

Plasma as a medium for processing

Citation for published version (APA):

Schram, D. C. (1985). Plasma as a medium for processing. In P. Masee, & W. F. H. Merck (Eds.), *Advanced course on low-pressure plasmas : technology and applications, Eindhoven University of Technology, Eindhoven, June 26-28, 1985 : lecture notes* (pp. 1.1-1.16). Eindhoven University of Technology.

Document status and date:

Published: 01/01/1985

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.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

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Plasma as a medium for processing

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A general introduction to two subsequent plasmacourses:

1. Course on thermal plasmas
2. Course on low pressure plasmas

1. Introduction

Plasmas are increasingly used for processes to modify surfaces, for chemical processing, and to cover surfaces with specific layers. To illustrate the specific use of plasmas we will first briefly list several applications, and to arrive at some specific characteristic features of plasma processing.

1.a. Examples of plasma treatments

The applications can be roughly divided into three classes:

- 1.a.1. Volume chemistry
- 1.a.2. Surface modification
- 1.a.3. Heating and acceleration of particulate matter

1.a.1. In Volume Chemistry the plasma is used to enhance the reactivity in the medium. In normal chemistry this is achieved by increasing the temperature and pressure. As a consequence particles with a higher energetic state are produced, which serve as intermediate in the chemical reaction. If the chemical process is exothermic, then energy is produced whence the reactions are started and the temperature is kept high by the process itself. In this case the initial temperature rise is only required to start the process which can be explosive if the energy input by the reactions is larger than the energy loss. A pertinent example is the diesel-engine.

In endothermic processes energy has to be added to compensate for the increase in internal energy and for the energy loss.

In these processes the reactivity of the medium can be determined on the basis of chemical equilibrium considerations, a situation which is usually not present in plasma chemistry. Here, the reactivity of the medium is artificially enhanced above the level at the prevailing heavy particle temperature by the use of a discharge. A pertinent example is the production of ozone in ozone-synthesis apparatus. A well known method is the use of a (negative) corona discharge.

It will be clear, that here the emphasis will be to reach a high specific reactivity, i.e. reactivity per unit volume at a minimum of electrical energy. The reactivity can be characterized by the number density of radicals. A radical is defined as a particle which has a larger internal energy than the gas particles present at normal conditions.

So, in this definition the nitrogen atom: N is a radical in a nitrogen molecules gas. Other examples are oxygen atoms, nitrogen oxide NO, etc. in air atmosphere.

The number density, i.e. the number of particles per unit volume, of radicals is directly related to the specific reactivity of the medium. If this number density is not in chemical equilibrium then kinetic models have to be used to calculate the reactivity of the medium.

1.a.2. The second application area is surface modification. Here the surface of a substrate is modified. Reasons may be deposition and etching of several layers of different materials on substrates, the alteration of the surface to allow adhesion, the hardening of surface layers and to improve corrosion resistance of the substrate. In many of these applications it is essential that the temperature of the substrate can be controlled and be much lower than the temperature needed for the reaction. So the plasma serves here to provide the reactive gases and so to promote the chemical reaction on the surface whereas the substrate may remain cold. We will list here several examples of such surface modifications.

- cleaning of the surface

It can be important to release from the surface adsorbed gases and to remove any impurities from the surface. This can be achieved by using plasmas, in the so-called discharge cleaning technique. Usually the surface to be cleaned forms a part of a electrode; if it is an isolator a RF discharge is advantageous. Depending in the application the process effectivity can be varied, by proper choice of power density in the plasma and the employed filling pressure.

- wetting of the surface

For some applications it may be necessary to provide a wettability of a surface made of smooth material. This may be necessary for writing (bank cards) or to improve adhesive properties.

etching

Another important technique of this second class is the so called dry etching of surfaces. This is an attractive alternative for the wet etching techniques and has several additional features. An important advantage is the possibility of anisotropic etching, i.e. vertical etching and no horizontal etching. Another important item is the selectivity of the etching process. One substance must be etched (e.g. SiO_2) whereas the other exposed substances must remain intact (e.g. photoresist, Si). Both items are of great relevance in (sub)micron technology.

