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Diagnostics of plasma particle interaction by SEERS and other methods

Holger Kersten

G. Thieme

D. Bojic

R. Hippler

(Institute for Physics, U of Greifswald)

M. Quaas

H. Wulff

(Dpeartment of Chemistry and Biochemistry, U of Greifswald)

www.inp-greifswald.de

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Dresden

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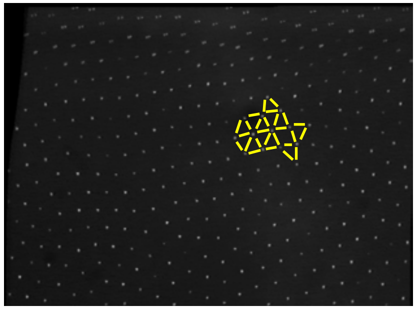
- introduction
- interaction plasma - powder
- modification of powder particles in process plasmas

  # deposition of protective coatings onto luminophore particles
  # coating of powder particles in a magnetron discharge
- summary

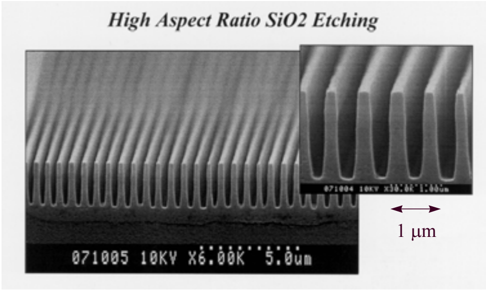
Why interest in complex (dusty) plasmas ?

- astrophysics
  (formation of stars, comets, planetary rings)

- basic research : plasma crystal



- dust as fault in semiconductor processing



- ***generation and modification of powders***
- *micro-probes for diagnostics*

interaction plasma - powder

charging and trapping of particles in plasma

starting point : particles (mono-disperse, spherical, R, ρ) are injected into rf-plasma (Maxwell, V_{pl}, n_e, kT_e, $\lambda_D >> R$, d_{sh})

↓

charging of particles

---

assumption : OML, Maxwell-distribution, $V_S = V_{fl} < V_{pl}$, $V_{bias} = V_{pl} - V_S$

currents to a particle : $j_e = j_{0e} exp(-e_0 V_{bias}/kT_e)$, $j_i = j_{0i}(1 + e_0 V_{bias}/kT_i)$

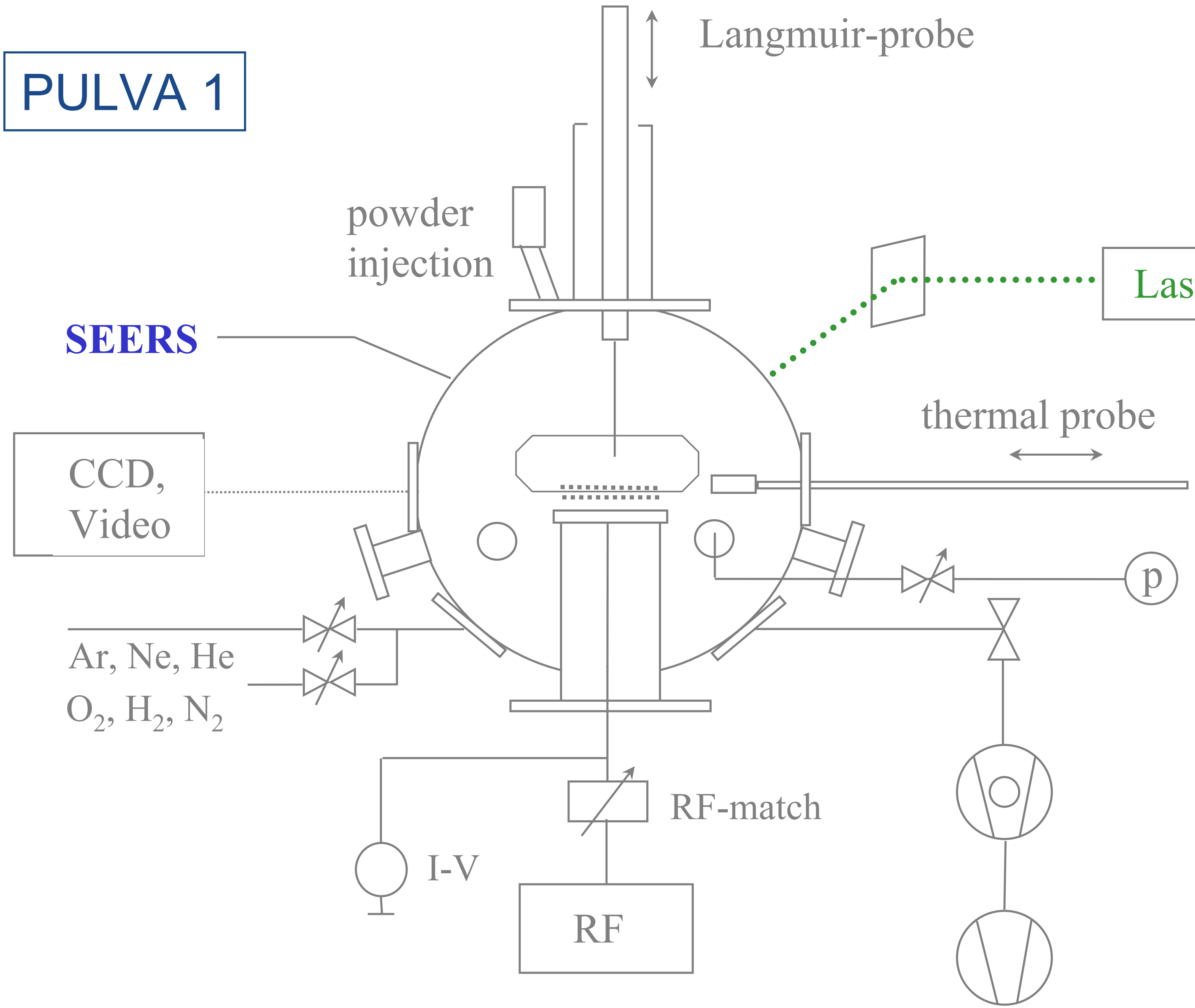
charge of a particle : $dQ/dt = \Sigma I_k$, $Q(t) = Ze = CV_{bias}(t) = 4\pi\varepsilon_0 R V_{bias}(t)$

equilibrium (e.g. particle completely charged), if $dQ/dt = 0$

$<V_S(t)>$, $<Q(t)>$, $t \rightarrow \tau$

interaction plasma - powder

PULVA 1

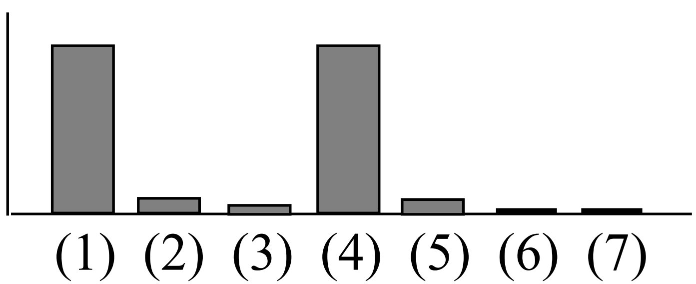


interaction plasma - powder

force balance of powder particles in plasma

onto negatively charged powder particles the following forces may act in a plasma:

1. **gravitation** : $\boldsymbol{F_g = m_P g \sim r_P^3}$
2. neutral drag force (vicosity) : $F_n \sim r_P^3 (v_P - v_n)$
3. ion drag force : $F_i \sim r_P^2 v_i$
4. **electrostatic force (E-field)** : $\boldsymbol{F_{el} = Q_P E \sim r_P}$
5. thermophoresis (temperature gradient) : $F_{th} \sim r_P^2 gradT_g$
6. photophoresis (radiation) : $F_{ph} \sim r_P^2$
7. inter grain force (Coulomb) : $F_d \sim Q_P^2/d^2$

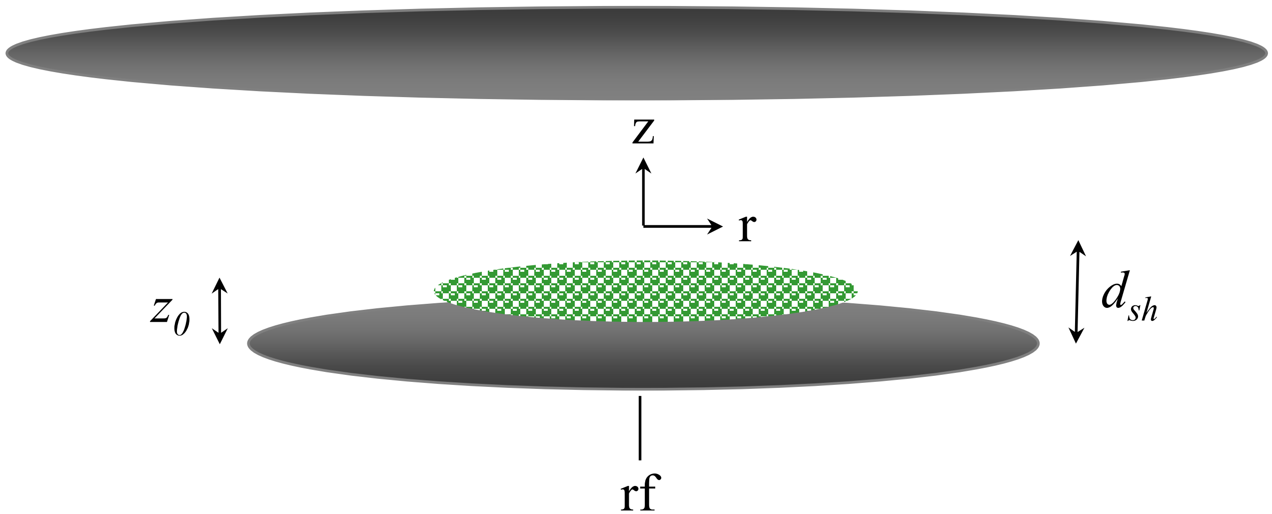


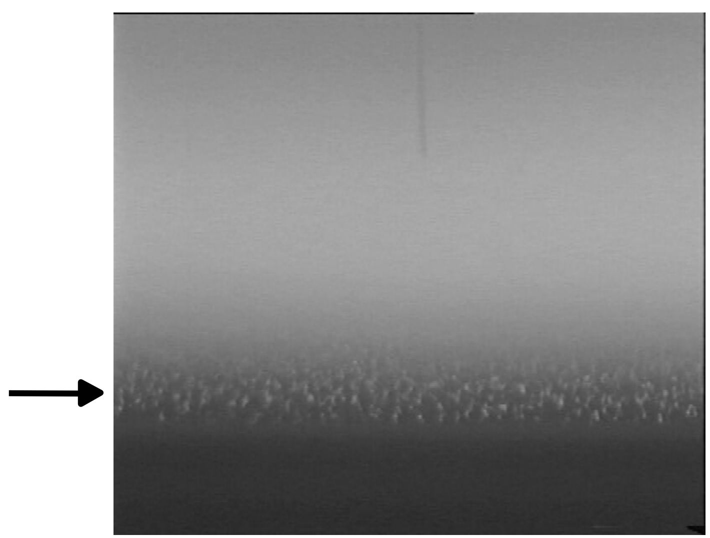
at positions, where $F_{ges} = \Sigma F_x = 0$, the particles are confined

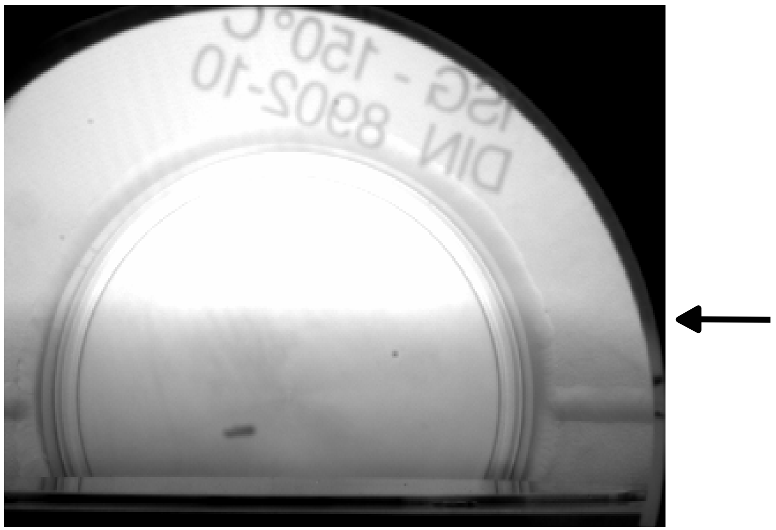
interaction plasma - powder

at positions, where $F_{ges} = \Sigma F_x = 0$, the particles are confined

dust particles are confined in plasma



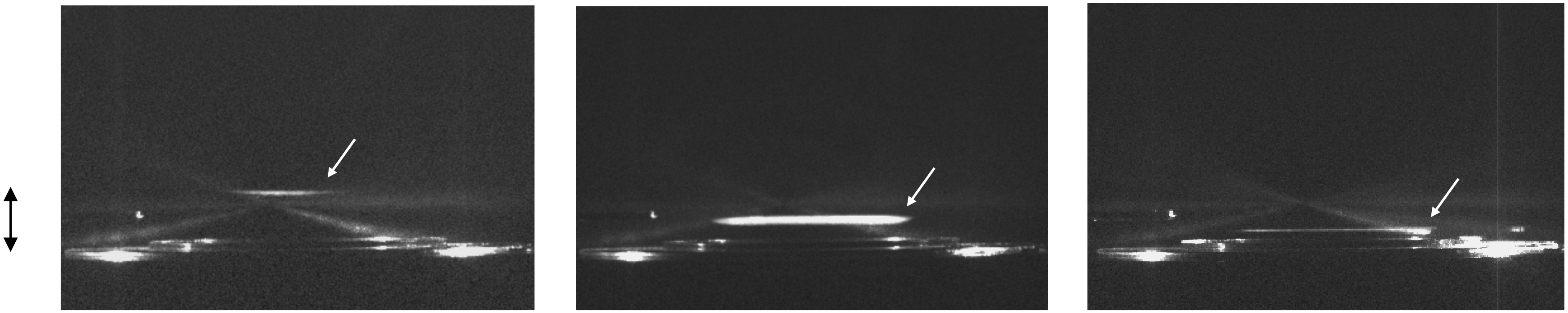




interaction plasma - powder

force balance depends on plasma conditions (pressure, gas)

