently fast production, a minimum electron temperature is required. A reasonable first guess for this important quantity is \( \frac{1}{4} \) of the ionization potential at low pressures down to \( \frac{1}{10} \) or lower at high (atmospheric) pressures.

The electron density, \( n_e \), and the ionization degree, \( \alpha = \frac{n_i}{n_e} \), defined as the ratio of electron density and gas density, \( n_g \), are the key parameters in plasmachemsistry.

Other important factors which determine the plasma appearance are the discharge geometry and the way the power is applied to the plasma. We will limit ourselves here to electrical discharges. One can distinguish between DC, RF and microwave discharges.

<table>
<thead>
<tr>
<th>Table 1. typical values for D.C. discharges</th>
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<tbody>
<tr>
<td>type</td>
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<tr>
<td>Townsend discharge</td>
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<tr>
<td>positive column normal glow</td>
</tr>
<tr>
<td>abnormal glow</td>
</tr>
<tr>
<td>medium pressure arc</td>
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<tr>
<td>Penning discharge</td>
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<tr>
<td>magnetron discharge</td>
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<tr>
<td>magnetized arc</td>
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RF discharge
RF plasmas depend primarily on the applied frequency: one uses low frequencies (10kHz-1MHz), intermediate frequencies (13.6, 27.2, 54.4 MHz) and ultra high frequencies (UHF; 100 MHz and higher). At lower and intermediate frequencies usually capacitive coupling is employed. RF discharges have the advantage above DC plasmas, that also insulating substrates can be treated.

In fact, potentials are built up which are important for directional (anisotropic) etching. The potential can be varied within certain limits by variation of the discharge geometry, e.g. larger or smaller electrodes, pressure and power.

Also inductive coupling is employed. As shown in Fig. 2, it can be constructed such that the plasma is only bounded by glasswalls. This enables very low levels of impurities as metals (smaller than ppB) which makes it suitable for plasmaspectrochemistry and for critical preparative applications. It has been modelled and analysed in detail by Boulon (1985).

Also microwave plasmas are used. They also can be dimensioned such that no metal walls surround the plasma. They usually burn stable and show somewhat higher electron densities than comparable RF discharges. Finally the corona discharge should be mentioned by using either sharp needles or thin wires with very small radii of curvature. At that electrode rather high field strengths exist, also because a large potential difference is applied (several kV).

The needle or wire can be either positive of negative (resp. positive and negative corona). In the latter one a repetitive discharge may exist (the so called richel pulses) especially in electronegative gases. In coronas large spatial and temporal variations in plasma density occur and these plasmas are difficult to classify.

5. Plasma characterization
It will be clear from the foregoing that a primary feature of plasmas is the presence of charged particles. As ionization in the majority of cases is primarily induced by electron collisions, electrons are the key characteristic even in very weakly ionized gases. It has already been stated that the presence of electrons leads to all kinds of radicals, whose densities can be even higher than \( n_e \). This leads to a large reactivity. Chemical equilibrium is by no means assured; only at high pressure and high power densities, plasmas may be close to local thermodynamic equilibrium (LITE), i.e. the system may be defined by only two thermodynamic variables. But as said, this is more an exception than a rule.

Therefore, it is advantageous to use as a first parameter: the electron density \( n_e \). In practically all cases it determines the reactivity since in any case in some step it takes care of excitation, dissociation and ionization. As a second parameter a quantity related to the gas density \( n_g \), is a good choice. This could be the total pressure, but we will use the ionization degree, defined as \( \alpha = n_e/n_g \). This choice has a very definite advantage for the division of the plasma into two distinct regimes: of low ionization degree and of "high" ionization degree. The boundary between these two regimes is about at \( \alpha \sim 10^{-2} \). There are several reasons to make this distinction useful.

The first reason is that of the dominance of either collisions with neutrals or Coulomb collisions. At low ionization degrees (below 1%) the collisions of electrons with neutral gas particles are more frequent than those with ions. As a consequence all transport properties, as e.g. the conductivity, are determined primarily by these electron-neutral collisions. This is the well known gasdischarge regime. At the other hand if the ionization degree is sufficiently high (\( \alpha > 1\% \)) electron-ion Coulomb collisions outweigh the collisions with neutrals. In this regime several transport properties as e.g. the resistivity are determined by Coulomb collisions: the resistivity does not depend on the neutral density and is a function of the electron temperature only.