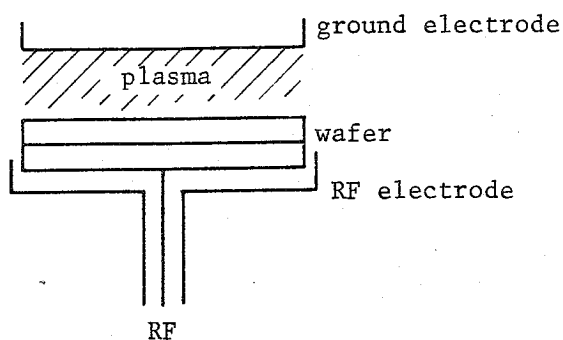


Fig.1. Schematic view of a single wafer etch apparatus

deposition

With plasmas it is also possible to deposit layers of all kind of materials on substrates. Plasma assisted chemical vapour deposition (PACVD) may be a good alternative to the well known chemical vapour deposition (CVD)-methods. Advantages are controllable substrate conditions, pressure, large freedom in choice of materials. Also the morphology of the layer can be influenced by the plasma and substrate conditions. Amorphous hydrogenated, polychrystalline etc. are possible. This technique is also of significance for sub-micron technology. Other important applications are a.o. solar cell fabrication, single mode glasfiber production (with profiled index of refraction), corrosion- and wear resistant layers.

polymerization

A related process is the procurement of layers of polymers. With appropriate materials and under specific conditions polymerization at the surface takes place during the deposition process. A polymer layer is the result. These techniques are a.o. being used in the optical and electronic industry.

boriding, carbonizing, nitriding

With the diffusion of several kinds of atoms into the surface of a substrate its surface properties can be changed. Well known examples are the hardening of steel by carbon or nitrogen. Also here plasma assisted techniques offer an attractive alternative for convential technologies.

They also have the advantage of a clean process.

"Ionitriding", i.e. nitriding by plasmas, is already used a long time. By the availability of new plasma techniques, the larger freedom of choice of materials and by conditioning, also here a further development is to be expected.

General features of surface modification processes are:
the fluxes of radicals, atoms and ions to the surface, the relation of these fluxes to the number densities in the

plasmas and the discharge parameters. Also the surface condition, the adsorbed layers, surface damage, are pertinent problems in this area.

Often limits are imposed to the fluxes of particles which eventually determine the rates of the processes, deposition rates, etching rates. This may be related to the surface conditions and adsorbed layers, to induced photon-damage or to the demand of anisotropy of the process.

1.a.3. 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; the plasma is a source of heat, to melt the material.

Plasmaspraying is one of the major applications here.

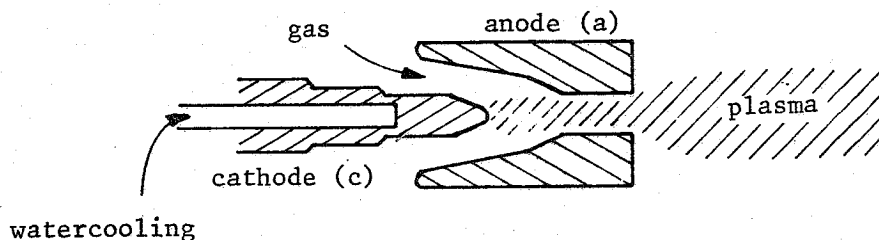


Fig.2. Schematic view of a plasma gun used for plasmaspraying

In the plasma gun, 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 50 μ 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.

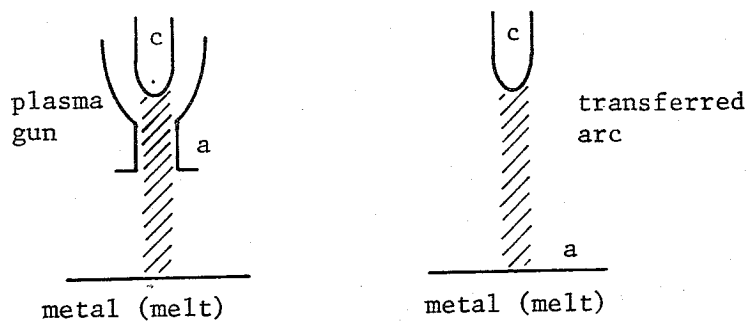


Fig.3. Schematic view of a plasma gun and a transferred arc used for plasma melting.