gas : Argon

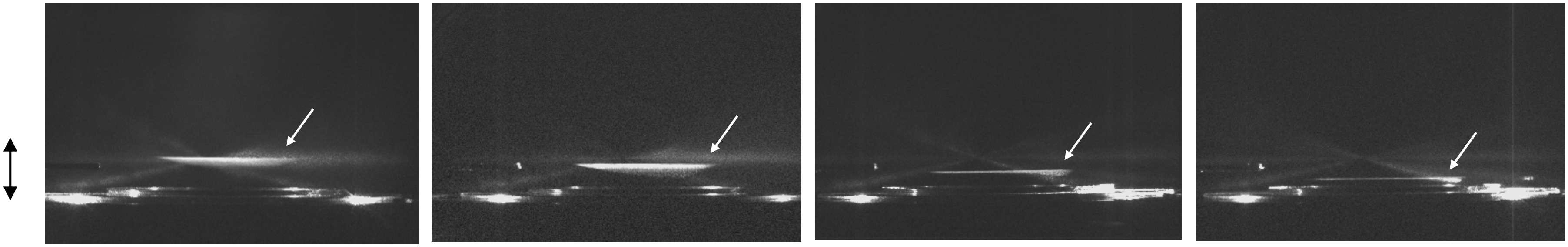


1 Pa 3 Pa 8 Pa

trapping of powder particles in plasma

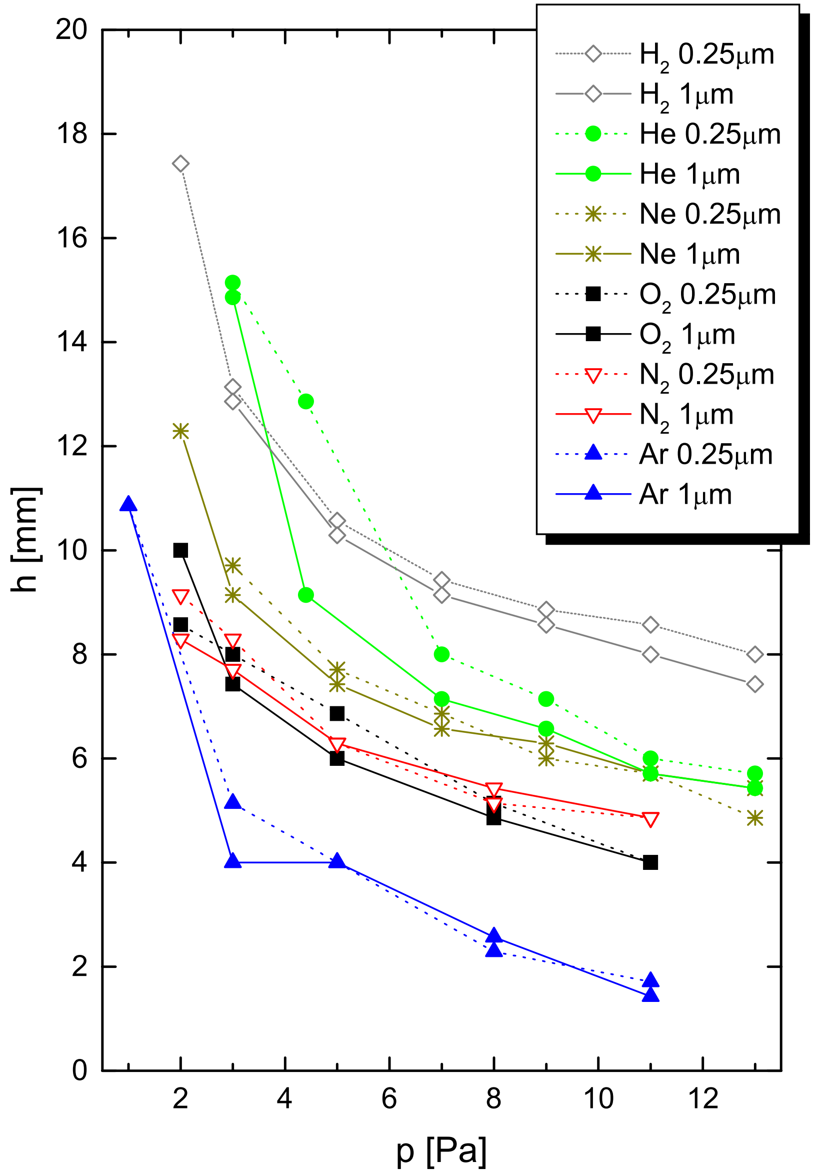
↕ 10mm

pressure : 8 Pa



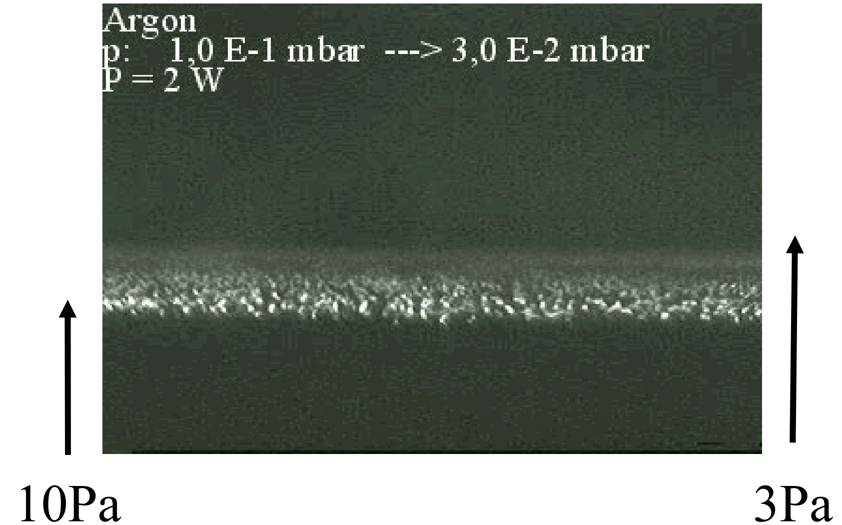
H_2 He O_2 Ar

interaction plasma - powder



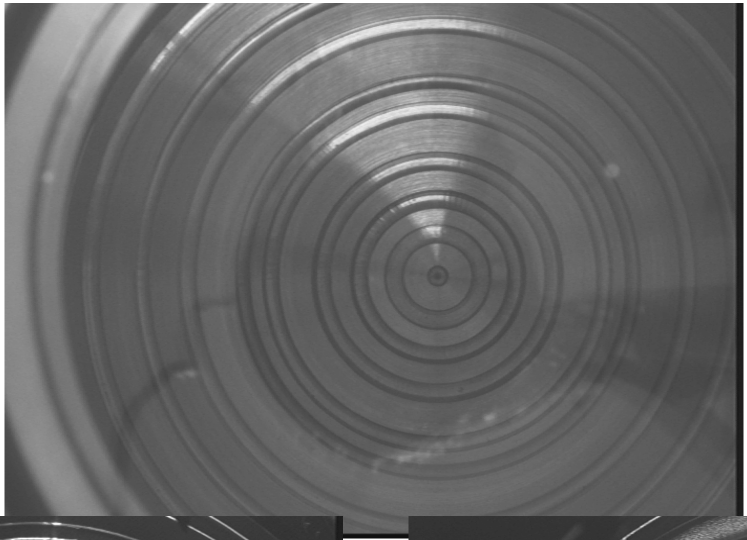
height of paricle cloud depends on :

- pressure
- gas composition
- particle size

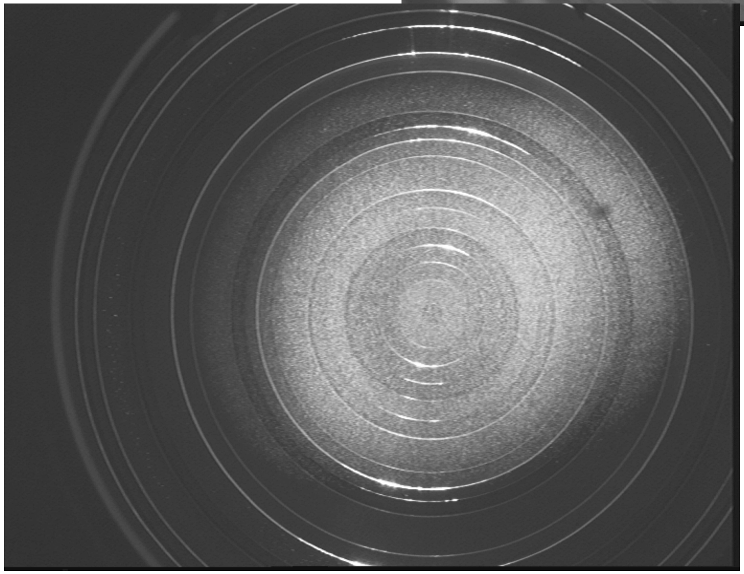


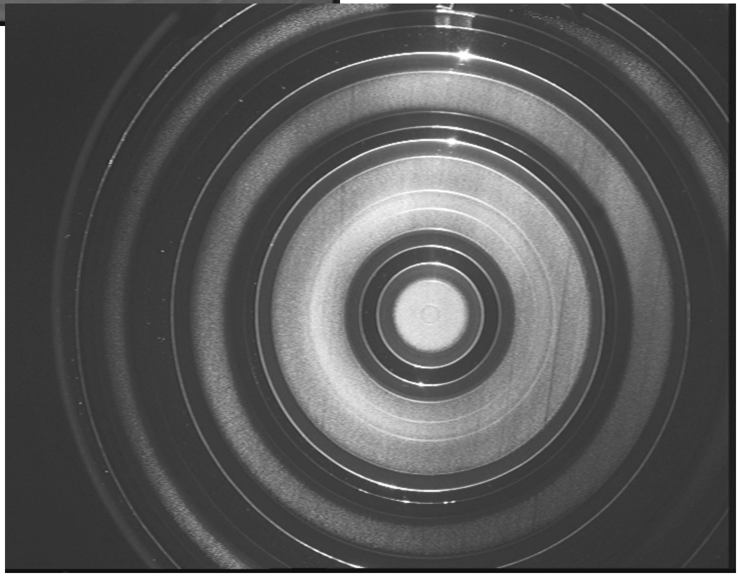
interaction plasma - powder

fragmentation / separation of powder mixtures (to sort)



Kersten,H., Deutsch,H., Stoffesl,E., Stoffels,W.W., Kroesen,G.M.W., Int.J.Mass Spectr. ***223-224****(2003), 313.*





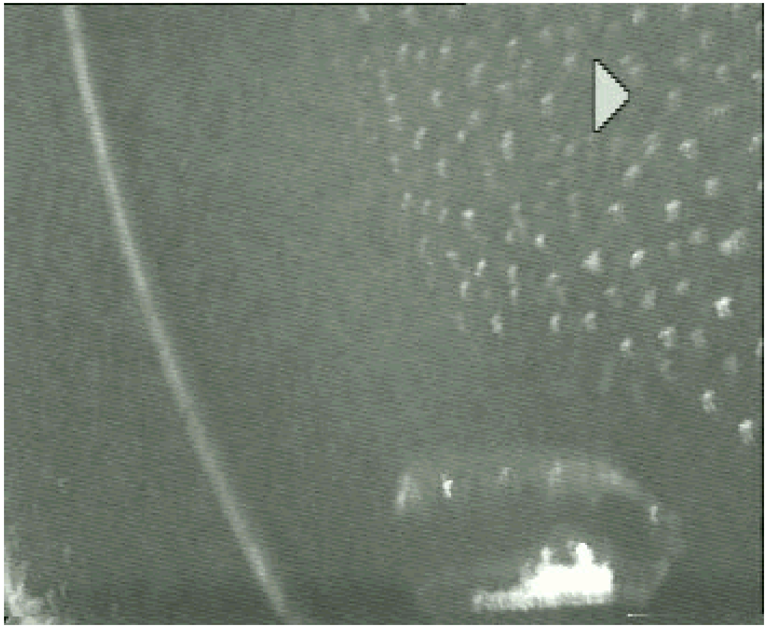
... by varaition of gas pressure (force balance) and grooves (equipotential planes) ...

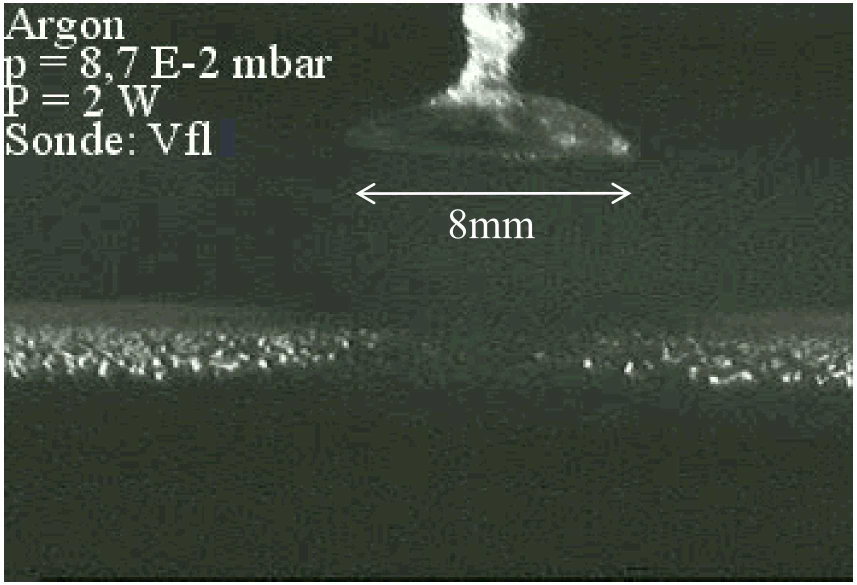
interaction plasma - powder

force balance depends on additional electric forces

electrostatic force + gravitation + additional E-field

- interaction of particls in the plasma sheath with „disturbances“ (charges, potential, E-field)
- characteristic pattern of particle movement in dependence on „disturbance“





- particles reflect very exact the sheath (shape, structure) surrounding inhomogeneities, here glass splinter at V_{fl}

- circulation of particles is strongly influenced by the potential of the probe in respect to plasma potential V_{pl}

