SEERS diagnostics at plasmas used in powder processing

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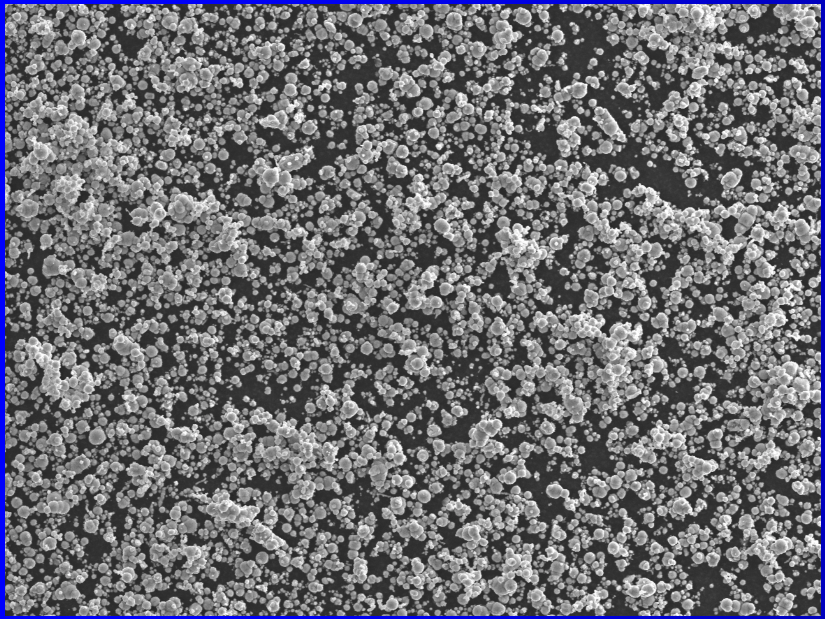
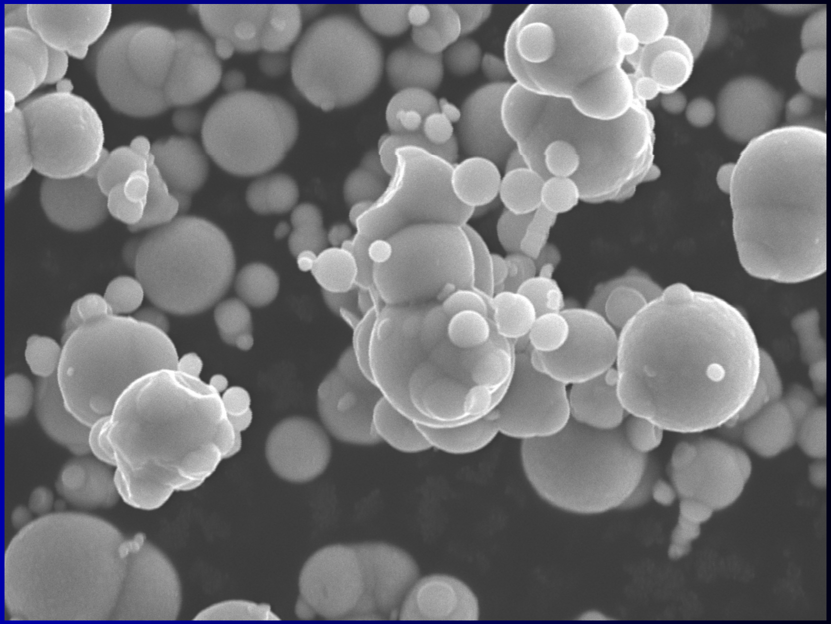
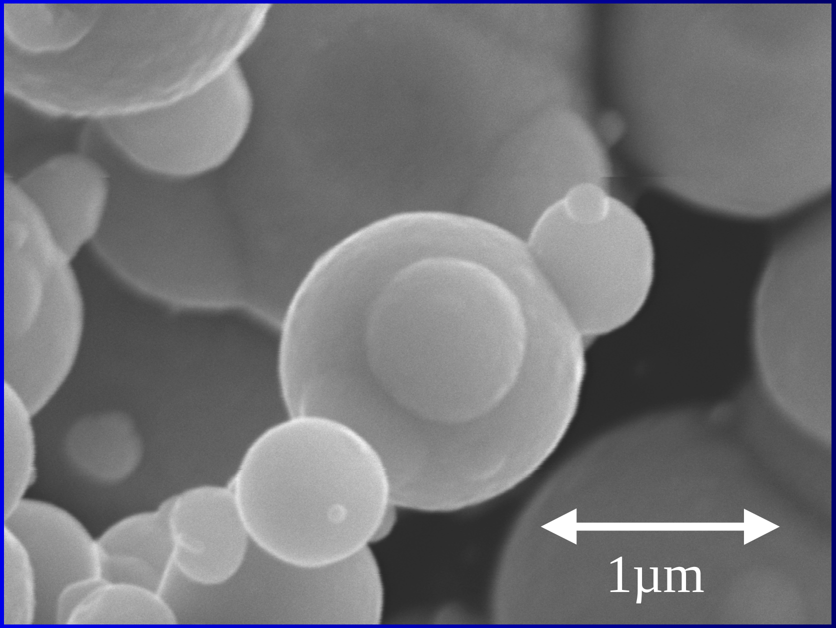
Introduction

Why dusty plasmas are of interest ?

- astrophysics : formation of stars in large interstellar clouds
- basic research : plasma crystal as model system
- semiconductor processing : avoid damaging effects by dust
- **particles as micro-probes for plasma diagnostics**
- **formation and modification of powders with tailored properties**







powder particle
(here c-Fe)

Dust particles as micro-probes

The interaction between plasma and injected micro-disperse powder particles might be used as a tool for the study of plasma wall processes in technological applications of low pressure plasmas as thin film deposition or etching. This idea has been triggered mainly by the basic research on plasma crystals. Hence, powder particles can be used as a kind of micro-probes for the determination of plasma parameters.

By observing the position and movement of the particles in dependence on the discharge parameters one can obtain information on the electric field in front of the electrodes and substrate surfaces where other plasma diagnostic methods fail.

The equilibrium net charge Q of a powder particle is the result of the charge carrier fluxes. Under our experimental conditions, where the diameter $2R$ of the particles ($\sim 10^{-6}m$) is always small in comparison to the Debye length λ_D ($\sim 10^{-4}m$) and the mean free path λ_{mfp} ($\sim 10^{-2}m$), the orbital motion limited (OML) theory for a spherical particle holds. The electron flux density j_e for a Maxwellian EEDF can be calculated by

$$j_e = n_e \sqrt{\frac{kT_e}{2\pi m_e}} \exp\left\{\frac{-e_0 V_{bias}}{kT_e}\right\}$$

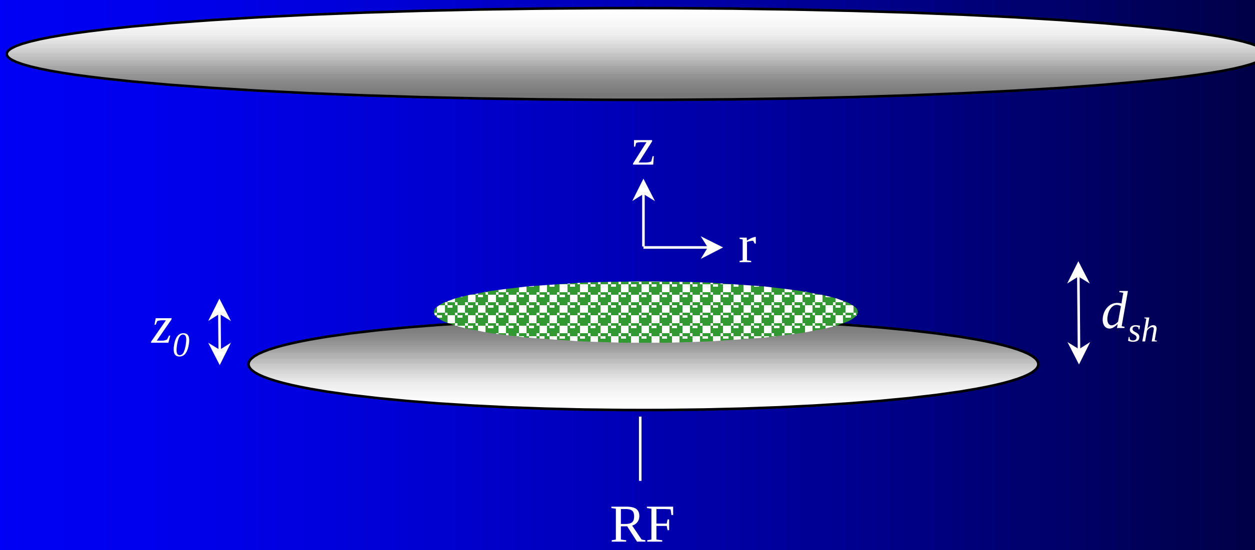
while the ion flux density j_i may be obtained by

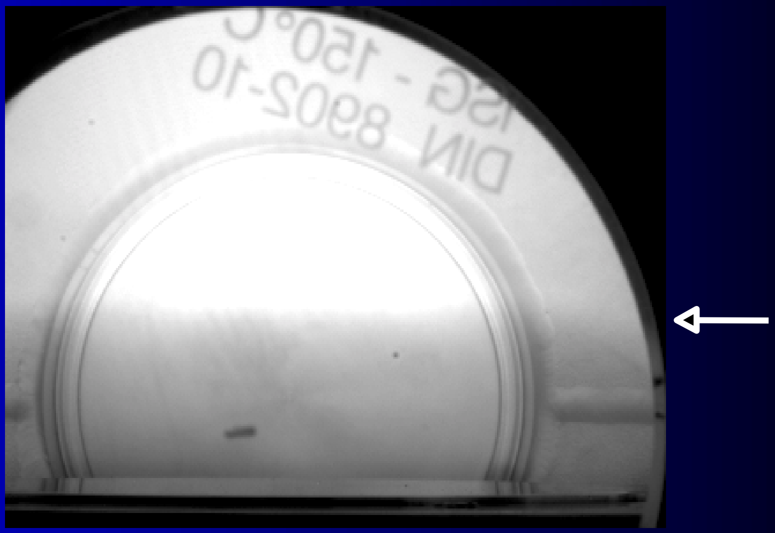
$$j_i = n_i \sqrt{\frac{kT_i}{2\pi m_i}} \left\{1 + \frac{e_0 V_{bias}}{kT_i}\right\}$$

The dust particles rest always at floating potential V_{fl} and it is $V_{bias} = V_{pl} - V_{fl}$.