A (related) second reason for this division into two regimes is found in the form of the electron energy distribution. For high ionization degrees (\( \alpha > 1\% \)) the electron-electron collisions are frequent and tend to maintain a Maxwell distribution. Hence, the electron energy distribution can be characterized by a temperature, \( T_e \), which facilitates the calculation of rates of inelastic processes.

For very low ionization degrees (\( \alpha < 1\% \)) substantial deviations may occur for several reasons and care has to be taken in the calculations. A third reason is the behaviour of the heavy particle temperature. The energy coupling between electron and heavy particles as ions and neutrals is poor in view of the large mass ratio. So, for low ionization degrees the neutrals are hardly heated and one speaks of "low temperature" plasmas. However at higher \( \alpha \)'s the heating of ions by electrons start to play a role and at even higher \( \alpha \)'s the heavy particle temperatures may approach the electron temperature. That is the regime of thermal plasmas, at least at higher pressures. In some literature one refers to this regime as high temperature plasmas, but this name is also used for the very much hotter thermonuclear plasmas.

Also the ion dynamics change around the discussed boundary for \( \alpha \sim 10^{-2} \). Above that value usually ion-ion Coulomb collisions outweigh ion-neutral collisions and again the ions can be defined by an ion temperature \( T_i \) (which does not need to be equal to \( T_e \)).
For all plasmas to be discussed ion-neutral collisions dominate the ambipolar diffusion process. This is so, even in the high ionization regime since the ion-ion collisions do not hamper the particle transport in first order.

There is an exception if a magnetic field is applied and the transverse diffusion is reduced. In order to elucidate the characterization, plasmas used in several applications are plotted in Fig. 4 where the coordinates are \( n_e \) as abscis and \( n_e/n_0 \) as ordinate.

\[
\frac{n_e}{n_0} \quad 10^{-8} \quad 10^{-6} \quad 10^{-4} \quad 1 \quad 10^2 \quad 10^4 \quad 10^6 \quad 10^8 \quad 10^{10} \quad 10^{12} \quad 10^{14} \quad 10^{16} \quad 10^{18} \quad 10^{20} \quad 10^{22} \quad 10^{24} \quad 10^{26} \quad p(W/m^3)
\]

Fig. 4. Plasma characterization: gd: glow discharge; ag: anomalous glow; a: arc; t: thermal plasmas.

It is observed that all non-magnetically confined plasmas group roughly along the line \( n_e/n_0 = (10^{-21} n_e)^6 \) where \( n_e \) is in \( m^{-3} \).

This is consistent with the requirement that the Debye length, \( \lambda_D \), has to be considerably smaller (100 times) than the ion-neutral mean free path, \( \lambda_{10} \). Apparently, the ambipolar field must be sufficiently small for the plasma to exist. In magnetically confined plasmas the constraints are different and a higher degree of ionization is achievable.

6. Plasmasurface modification.

Plasmasurface modification is the most important branch of plasmachemistry and deserves a more elaborate discussion. It is also an important item in thermonuclear fusion and many of the underlying physical mechanisms as sputtering and redeposition have been studied in detail by thermonuclear physicists active in surface physics. The elementary reactions at the surface have also been investigated by several plasmachemical groups. It is generally assumed that radicals, ions and possible photons and vibrationally excited parentor molecules play an important role (Agostino 1985). In specifically designed experiments the role of simultaneous impact of ions and adsorption of radicals have been studied. In these experiments a surface, e.g. Si, is bombarded with an ion beam whereas it can be simultaneously flushed with an unsaturated fluor, or chlorine compound or atom. The resulting etched products are ionized and subsequently mass selected and energy analysed by time of flight analysis. A typical experiment conducted by Sanders et al. (1985) is illustrated in Fig. 5a, with a typical time of flight spectrum converted to an energy spectrum in Fig. 5b. In this paper the authors conclude from the dominance of a high energy tail of the spectrum that the mechanism is sputtering by ions from a surface layer which is chemically modified by the incident flux of chlorine molecules. In this interpretation the chemical part of the process is limited to the chemical modification of the surface atoms of the substrate. A similar experiment conducted at Bell [Mc. Nevin and Becker, 1985] lead the authors to a somewhat
different conclusion. They tend to prefer an explanation which is labelled ion-enhanced chemical reaction, where the incident ion provides energy to the surface and this energetically excited surface then has an enhanced reaction probability to form the silicon chloride products. Whichever reaction is dominant may depend on the conditions of the experiment as ion energy and the incident neutral chlorine flux. In any rate the fact that the results of incident radicals and ions can be larger than the sum of the two fluxes separate can well be deduced from Fig. 6, which is taken from a paper by Coburn and Winters (1979) which is generally regarded as pioneering work in the area of plasma chemistry by halogens. In this figure it is clearly observed that the etching rate of the combined actions of ions and radicals is an order of magnitude larger than that of the separate fluxes alone.