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interaction plasma - powder

$$E(z) = F_{el}(z) / Q(z) = F_{el}(z) / Z(z)e$$

in equilibrium $z = z_0$: $F_{el} = F_g = mg$

$\Rightarrow$ determination of *m* and Q nessecary

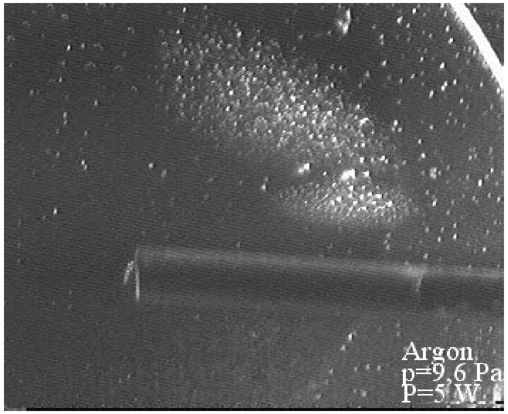
***m* :**

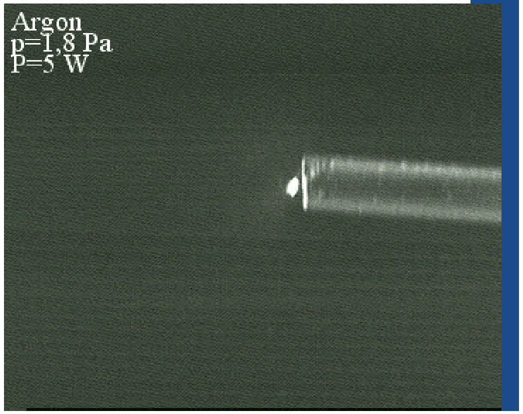
- REM, size measurement
- MIE scattering ellipsometry
- monodisperse particles

***Q* :**

- **driven oscillation method**
- **SEERS**
- MACH cones
- laser-induced photodetachment
- model : spherical capacitor
- model : currents towards particle

powder injection :





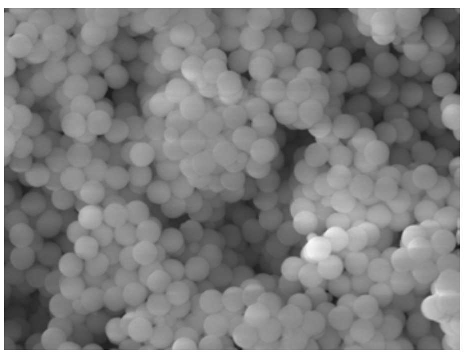
interaction plasma - powder

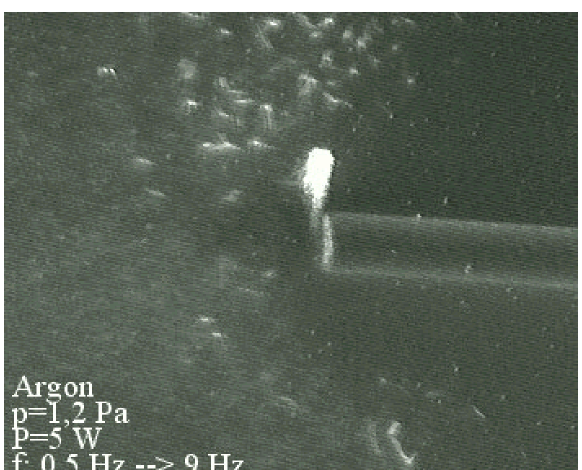
determination of charge by resonance

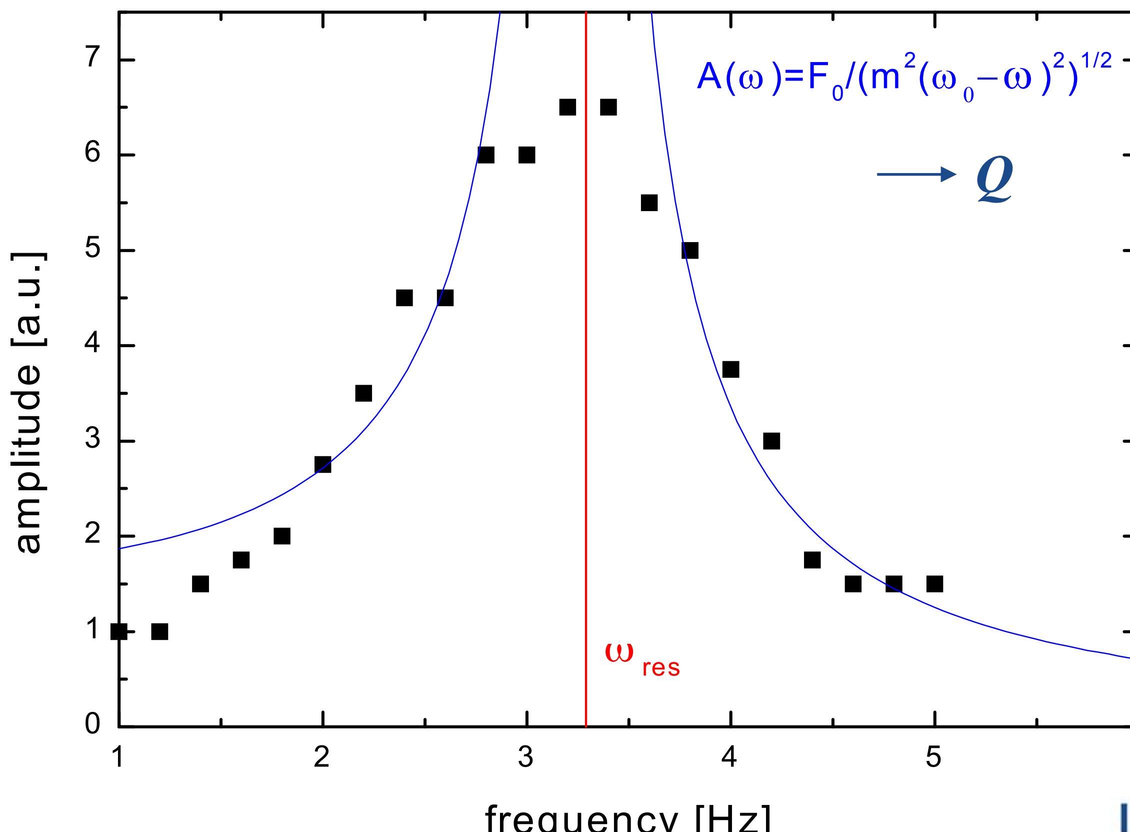
superposition of a driven harmonic E-oscillation : $F = F_0 \cos(\omega t) = m\ddot{z} + mg - QE$

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

$$\ddot{z} + \frac{Q}{m}\frac{e_0 n_i}{\varepsilon_0} z = F_0 \cos(\omega t) \quad \text{with} \quad \omega_0^2 = \frac{Q}{m}\frac{e_0 n_i}{\varepsilon_0} \qquad \text{resonance at : } \quad A(\omega) = \frac{F_0}{m\sqrt{(\omega_0^2 - \omega^2)^2}}$$







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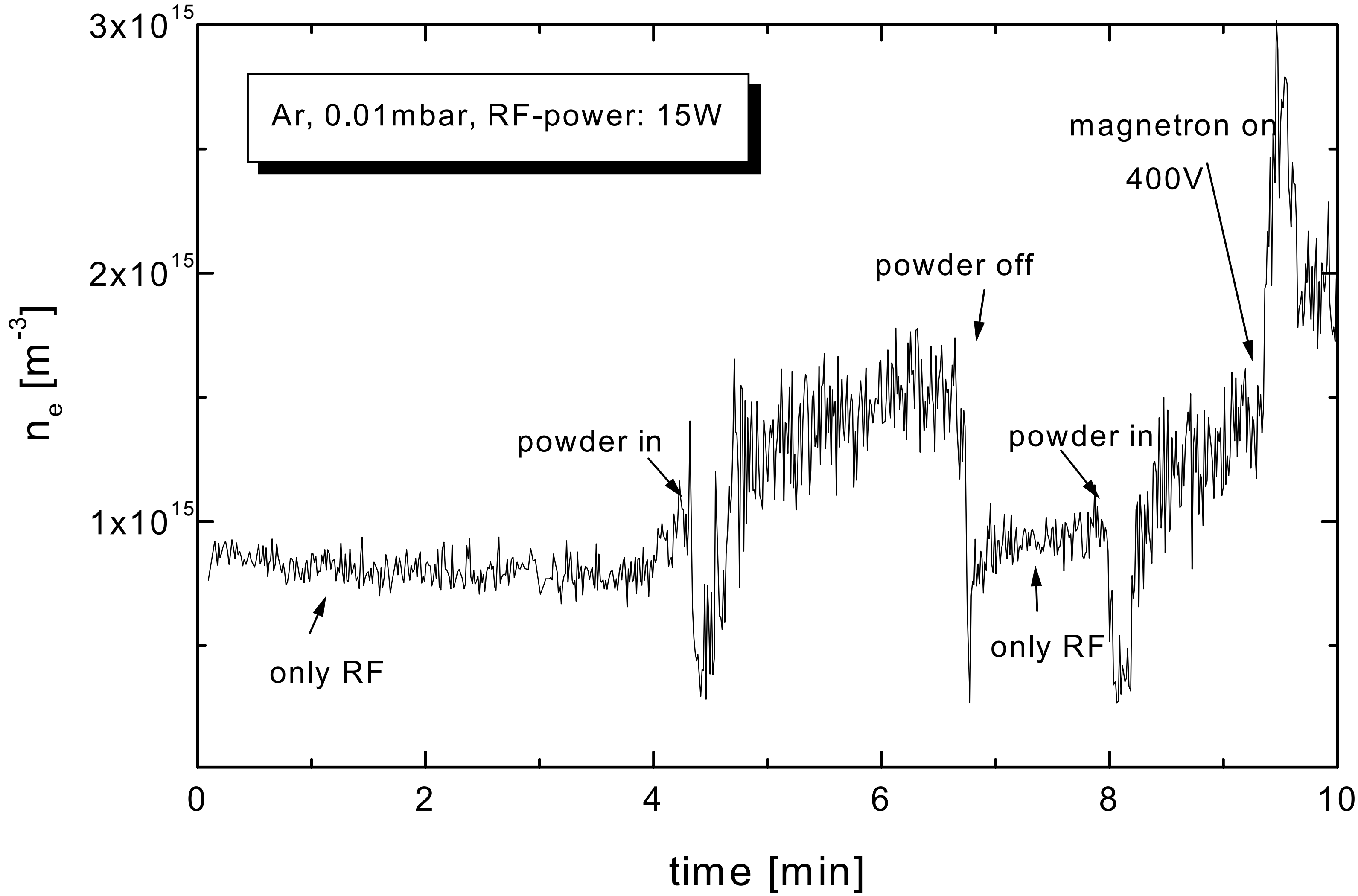
interaction plasma - powder

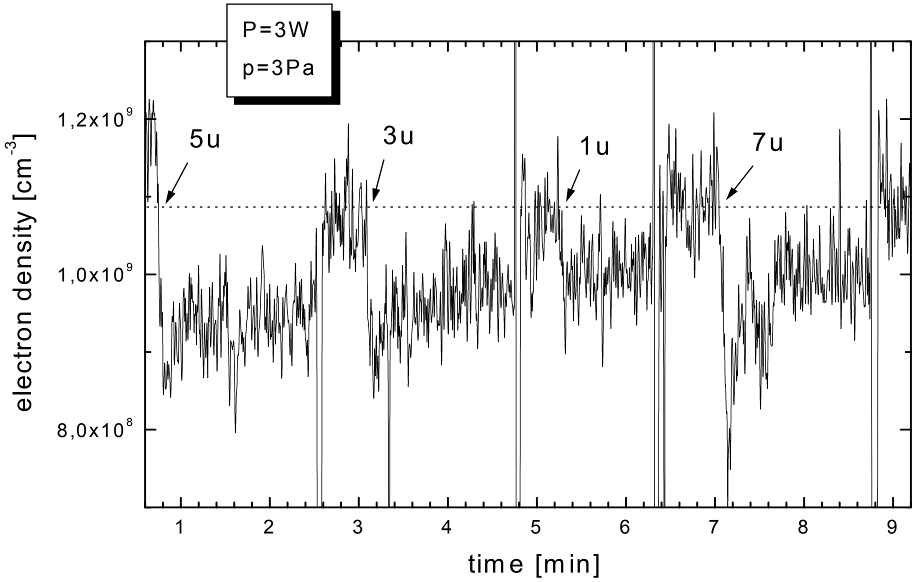
determination by SEERS



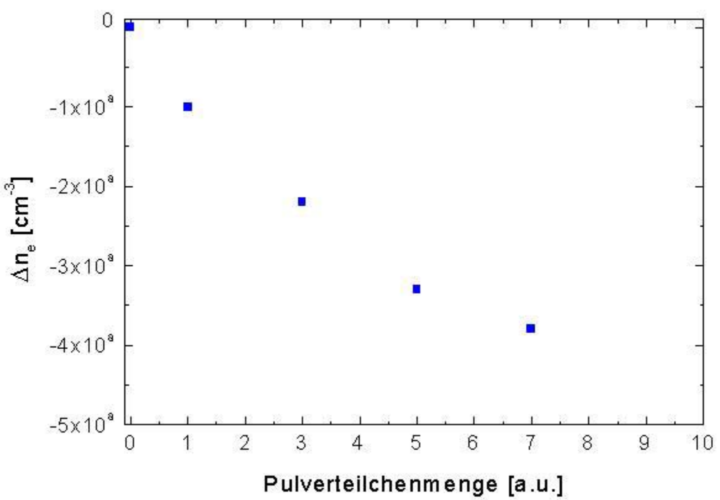
interaction plasma - powder

- plasma without dust : n_e
- plasma with dust : n_e^{dusty}
- dust density : n_P

- at first n_e, after powder injection : $n_e^{dusty} < n_e$
- $\Delta n_e = n_e - n_e^{dusty} = Zn_P$: electrons at dust particles



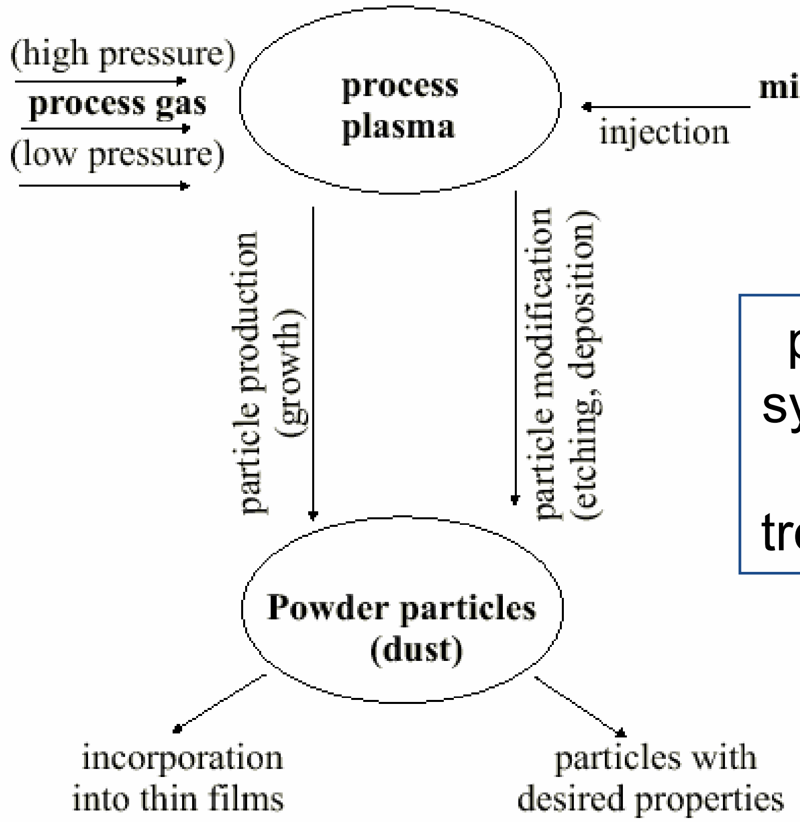
Kersten,H., Deutsch,H., Otte,M., Swinkels,G., Kroesen,G.M.W., Thin Solid Films 377-378(2000), 530.



