Capacitively Coupled Plasma Reactors and Etching

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Concept of a positive plasma potential

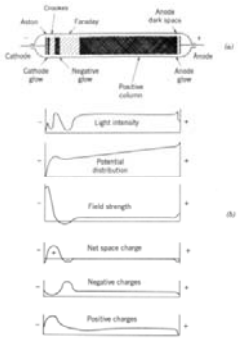
Electron temperature and energy distribution

Potential necessary for equal fluxes to walls

Energetic ions and electrons

- Plasmas are everywhere and most of the universe is in a plasma state.
- The plasma state is mainly characterised by very hot electrons.
- The electrons serve a number of purposes:
- 1) Ionise neutral atoms
- 2) Excite neutrals and ions
- 3) Dissociate molecules
- These collisions result in the creation of ions, photons and active radicals all of which can be used to modify surfaces.

Plasmas fill their containers and since electrons are much more mobile than ions, the plasma sits at a positive potential to prevent all the electrons leaving.
Hence a high voltage cathode will only produce a sheath close by.
Plasma ions are accelerated through the sheath to the cathode where they release about 10% secondary electrons which are also accelerated through the sheath and ionise the gas to produce the negative glow.
The ions have sufficient energy to sputter the cathode material and these systems are used as sources of metallic ions and neutrals for making thin films

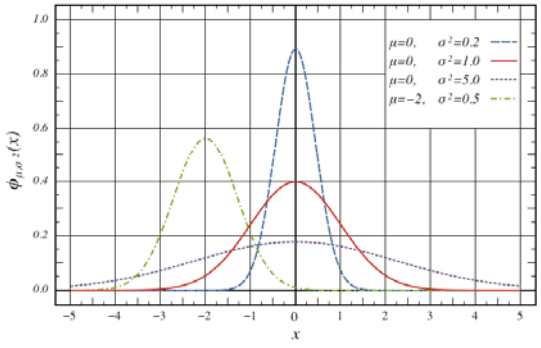


Discussion of Maxwellian distributions

Derivation of the plasma potential

Discussion on sheaths

Maxwell Boltzmann distribution



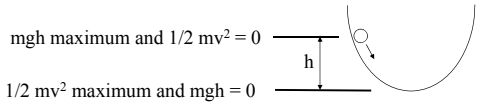
Maxwell 1860 proposition IV

One of Maxwell's chief aims was to show that the number of particles whose velocity lies between v and v + dv is proportional to $v^2 \exp -v^2/a^2$ where a is a parameter to be determined later.
Maxwell proved this in his Proposition IV by assuming that the velocity components of each particle in any arbitrarily chosen rectangular coordinate system are independent. This is a result of statistical physics.

Conservation of potential and kinetic energy

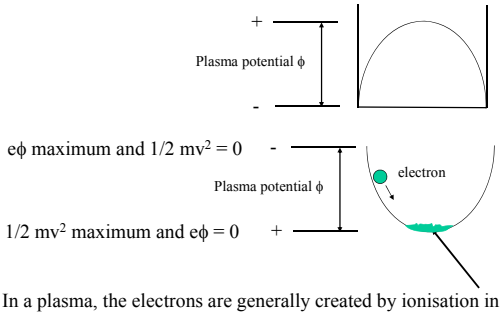
for example:
A ball mass m rolling with a velocity v down a slope in a gravitational field g

Total energy = potential + kinetic
= $mgh + 1/2\ mv^2$



For an electron in the well of the plasma potential it is the same

Electrons trapped in the potential well of the plasma
Potential energy = eϕ and kinetic energy $1/2\ mv^2$



In a plasma, the electrons are generally created by ionisation in the most positive region of the plasma potential.

Distribution of random non-correlated events:

$$P = 1/\sigma(2\pi)^{1/2} \exp -(x - \mu)^2/2\sigma^2$$

Now we use $(kTe)^{1/2}$ for s, v for x and have no drift ie. $\mu = 0$ to get:

$$P(v) = (m/\ 2\pi kT_e)^{1/2} \exp -(1/2mv^2 - e\phi)/kT_e$$

v KE PE

Maxwellian distribution for plasma particles

The plasma potential

Due to the high mobility of the light electrons, a plasma will initially loose electrons and hence charge up positively. This accelerates ions out of the plasma and prevents more electrons escaping. For an equilibrium situation:

Flux of escaping electrons = Flux of escaping ions

$$\Gamma_e = \Gamma_i$$

As the electron flux is from all directions but ion flux is directed:

$$1/4 \times n_e v_e = n_i v_i$$

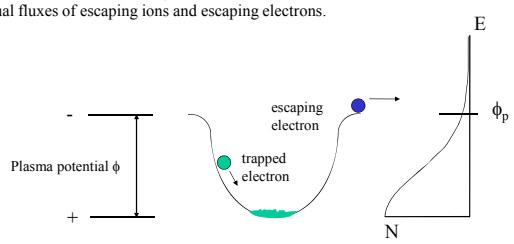
BUT $v_e \sim 10^8$ cmsec^{-1}
and $v_i \sim 3 \times 10^4$ cmsec^{-1}

hence $v_e > v_i$

Therefore there is something wrong with $n_e = n_i$

Getting the ion and electron densities the same at the wall.