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**Fig. 5a.**
Schematic view of TOF apparatus used for the study of surface interaction. 1-4, ion source including mass and energy vibration and chopping; 5, oven on which target, 6, is mounted; 7, reactive gas inlet; 8, diaphragm; 9, ionizator; 10, quadrupole mass spectrometer; 11, detector. From Zalm (1985).

**Fig. 5b.**
Time-of-flight spectrum of SiCl obtained by bombarding Si at 300°C with 3 keV Ar⁺ ions (flux approx. 5x10¹⁴/cm²/s) under simultaneous exposure to a Cl₂ gas flux of about 5x10¹⁵/cm²/s.

Insert. Corresponding energy distribution curve. The fitted substrate temperature Maxwell-Boltzmann distribution (1) as well as a local thermal equilibrium contribution (2), fitted to the high energy tail, and a collision cascade contribution (3) are indicated. From Zalm (1985).

**Fig. 6.**
Experimental proof of ion-enhanced gas-surface chemistry, as taken from Coburn and Winters (1979). It concerns a Si-surface, irradiated by XeF₂ molecules (2.10¹⁸ mol/s) and Ar⁺-ions (2.5 μm).
So, the conclusion can be drawn that the plasma serves to provide radical and ion fluxes and that the plasma physics task is to optimize conditions regarding the magnitudes of these fluxes. One element of the etching which is important in the explanation of the mechanism is the anisotropy, which at the same time is also a very important characteristic of the plasma etching in IC technology. This underlines the role of ions; Flamm (1981) proposes two possible mechanisms. One involves damage induced by ions and subsequent chemical etching, the other the activation of adsorbates at the surface by ion impact.

A third information can be obtained from the selectivity. Several systems show selectivity with regard to the etching rates of various substrate materials; also this is a favourite aspect of the plasma etching process. Selectivity indicates at least one chemical step; activation of adsorbed radicals by ions would explain the accompanying anisotropy.

It should be noted that dominance of physical or chemical processes may well depend on the conditions in plasmachemical situation. At low pressures and high powers sputtering may be dominant, and the process is called ion milling, with good anisotropy and poor selectivity. With increasing pressure and decreasing ion energies the process changes via reactive ion etching. Ion assisted plasma etching to chemical etching. With the decreasing role of energetic ions the anisotropy deteriorates whereas selectivity becomes better.

In the following section where we discuss the plasma etching process from the plasma physics point of view we will assume the existence of an adsorbed layer of radicals, referred to as gasadsorbed layer. The actual composition of this layer will depend on an effective temperature, which in turn depends on the incident power flux and substrate temperature. Incident ions with energies of 100 eV will pass and activate the layer and modify the surface of the substrate. In this picture the plasma physics part is to specify the net radical fluxes, the ion fluxes and ion energies.

7. Plasma etching.

In this section plasma etching will be described to illustrate the various processes which play a role in capacively coupled RF excited low pressure plasmas which are commonly used for etching, polymerization and deposition. In principle the method is simple; to a pair of electrodes a RF voltage difference is applied with frequencies from 100 kHz to several terms of megahertz. The electrodes can either be AC or DC coupled. In both variants sheath potentials will develop which play an important role in the surface modification process.