- with $\Delta n_e = 4{\cdot}10^8 cm^{-3}$ for 7u (amount of dust) and $n_P = 2{\cdot}10^5 cm^{-3}$ one obtains $Q = Ze_0 \sim 2{\cdot}10^3 e_0$
- relaxation in ~10 ... 100s due to particle interaction

modification of particles in process plasmas

The increased knowledge and ability to control particles in a plasma environment has recently led to new lines of technological research, namely the **tailoring of particles with desired surface properties**.



Kersten,H., Deutsch,H., Stoffels,E., Stoffels,W.W., Kroesen,G.M.W., Hippler,R. Contrib.Plasma Phys. ***41****(2001), 598.*

particle synthesis and treatment

- A. Bouchoule et.al.
- G. Kroesen et.al.
- G. Selwyn et.al.
- J. Winter et.al.
- P. Roca i Cabarocas et.al.
- N. Sato et.al.
- C. Hollenstein et.al.
- S. Girshick et.al.
- etc.

modification of particles in process plasmas

some applications and new prospects for application :

- treatment of soot and aerosols for environmental protection

- powder particle synthesis in high pressure and low pressure plasmas
- ***enhancement of adhesive, mechanical and protective properties of powder particles***
- fragmentation of powder mixtures in order to sort them

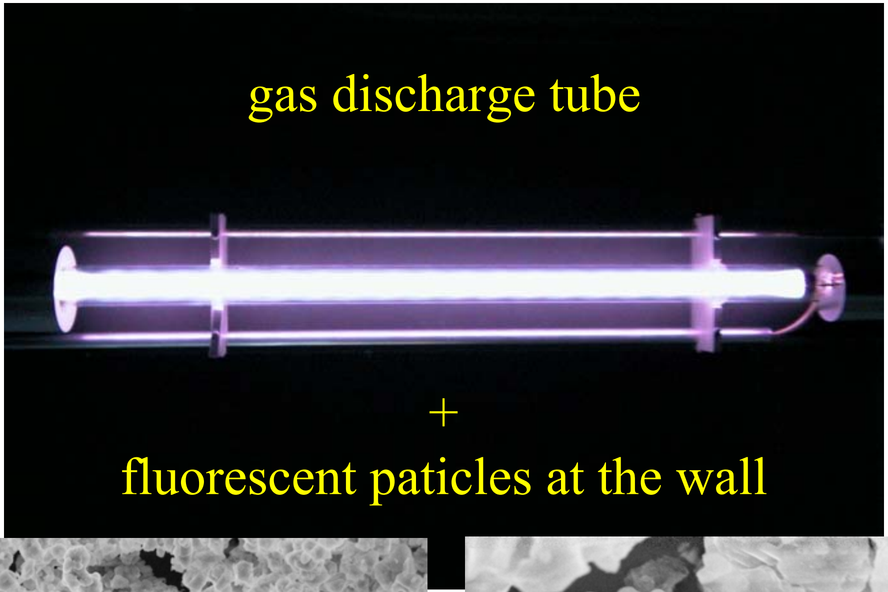
- improvement of thin film properties by incorporation of nanocrystallites for amorphous solar cells and hard coatings
- coating of lubricant particles

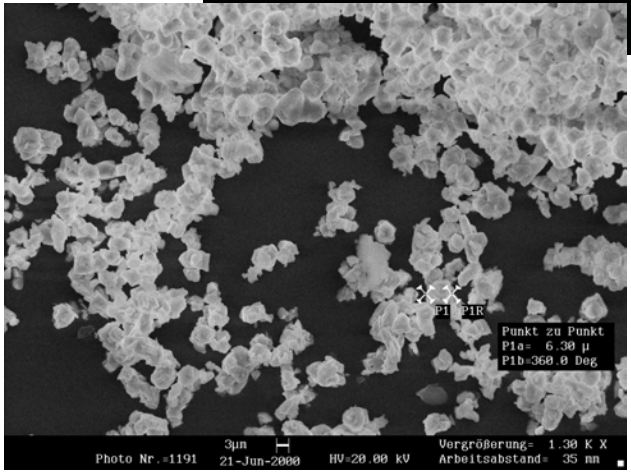
- application of tailored powder particles for chemical catalysis
- functionalization of micro-particles for pharmaceutic and medical application

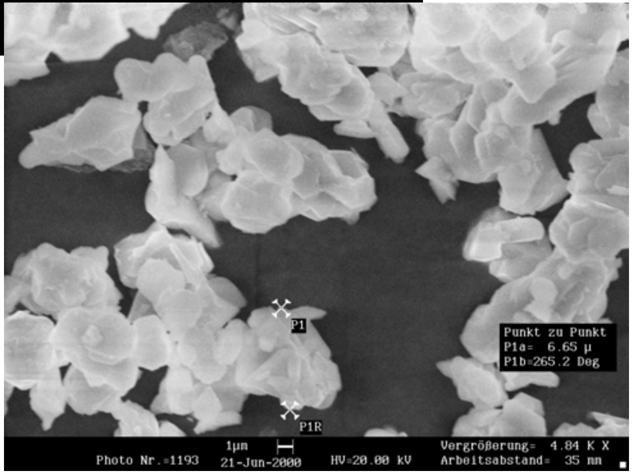
- production of colour pigments for paints
- ***improvement of surface protection against corrosion of fluorescent particles***
- tailoring of optical surface properties of toner particles ..... etc.

modification of particles in process plasmas

deposition of protective coatings onto fluorescent particles







$BaMg_2Al_{16}O_{27}:Eu^{2+}$ grains (blue luminophores)
should be coated by an alumina layer (protection, aging, adhesion)

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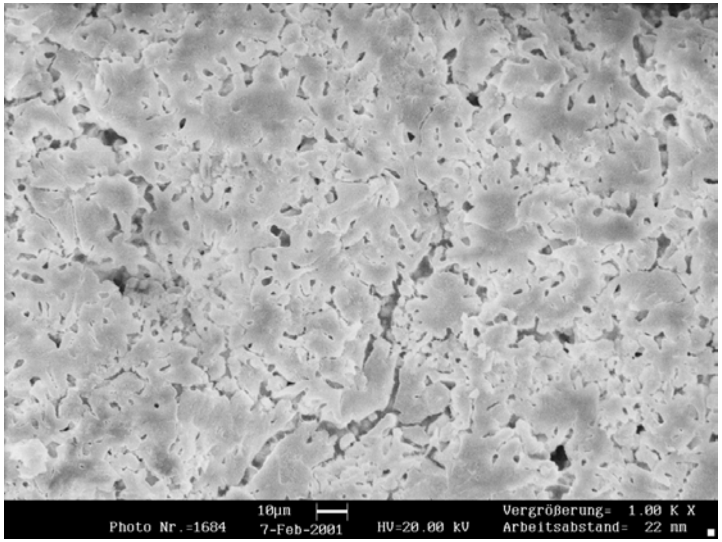
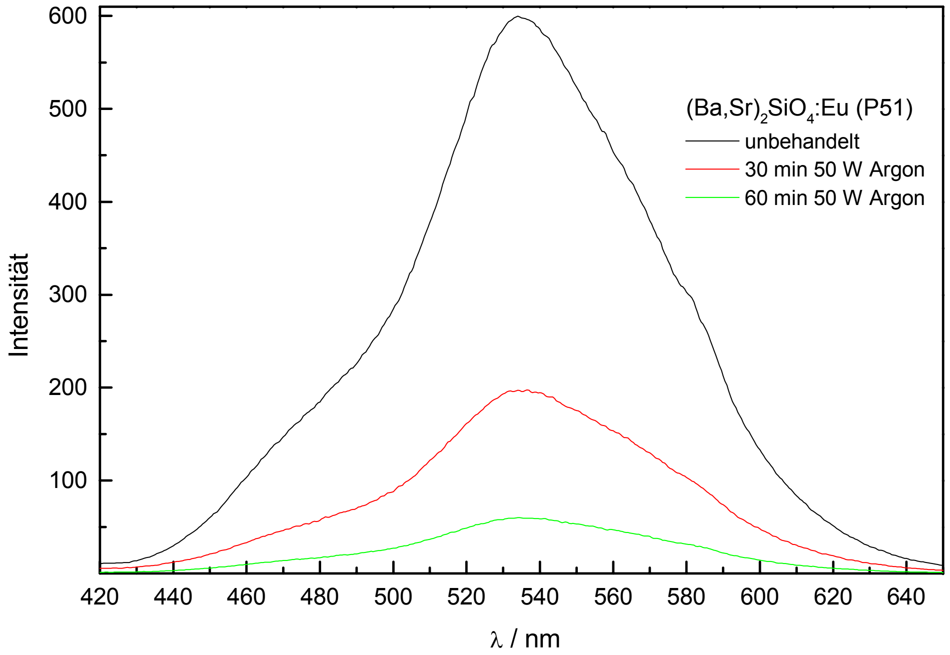
modification of particles in process plasmas

degradation of luminophores after plasma irradation



original material : fluorescent particles, non-treated
decrease of light intensity after irradiation



modification of particles in process plasmas

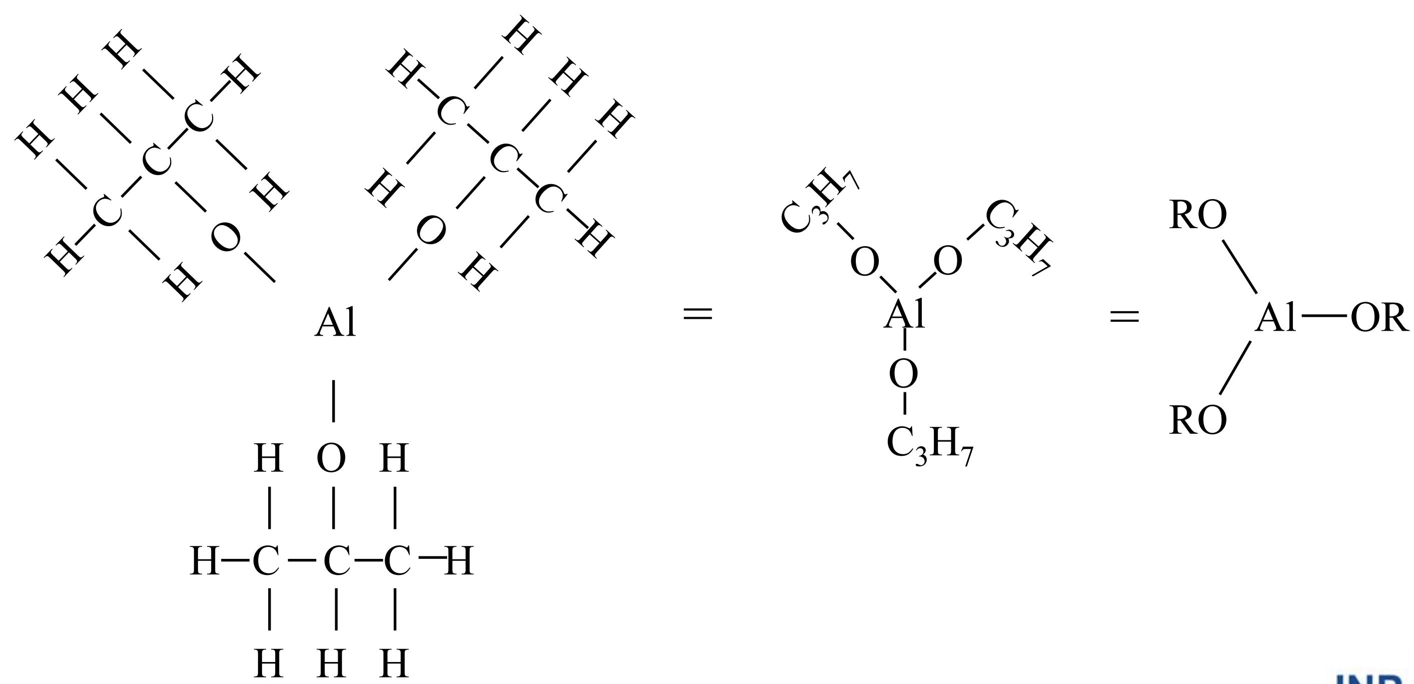
a solution :
PECVD of aluminum oxide by a metal-organic precursor ATI

Aluminum-Tri-Isopropyloxide (ATI) in plasma $\longrightarrow$ **Al-oxide layer**

reaction for deposition of oxide : $2\ Al(i\text{-}OC_3H_7)_3 \longrightarrow \mathbf{Al_2O_3} + 3\ C_3H_6 + 3\ C_3H_7OH$