The plasma approximation states that there are equal densities of ions and electrons $n_e = n_i = n_0$ in the bulk of the plasma, or there will be electric fields and currents. But, at the walls, n_e cannot equal n_i and must be much smaller to allow equal fluxes of escaping ions and escaping electrons.



The electrons that can escape must have an initial energy > ϕ_p

from Boltzmann: $n = n_0 \exp - e\phi_p/kTe$ for the escaping electrons

Recap on the plasma potential

High voltage sheaths

Determine plasma density from input power

Start on capacitive discharges

Electrons escape at their thermal speed, ie. $v_e = (8kTe/\pi m_e)^{1/2}$ so the flux of escaping electrons is:

$nv_e = 1/4\ n_0 \exp -(e\phi_p/kT_e)\ (8kT_e/\pi m_e)^{1/2} = n_i\ v_i = n_0\ v_i$

If we take the ion speed $v_i \sim 300\ msec^{-1}$ then we get a plasma potential that does not agree with experiment.

It was shown by David Bohm in 1949 that a necessary condition for a positive sheath is that ions escape at the sound speed (C_s or $v_B = (kT_e/m_i)^{1/2}$, hence:

$1/4\ n_0 \exp - (e\phi_p/kT_e)\ (8kTe/\pi m_e)^{1/2} = n_0\ v_B = n_0\ (kT_e/m_i)^{1/2}$

$\phi = kT_e/e \times \ln[(8kT_e/\pi m_e)^{1/2}/\ 4(kT_e/m_i)^{1/2}]$

$\phi = kT_e/e \times \ln[m_i/2\pi m_e]^{1/2}$

For argon, $V_p = \phi \sim 5kT_e$ and the plasma electron temperature is typically 30,000 K, ie. about 3 eV hence the plasma potential is 15 volts above the grounded walls.

A note on plasma existence

If the plasma potential is 15 Volts and the ionisation potential for, say, argon is 15.75 eV, then all electrons that can ionise will only have one pass through the plasma before they are lost.

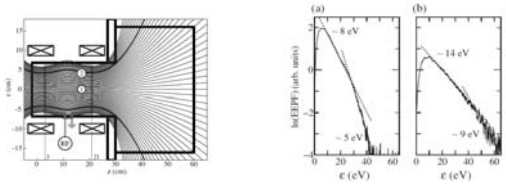
Hence for the plasma to exist, it would be best if the plasma potential were somewhat greater than 15.75 Volts.

A note on electron energy probability functions

Electrons less energetic than V_p will be trapped for ever whereas more energetic electrons will escape.

Trapped electrons will have many collisions and will form a Maxwellian distribution up to V_p.

Free electrons have an energy greater than V_p and their distribution reflects the heating mechanism



Sheaths around electrodes

A consequence of the high electron mobility is that a plasma is a very good electrical conductor and will not happily support electric fields. The potential difference between the plasma and the walls is taken up in a thin region next to the walls called a sheath (since it protects the plasma from the walls).

If a potential more positive than V_p is applied to an electrode, it will remove electrons until the plasma is once again a potential of V_p higher than this electrode. If a negative potential is applied then a larger sheath forms on the electrode but the potential of the plasma is unchanged. The

thickness of the "Child-Langmuir" sheath in this case is given by: $S = 400\frac{V^{3/4}}{n^{1/2}T_e^{1/4}}$

The sheath is not a plasma as the density of electrons is not equal to the density of ions, the difference in charge creating the sheath potential. As well as reflecting the majority of electrons back into the plasma the sheath accelerates the ions onto the electrode and this can be used to sputter material for coating onto adjacent targets, accelerate active species to a silicon wafer clamped to the electrode to produce reactive ion etching, to implant ions into the sub-surface layers and to densify growing film of SiO_2 for example.

The sheath can be considered as a capacitor and it stores energy the same as a capacitor.

Calculate plasma density from input power

Consider a box with sides of 20 cm. And we create an argon plasma in it with 100 Watts of power and assume the electrons have a temperature $T_e = 3$ eV. The power coming out of the plasma has to equal the power 'in'.

Escaping from the plasma are ions and electrons in equal amounts, photons and radicals. We will neglect the radical contribution as it is normally less than 10% of the total power coming from electron energy loss in breaking molecular bonds.

Consider the ions; each ion that leaves and hits a wall takes the ionisation energy (E_i) and the energy it gains falling down the plasma potential ($V_p = 5kT_e$).

Electrons are lost at the same rate as the ions and take $2kT_e$ each

Photons (one visible of 2 eV and a UV photon of 12 eV) are lost at the same rate as the ions since the cross section for excitation is approximately the same as that for ionisation.