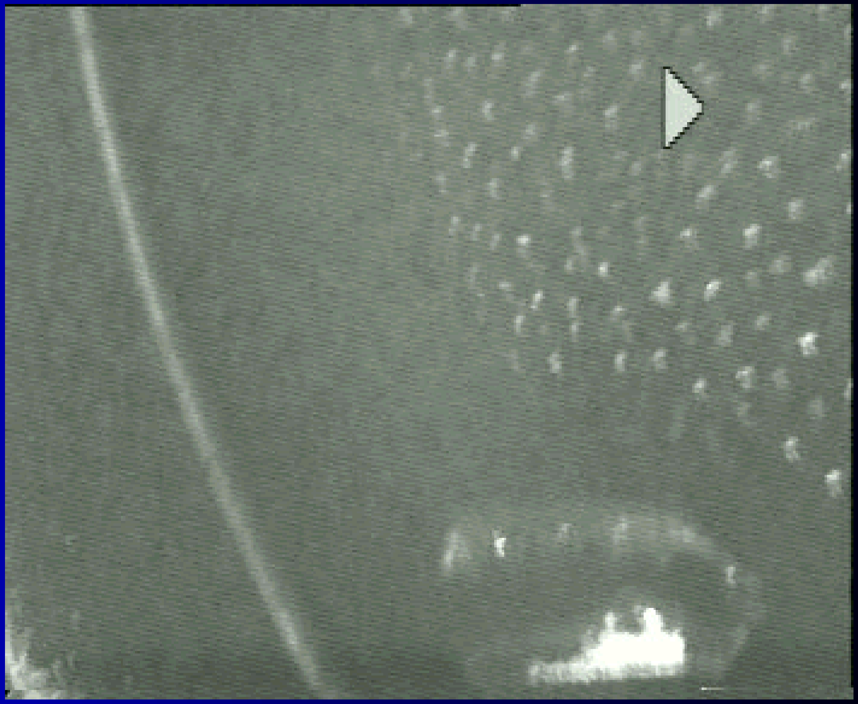
In this equilibrium state the electron and ion currents towards the particles are equal : $j_e = j_i$.

The particles are confined near the sheath edge and in the sheath.
They reflect structures and inhomogeneities of the surfaces quite well.



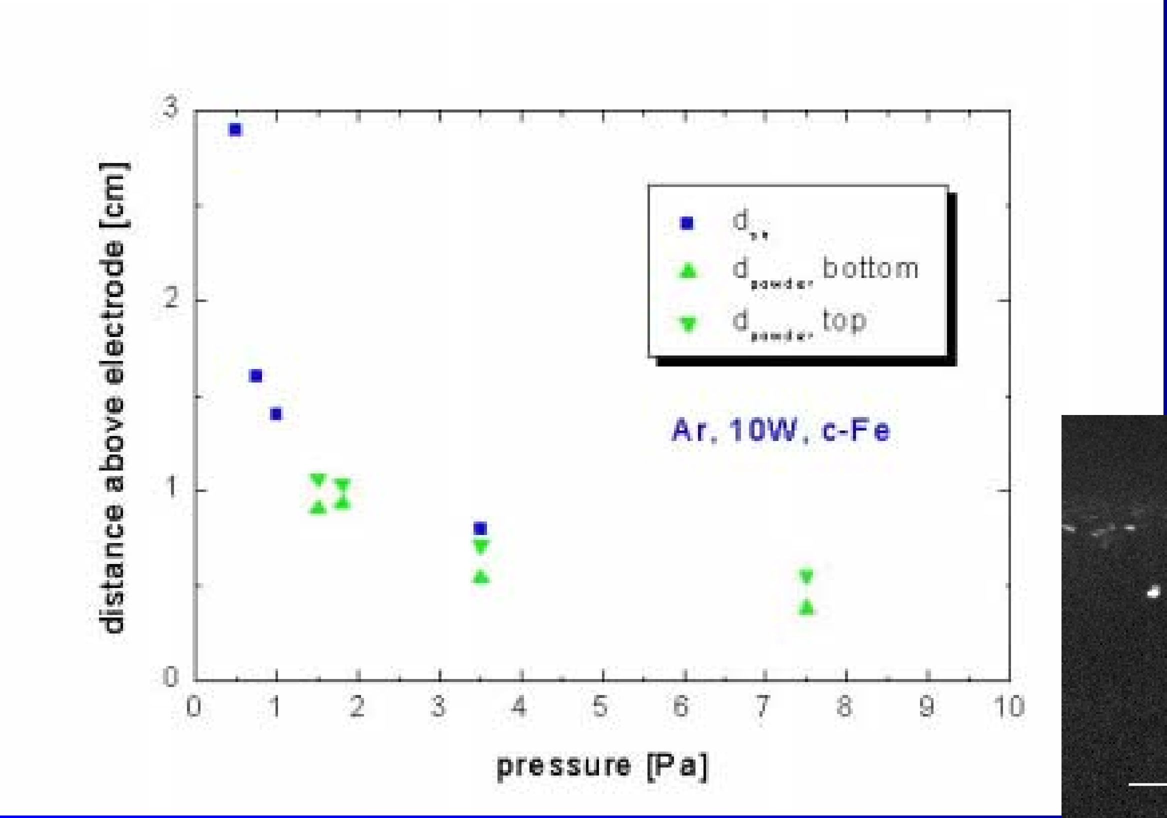


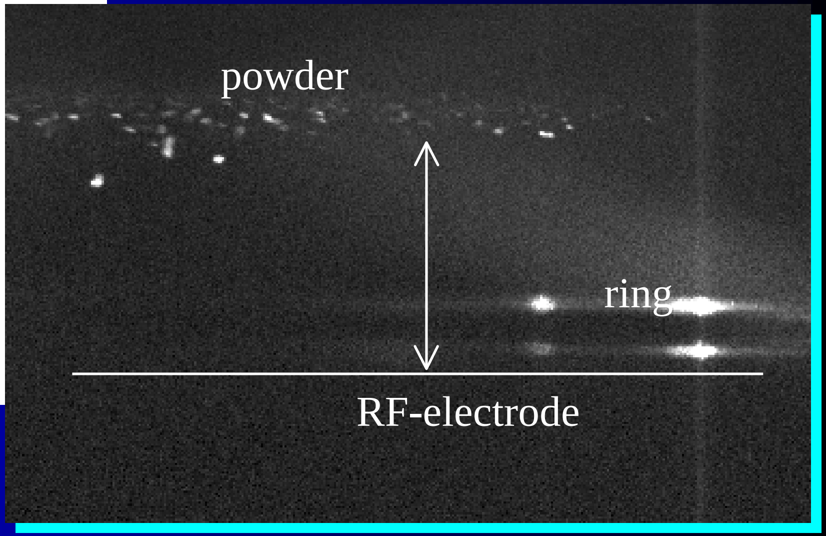
The distribution of the confined iron particles is determined by a variety of forces acting on the powder particles. It can be easily observed by a laser scan that the particles in the plasma are radially and axially confined in a plane where the net force on them is zero.



rf-plasma Ar, 3W, 0.01 ... 0.1mbar

Kersten,H., Otte,M.,Deutsch,H., Hippler,R.
IVth European Workshop on Dusty Plasmas, Lissabon, June 2000.





By determining the particle charge one obtains an electrical field strength ***E*** at trapping position $z=z_0$. Vice versa, knowledge of the field distribution in the sheath region is useful to determine the equilibrium charge carrier densities by this method.

How can the particle charge still be obtained ???

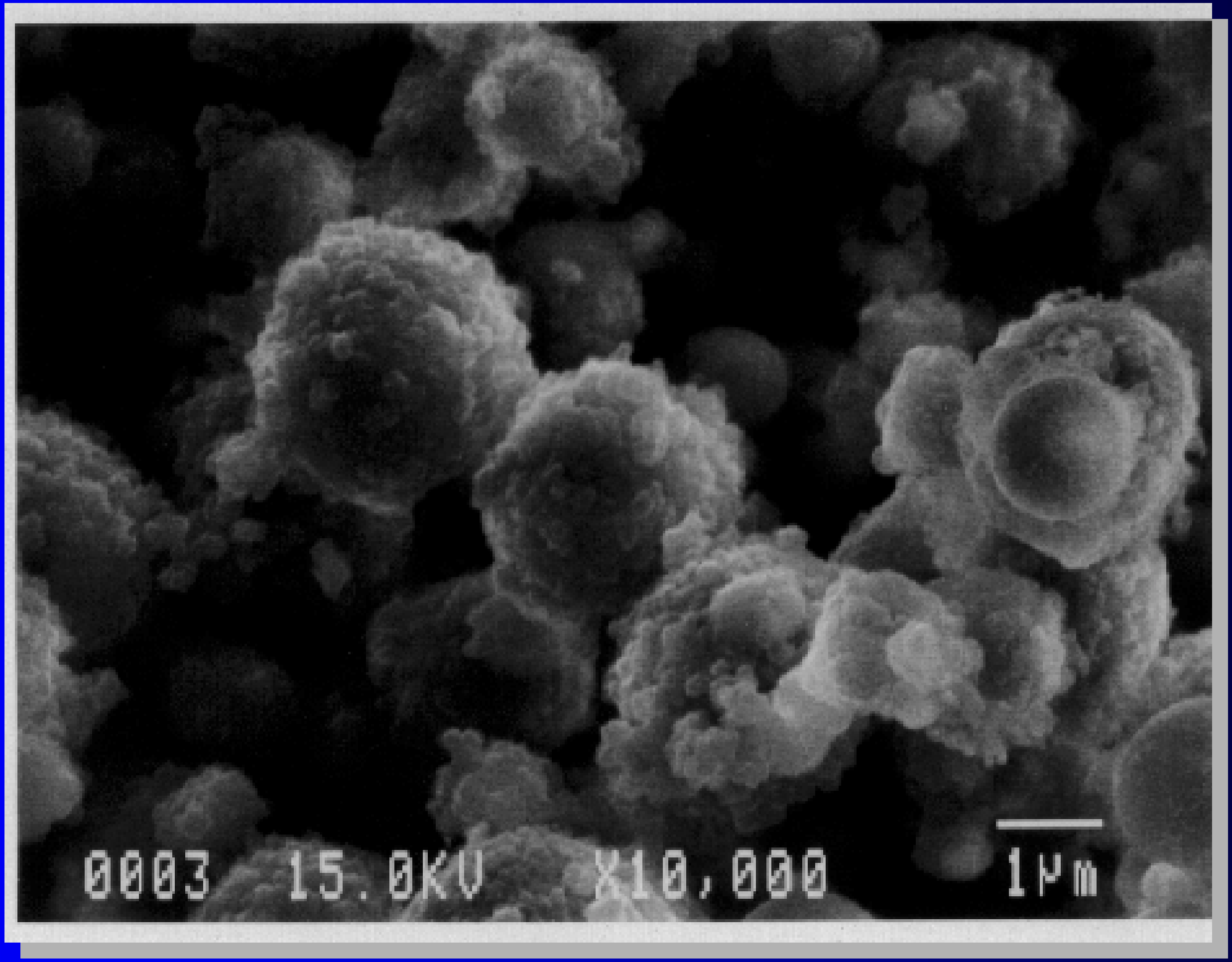
Formation and modification of nano- and microdisperse powder particles in plasma