Another related area is plasma spectrochemical analysis. Here there is a chemical use of the internal energy of the plasma for the ionization and excitation of the

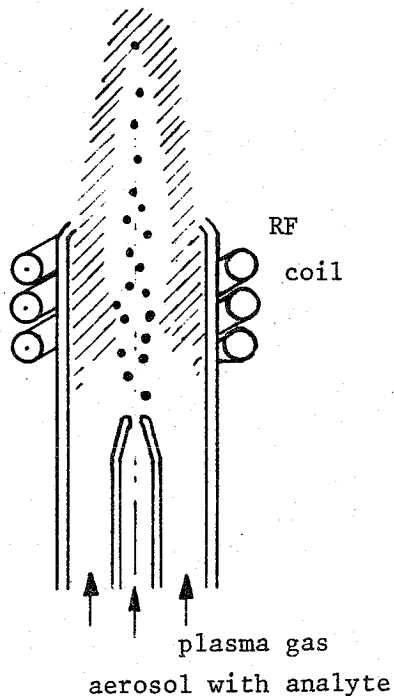
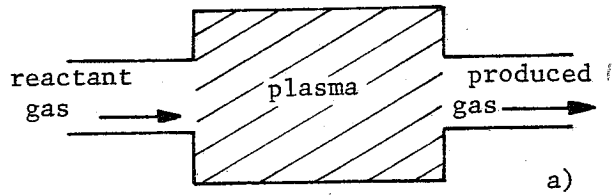


Fig.4. Schematic view of an ICP plasma used for spectrochemical analysis.

material to be analysed. However, the relative content of the sample in the plasma is small and the primary use of the plasma is again as a source of energy and momentum. One of the most important designs is the so-called Inductively Coupled Plasma (ICP). This has the advantage of clean operation and is also potentially useful for preparational techniques as plasma deposition.

To summarize, we have:

1.a.1. Volume chemistry



important parameters: Fig.5a

- volume of the plasma
- specific plasma reactivity
 - number density of radicals
 - (a.o. free atoms, ions, electrons)
- flow, throughput

1.a.2. Surface modification

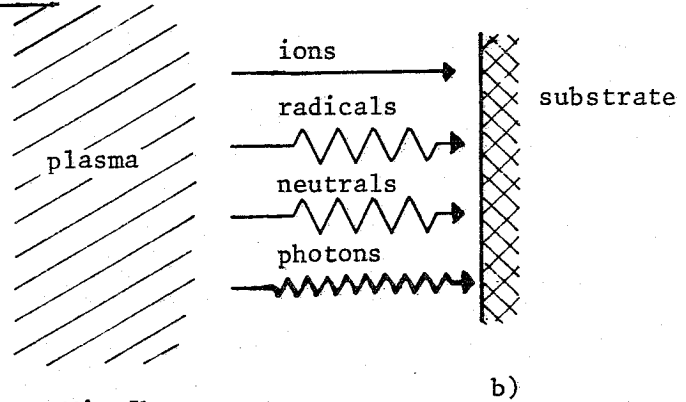


Fig.5b

- fluxes to substrate
- directionality of ion fluxes
- determined by power, pressure, flow

1.a.3. Surface covering and melting

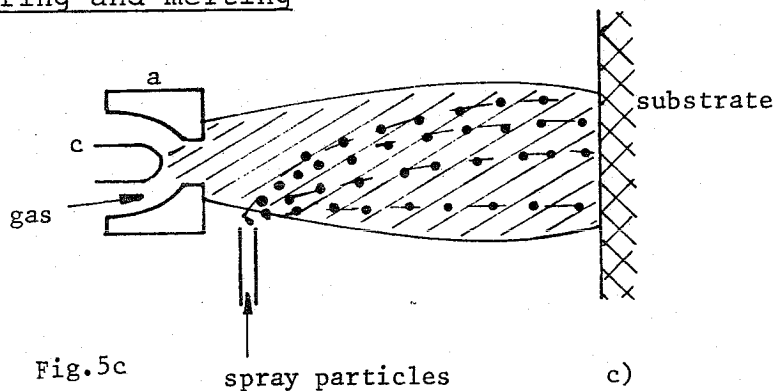


Fig.5c

- energy flow/content
- temperature
- momentum/velocity
- determined by power, pressure, flow

1.b. Why the use of plasmas

From the quoted examples of plasma treatments it is evident that the primary reason of the use of plasmas is the provision of a high temperature. Of course a high temperature does not necessarily require a plasma. In fact usually the plasma is electrically heated and this may not be the cheapest form of

energy.