Power 'out' = Area x flux x voltage

$= 6 \times 0.2 \times 0.2 \times n_p \times e \times v_B \times (E_i + V_p + E_{ex} + 2kT_e)$

$= 0.24 \times n_p \times 1.6 \times 10^{-19} \times 2.5 \times 10^3 \times (15 + 15 + 14 + 6)$

$= 50 \times 10^{-16} \times n_p$ = power 'in' = 100

$n_p = 2 \times 10^{16}\ m^{-3}$

Recap on earlier course material

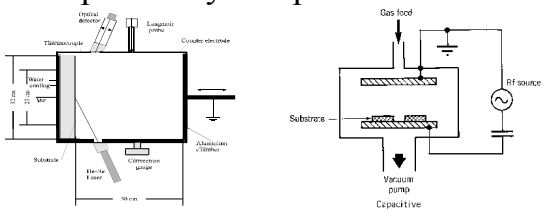
Symmetric capacitive discharges

Asymmetric capacitive discharges

Sheath voltage division

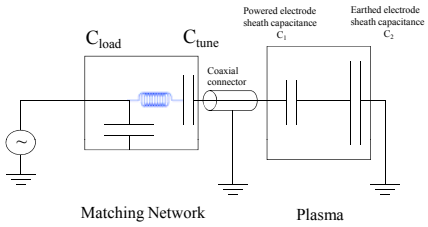
Sparks

Radio Frequency Generated Capacitively Coupled Plasmas



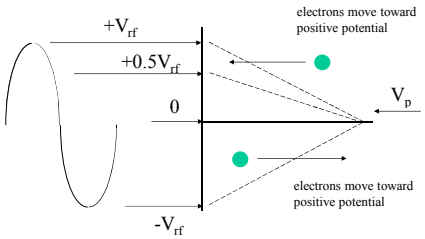
Capacitively coupled plasmas have been used since 1975 for anisotropic reactive ion etching (RIE). 13.56 MHz (an industrial frequency) is coupled via a matching network (capacitors and inductors) to an electrode in a low pressure reactive gas such as CF_4 or SF_6.

Capacitively coupled plasma reactor



The area of the powered electrode is generally much smaller than the earthed electrode (the walls of the vacuum vessel) hence the sheath protecting the plasma from the electrodes is smaller and the capacitance of the sheaths is smaller.

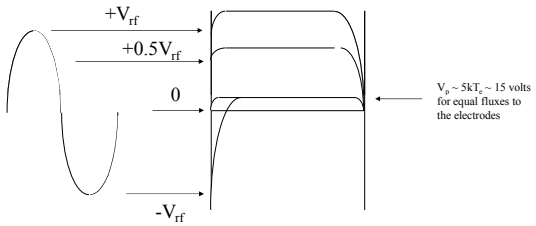
Potentials in a symmetric parallel plate reactor with a varying voltage applied to the powered electrode.



With no plasma we have a simple capacitor with potentials given by the dashed lines.

Electrons move toward positive potential on electrodes and create a more positive potential by their absence

Potentials in a symmetric parallel plate reactor with a varying voltage applied to the powered electrode.



With a plasma and 0 volts rf applied to the electrode, the plasma sits at a positive potential which decreases the escaping electron flux until it is equal to the escaping ion flux: $V_p \sim 5kT_e \sim 15$ volts for a 3 eV argon plasma. At $+V_{rf}$ electrons flow into the powered electrode until the potential is $5kT_e$ above V_d causing a sheath of $5kT_e + V_d$ on the ground electrode. As the rf voltage decreases, the potential of the plasma decreases until it reaches $5kT_e$. Further lowering the voltage produces a sheath on the powered electrode, but the plasma potential remains at $5kT_e$.

System voltages, symmetric system

If we take 100 Watts of input rf power (P) and a system impedance (Z) of 50 Ω, then the voltage (V) at the input to the matching network is given by:
$V_{rms} = (PZ)^{0.5} \sim 70$ Volts.
Hence $V_{rf} = 1.4 \times V_{rms} \sim 100$ Volts.

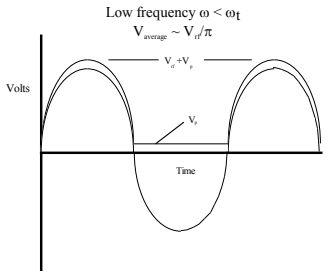
The matching network is a resonant system with a quality factor of typically Q = 5, hence at the output of the matching network, the V_{rf} is multiplied by a factor of five resulting in $V_{rf} \sim 500$ Volts and it is this voltage which is applied to the electrode.

In the plasma we can generally ignore the plasma resistance and concentrate on the two capacitors in series, C_1 and C_2 represented by the sheaths on the powered and earthed electrodes. In the symmetric system, the size of the two sheaths is about the same so they have equal capacitances.

The plasma impedance is given by $Z = 1/\omega C_1 + 1/\omega C_2$ and since the capacitances are equal, the applied voltage is divided equally between the two sheaths.