applications and perspectives :

- treatment of flue gas, aerosols, flames
- light sources (cluster lamps)
- powder metallurgy (synthesis, coating, sort)
- film deposition (nanostructured films, hard coatings, lubricants)
- nanostructured amorphe Si films (solar cells)
- chemical catalysis (large specific surface area)
- diffusion barriers for pharmaceutic powders
- improvement of optical, mechanical, and thermal properties of small particles (pigments, luminophores)
- corrosive protection of magnetic metal particles
- etc. etc. etc.

Example:
micro-disperse particles are coated by a thin metallic film
(particles are confined in a rf-plasma and processed by a dc-magnetron)

SEM



Kersten,H., Schmetz,P., Kroesen,G.M.W., Surface and Coatings Technology 108-109(1998), 507.

deposition of Al (150 ... 200nm) onto particles

⇨ each particle is surrounded by a compact layer

⇨ change of properties

Experimental Set-up

PULVA : aluminum electrode, D=130mm,

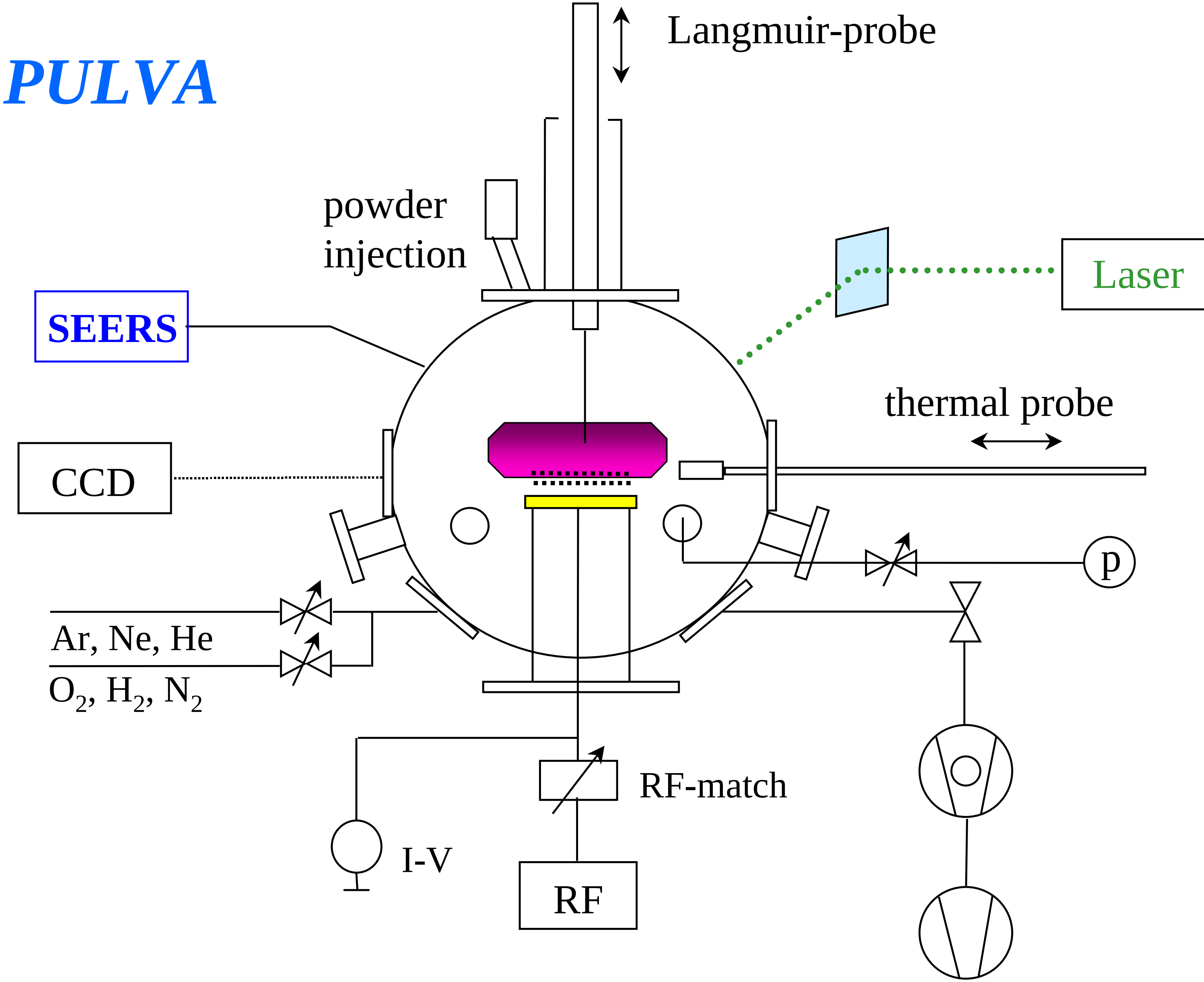
Particles : Fe-powder particles R~1µm, (0.2 ... 5µm)

SiO_2-powder particles (R = 0.13µm, 0.5µm)

Discharge conditions :

rf-voltage :	100 … 400V
power :	1 … 20W
pressure (Ar) :	0.5 ... 15Pa
gas flow :	6sccm

PULVA



Langmuir-probe
powder
injection
Laser
SEERS
thermal probe
CCD
p
Ar, Ne, He
O2, H2, N2
RF-match
I-V
RF

Diagnostics

Langmuir-probes :   *EEDF*, n_e, kT_e, V_{pl}, V_{fl},

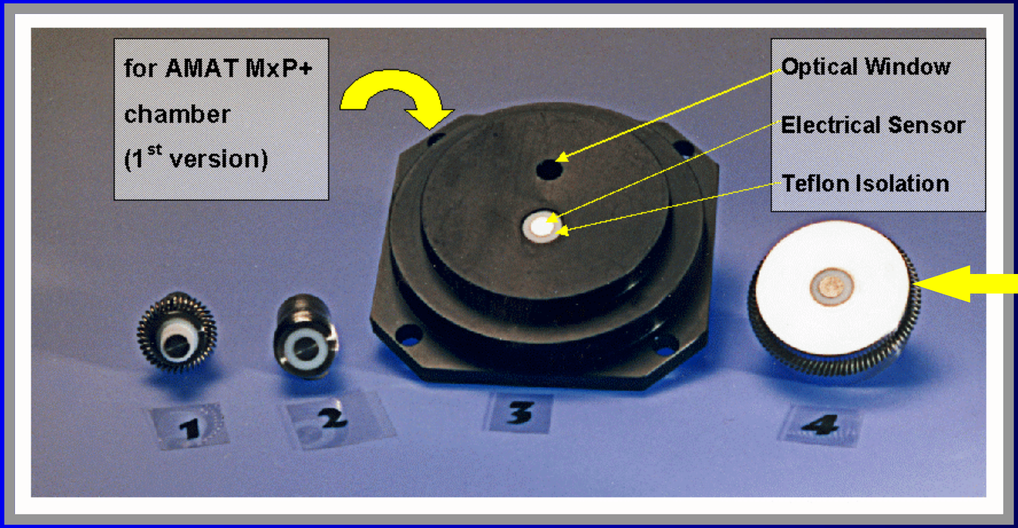
 # SEERS (*ASI Hercules*) : n_e

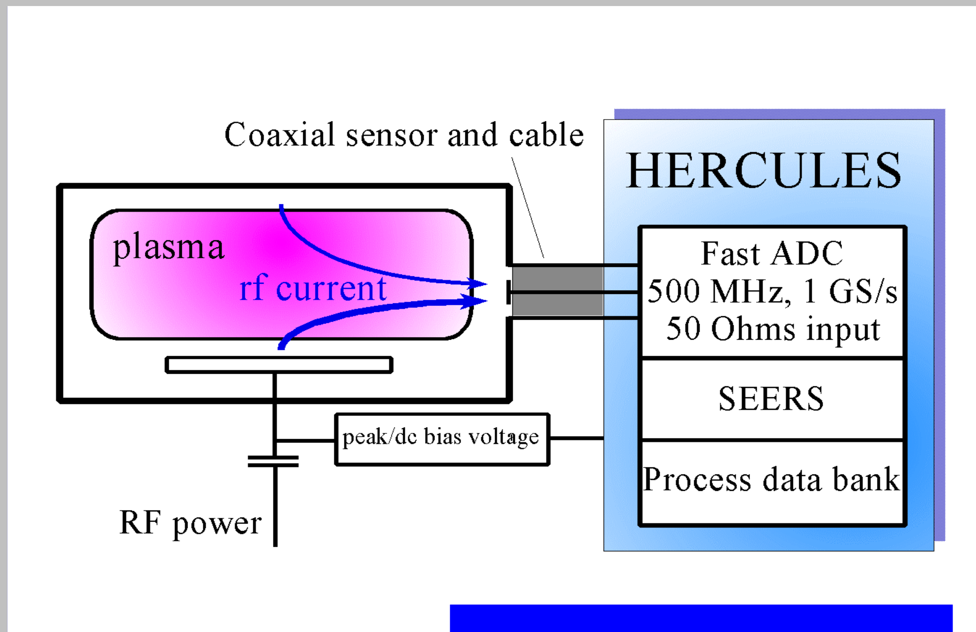
thermal sensor (temperature raise dT_S/dt) : total energy influx J_{in}