Special advantages accompany the use of plasmas; generally plasma processing can be done in relatively small units without increasing the price significantly. More important is the large specific reactivity achievable in plasmas. This relates as well to reactivity per unit volume as per particle (atom or molecule). The reactivity is usually determined by the electron temperature, T_e , which does not need to be in equilibrium with the heavy particle temperature. In most discharges T_e is in the range of a few eV* ($1\text{eV} \underline{\Delta} 11.600\text{ K}$), whereas the heavy particle, or gas temperature is close to ambient temperature. Even though, particularly at low pressure, the system is not in chemical equilibrium, the reactivity is appreciably higher than the one of a gas at the gas temperature. So even though the reactivity is usually lower than the one in chemical equilibrium at the electron temperature, the reactivity is very large since T_e is high. This is probably the most pertinent advantage of the use of a plasma.

This feature enables one to have a high reactivity without necessarily the associated bulk heat content of a system in chemical equilibrium. The background gas particles which may be the majority 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.

Another related quality of plasma assisted methods is, that 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 or aerosols, or as a solid by sputtering or vaporization.

A lot of attention is paid to the material efficiency in plasma processing.

In some 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 this aspects.

Finally the achievable quality of the product is one of the major reasons to use plasma assisted technologies. Again, to optimize, skillful handling and careful treatment on the basis

*The unit eV is commonly used in plasmachemistry.
 $1\text{eV} \underline{\Delta} 11.6000\text{ Kelvin}$. The unit eV can also be used
 as energy unit; then it is equivalent to $1.6 \cdot 10^{-19}$ Joule

of models and diagnosis helps to obtain the best achievable quality.

In the subsequent lectures one will touch in detail many of the mentioned aspects of plasma treatments.

1.c. 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 plasmaparameters and the plasmacomposition. As loss of electrons has to be compensated for by sufficiently fast production a minimum electron temperature is required. A reasonably first guess for this important quantity is $1/4$ of the ionization potential at low pressures down to $1/10$ or lower at high pressures.

As the ionization potential differs for many gases also T_e will vary. In part also dependent on the power density are the electron density, n_e , and the ionization degree, n_e/n_g here defined as the ratio of electron density and gas density, n_g . In the second section we will argue that characterization of the plasma by n_e and n_e/n_g is a good guide in plasma chemistry.

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.

Tabel 1.

typical values for

D.C. discharges	type	current density	n_e	n_e/n_g	p
	Townsend discharge	10^{-1} A/m ²	10^{14} /m ³	10^{-7}	
	positive column normal glow	10 A/m ²	10^{17} /m ³	10^{-4}	
	abnormal glow	10^3 A/m ²	10^{18} /m ³	10^{-3}	around 10^{-3} at
	medium pressure arc	10^6 A/m ²	10^{19} /m ³	10^{-2}	
	atmospheric arc	10^7 A/m ²	10^{23} /m ³	1	1 at
	Penning discharge	10^4 A/m ²	10^{18} /m ³	10^{-3}	10^{-1} Torr
	magnetron discharge	10^4 A/m ²	10^{18} /m ³	10^{-4}	1 Torr
	magnetized arc	10^6 A/m ²	10^{20} /m ³	1	10^{-3} Torr

Electrode design is very important and needs much attention.

RF discharges

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 D.C. plasmas, that also insulating substrates can be treated.