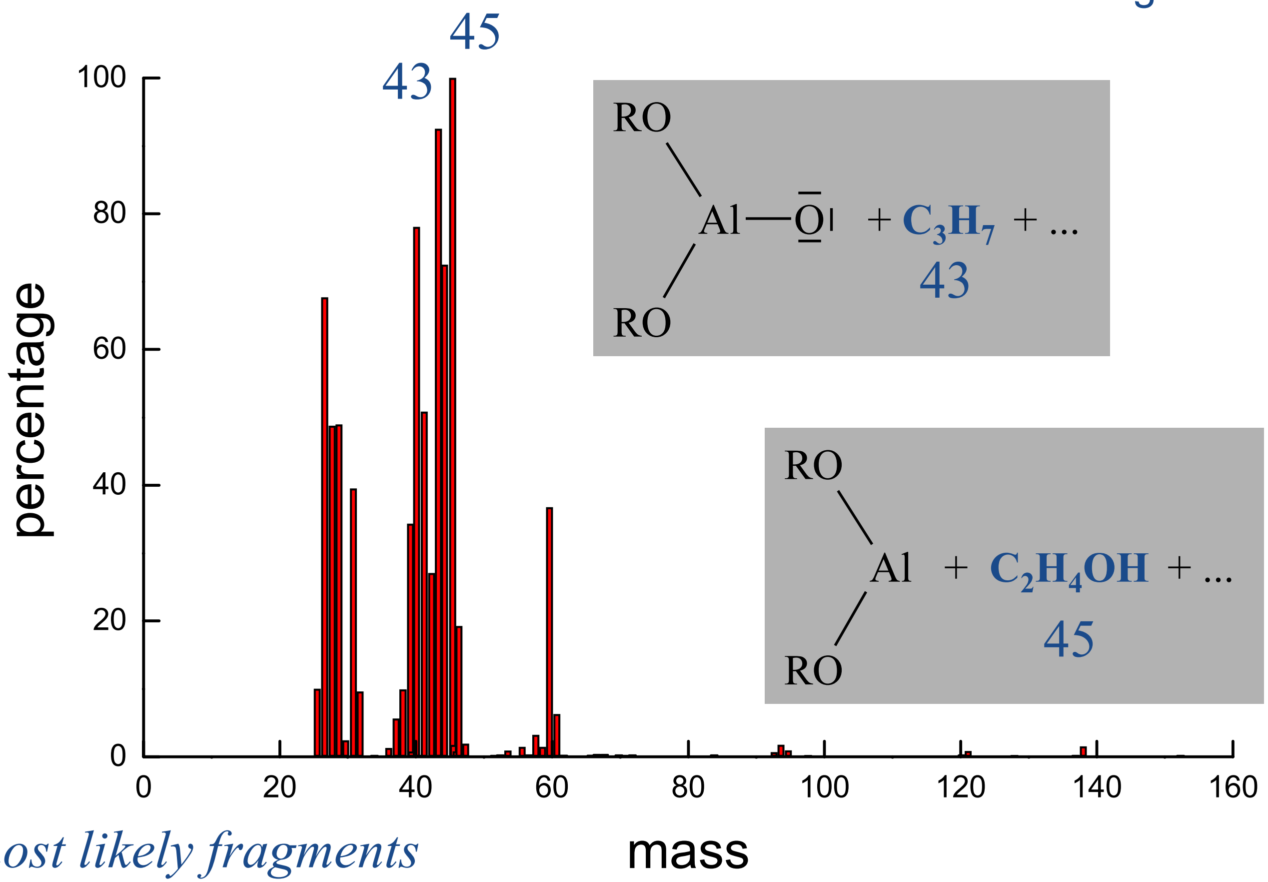
use of ATI :

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

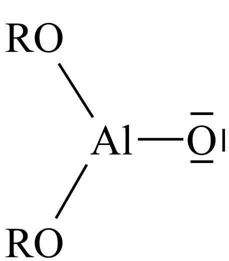


modification of particles in process plasmas

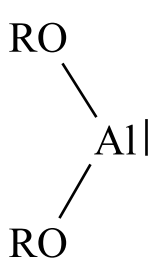
PECVD of a metal-organic monomer



most likely fragments

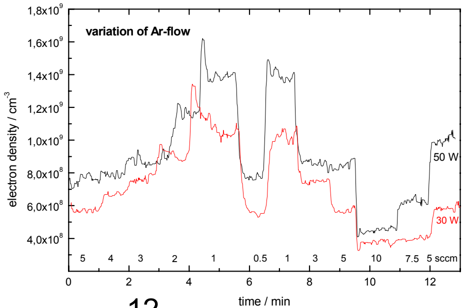


and

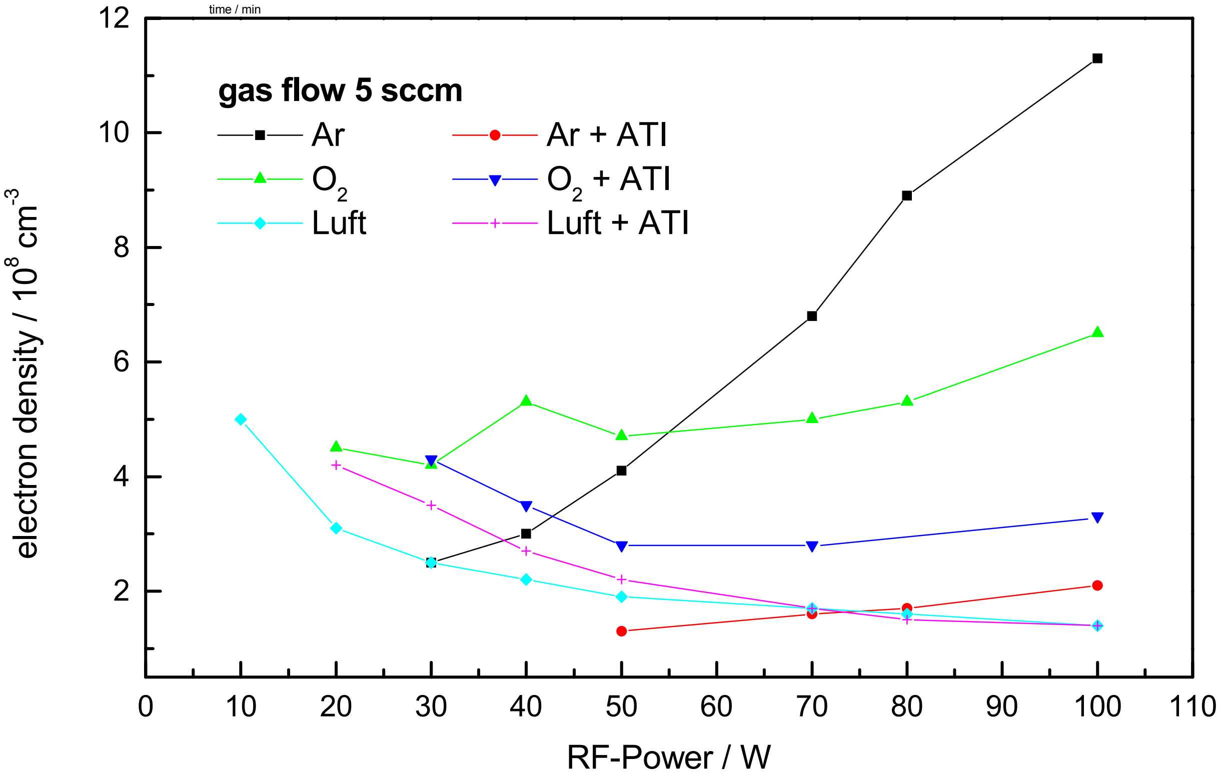


tend to form negative ions by electron capture
(electron drain)

modification of particles in process plasmas



plasma measurements by SEERS
n_e vs. rf-power



Ar: electropositive,
$P \uparrow \; n_+ \uparrow \; n_e \uparrow$

O_2: electronegative,
$P \uparrow \; n_O \uparrow \; n_- \uparrow \; n_e \rightarrow$

ATI: electronegative,
$P \uparrow \; n_R \uparrow \; n_- \uparrow \; n_e \rightarrow$

The different order of magnitude and the tendency in the electron densities for the different process conditions allow conlusions in respect to the dissociation and ionizaition mechanisms and reveal informations on thin film deposition on the fluorescent grains.

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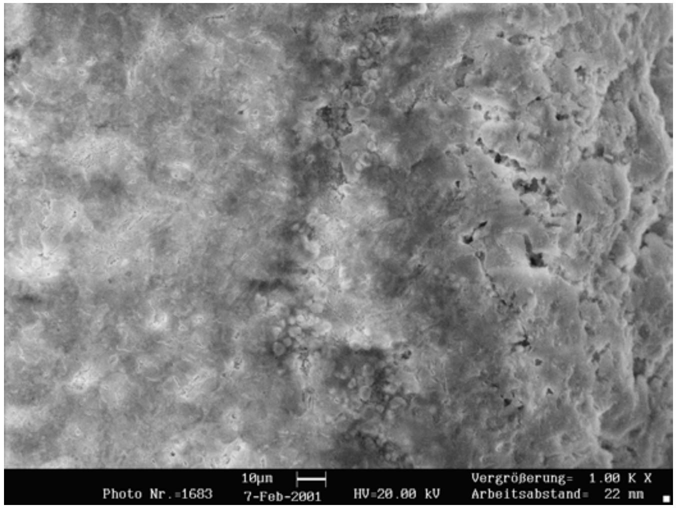
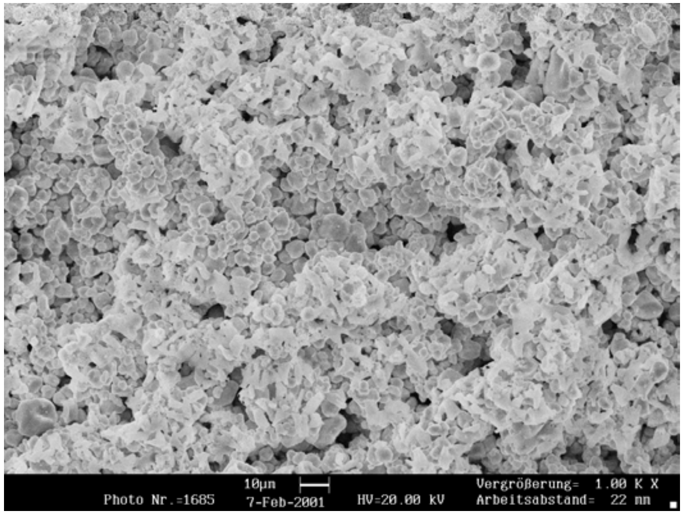
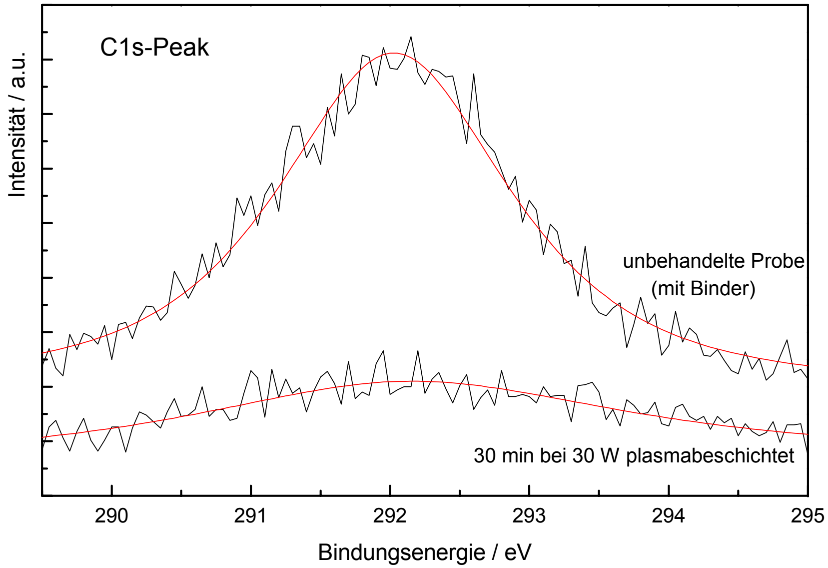
modification of particles in process plasmas

PECVD of aluminum oxide onto fluorescent particles





before deposition,
no decomposition
by the plasma,
still CH-groups



after deposition
(protective layer),
Al_2O_3
no CH-groups

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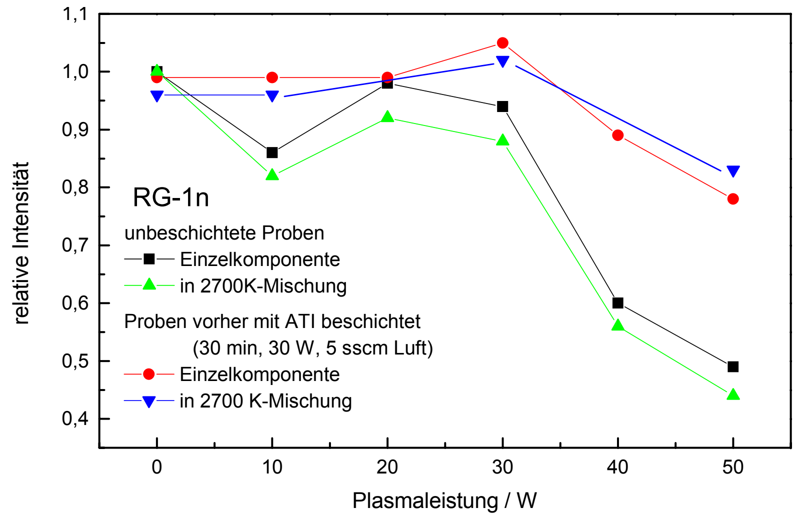
modification of particles in process plasmas

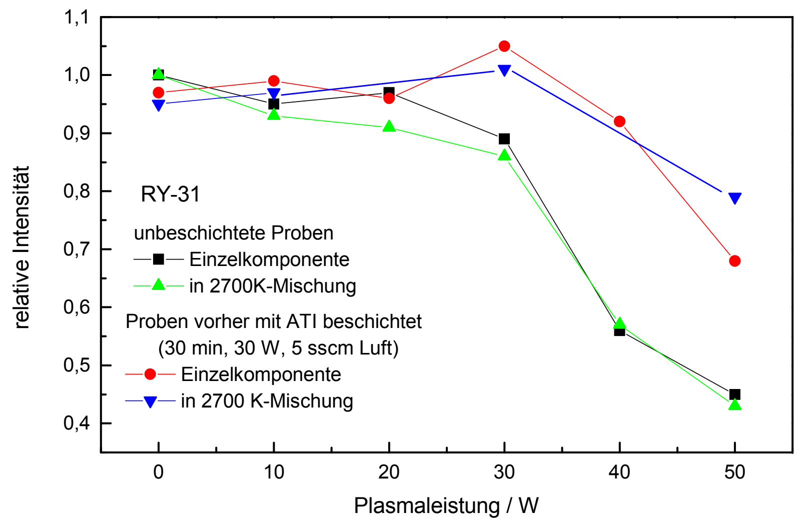
alumina coated particles are stabilized against irradiation (protective layer)



fluorescent particles, coated
light intensity by irradiation stays stable

fluorescent particles, non-treated
decrease of light intensity by irradiation

green component



red component

Kersten,H., Wiese,R., Thieme,G., Fröhlich,M., Kopitov,A., Bojic,D., Scholze,F., Neumann,H., Quaas,M., Wulff,H., Hippler,R., New J. Phys. ***5****(2003), 93.1*

results of particle coating

1. PECVD by decomposition of ATI in an rf-plasma results in deposition of transparent Al_2O_3 films onto fluorescent particles