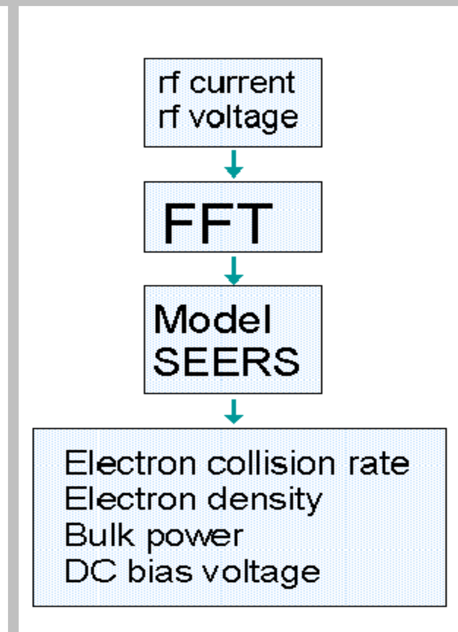
analytical CCD photometry : d_{sh} , powder location

electron microscopy (REM) :   particle mass *m* , size distribution

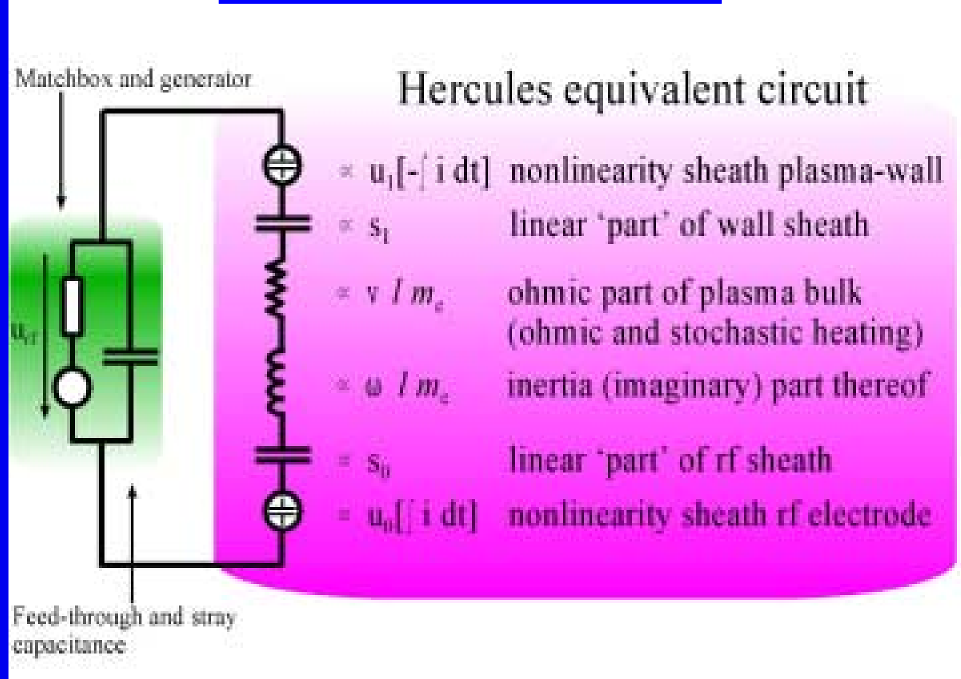
low frequency superposition :   particle charge *Q*







SEERS



ASI Berlin,
Information Brochure

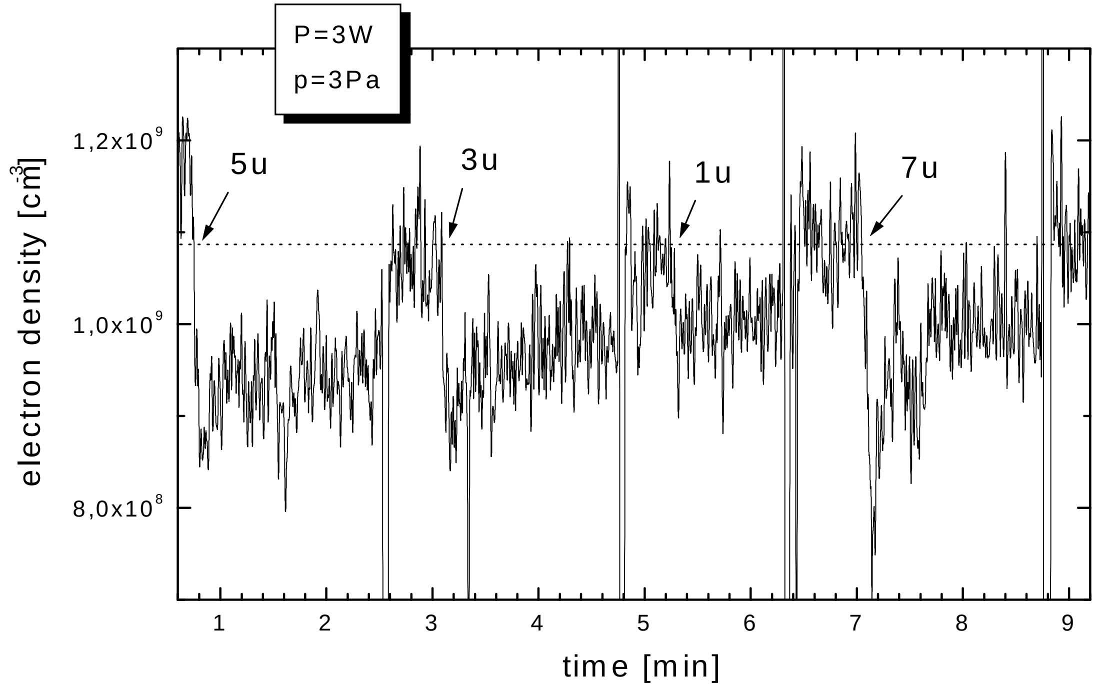
Determination of the particle charge

Since the net charge of the dust particles is a crucial parameter for a description of the particle behavior in a surrounding plasma, different methods for determining the net charge may be used :

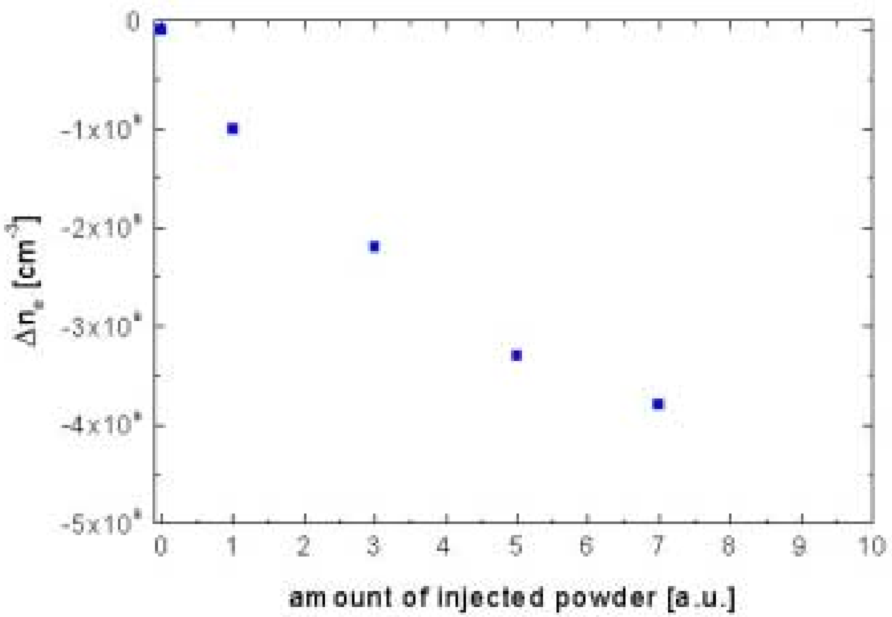
- an adapted model based on elementary plasma-wall-interaction
- common resonance method
- observation of the particles gyration ???
- **estimation by SEERS**

powder injection :

• injected powder particles catch electrons from the plasma
• relaxation of electron density



SEERS measurements

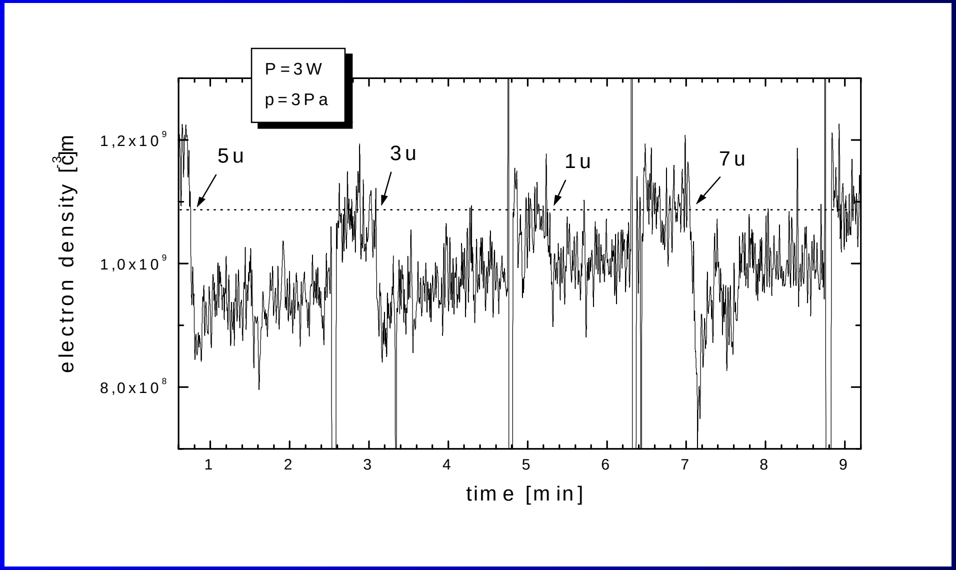


By taking into account the dust particle density n_D it is possible to estimate the particle charge Q.