We will first discuss the basic reaction path and underline the conclusion with measured electron densities and ion fluxes to the surface. Also the occurrence of negative ions will be discussed.

The mechanisms operative for plasma etching can be ion milling at low pressure, ion assisted plasma etching at intermediate pressures and chemical etching at high pressures. Anisotropic etching is primarily caused by ion assisted processes; the in the sheath potential accelerated ions cause the etching to be mainly vertical. This is of great importance in the (sub) micron - technology, where in the production process several patterns of isolators, dopants, conductors and passivation layers have to be reproduced. To this end a mask is produced in which the patterns are produced by photolithographic techniques as shown in Fig. 7.

Fig. 7. Schematic representation of a part of an etched device. The pattern of the mask is reproduced in a functional layer (e.g. insulator). Isotropic etching results in undercutting, anisotropic etching results in vertical walls.

Several discharges types can be used. Low frequency, intermediate frequency and high frequency capacitively coupled discharges. Also microwaves are used sometimes in combination with electron cyclotron resonance (ECR). see Mejia and co-workers, 1985. In this section we will describe the physics of a 13.56 MHz RF single wafer plasma etch reactor. A single wafer etcher is an alternative for the larger so called batch reactor in which several wafers are treated, with lower rates. The simple wafer reactor is operated at larger power densities, so that the etch rate is usually larger. The smaller dimensions of the plasma permits better diagnostic access and a detailed description supported by measurements allows for a more general description of the physics of RF plasma.
Fig. 8. Sketch of the single wafer plasma etcher. a) normal set-up, b) enclosed in microwave cavity.

In Fig. 8 schematic sketch of the employed etch reactor is given. Two geometries are used: one is the common symmetric two plate RF geometry: in the second the ground electrode is replaced by an enclosure which serves with the RF electrode as a microwave cavity to permit the measurement of the electron density.

In the plasma electrons (e\(^{-}\)) and positive ions (+) are produced by electron impact ionization:
\[ \text{e} + \text{CF}_4 \rightarrow \text{CF}_3^{-} + 2\text{e} + \text{F} \quad (1) \]

Radicals are generated by ionizative dissociation, cf. eq. (1), by electron impact dissociation (eq.):
\[ \text{e} + \text{CF}_4 \rightarrow \text{CF}_3 + \text{F} + \text{e} \quad (2) \]

and by recombination of positive and negative ions:
\[ \text{CF}_3^{-} + \text{F}^{+} \rightarrow \text{CF}_3 + \text{F} \quad (3) \]

Negative ions are mainly formed by direct association
\[ \text{CF}_4 + \text{e} \rightarrow \text{CF}_3^{-} + \text{F}^{-} \quad (4) \]

The listed reactions provide for the dominant kinetics as shown by Bisschops (1987). Of course side and subsequent reactions may produce other positive and negative ions as CF\(_2\). CF\(^{+}\), CF\(_3\)\(^{-}\) and radicals CF\(_2\), CF, CF\(_2\)F\(_2\) and others as discussed in detail in a numerical study by Edelson and Flamm (1984). In following the dominant kinetic path we will obtain with reasonable accuracy the required fluxes to the surface.

So, for radicals, production, diffusion, adsorption, reaction or desorption in the gas layer are the relevant processes. For ions the production and ambipolar diffusion are important.

The mass balances for electrons (e) positive ions (+) and negative ions(-) read:
\[ \text{e} \quad n_\text{e} k_{\text{ion}} - n_\text{e} k_{\text{at}} = v_\text{e} \ell_\text{e} : \ell_\text{e} = -D_\text{e} v_\text{e} + \mu_\text{e} n_\text{e} v_\phi \quad (5a) \]
\[ (+) \quad n_\text{+} k_{\text{ion}} - n_\text{+} k_{\text{at}} = v_\text{+} \ell_\text{+} : \ell_\text{+} = -D_\text{+} v_\text{+} - \mu_\text{+} n_\text{+} v_\phi \quad (5b) \]
\[ (-) \quad n_\text{-} k_{\text{ion}} - n_\text{-} k_{\text{at}} = v_\text{-} \ell_\text{-} : \ell_\text{-} = -D_\text{-} v_\text{-} + \mu_\text{-} n_\text{-} v_\phi \quad (5c) \]

where \( n_\text{e} \) is the density of parent gas molecules (CF\(_4\)) and \( \ell_\text{e} = -e \Phi \) the e.s. field strength.