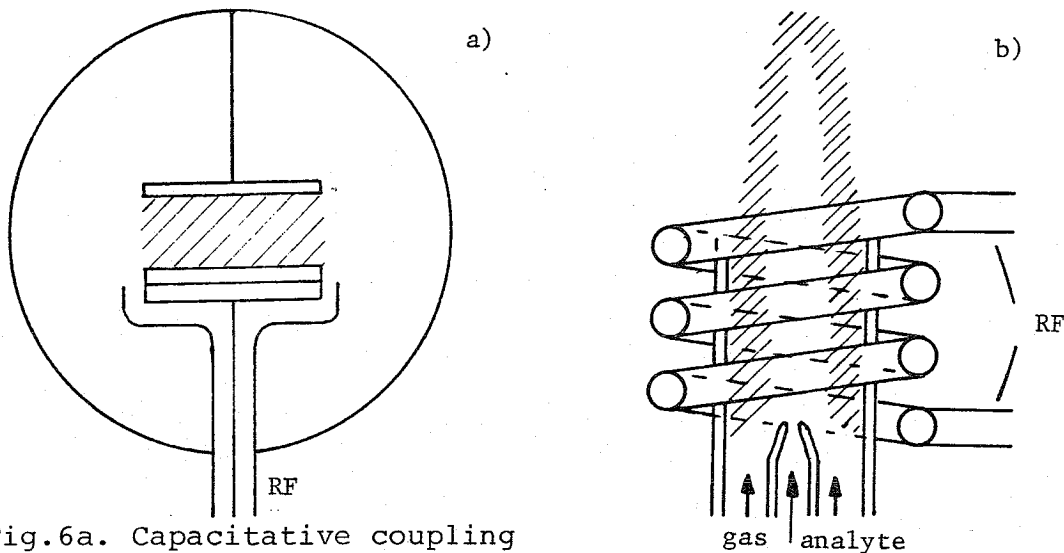


Fig. 6a. Capacitive coupling (single wafer etcher)

Fig. 6b. Inductive coupling (ICP-plasma)

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.

At intermediate and higher frequencies also inductive coupling is employed. As shown in fig. 6b 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.

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 as a special case. At one electrode, field amplification is achieved by using either sharp needles or thin wires with very small radii of curvature. At that electrode rather high field strength exist, also because a large potential difference is applied (several kV).

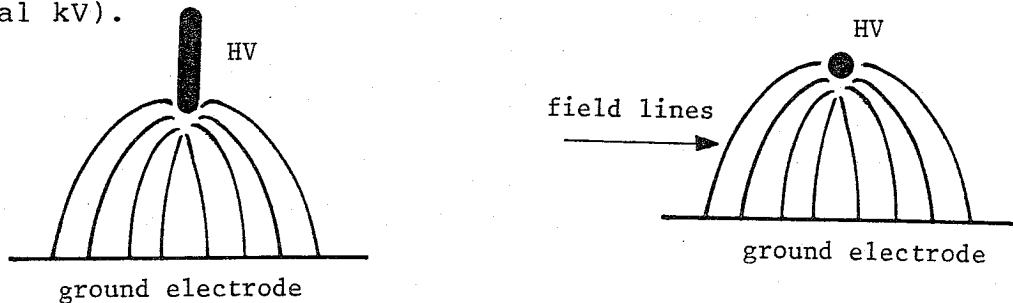


Fig. 7. Corona geometries: a) point-plate, b) wire plate.

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

Finally, the influence of the chemical processes, either in the volume or at the wall should be mentioned. They may influence the composition, the electron temperature, and give rise to negative ion formation. Also the importance of electrodes has already been referred to; it is also an important item in reliability considerations.

1.c.2. Some essential characteristics

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 kind 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 in high pressure, high power density plasmas the system may be close to local thermodynamic equilibrium (LTE), i.e. the system may be defined by only two thermodynamic variables. But as said, this is more an exception than a rule.

Another characteristic is that plasmas tend to maintain charge neutrality, i.e. to keep the positive charge density (ions) equal to the negative charge density (electrons and sometimes negative ions). Only in a layer adjacent to the wall a substantial electric field strength may be built up caused by very small excess of positive charges in the discharge. Hence, the name quasi neutrality is used:

$$n_e = n_+ \quad (1)$$

but large electric fields may exist in the sheaths because of a small unbalance. Another way to illustrate this, is to follow in time the evolution of a plasma.



Fig. 8. Ambipolar diffusion.