- pristine plasma : n_e
- dusty plasma : n_e^{dusty}
- dust density : n_D

- firstly n_e, by dust injection : $n_e^{dusty} < n_e$

- $\Delta n_e = n_e - n_e^{dusty} = Zn_D$: number of electrons captured by the dust particles



Kersten,H., Deutsch,H., Otte,M., Swinkels,G., Kroesen,G.M.W., Thin Solid Films 377-378(2000), 530.

- with $\Delta n_e = 4{\cdot}10^8 cm^{-3}$ for 7u amount of dust and $Q = Ze_0 \sim 10^3$ one obtains $n_D = 4{\cdot}10^5 cm^{-3}$ which is a realistic value

- relaxation of n_e needs ~10 ... 100s due to dust interaction

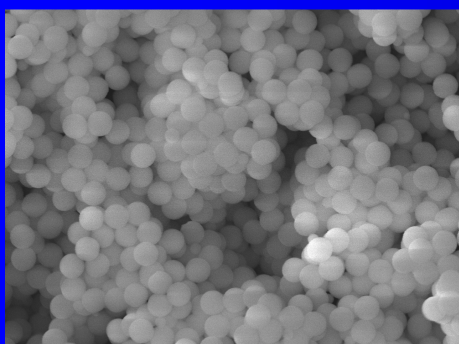
determination of charge by resonance method

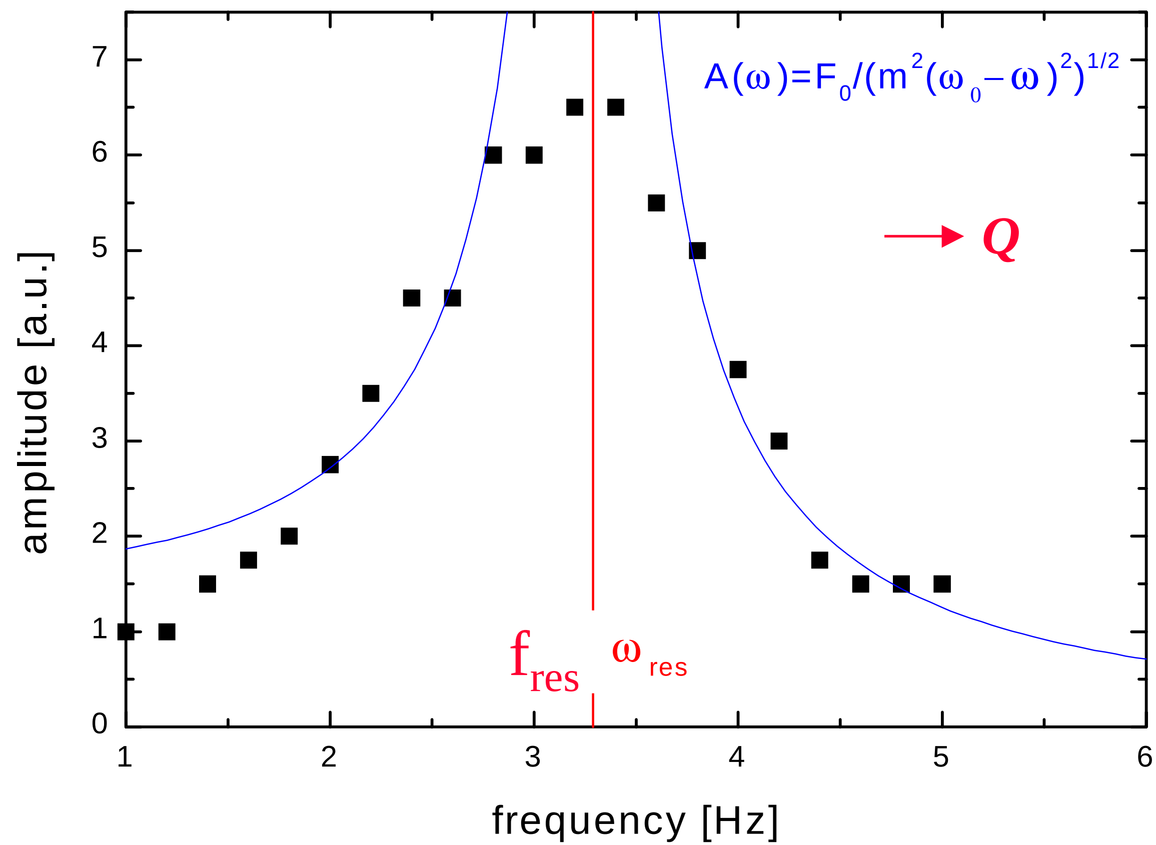
superposition of forced harmonic E-oscillation : $F = F_0 \cos(\omega t) = m\ddot{z} + mg - QE$

$$QE = QE(z) = Q\left(E_0 + \frac{dE}{dz}\right) \text{with } QE_0 = mg \longrightarrow F_0 \cos(\omega t) = m\ddot{z} - Qz\frac{dE}{dz} \quad \text{with } \frac{dE}{dz} = -\frac{e_0 n_i}{\varepsilon_0}$$

$$\ddot{z} + \frac{Q}{m}\frac{e_0 n_i}{\varepsilon_0} z = F_0 \cos(\omega t) \quad \text{with } \omega_0^2 = \frac{Q}{m}\frac{e_0 n_i}{\varepsilon_0}$$

resonance at : $A(\omega) = \dfrac{F_0}{m\sqrt{(\omega_0^2 - \omega^2)^2}}$





determination of charge by a simple model

In order to determine the charging of “insulated” dust particles the following elementary processes at the surface have to be considered:

- adsorption of incoming charge carriers (negative and positive),
- desorption of charge carriers, and
- surface recombination of the incoming charge carriers including the concept of their surface diffusion

$$\frac{d\sigma_e}{dt} = (1-\Theta_e) S_e j_e - \frac{\sigma_e}{\tau_e} - \alpha_R \sigma_e \sigma_i \,, \quad \frac{d\sigma_i}{dt} = (1-\Theta_i) S_i j_i - \frac{\sigma_i}{\tau_i} - \alpha_R \sigma_e \sigma_i \,,$$

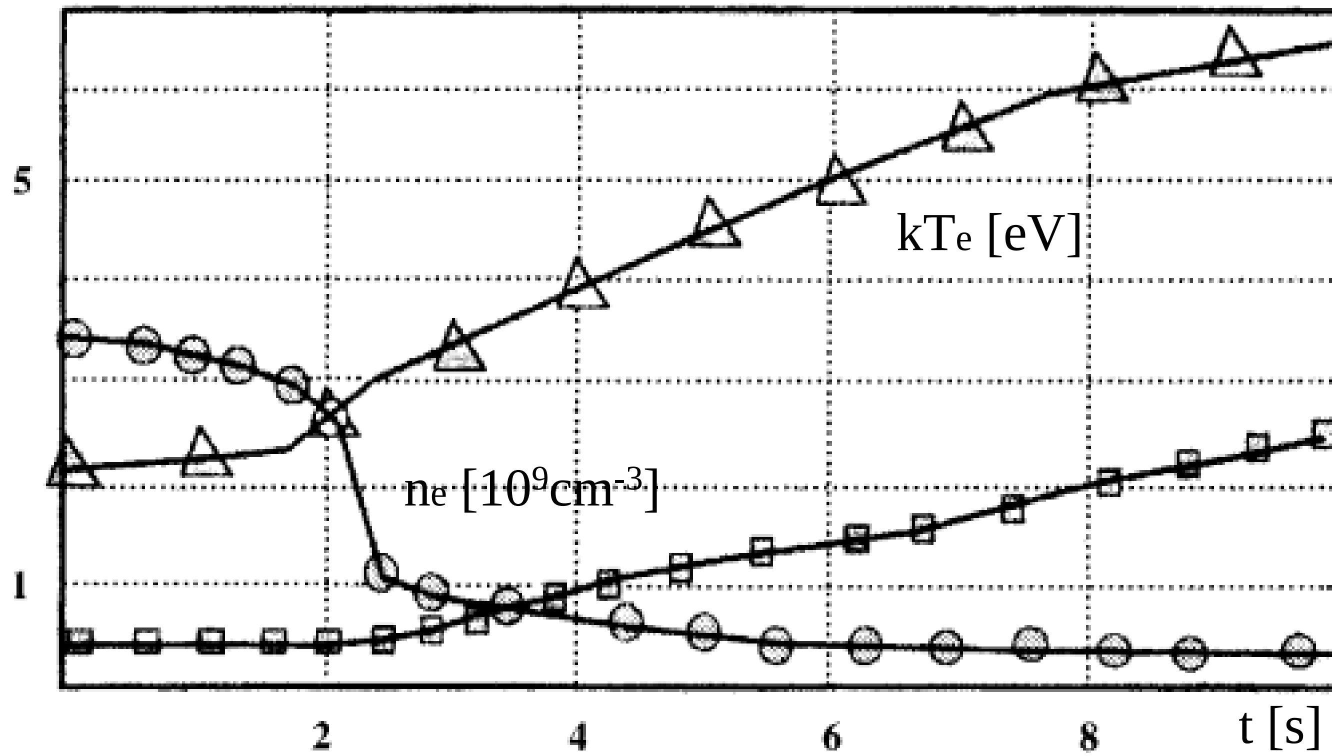
$$\tau_k = \tau_{k,0} \exp\left(\frac{E_{a,k}}{kT_p}\right), \quad k = e, \mathrm{i} \qquad \Delta\sigma_e = \sigma_\mathrm{e} - \sigma_i = \frac{\mathrm{Q}}{\mathrm{A_p}} \,,$$