Two ways can be followed for calculating the number densities and reactive flows. The first is to solve the eqs. (5a-c) with the quasineutrality conditions
\[ n_\text{e} + n_\text{-} = n_\text{+} \quad (6) \]

and substitution of the relevant diffusion coefficients and mobilities. In the absence of negative ions the so called ambipolar diffusion is retained with coefficient
\[ D_\text{a} = \frac{D_\text{e} D_\text{+}}{D_\text{e} + D_\text{+}} \quad (7) \]

and the mass balance reads:
\[ n_\text{+} k_{\text{ion}} = v_\text{+} \ell_\text{+} : \ell_\text{+} = v_\text{+} D_\text{a} v_\text{+} \quad (8) \]

In the presence of negative ions the situation is more complex. The electron current density can then be expressed in terms of a more complicated diffusion coefficient, as described in Hollehan and Bell (1975).

However, this procedure leads to unequal results for the positive ion and electron currents to the substrate which is an unlikely results. The reason may be that quasineutrality is these low density plasmas may only be approximately fullfilled.

It is more straightforward to calculate the mass flow of positive ions just prior to the sheath from the balance integrated over the volume. By Gauss theorem we obtain
\[ \int \int \int n_\text{+} k_{\text{ion}} dV = \int \int \ell_\text{+} dS = \int (\ell_\text{+} - \ell_\text{-}) \quad (9) \]
At the electrode surface no negative ion current is expected nor it is observed. Even sideways negative ions are hardly observed. By stating the positive ion current to be mainly directed towards the RF and grounded electrodes we obtain

$$\int \int L_+ \, dS = \iiint n_e n_o (k_{ion} - k_{att}) \, dV$$

through which we expressed the positive ion flux in terms of a volume integral of the electron density and the ionization and attachment rates. A negligible negative ion current implies also the volume integral of the net production to be zero:

$$\int \int \int (n_e n_o k_{ion} - n_e n_o k_{rec}) \, dV = 0$$

This yields an estimate for the ratio (volume averaged) of $n_e/n_o$:

$$\frac{n_e}{n_o} \approx \frac{\frac{P}{V_0}}{}$$

From the rate coefficient and measured $T_e$ (see further) we infer $n_e/n_o$ ranging from $O(1)$ at 10 pascal to $O(10)$ at 100 pascal. Still eq.(10) proves that the positive ion flow to the substrate can be calculated from the production of electrons; so only the electron density and temperature are needed. From the electron mass balance we can learn that the temperature (more general electron energy distribution) must be in the range of $T_e \sim 3 - 4 \text{ eV}$. It illustrates again that $T_e$ is not a very indicative parameter; it is prescribed by the existence demand: at lower pressures it is approximately $1/4$ of the ionization potential, at higher pressures $1/8$ $E_{ion}$.

The electron density is more or less prescribed by the energy balance. For a molecular gas it reads:

$$n_e n_o [k_{ion} (E_{ion} + eV_{bias}) + k_{dis} E_{dis} + k_{vibr} E_{vibr}] = \frac{P}{V_0}.$$  

Since the rate constant for vibrational excitation is very large compared to $k_{dis}$ and $k_{ion}$ we find that the major energy losses are caused by ionization and subsequent acceleration in the sheath of positive ions and vibrational excitation of parent molecules in the bulk of the plasma. Again plugging in numbers we obtain $10^{16}/\text{m}^3$ for power densities of $1\text{W/cc}$ which proves to be the observed density.

In order to obtain an estimate of the expected etch rate we note that equating the volume integrated production of radicals and ions should be equal to the net flow (incident - desorption fluxes) to the wall. From this it is clear that the net radical flux will be somewhat larger than the ion flux incident on the wall. If we assume only 1 reaction per incident ion, which is probably a good estimate for $\text{CF}_4 - \text{SiO}_2$ etching we obtain $1 - 2 \text{ nm/s}$ for electron densities in the order of $10^{16}/\text{m}^3$ and ionization rates of $10^{-16}\text{m}^3/\text{s}$ at effective electron temperature of $3.5 \text{ eV}$. The etch rates have been measured in the open geometry: as can be observed in Fig. 9a. They are approximately proportional to the $\text{F}/\text{Ar}$ excitation also shown in Fig. 9a. In Fig. 9b the $\text{Ar}$ excitation is compared to the measured electron density in the closed geometry. From these two figures it appears likely that the etch rate is nearly proportional to the electron density, which on its turn is proportional to the power density.