Imagine the charged particles to diffuse freely and independent. Because of the small electron mass and high mobility, electrons tend to diffuse faster out of the discharge than the colder and much heavier ions. Then even a small unbalance, a deficit of electrons, leads immediately to large positive space charges which hampers the electron

diffusion and helps the ion diffusion. This process continues up to the point when ions and electrons diffuse together, the so called ambipolar diffusion. Only in the sheath adjacent to the wall a strong unbalance in electron and ion densities can occur. The thickness of this sheath is related to the Debye shielding length, defined as:

$$\lambda_{DC} = \sqrt{\frac{\epsilon_0 k T_e}{n_e e^2}} \approx 7.10^3 \sqrt{\frac{\hat{T}_e \text{ (eV)}}{n_e}} \approx \frac{10^4}{\sqrt{n_e}} \quad (2)$$

Typical values are 100 μm for low density plasmas and .1 μm for very high density plasmas.

This sheath with associated potential difference which may accelerate ions to the wall is very important for plasma processing. It is an essential factor in the unidirectionality of plasma etching.

2. Plasma characterization

It has been clear from the foregoing that plasmas can appear in a large variety. The particular application of the plasma medium will determine which plasma parameters and which geometry and excitation is most appropriate. In the two subsequent courses several application areas will be covered, so here only a few general remarks will be made.

One of the most important parameters is the electron temperature T_e . For low ionization degrees, $\alpha = n_e/n_g < 10^{-2}$ significant deviations from Maxwell Boltzmann distributions may occur and it is better to use a average electron energy $\langle \epsilon_e \rangle$. However, the electron temperature (or $\langle \epsilon_e \rangle$) does not vary appreciably; it has to be at a certain minimum value for the plasma to exist and it can not rise fast with increasing power because of fast increasing radiation losses. So, at low and intermediate pressures a very reasonable first guess for the electron temperature of active plasmas (where the power is dissipated) is around $1/4 \epsilon_{ion}$, where ϵ_{ion} is the ionisation energy. At higher pressures (around 1 at. $\Delta 10^5 \text{ N/m}^2$) the temperature can be lower, typically around 1 eV ($\sim (1/15) \epsilon_{ion}$). So, the electron temperature is not a very good parametrizing quantity. The relative amount of excitation, which is related to T_e by at least an exponential Boltzmann factor would be a better choice, but is not very convenient in use and is rather abstract. Of course the reactivity is determined by excitation and in view of chemical use it would be appropriate to find a parameter related to reactivity.

To obtain a first insight 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 etc.

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 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 (the subjects of the two courses) is about at $\alpha \approx 10^{-2}$. 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 wellknown 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 low ionization degrees ($< 1\%$) 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 or average energies. 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 about "low temperature" plasmas. However at higher α 's the heating of ions by electrons start to play a role and at even higher α '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 changes around the discussed boundary for $\alpha \approx 10^{-2}$.

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. Like-Like (ion-ion) particle collisions do not change the total momentum of the total (ion) distribution.

There is an exception if a magnetic field is applied and when the electrons gyrate freely around the magnetic field lines. This is however beyond the scope of the present discussion.

In order to elucidate the characterization, plasmas used in several applications are plotted in fig.9, where the coordinates are n_e as abscis and n_e/n_g as ordinate.