$\tau_{e,o}: 1.9 \cdot 10^{-9}$ s	$\tau_{i,o}: 1 \cdot 10^{-11}\, s$	$S_e: 0.95$	$\alpha_R: 0.32 \ldots 0.37 \, \frac{cm^2}{s}$
$E_{a,e}: 0.185\, eV$	$E_{a,i}: 0.10\, eV$	$S_i: 1.00$	

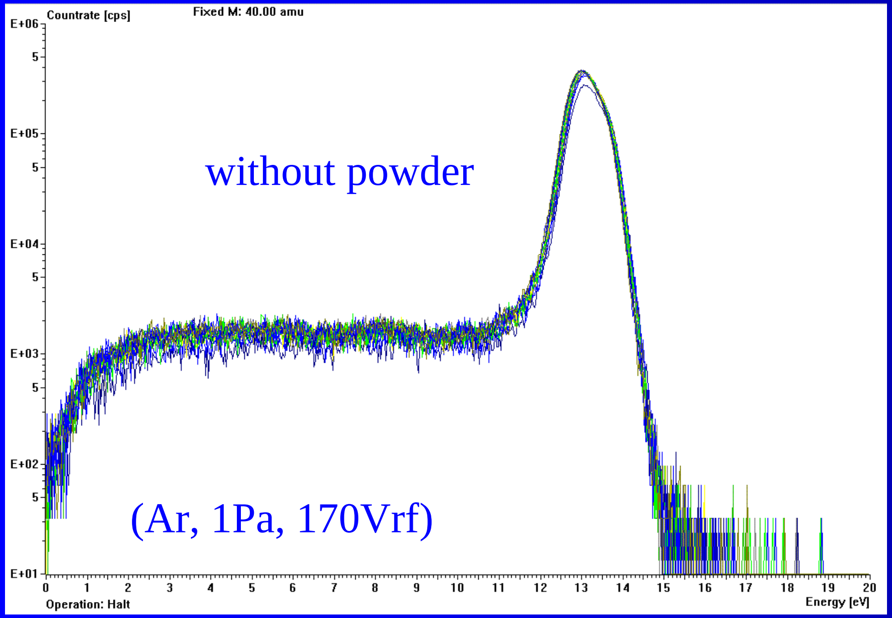
J.F. Behnke, T.Bindemann, H.Deutsch, K.Becker, Contrib.Plasma Phys. 37(1997), 345.
Kersten,H., Deutsch,H., Otte,M.,Swinkels,G., Kroesen,G.M.W., Thin Solid Films 377-378(2000), 530.

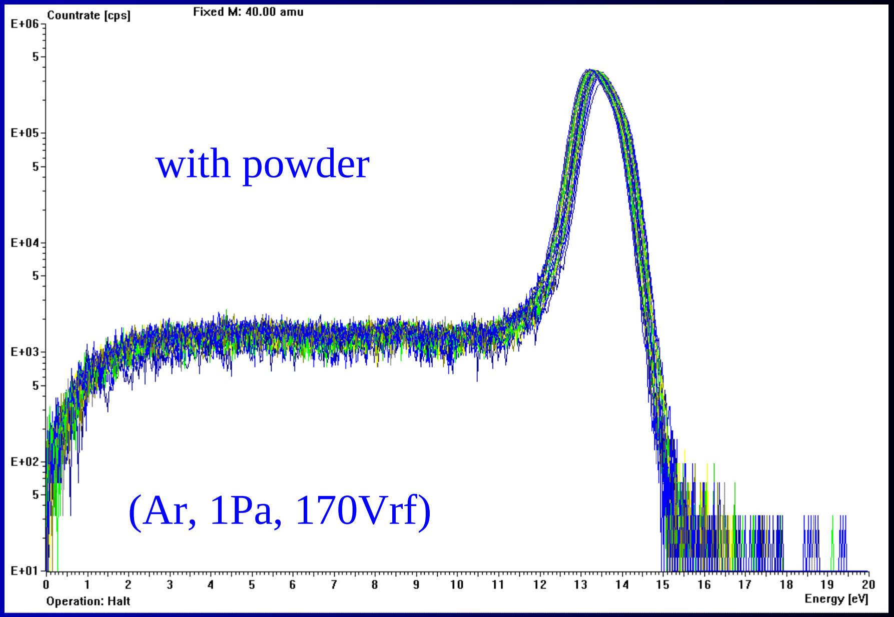
- rf plasma (Silan, Ar, He) : formation of particles
- decrease of free electron density
- simultaneous increase of ionization rate,
  in order to compensate particle recombination

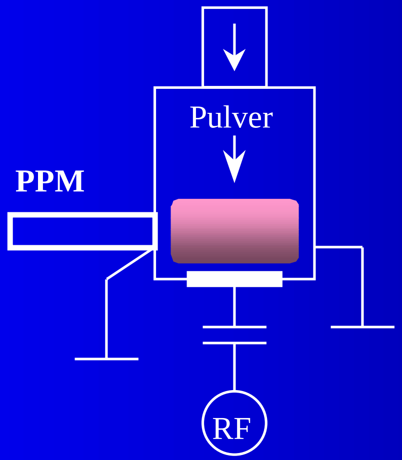
L.Boufendi, A.Bouchoule, T.Hbid, J.Vac.Sci.Technol.A14/2(1996), 572.



influence on ion component :







- only very weak effect on IEDF

Particle coating for fluorescent lamps

The improvement of lumen maintenance in fluorescent lamps is a well known problem. A variety of factors contribute to the drop-off in light output during lamp operation. It is believed that one of the primary causes of the drop-off in light output during operation is the formation of mercury compounds, particularly on the surface of phosphor particles.
Various uses of alumina have been proposed to overcome this problem and to improve lamp performance. One such use is the application of a thin layer of alumina over the phosphor particles.

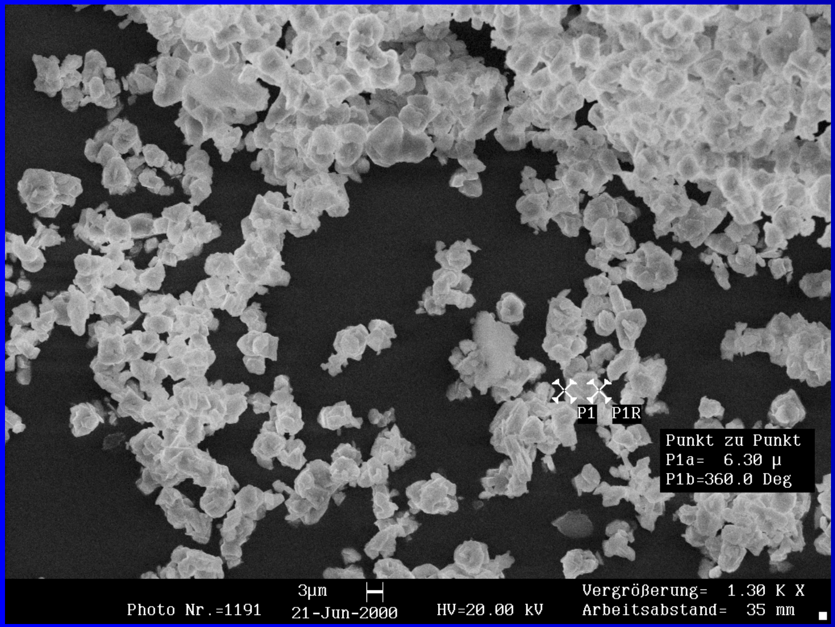
Volatile organo-, alcoxide and acetylacetonate compounds of aluminum may be used as coating precursor materials in plasma (PECVD).

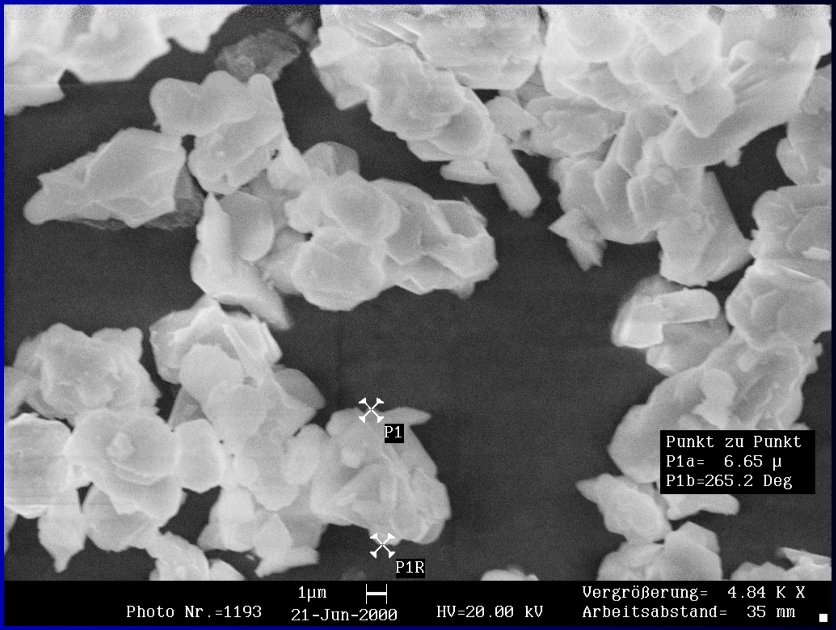
But the first obstacle is that very little is known about plasma species and plasma reactions ..... → SEERS ???