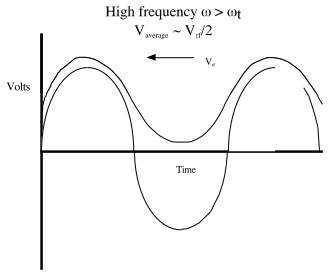
Potentials in a symmetric plasma

for rf frequencies lower than the transit time for an ion to cross the sheath



Potentials in a symmetric plasma

for rf frequencies higher than the transit time for an ion to cross the sheath



Calculate plasma density for high frequency symmetric system consisting of two 20 cm. x 20 cm. electrodes with 100 watts applied to the matching network.

Once again we use
Power in = Power out

Since the sheath is the same height on both electrodes, the capacitances and hence the impedances are equal resulting in the same voltage drop across each sheath ie. $V_{rf}/2 \sim 250$ Volts.
The loss area is $2 \times 0.2 \times 0.2 = 0.08$ m^2. and we assume $kT_e = 3$eV.

$$100 = 0.08 \times n \times e \times v_B \times (E_i + V_p + E_{ex} + 2kT_e + V_{rf}/2)$$
$$100 = 0.08 \times n \times 1.9 \times 10^{-19} \times 2.5 \times 10^3 \times (15 + 15 + 14 + 6 + 250)$$
Hence: $n = 10^{16}$ m^{-3}

This is less than the density calculated for the 6 sided box because ions lose power in falling through the rf sheaths.

System Voltages in an asymmetric system, one powered and five sides at earth

Clearly, the capacitance of the sheath on the earthed electrode is five times larger in area than the sheath on the powered electrode (actually it is still larger because the powered electrode sheath is thicker because of the large V_{bias}).

The plasma impedance is given by $Z = 1/\omega C_1 + 1/\omega C_2$ and since $C_2 > 5C_1$, most of the applied potential will be dropped across the powered electrode.

This will make the plasma near the powered electrode oscillate to over 500 Volts positive and since the plasma is a good conductor, there will be a drop of 500 volts all around the earthed walls of the reactor.

Hence the sheath on the earthed walls is being forced to be at 500 volts but its impedance requires it to have only a few 10s of Volts and so there is a conflict.

Note, we assume that the rf is connected directly to the powered electrode, there is no matching network, or there is no blocking capacitor in the matching network.

Sparks and the blocking capacitor

As the plasma is a good conductor, electrons will move from the region of the earthed sheath to the region of the powered sheath to short circuit the electric fields.

The sheath on the earthed electrode will be overvoltaged and the sheath capacitance will break-down in a spark.

These micro-discharges have an energy given by $0.5\ CV^2$
The earthed sheath capacitance $C = \varepsilon A/d = 8.8\ 10^{-12}(\text{Fm}^{-1}) / 10^{-4} \sim 10^{-7}$ Farads
This is HUGE!!
So energy stored is: $0.5\ 10^{-7} \times 500^2 \sim 10$ mJoules

This is sufficient to melt little craters of about 50 μmetres in the metal walls.

Which is rather distressing as evaporated material from the wall will enter the plasma and change its properties as well as the properties of the wafers being processed.

Recap on capacitive systems

Forming the bias voltage

Determine plasma density from input power

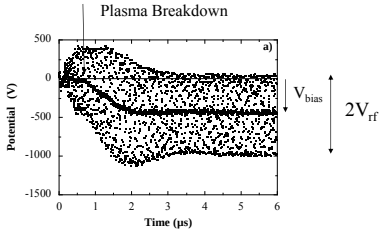
Intro to sheath heating

Intro to ionisation

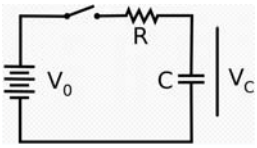
Examples of LAM reactors

Formation of a self bias voltage

Fortunately, there is a blocking series capacitor (tune) in the matching network and this charges up negatively to V_{rf} thereby allowing the plasma potential to revert to its equilibrium value of around 15 Volts. This voltage is called the self bias because it is created automatically by the plasma in an attempt at self preservation. For the 100 Watts of input power, the $V_{bias} = V_{rf} = 500$



Charging a capacitor

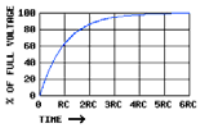


V_C is Voltage across capacitor C which has a charge Q

$V_C = Q/C$ and $I = dQ/dt$

$V_0 = V_R + V_C$ and V = IR hence:
$= IR + Q/C$
$= RdQ/dt + Q/C$

$Q = CV_0[1 - \exp(-t/RC)]$ or



$V_C = V_0[1 - \exp(-t/RC)]$

Approximate with a Taylor series:

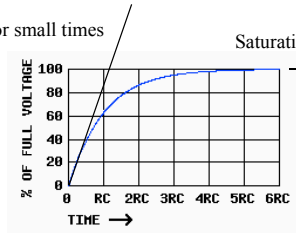
$V_C = V_0[1 - 1 - t/RC + 1/2(t/RC)^2 \ldots\ldots]$