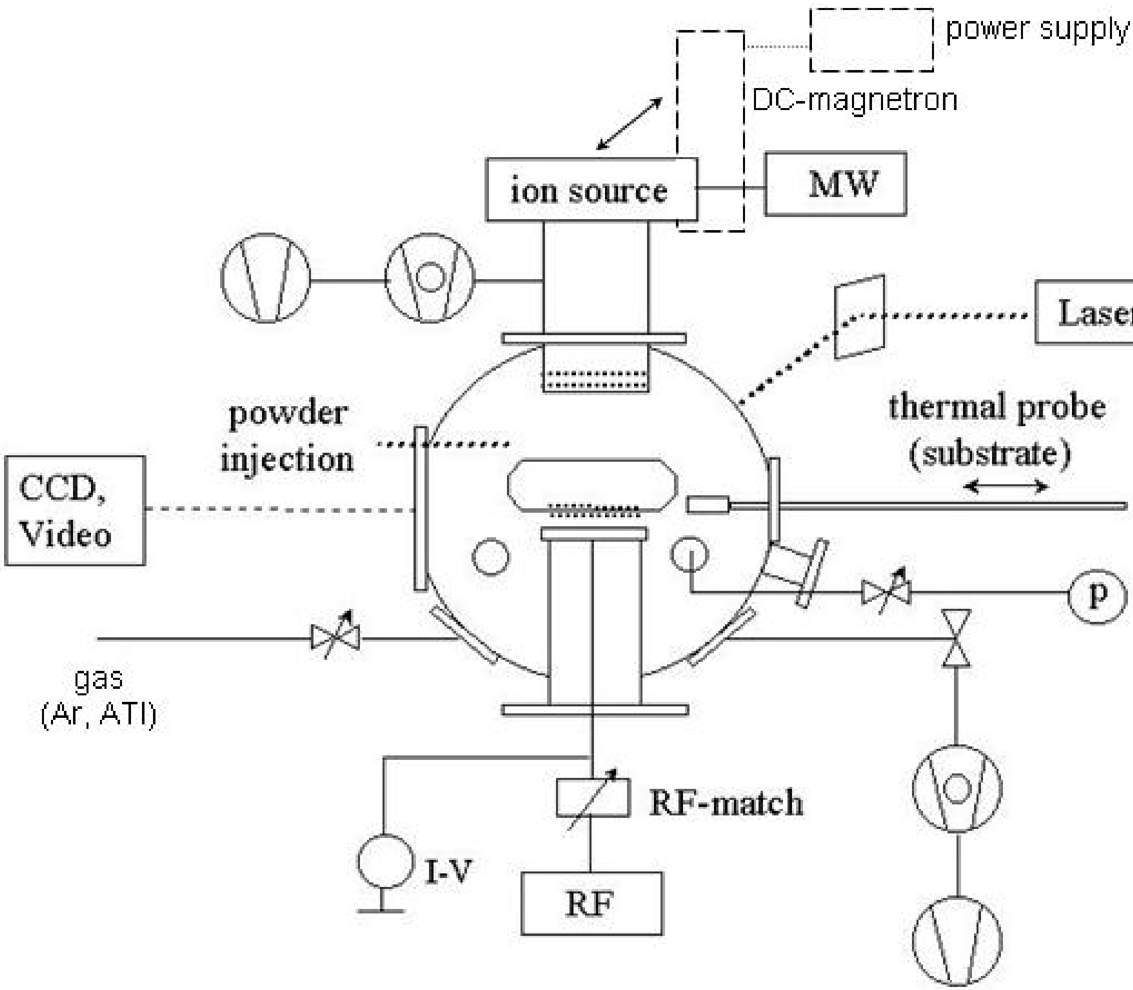
2. no change of the emission spectra by the Al_2O_3 (particles are not influenced by the protective layers)

3. Al_2O_3 protective films onto fluorescent material result in a remarkably higher stability against plasma irradiation, e.g. against UV radiation and particle bombardment at low energies

4. plasma deposition under optimized conditions (30W, 5sccm air/ATI, 30 min) results also in a decomposition of the glue material, additional annealing is not necessary

modification of particles in process plasmas

coating of powder particles in a magnetron discharge



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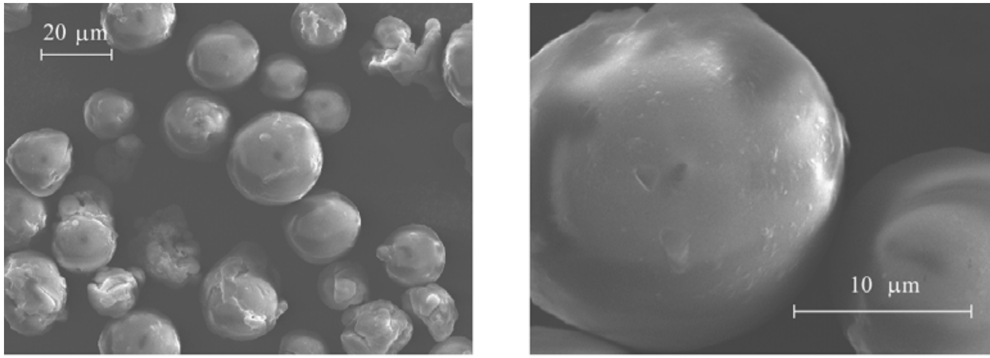
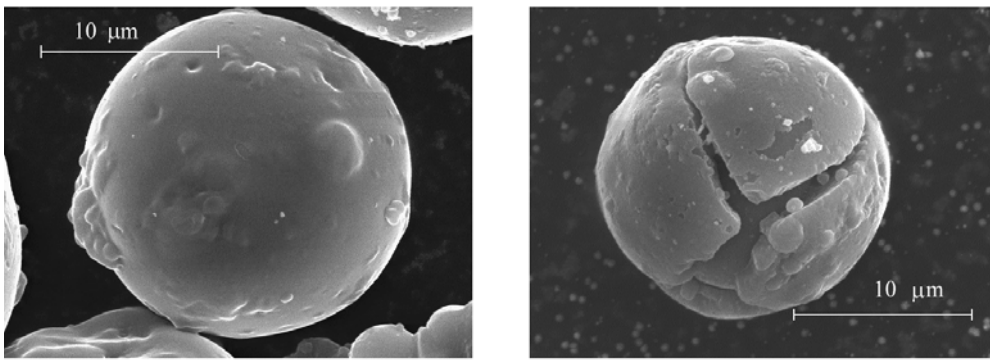
modification of particles in process plasmas

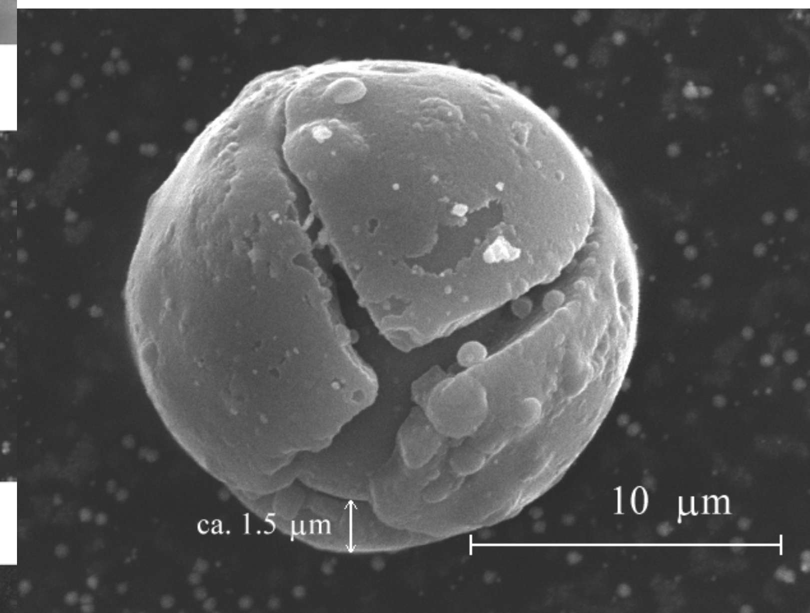
treated micro-particles

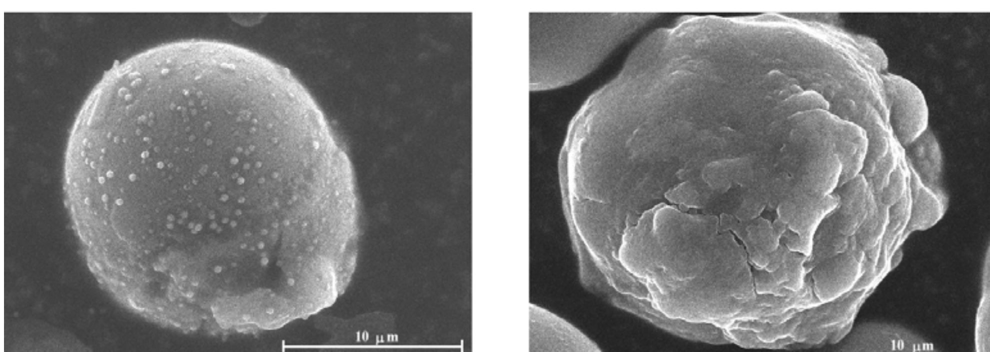


(a) Silicon oxide particles uncoated (b)



(c) Cu-coated (d)





(e) Ti-coated Al-coated (f)

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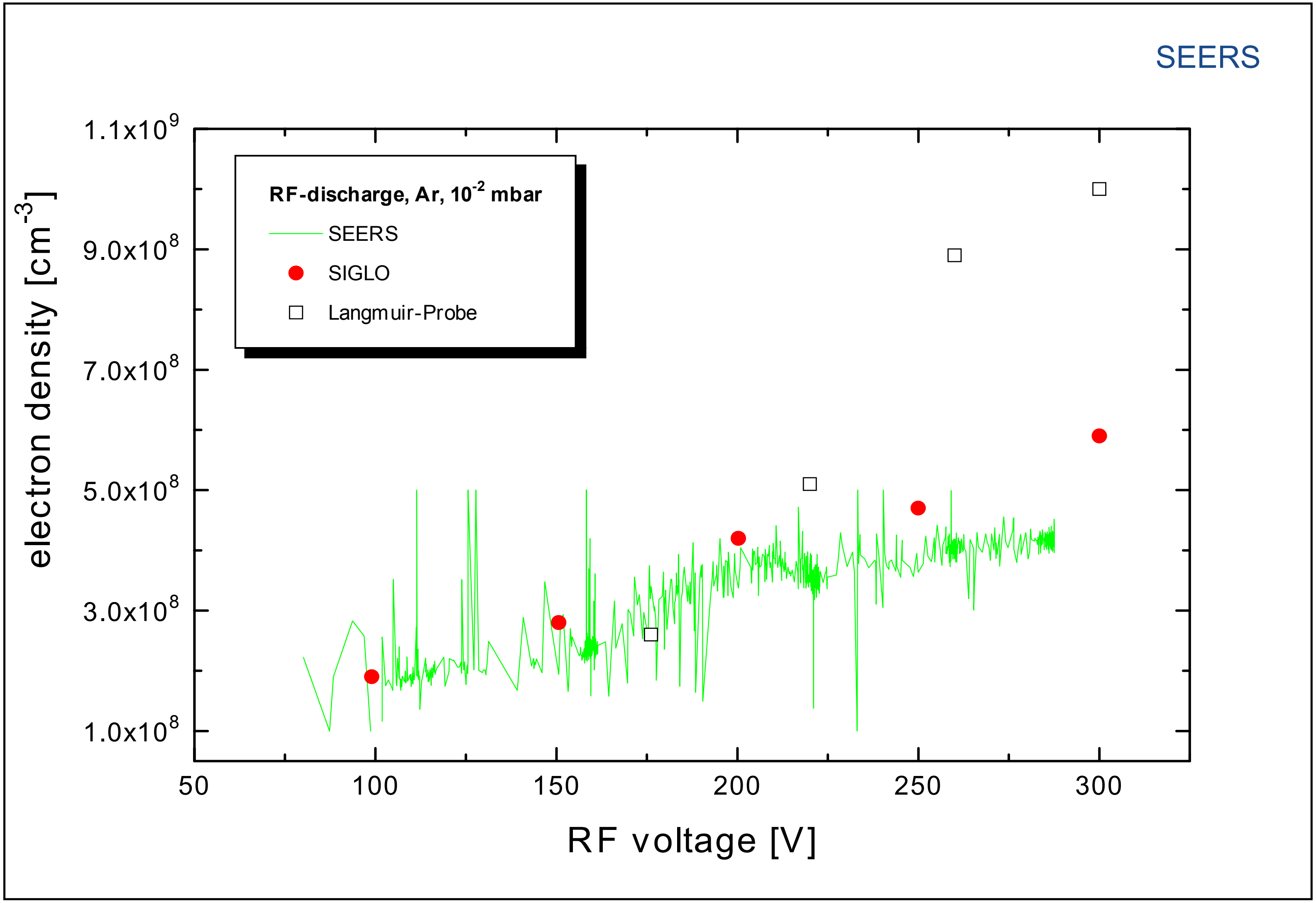
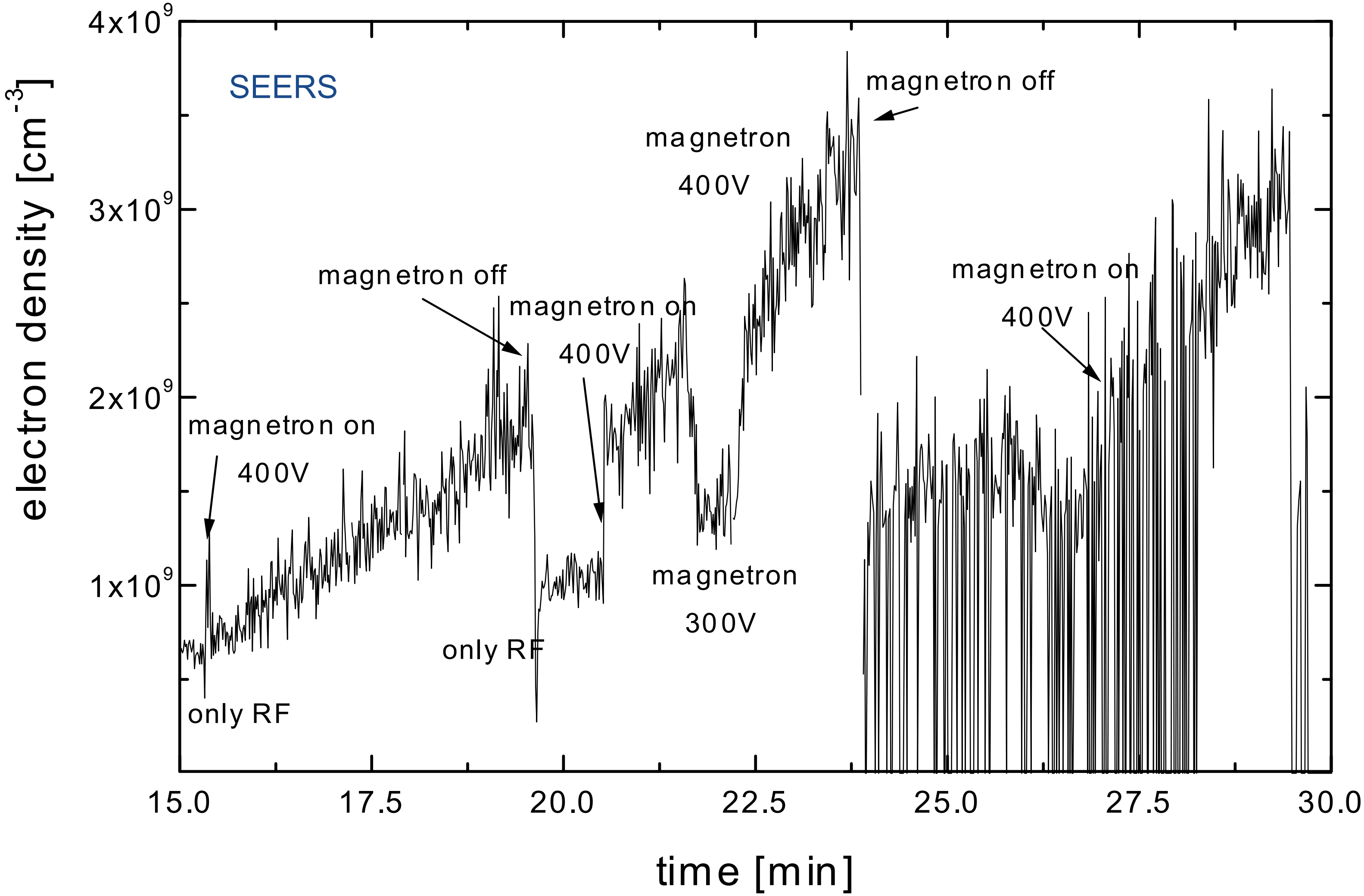
modification of particles in process plasmas