gas discharge tube

+

fluorescent particles at glass wall





$BaMg_2Al_{16}O_{27}:Eu^{2+}$ particles

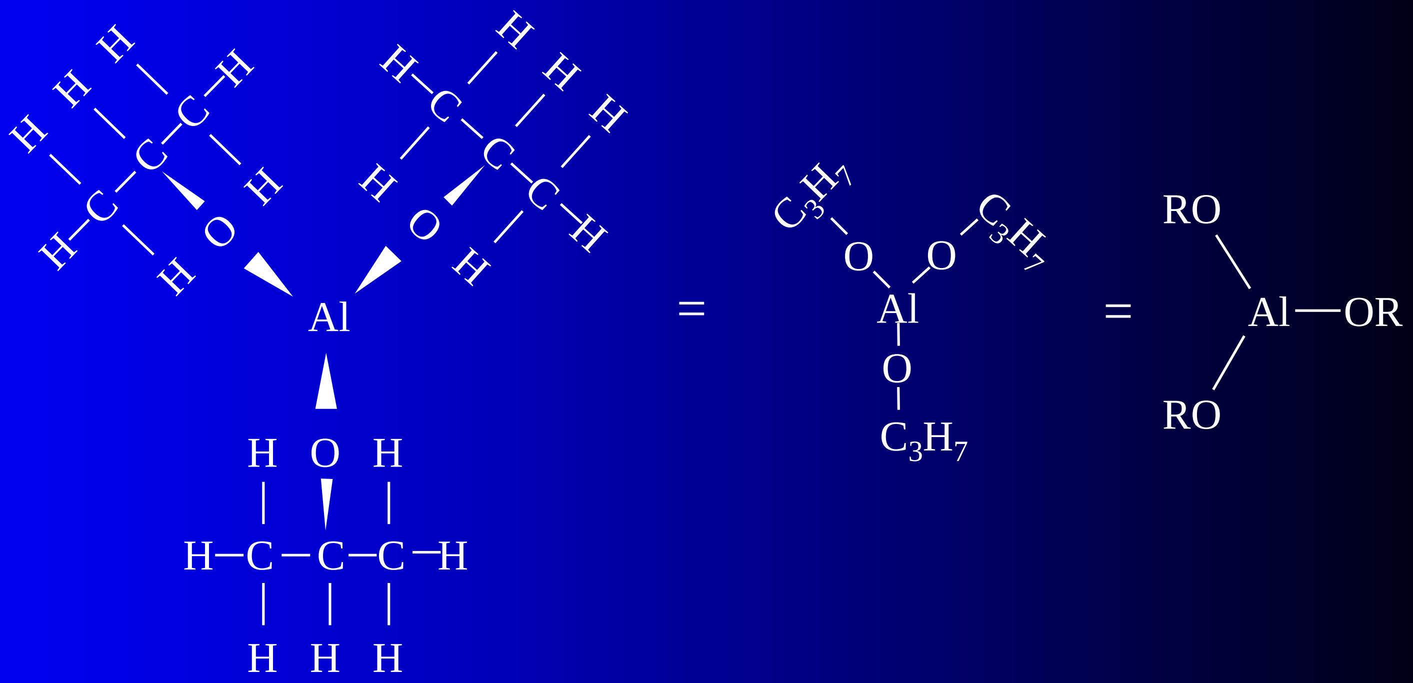
have to be coated by an alumina thin film (protection, adhesion) aluminum-tri-isopropyloxide (ATI) in plasma $\longrightarrow$ **alumina** layer

brutto reaction for deposition of alumina :

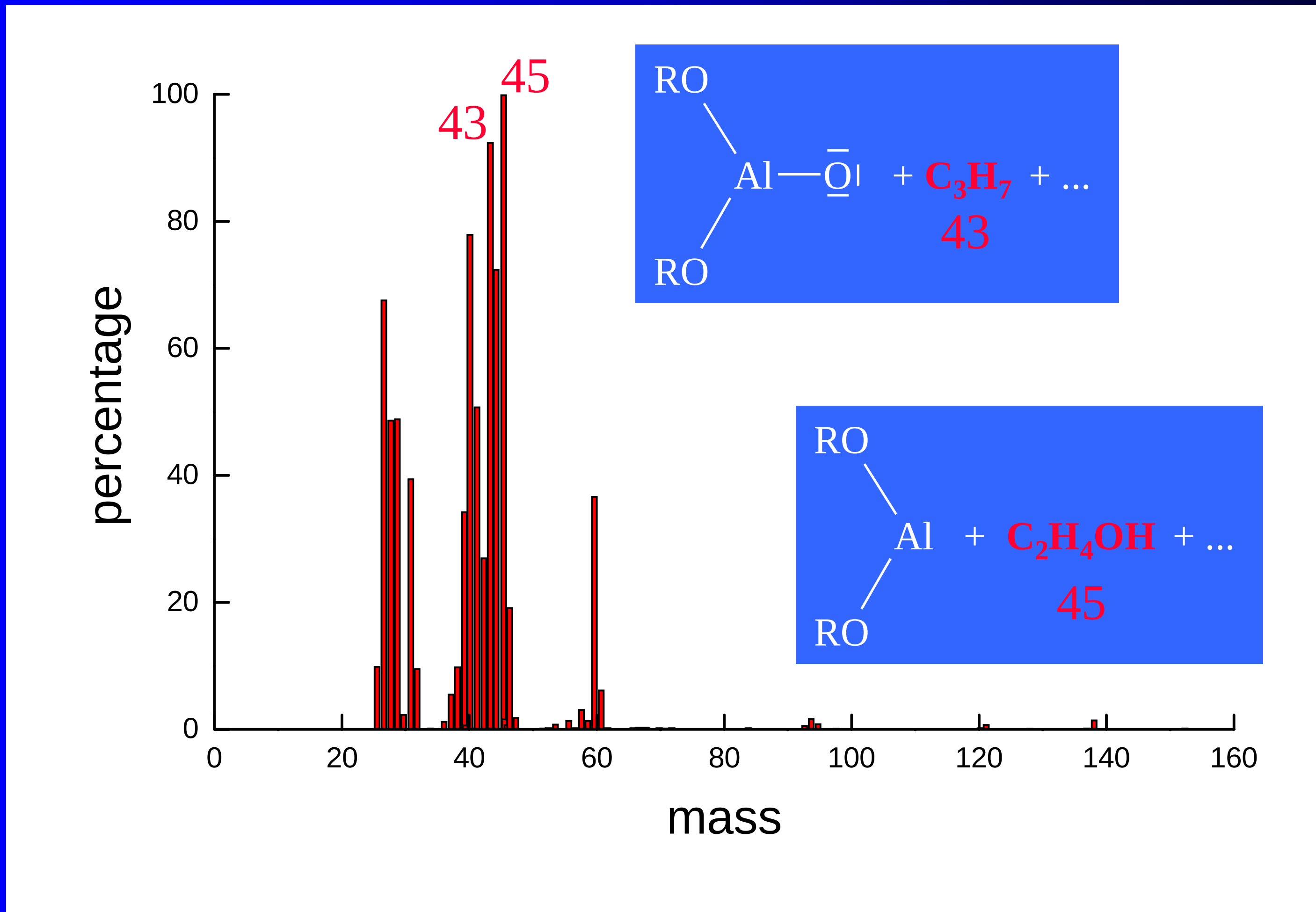
$$2\ Al(i\text{-}OC_3H_7)_3 \longrightarrow \mathbf{Al_2O_3} + 3\ C_3H_6 + 3\ C_3H_7OH$$

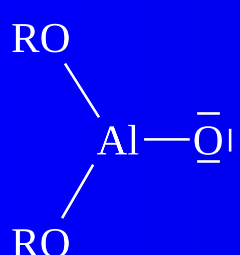
use of ATI :

$Al(i\text{-}OC_3H_7)_3$ =

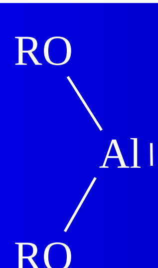


most likely fragments :

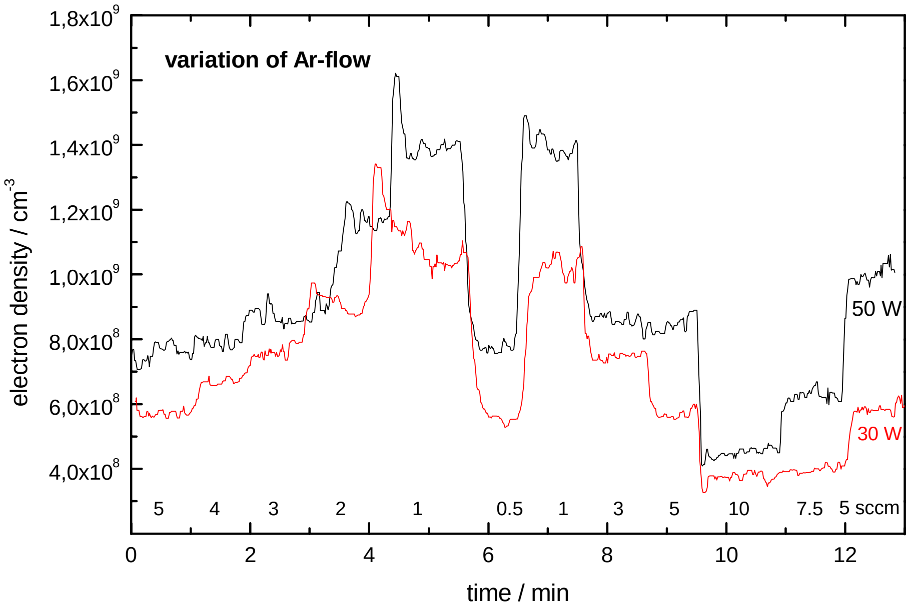




and



tend to form negative ions by electron capture
(electron drain)