Fig. 9. Comparison of RF power dependence of etch rate with that of the fluor and argon line intensities in open geometry a) and with the dependence of electron densities in closed geometry b).
In Figs. 10 and 11 the electron density is shown as functions of power and pressure. The decrease for higher pressures is connected with the presence of negative ions. Finally, the ion energies and ion fluxes have been measured as functions of power and pressure as shown in Figs. 12 and 13. The typical shape of the ion energy distribution can be explained by the time varying sheath potential and by collisions in the sheath. If we take the observed ion energies as being equal to the sheath potential we find also here a decrease with increasing pressure. Again this is most likely due to the occurrence of negative ions. Detailed results have been obtained by Gottscho (1987), who measured the electrostatic potential spatially resolved by laser induced fluorescence. He also obtained time dependent results.

Conclusively, the electron density is the rate determining parameter. With wall loadings of 1 W/cm² corresponding to 1 W/cc power densities the electron density is limited in CF₄ to 10¹⁶/m³ which prescribes etching rates (and deposition rates) of 1 nm/s in the case of SiO₂. For Si surfaces the rates are higher, as in that case the number of etched atoms per incident ion apparently is larger than one.

In microwave plasmas the electron densities are somewhat higher, up to 10¹⁷/m³; However, this goes with comparable power densities at the expense of the sheath potential therewith degrading the anisotropy of the etching. For deposition it is an interesting alternative; it is employed in glass fiber fabrication (Bachman, (1985)) and for other deposition purposes.

**Plasma deposition.**

As concluded in the preceding section, deposition and etching rates are limited by existence demands if the plasma is generated adjacent to the surface to be modified. There is a prescribed range of pressure (~ 10 pascal), size (~ 1 cm), electron density (10¹⁶/m³), rate (1nm/s) and power density (W/cc).

There are fundamentally two escapes from these existence demands. The first and obvious way is to apply a magnetic field. This limits the sideways diffusion there with cutting down on transport.
This in turn enables a larger electron density at lower pressures. This principle is applied e.g. in multipole configuration (cf. Drevillon and co-authors, 1983), which enables operation at relatively low pressures, which influences the film properties favourably. Other examples of the use of magnetic fields are Penning and magnetron discharges. A relatively new line is the combination of a magnetic field and microwave excitation under electron cyclotron resonance conditions. This line can be seen as another example of the favourable use of ECR as already was clear from the successful ECR-ion sources as developed by Geller (1986). Still other examples can be found in the "Wissensspeicher Plasma-technik" edited by A. Rutscher and H. Deutsch (1983). The other principle way out from the existence demands limitations is to separate plasma production geometrically from the plasma treatment section. Then the production can take place at high pressures, high power densities and electron densities. Even though this implies somewhat smaller dimensions the production power of electrons and ions is very large compared to lower pressure RF, operation. As treatment requires low pressures an expansion from the high to low pressure is a consequence which at the same time accelerates the produced plasma in the direction of the substrate. As the plasma production takes place at high pressure more or less complete dissociation occurs. The resulting ion densities and systematic velocities lead to very large particle fluxes and very large deposition rates up to 100 nm/s. This favourable behaviour is accompanied by relatively good material efficiencies at still moderate power fluxes.

These new lines in approaches of the surface modification processes proves the necessity of a plasmaphysics approach. It leads to the final conclusion of this paper that the area of plasmachemistry provides a new challenge to the plasma physics community to direct their skill to model and diagnose these plasmas and on basis of a further development of our discipline at the same time add new and advanced techniques for further optimization of plasma processing techniques. It forms also a basis to further develop the science of the combined system of plasma - solid state systems which already finds wide interest in the fusion community.

REFERENCES