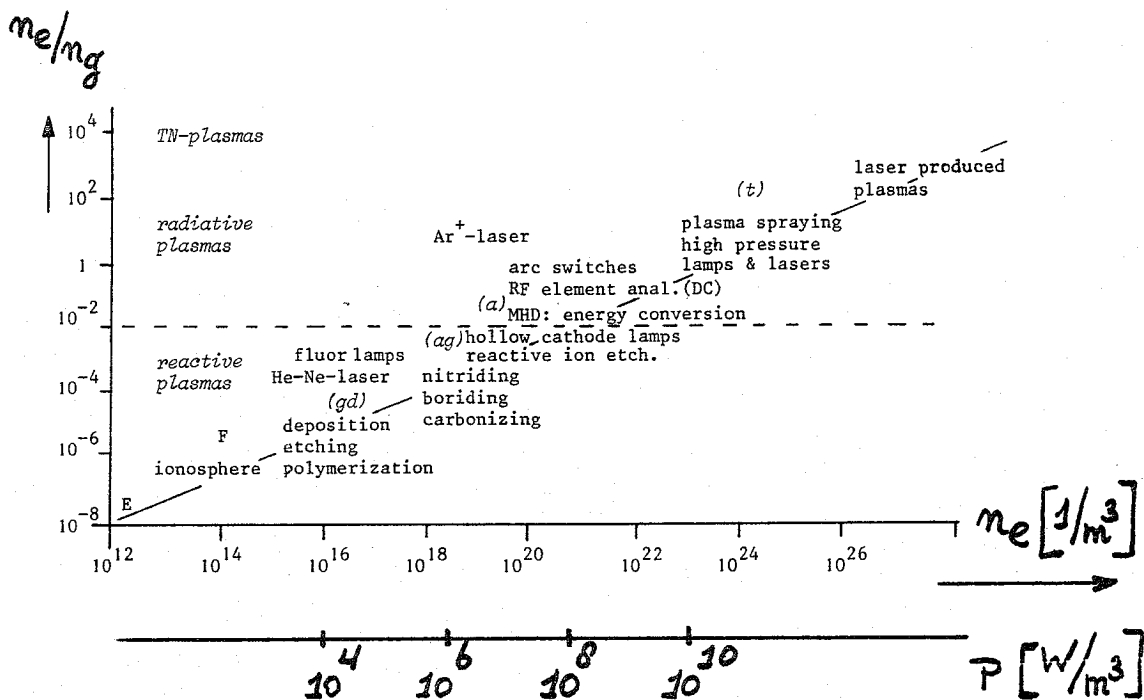


Fig. 9. Plasma characterization; gd: glow discharge; ag: anomalous glow;

a: arc; t: thermal plasmas.

It can be observed that there is a definite alignment in this figure. Apparently, plasma production imposes restraints. Note also, that the Ar^+ -ion laser plasma does appear somewhat higher in this figure. The reason is the application of a magnetic field which helps to cut down on plasma transport. As a consequence the plasma is hotter and the main heavy particle is now the ion rather than the neutral particle. This of course is essential in this application since Ar^+ -ions have to be excited to produce laser emission.

As a rule, however, plasmas group around the line:

$$\frac{n_e}{n_g} \approx (10^{-24} n_e)^{2/3} \quad (3)$$

where n_e is in units of $[1/\text{m}^3]$.

There is a definite relationship between the required power density and the electron density. This can be argued quite easily on the basis of the basic formulation of mass- and energybalances. For simplicity we will assume a simple plasma in the sense that one neutral atom or molecule forms the major neutral particle. Further, in the mass balance we will assume ambipolar diffusion to dominate. Finally, in the energy balance we will take the increase of internal energy as the major energy loss term. Also we will limit ourselves for plasmas which are relatively far out of equilibrium.

Then the mass balance reads:

Net production of charged particles = ambipolar loss

or in formula:

$$n_e n_g K_1 (T_e) = - \nabla \cdot D_A \nabla n_e \sim \frac{D_A n_e}{L^2} \quad (4)$$

in which K_1 stands for the total excitation and ionization rate, D_A for the ambipolar diffusion coefficient and L for a typical dimension of the plasma. If, as usual, ion neutral collisions determine the diffusion (enhanced by the ambipolar factor T_e/T_i) then D_A is primarily dependent on neutral gas density (inversely proportional) and of course the temperature. In fact, from this equation immediately the conclusion can be drawn that the dimensions of the plasma are not free. Extracting the gas density from D_A by using $D_A n_g$ which is independent of the gas density, immediately the following relation results:

$$n_g L \sim \sqrt{\frac{(D_A n_g)}{K_1 (T_e)}} = \text{only a function of temperature} \quad (5)$$

Working out the details for e.g. argon at $T_e \sim 3\text{eV}$ we find $n_g L \sim 10^{19} / \text{m}^2$ which is indeed a typical value for gas discharge plasmas. So, in using plasmas, one has to take care to obey the plasma rules. There are ways to escape them but they are limited and have to be designed with great care.

In fact, the situation is a little bit more complicated as not necessarily all excitations need to lead to ionization. Particularly at low electron densities ($< 10^{19} / \text{m}^3$) radiation back to the ground state may make it necessary to "hit" the neutral several times (typically a number between 1-10) before ionization is successful. We can account for this by the multiplication of the LHS of the mass balance (4) a factor γ which is between .1 and 1.