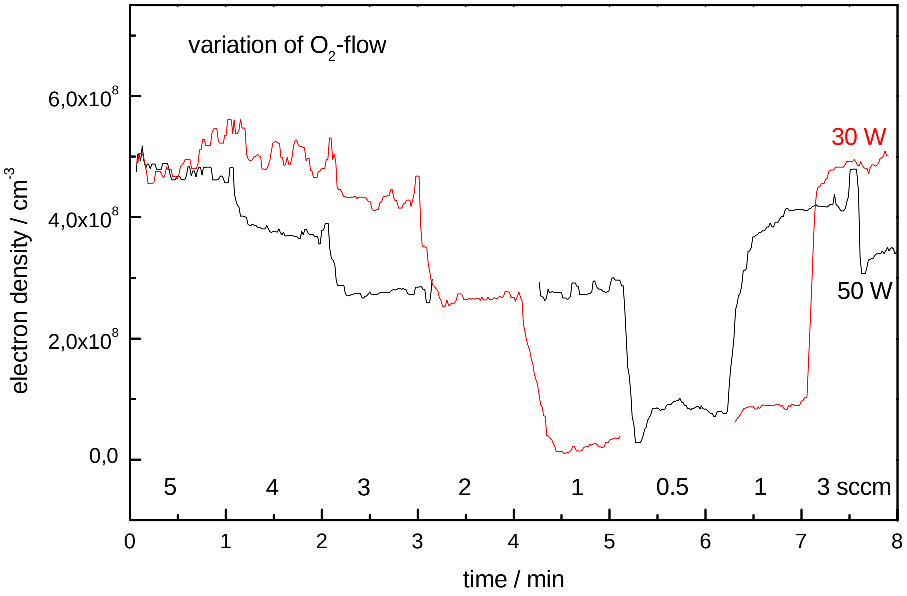
measurement of n_e

by SEERS
in rf plasma
(process chamber)

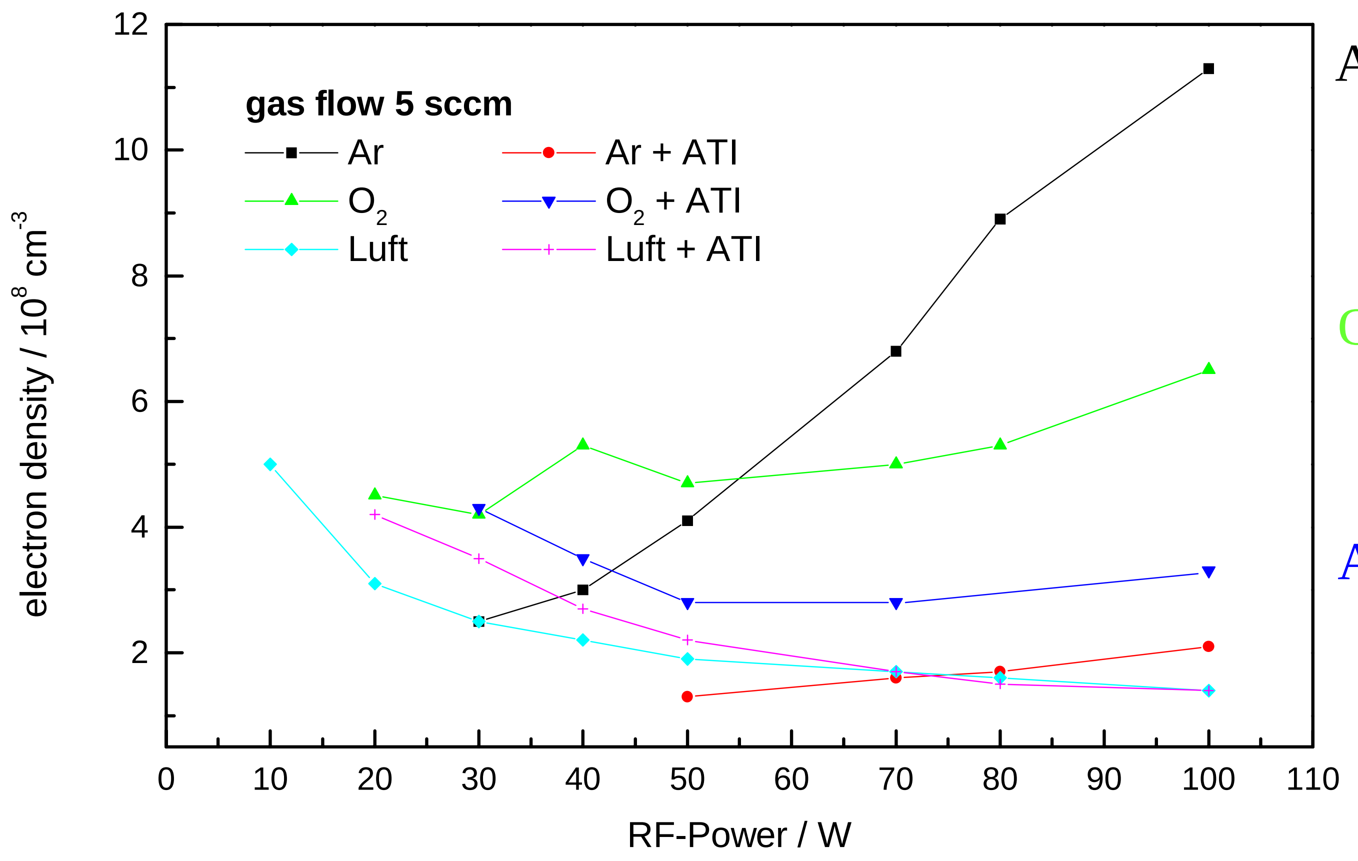
argon

for the carrier gases

oxygen



measurement of n_e vs. rf power

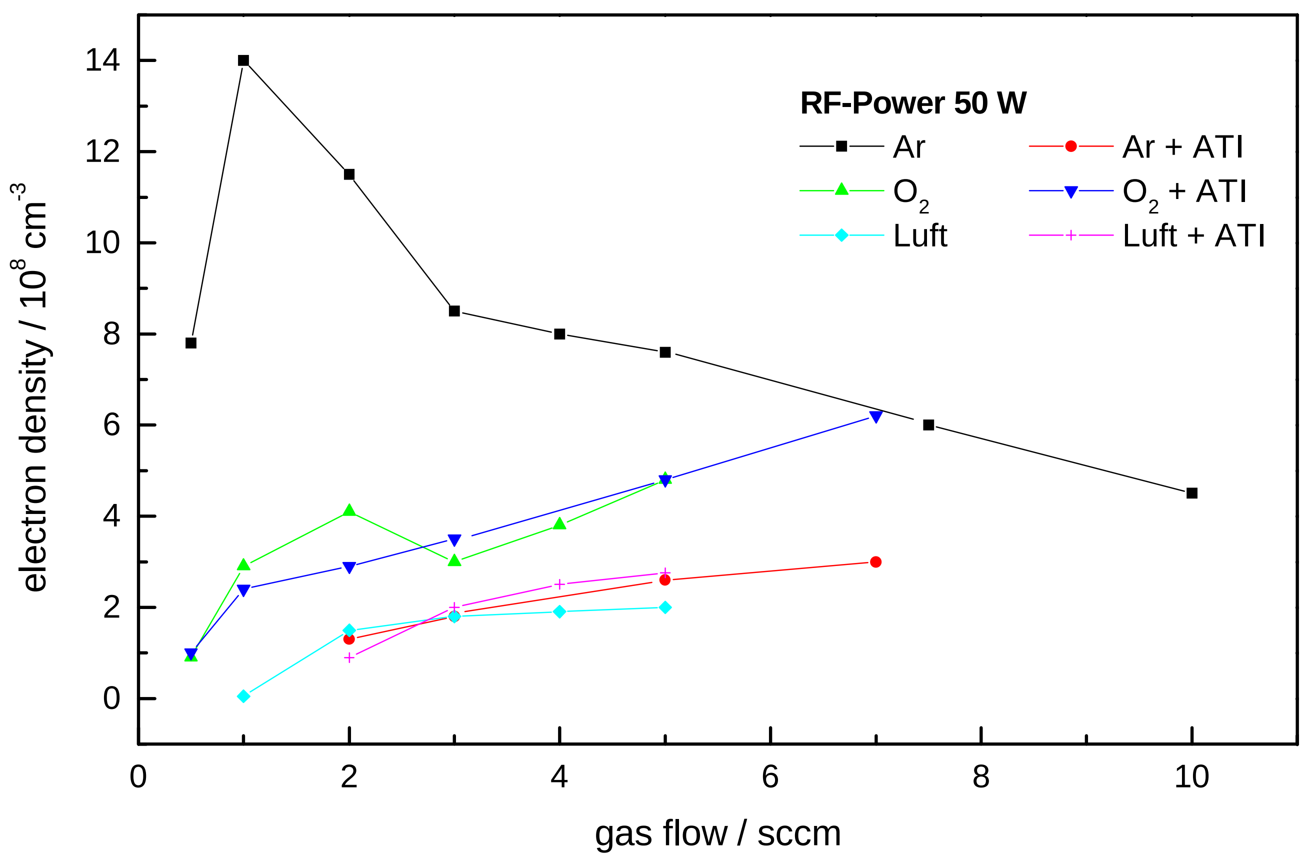


Ar: electropositive, P ↑ n_+ ↑ n_e ↑

O_2: electronegative, P ↑ n_O ↑ n_- ↑ n_e →

ATI: electronegative, P ↑ n_R ↑ n_- ↑ n_e →

measurement of n_e vs. pressure (gas flow)



Ar: electropositive,

$p \uparrow\ n_+ \downarrow\ n_e \downarrow$

O_2: electronegative,

$p \uparrow\ n_O \downarrow\ n_- \downarrow\ n_e \uparrow$

ATI: electronegative,

$p \uparrow\ n_R \downarrow\ n_- \downarrow\ n_e \uparrow$

Conclusion

- *in situ* measurement of n_e during powder processing in plasma is possible

- change in n_e provides information on electron capture by dust particles and, hence, on particle charge or dust denstity, respectively
(comparison with other methods !)

- determination of n_e during powder treatment by a thin film depositing plasma (PECVD, MOCVD)
- different order of magnitudes and tendency of n_e at different process conditions (Ar, O_2, ATI) give information on dissociation, ionization, fragmentation and, thus, information on layer deposition