rf-plasma for charging and trapping of particles



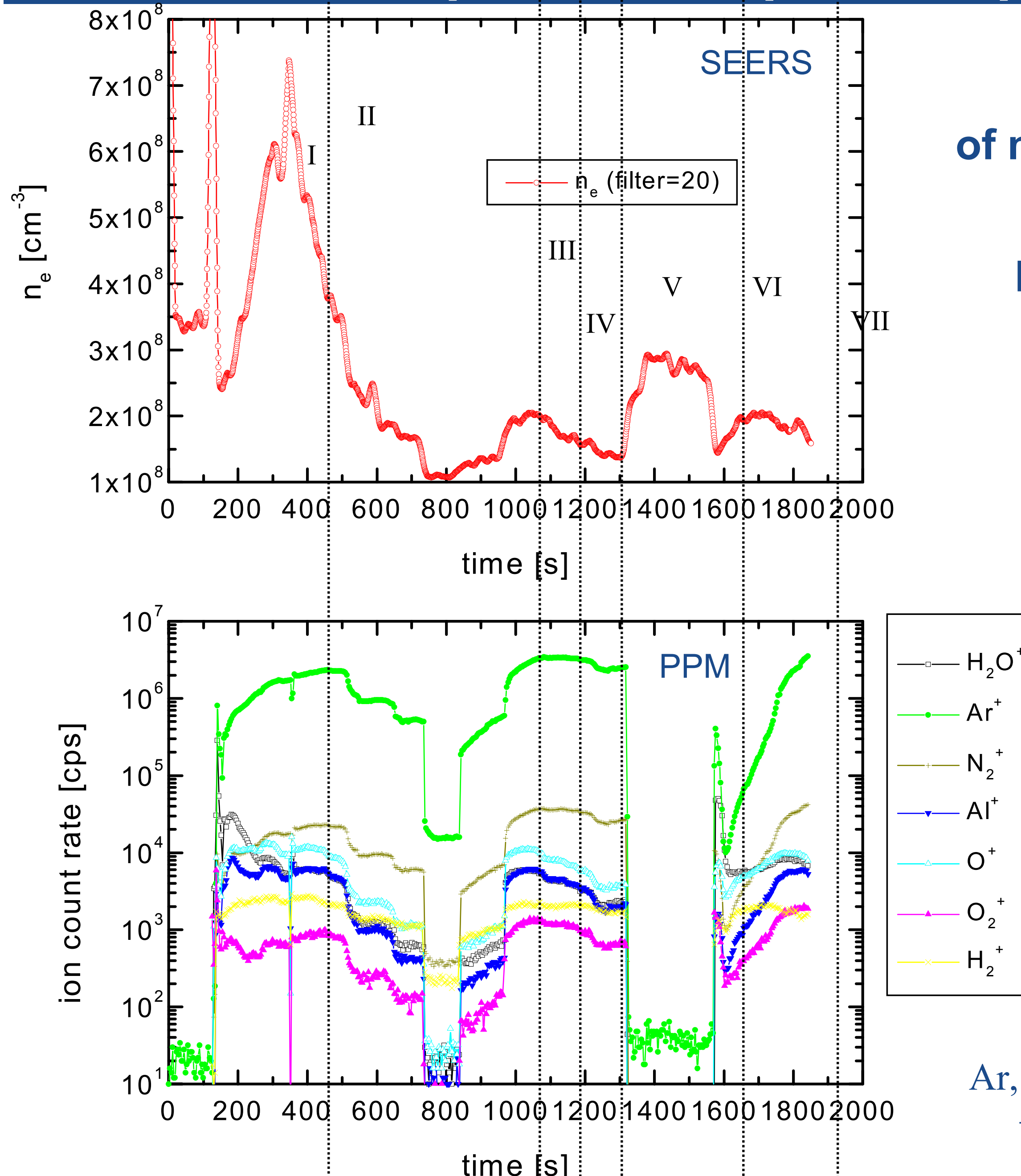
modification of particles in process plasmas

rf-plasma + dc-magnetron for particle coating



electron density in substrate region

modification of particles in process plasmas



strong effect of magnetron operation

process :

I only RF

II magnetron on: 515V … 545V 70mA … 50mA

III magnetron lower: 500V, 36mA

IV magnetron higher: 540V, 42mA

V magnetron higher: 585V … 595V 50mA … 46mA

VI magnetron off: only RF

VII magnetron on: 590V, 48mA

Ar, 1Pa, Vrf=185V
+ magnetron

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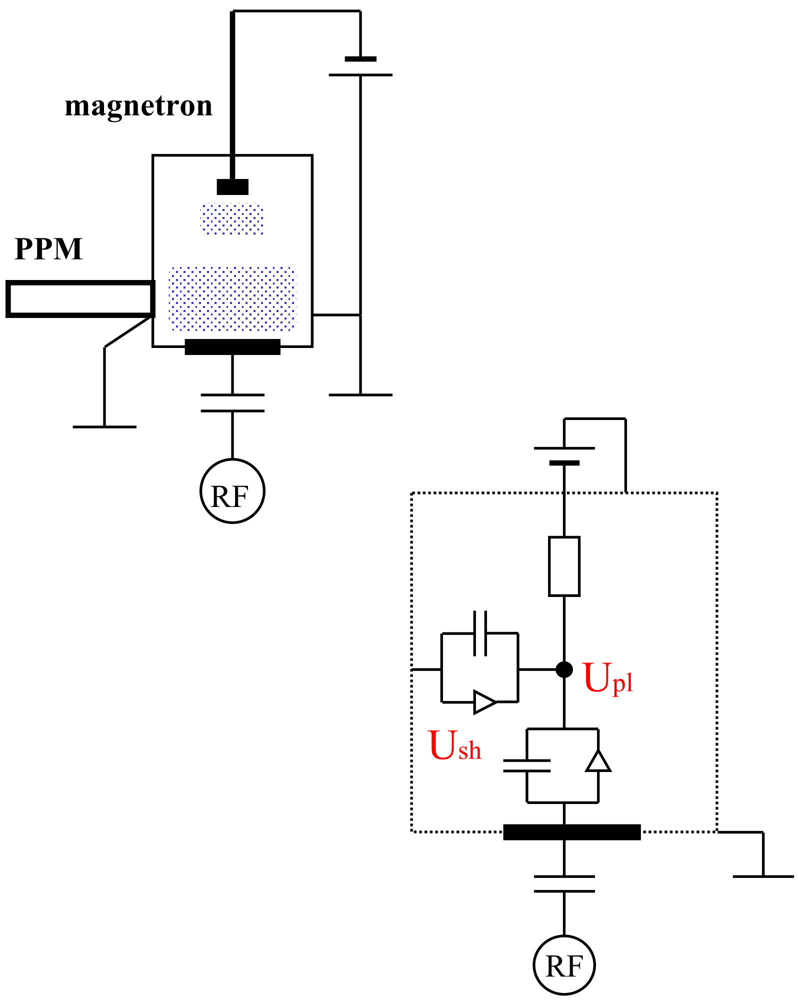
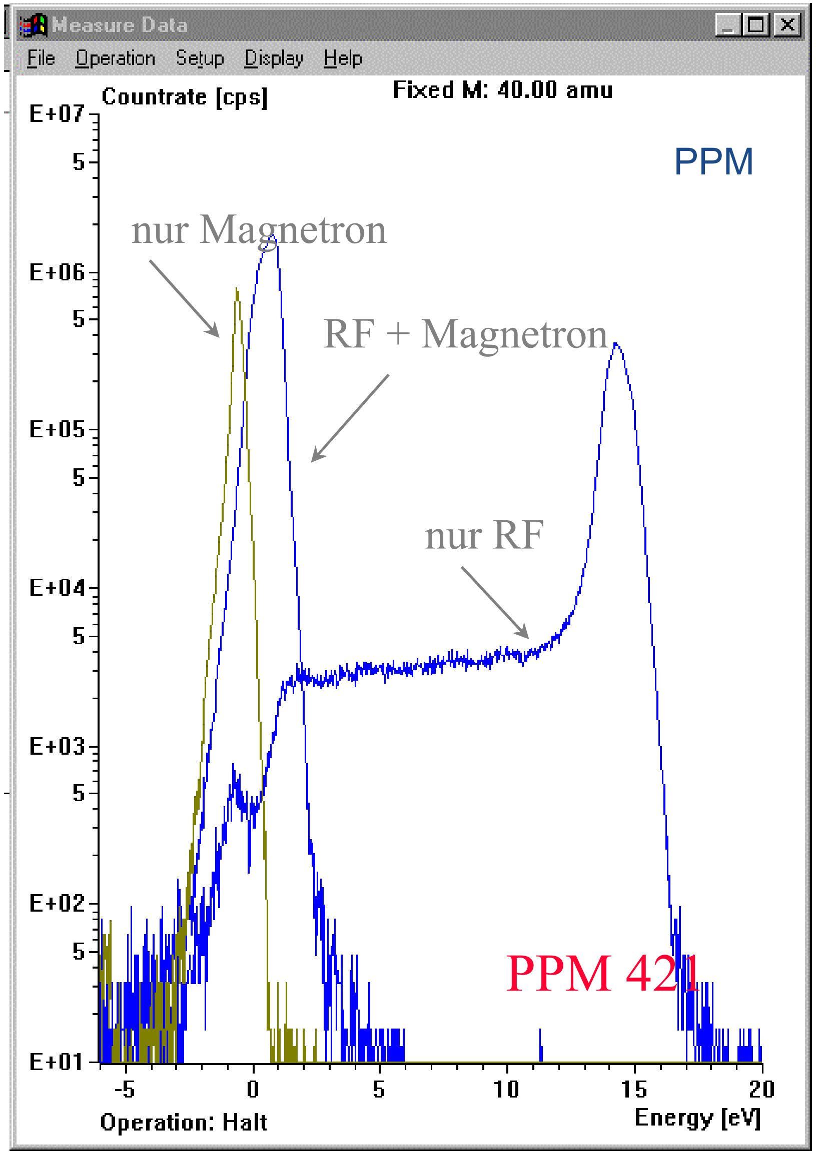
ion component in rf-plasma + dc-magnetron





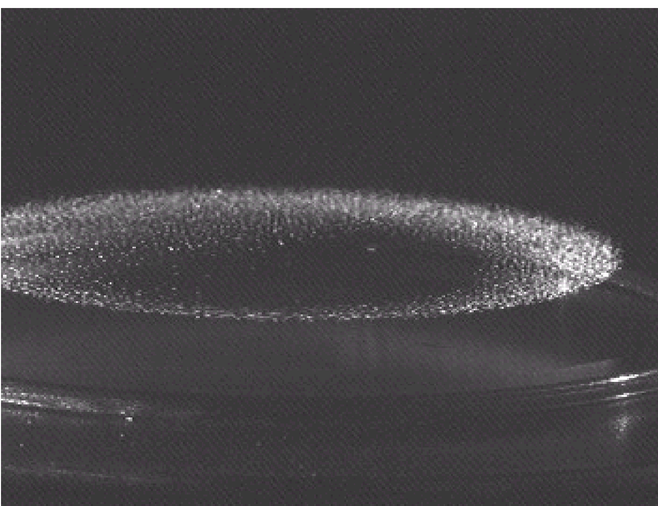
Ar, p=10^{-2} mbar, V_{RF}=340V

modification of particles in process plasmas

external dc-magnetron and particles in plasma

In these experiments the influence of a DC-magnetron (PPM 50) has been studied. The effect in respect to the confinement is due to :

- ***changes of the plasma sheath and the field (plasma density in trappping region),***
- ***charge of the powder particles (additional electron flux),***
- ***deposition of films onto particles (and heating).***