Hence for small time $V_C \alpha t$

Capacitor Charging revisited

Linear for small times

Saturation for longer times



Rearranging the equations of the previous page:
$dQ/dt \alpha Q$

ie. the rate of change of stuff depends on the amount of stuff

Capacitor discharging

For small times when shut off bias:

I = V/R and I is the ambipolar current flowing to the capacitor:
$I = Anev_B = V/R$

where A is the area of the rf chuck, n is the plasma density, e is the electronic charge 1.6×10^{-19} Coulombs and v_B is the Bohm velocity or the ion sound speed (kT_e/m_i). Hence:

$$V \alpha (T_e)^{1/2}$$

So, if you pulse the bias voltage off you can measure the electron temperature

Plasma density for high frequency asymmetric box consisting of a 20 cm. powered electrode and the other 5 walls at earth potential. 100 watts applied to the matching network.

Power in = Power out

Here the sheath on the powered electrode can be considered as a DC sheath at the bias voltage $V_{bias} = V_{rf} = 500$ Volts.
The voltage on the sheath on the earthed sides of the box is about the plasma potential $V_p \sim 15$ Volts if we assume $kT_e = 3eV$.
Assume the plasma density is constant over the volume.

Powered electrode area $0.2 \times 0.2 = 0.04m^2$. Earthed electrodes area $= 5 \times 0.04 = 0.2m^{-2}$

Power out = $n \times 1.6 \times 10^{-19} \times 2.5 \times 10^3 \times [0.04(50 + 500) + 0.2(50)]$
$100 = n \times 4 \times 10^{-16} \times [22 + 10]$
$n = 7.8 \times 10^{15} m^{-3}$
ie. about 3 times less than the simple (inductive) box

Sheath heating vs gamma discharges

Sheath heating is simply the result of the collision of a light object with with a moving hard wall.
eg. A game of tennis:

When the player hits the ball, it changes direction and acquires twice the velocity of the racket (4 times the energy)

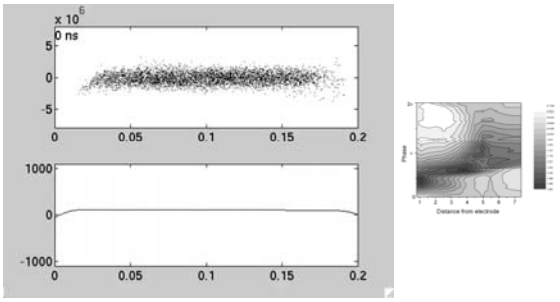
In a plasma, the advancing sheath has to move at 10^8 cms^{-1} at least.

This can be approximated by assuming the sheath advances to its full extension in 1/4 of a rf cycle

A blast from the past

ANU 1D particle in cell simulation circa 1987

Newer PIC agrees with experiment at Bochum



watch the red electrons!

In Gamma discharges, fast ions generate secondary electrons on the substrate that subsequently, are accelerated by the electric field of the chuck bias.

Mean free path for ionisation $\lambda_{imfp} = 1/n\sigma$
$\sigma$is the ionisation cross section that can be taken to be ~ 1 to 3 10^{-16} cm^{-2}, ie. 1 to 3 $Å^2$. n is the neutral density.

For 1 mTorr, n = 3.4 10^{13} cm^{-3} hence λ_{imfp} ~ 100 cm

For 100 mTorr λ_{imfp} ~ 1 cm

Review sheath heating

More on gamma discharges

Introduction to frequency effects in CCP

Frequency effects in simple RC circuit

following Howling 1995

Assume the CCP is symmetric, ie equal sheaths on each electrode, hence the sheath capacitances are equal $C_t = C_w = C$ and the plasma presents a simple resistance R.

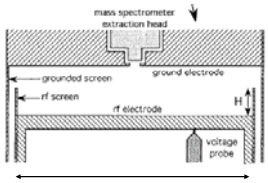
$$V_{rf}^2/P_p = [R^2 + (2/\omega C)^2]/R \sim 4/\omega^2C^2R = f(\omega)$$

Assuming C and R do not change with frequency (false but not too bad) and that plasma impedance R is small cf. sheath impedance 1/ ωC (good).

Hence the V_{rf} decreases with the frequency, for constant power.
$V_{rf} \alpha 1/\omega$

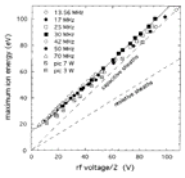
Is this true??

Use experiments and PIC simulation done by: W. Schwarzenbach, A. A. Howling, M. Fivaz, S. Brunner, and Ch. HollensteinW. Schwarzenbach, A. A. Howling,a) M. Fivaz, S. Brunner, and Ch. Hollenstein, **J. Vac. Sci. Technol. A 14(1), 132, 1996**



130 mm

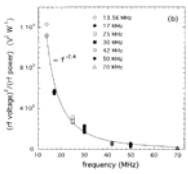
The rf screen is adjusted so that $V_{dc} = 0$, ie. symmetric discharge rf power remains constant at 14 Watts and frequency varied from 13.56 to 70 MHz, argon pressure 100 mTorr with 50 sccm.