A similar relation is a "bare" energy balance, in which we assume that all the consumed power is used to excite and ionize particles. In this way radiative losses (at least in the neutral system) are taken care of, since they are accounted for during the excitation:

$$n_e n_g K_1 (\epsilon_{1+} + \frac{5}{2} k T_e) \approx P = \underline{j} \cdot \underline{E} \quad (6)$$

Note, that the required power density, P , would be even larger if other losses as heat conduction, convection etc., would play a role. The term $\frac{5}{2} k T_e$ stands for the contributions of the required heating of the newborn electrons ($\frac{3}{2} k T_e$) and the expansion energy ($k T_e$).

By now combining the mass balance and energy balance one can write immediately:

$$P \sim \frac{(D_A n_g) (\epsilon_{1+} + \frac{5}{2} k T_e)}{\gamma L^2} \cdot \frac{n_e}{n_g} \quad (7)$$

So we conclude, that as a general rule to obtain more density and more ionization degree more power consumption is required. In fig.9. we have indicated several typical values for P which are in good agreement with the estimates based on eq. (7).

We have stated already, that the use of balances have only an illustrative meaning. We have not treated plasmas which are close to equilibrium where also recombination has to be taken care of. Nevertheless it illustrates two basic rules:

1) The size of plasma and its form are also chosen by the plasma itself and in the design this has to be taken into account.

2) To arrive at a higher reactivity a larger power density has to be used. Roughly speaking there is a proportionality.

Of course any detail is beyond the scope of this introduction. It illustrates the way the conservation laws in a more elaborate form are used for the modelling of plasmas. To study plasmaflow also the conservation law for momentum has to be used.

Particle balance: diffusion, transport \longleftrightarrow
ionization/recombination
(mass)

momentum balance: forces (e.g. $e\mathbf{E}$, ∇p) \longleftrightarrow flow of plasma

energy balance: power consumption \longleftrightarrow plasma heating

3. To summarize, there are two limiting plasma regimes:

1. Low temperature (T_g low), low ionization degree ($\frac{n_e}{n_0}$ low) low electron density plasmas. The electron temperature is substantially higher than the gas temperature which is close to ambient temperature. The plasmas are out of chemical equilibrium; the reactivity is high; it is very much higher than the equilibrium value at gas temperature, but lower than that at electron temperature.

There is a definite relation between power density and radical and ion density, thus specific reactivity. These plasmas are used for volume chemistry and many applications on surface modification.

2. "high" temperature (T_g "high") plasmas, thermal plasmas, relatively high ionization degree ($> 1\%$), high electron density plasmas. At atmospheric plasmas they are usually referred to as thermal plasmas since they are commonly not too far from local thermodynamic equilibrium.

As a consequence of the higher ionization degrees and relative large electron and thus ion densities the heavy particle (read gas-) temperature is close to the electron temperature. Even though in this plasmas also high reactivities are achieved, the use of the large (kinetic and internal) energy density and/or large momentum is primary here.

So the division into the two subsequent courses finds its basis in this subdivision.

It is however obvious, that the transition between the two regimes is gradually and it is useful to consider for any application the plasma regime as a whole.

To illustrate this we will end this introduction by referring to two examples where within the used classifications both kinds of plasmas are encountered.

The first is the negative corona discharge which is used for a long time for ozon production. In electro-negative coronas there is a definite time structure and the discharge is very inhomogeneous. During the very short discharge pulses (the so called Trichel pulses) relative high electron densities are achieved near the corona wire or point^{and} classification as high temperature plasma is appropriate. The dimensions of this initial plasma are small and it starts very soon to expand during the interval between the Trichel pulses. This expanding plasma consumes the energy deposited during the short pulse and there is no need for Joule dissipation; also there is no requirement of stationarity. This decaying plasma (a miniaturized afterglow) could be classified as weakly ionized plasma.

The second example is the use of a thermal plasma (either D.C. or inductively coupled) as a particle source to be used in a surface modification process. Now it is possible to use the thermal plasma in the active domain with high power density, high specific reactivity, but also with high fluxes. This flux is allowed to expand and a low density plasma of large size is produced. Since again this is a flowing afterglow the basic limitations do not apply and more freedom in use of plasmas is achieved.

In both examples use is made of convective energy transport from the high density active regime to the low density "preparation" regime. It is one way to escape some of the limitations of active plasmas, where the power is dissipated at the spot of chemical action.

By the same examples it may have become clear that a thorough knowledge of plasma physics and plasma chemistry is of advantage in optimizing plasma processing.

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