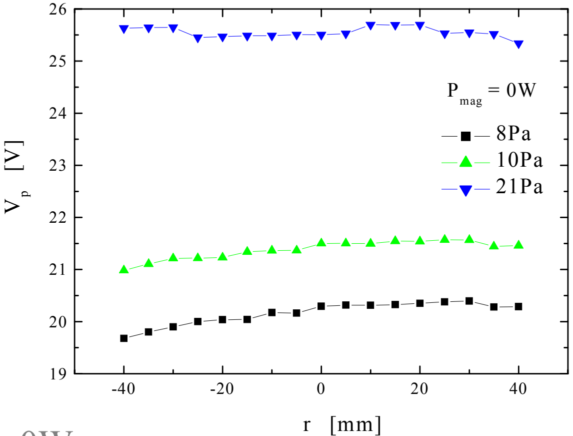
• Ar, 5 Pa
• rf-plasma, 5 W
• large ring, SiO_2 ~15µm
• magnetron on / off, 50 W

• small ring, SiO_2 ~15µm
• magnetron on / off, 50 W
• Ar, 5 Pa
• rf-plasma, 5 W

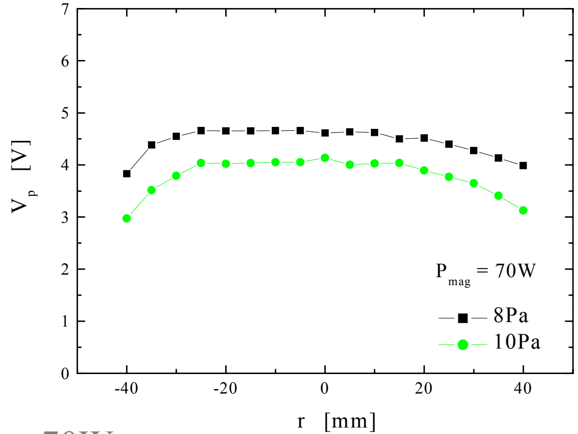
• no rf-plasma, 0 W
• small ring, Ti ~100nm
• magnetron variation, 10-80W

modification of particles in process plasmas

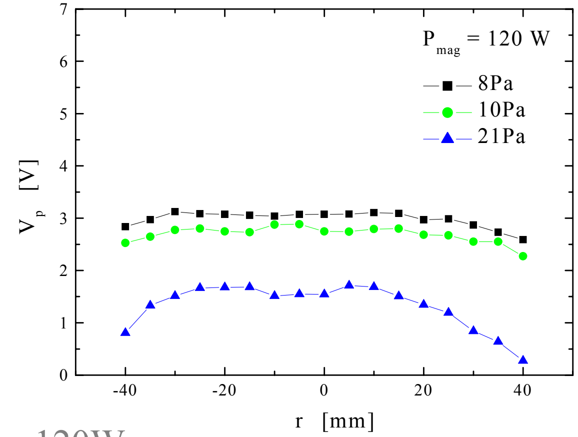
plasma potential



0W

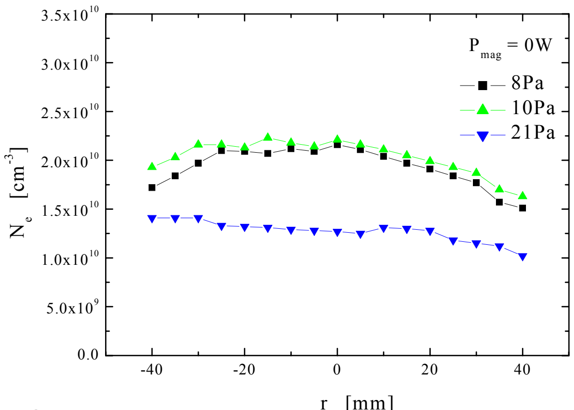


70W

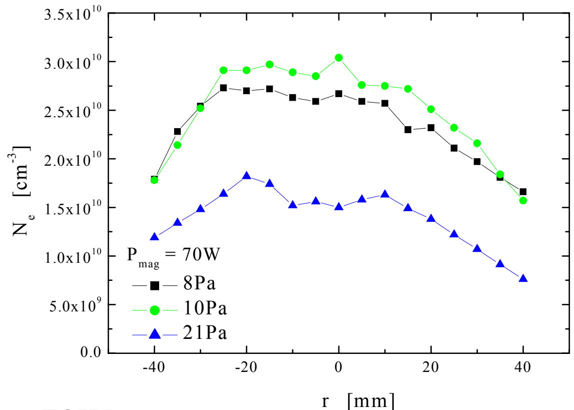


120W

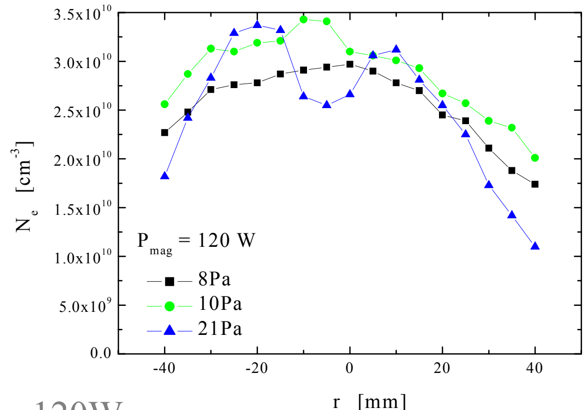
electron density



0W

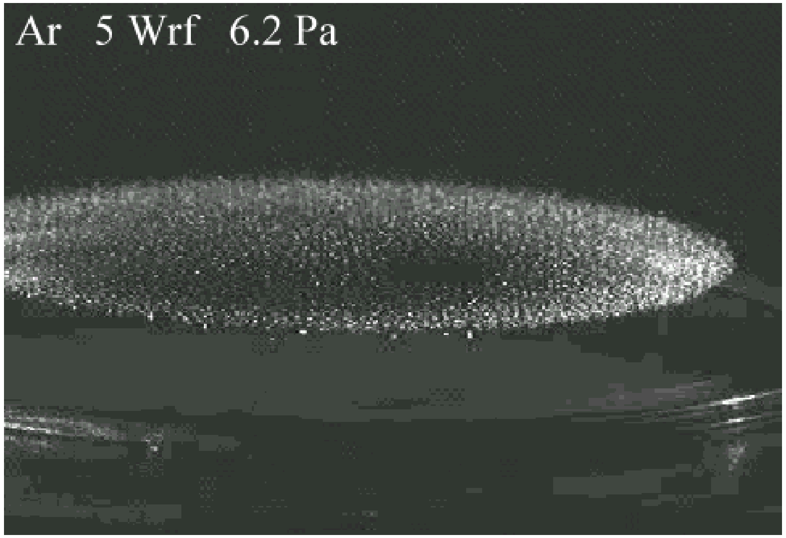


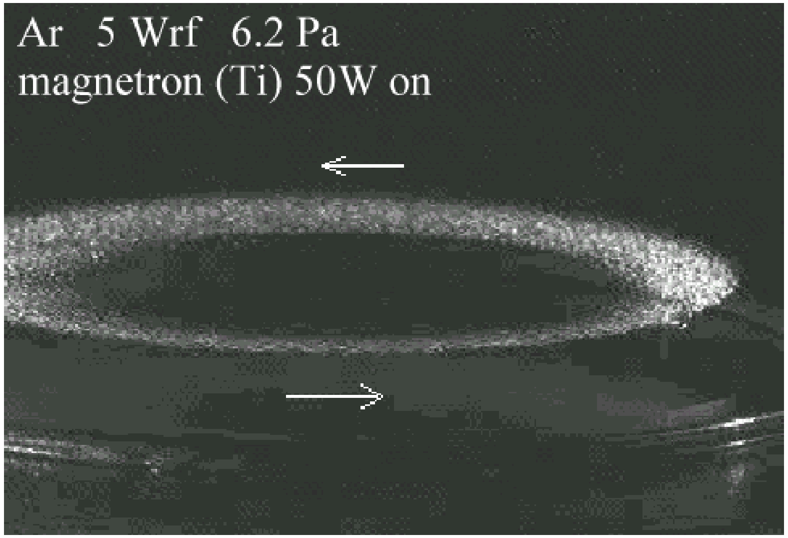
70W

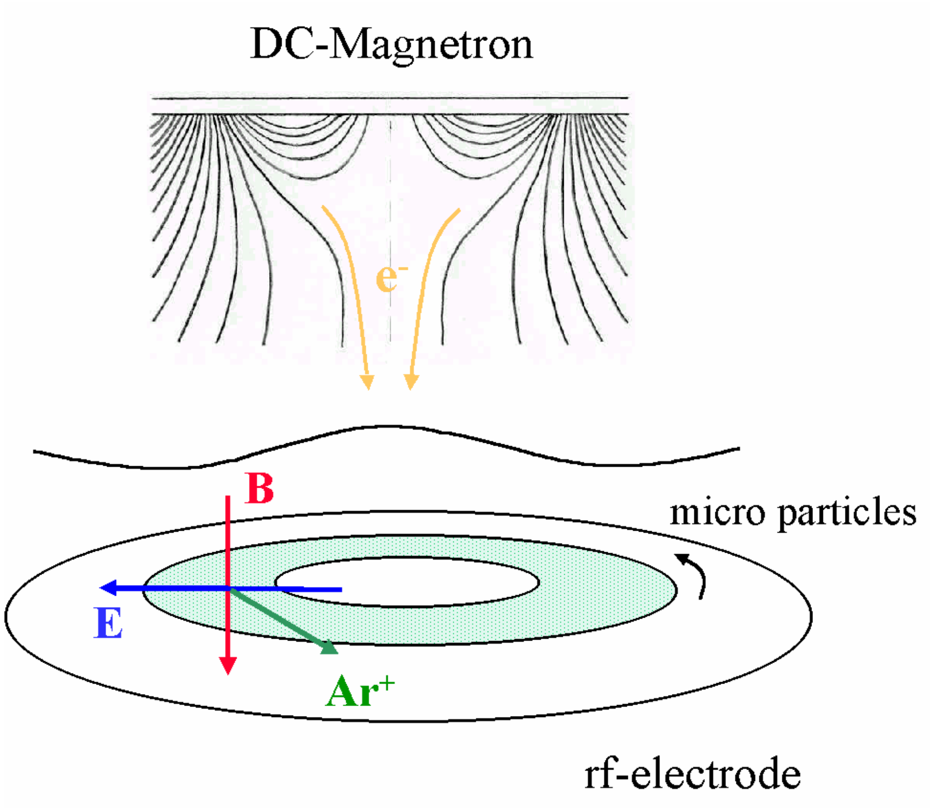


120W

modification of particles in process plasmas







Kersten,H., Wiese,R., Thieme,G., Fröhlich,M., Kopitov,A., Bojic,D., Scholze,F., Neumann,H., Quaas,M., Wulff,H., Hippler,R., New J. Phys. ***5****(2003), 93.1*

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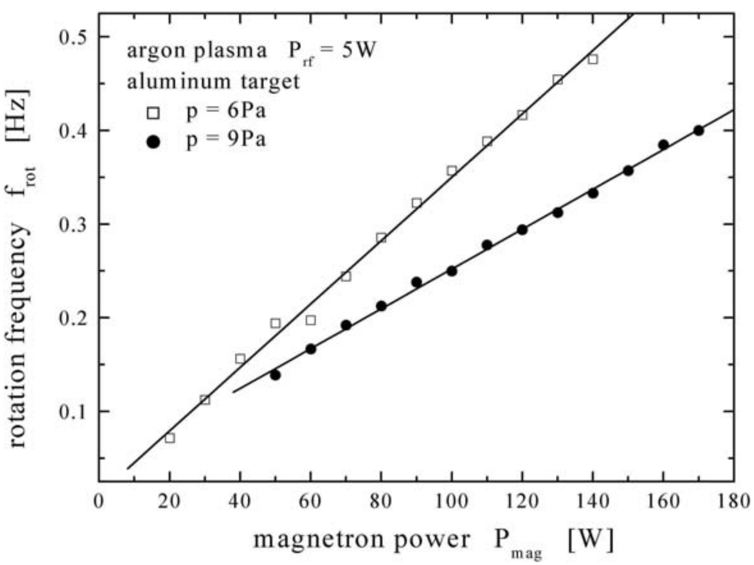
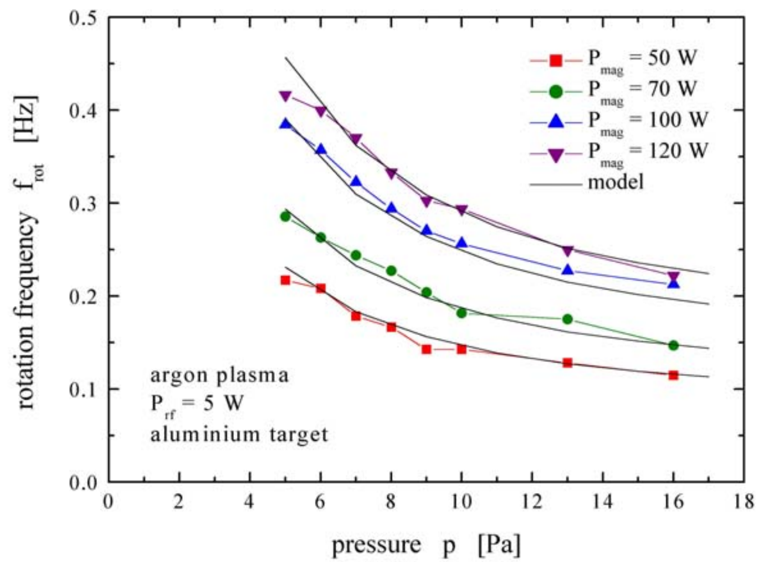
modification of particles in process plasmas

external dc-magnetron and particles in plasma





estimation for the driving rotational force :

$$f_{rot} = \frac{F}{2\pi \frac{\delta\, m_S}{\rho_S\, r_S} \sqrt{\frac{8}{\pi} \frac{m_N}{k_B T_N}}\, r} \cdot \frac{1}{p} \longrightarrow F \approx 4{,}8 \cdot 10^{-13}\ \mathrm{N}$$

summary

• unique possibillity of dust particle confinement and control in the gas phase makes plasmas to excellent media for particle handling and treatment

• applications of dust particles are numerous, most of them emerging in modern material science

• detailed knowledge of plasma particle interaction is necessary for optimization of the processes
• interaction can also be used as a diagnostic tool
• by observing the position and movement of the particles in dependence on the discharge parameters, informations are obtained on the electric field in front of surfaces and on sheath structure

• different applications make complex plasmas a rapidly expanding field of research between plasma physics, material processing, and diagnostics

• SEERS is a suitable method for determination of plasma parameters and particle charge