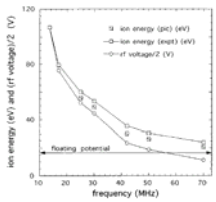
Ion energy measured by the Hiden is proportional to the V_{rf} for a capacitive sheath, agrees with the PIC too.

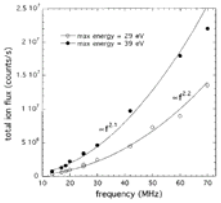
Showing that the square of the applied V_{rf} divided by the applied power is approximately inversely proportional to the applied frequency squared

$V_{rf}^2/P_p \sim 4/\omega^2C^2R$



As the applied frequency increases, ion energy decreases and the plasma density increases. Hence the total power out will remain equal to the power in.





Notes on capacitive and inductive discharges

Typically, capacitively coupled plasmas have a skin depth that is much greater than the dimensions of the system and in analysis, the speed of light is assumed to be infinite

the skin depth is the distance required for the field at an interface to fall off by 1/e, examples would be total internal reflection of light on the surface of water and microwave ovens. In conductors, the rf current flows in the skin of the conductor, not the bulk.

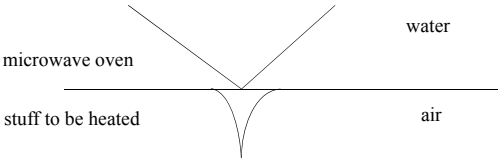
$\delta \sim c/\omega_{pe}$ for collisionless systems and where the rf frequency is much greater than the electron neutral collision frequency.
$\delta \alpha (1/\omega_{rf})^{1/2}$ for collisional systems $\omega_{rf} << \nu_{en}$

at 1 mTorr $\nu_{en} \sim 10^7$ and for 13.56 MHz $\omega_{rf} = 2\pi f \sim 10^8 >> \nu_{en}$
but at 100 mTorr $\nu_{en} >> \omega_{rf}$ hence collisional.

Evanescent waves

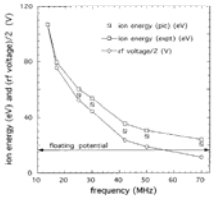
Assume wave propagates as $E = E_0 \exp i(\omega t - kz)$
normally, $k = k_r + ik_i$ the sum of the real and imaginary parts
if k is purely imaginary ie. $k = ik_i$, no real wavelength $k_r = 0$.

Then $E = E_0 \exp i(\omega t - ikz)$ ie. $E = E_0 \exp(i\omega t) \times \exp - k_i$
A temporally oscillating field with an exponentially decreasing amplitude.



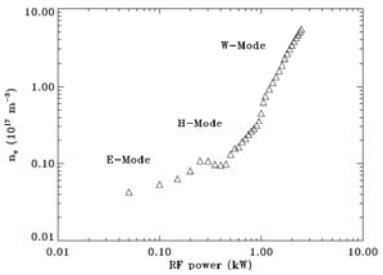
Skin depth for low pressure plasma a few mTorr and 5×10^{10} cm^{-3}
$\omega_{pe} \sim 2\pi \times 10^4 \times (n_e)^{1/2} \sim 1.3 \times 10^9$
$\delta \sim c/\omega_{pe} \sim 3 \times 10^{10}/1.3 \times 10^9 \sim 20$ cm.

ie. close to the plasma dimension for common industrial reactors and and hence we would expect inductive effects, even with a CCP.



From Howling's system, we would expect that the plasma would behave inductively for frequencies greater than 70 MHz. since the ion energy is then equal to the simple plasma potential and the plasma density would scale proportionally with the power.

E to H to W transition in the large "helicon" plasma WOMBAT



In E mode n α $P^{1/2}$ in H mode n α P in W mode n exponential

What are the important impedances involved?

Plasma resistance R is typically about 1 to 2 Ohms for densities of 10^{11} cm^{-3} measured at ANU and elsewhere.

Sheath impedance depends on area of reactor and sheath width.
Taking Howling's reactor with 13.56 MHz, $V_b \sim V_{ion} \sim 100$Volts, electrode area $A \sim \pi \times 6.5^2 \sim cm^2$. and power in ~ 10 Watts then calculate plasma density:
$10 = 2 \times A \times n \times e \times V_B \times(100 +15 + 13 + 6)$
$10 = 2 \times 43 \times n \times 1.6 \times 10^{-19} \times 2.5 \times 10^5 \times 132$
ie. $n = 2 \times 10^{10}$ cm^{-3}

hence sheath width ~ $400 \times V^{3/4}/(n^{1/2} \times T^{1/4})$ cm ~ 0.07 cm.

capacitance of powered sheath:
$= \varepsilon A/d \sim 8.8 \times 10^{-12} \times 43 \times 10^{-4}/7 \times 10^{-4} \sim 52$ pF

Impedance = $1/\omega C \sim 1/(2 \times \pi \times 13.56 \times 10^6 \times 52 \times 10^{-12}) \sim 200\ \Omega$

ie. the capacitive impedance is much greater than the plasma resistance!

When does the change from capacitive to inductive occur?

To reduce the capacitive impedance; the excitation frequency, plasma density and electrode area need to be increased.
Take a commercial reactor with electrode diameter 13" (area 0.1 m^2), excitation frequency 60 MHz and the same plasma density.
The capacitive impedance is reduced by the inverse frequency ratio (13.56/60 ~ 0.23) and the inverse area ratio (0.013/0.1 ~ 0.13)

$Z_C \sim 200 \times 0.23 \times 0.13 \sim 10\ \Omega$

so the system is some 10% inductive and we would expect plasma to appear in surprising places.

NB. In a CCP the impedance is dominated by the largest impedance ie. the smallest capacitor, which is commonly found on the powered electrode.

So CCP reactors can behave like inductively coupled reactors, and the inductively coupled reactors can behave like capacitively coupled reactors!

Introduction to etching:

SF6 and Silicon
SF6 and SiO2

Concepts of passivation

Etching involves the creation of a gas phase product that is volatile and will not stick to the feature being etched. Firstly, gas phase plasma electron collisions produce the etchant species:

$SF_6 \rightarrow SF_2 + 4F$

gas phase fluorine and surface silicon spontaneously react to create volatile SiF_4

$4F + Si \rightarrow SiF_4$

MD simulation by Pascal Brault have been carried out using Bagus potential. The simulation used a fitted/extrapolated version of the original potential of F interaction with cluster Si10H13F mimicking F-Si(111) interaction [1] at the open site [2]. This is a two-well interaction potential. The wells are separated by the Si atomic plane.

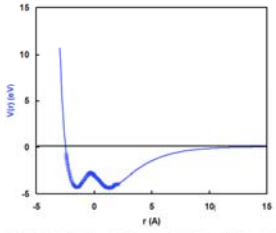


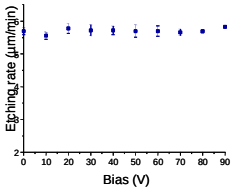
Fig. 1 : fitted and extrapolated potential. Circle originates from ab-initio calculation of Bagus [1]

[1] Materials Research Symposium Proceedings 38 (1985) 179-186, which make some corrections to
[2] M. Seel and P.S. Bagus, Phys. Rev. B 28 (1983) 2023-2038.

Role of the electrons and ions in silicon etching with SF_6

The electrons in the plasma maintain the plasma and dissociate the SF_6, at the periphery of the plasma the electrons attach to neutrals to form negative ions.

The ion neither help nor hinder deep silicon etching as can been seen from the ANU results and the Orleans (French) results.



At low pressures, most of the SF_6 is utilised and, generally, the etching proceeds as:
$Si + 2F \rightarrow SiF_2$ followed by the gas phase or surface reaction:
$SiF_2 + 2F \rightarrow SiF_4$
and so all the available fluorine is used.

For the ANU (13.56 MHz) and French (distributed microwave) experiments SF_6 was used at about 1 mTorr, 10 sccm and 400 Watts of rf power (ie. a pumping rate of 100 $lsec^{-1}$ and residence time of 100 msec.
The measured etch rate of 1 $\mu m.min^{-1}$ was gas limited.
Not influenced by ion bombardment energy or current flux.

The etch was completely chemical and the profile was "isotropic"

Estimate power needed for dissociation of SF_6:
typically a covalent bond is about 2 eV (40,000 kiloCalories) but SF_6 can absorb a lot of vibrational energy (20 eV??) so we take 10 eV for the production of the 4 atoms of fluorine.

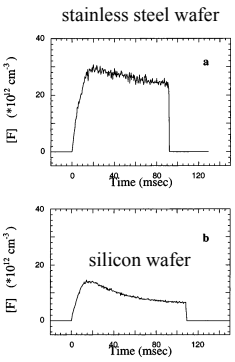
10 sccm $\equiv 10 \times 2 \times 10^{19}/60 \sim 3 \times 10^{18}$ molecules.sec^{-1}

each molecule absorbs 10 eV, yielding power absorbed
$P_{SF6} \sim 1.6 \times 10^{-19} \times 10 \times 3 \times 10^{18}$
~ 5 watts ie, about 1% of the input power.

Nota bene: for some commercial systems, the SF_6 flow is 500 sccm and then the power absorbed by the SF_6 could be 250 Watts.

This would probably result in the incomplete dissociation of SF6 yielding SFx fragments that are not as active as atomic fluorine.

For low pressure etching we can account for all of the SF_6 and atomic fluorine entering and leaving the system.
For the previous example at ANU, actinometry of atomic fluorine showed that a full 4" wafer reduced the fluorine density by a factor of about 4, and that the etch product was SiF, hence it was not possible to etch faster.



However, by assuming the SiF picked up another 3 atoms of fluorine in the gas phase or on the walls of the reactor or in the pumping system to form SF_4, then all the SF_6 can be accounted for: entering, dissociating to yield 4 atoms of fluorine, etching to form SiF and subsequently SiF_4 being pumped out.

$SF_6 + Si \rightarrow SF_2 + SiF_4$

In fast silicon etch systems (and other systems operating above about 5 mTorr) the etch rate is about 10 times slower at 10 $\mu m.min^{-1}$ at 100 mTorr, AND the etch profiles suggest that the reactivity of the etchant is only 10%.

Why this is so probably depends on the flow lines in this high pressure systems.

Etching a full 8" silicon wafer with SF_6

Silicon wafer 8 inch diameter (20 cm. and area of ~ 300 cm^2) on the powered electrode and we want an etch rate of 0.5 micro-metres per minute.
Take the ANU parallel plate etcher, 30 cm. diameter and 30 cm. long with a 100 litre per second turbo-molecular pump. This gives a residence time of around 200 milliseconds before the particle is pumped out.

Assume $SF_6 \rightarrow SF_2 + 4F$ and $Si + 4F \rightarrow SiF_4$

There are 5×10^{14} atoms of silicon per cm^2 per Angstrom hence $5 \times 10^{14} \times 300 \times 5000$ atoms of silicon ie. 7.5×10^{20}, need to be removed per minute. This will require (eventually) 4 times as many atoms of fluorine ie. 3×10^{21}.
Therefore 7.5×10^{20} molecules of SF_6 are needed per minute which is equivalent to 36 sccm.
With a pumping speed of 100 litres.sec^{-1} this gives a pressure of 6×10^{-6} Bar for complete fluorine consumption (about 5 milliTorr).
For safety (to remove fluctuations) usually take a 10 times higher flow.

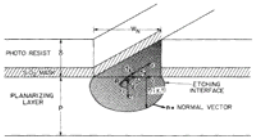
The fluorine accounting suggests that a full 8" wafer etched at 5 μm.min^{-1} would require 360 sccm of SF_6 at 50 mTorr (with the same pumping speed of 100 l.sec^{-1}).
This assumes that flow fields and dissociation remain the same, BUT about 200 Watts would be absorbed by the SF_6 so considerably more rf power would be required, some kiloWatts.

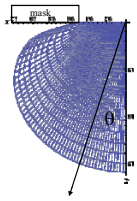
However, the pressure will have an effect: the plasma electrons will be cooled by the collisions and the electropositive plasma near the antenna (powered electrode) will be surrounded by an electro-negative plasma. Additionally, the fluorine atoms will suffer attaching collisions with various molecules and their density will decrease away from the visible (electro-positive) plasma.

Assuming fluorine atoms are very sticky (looking for an electron) then their mean free path at 100 mTorr would be about 1 cm.

Etch profiles and chemical etching isotropic etching

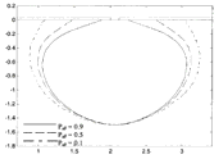
Shaqfeh and Jurgensen Bell Labs 1989, solid angle subtended by the mask as seen on the etch face assuming etchant comes through the hole. Discovered the etch front propagates as a wave.



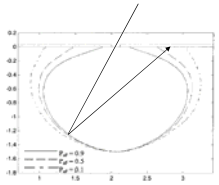


Use Mathematica (Bob Dewar) to calculate stream lines and etch front as a wave progressing into the silicon as a function of time. Assuming just chemical etching of silicon by fluorine. For great distances from the hole, etch rate $\alpha \cos\theta/r^2$ due to flux conservation. The shape of the etch surface with a small hole is a sphere.

Marcos, Rhallabi and Ranson in France used particle pushing and Monte/Carlo collisions to simulate the etch front for different sticking (etching efficiency) coefficient. Very similar to the analytical derivation.

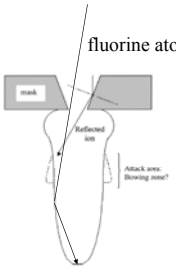


Effect of sticking coefficient, basically fluorine usage



fluorine atom enters the hole and reflects from the far wall to the top where it sticks and subsequently etches. The smaller the sticking coefficient, the less overhang, ie. the shape becomes hemispherical rather than spherical. But the absolute etch rate drops.

Anisotropic etching of silicon requires sidewall protection



This is commonly achieved by an alternating deposition/etch proceedure eg. C_4F_8/SF_6 or mixing in oxygen with SF_6 to produce an oxide on the side walls.
Fluorine etches oxide much slower than silicon and is reflected more easily from oxide.

Hence the etch rate at the bottom of the via does not proceed as $\cos\theta/r^2$ but should be proportional to the flux of fluorine arriving at the top of the hole.