On the plasma modification of micro-disperse powder particles

H. Kersten

(Department of Physics, University of Greifswald)

P. Schmetz, G.M.W Kroesen, W.Stoffels, E.Stoffels,
M.Otte, H.Deutsch, R.Hippler

Workshop on SEERS, Dresden, 08.-09.06.1999

- motivation
- plasma - powder interaction
- plasma diagnostics at powder treatment
- thermal balance of (micro)substrates

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
- formation and modification of powders with tailored properties

Motivation :
Interest in particle-containing plasmas

Five reasons for the growing interest :

- plasma crystal
- astrophysics, formation of stars
- disturbing influences at µ-processing
- formation and modification of powders
- plasma characterization by particle probing

1. Astrophysik, Sternentstehung

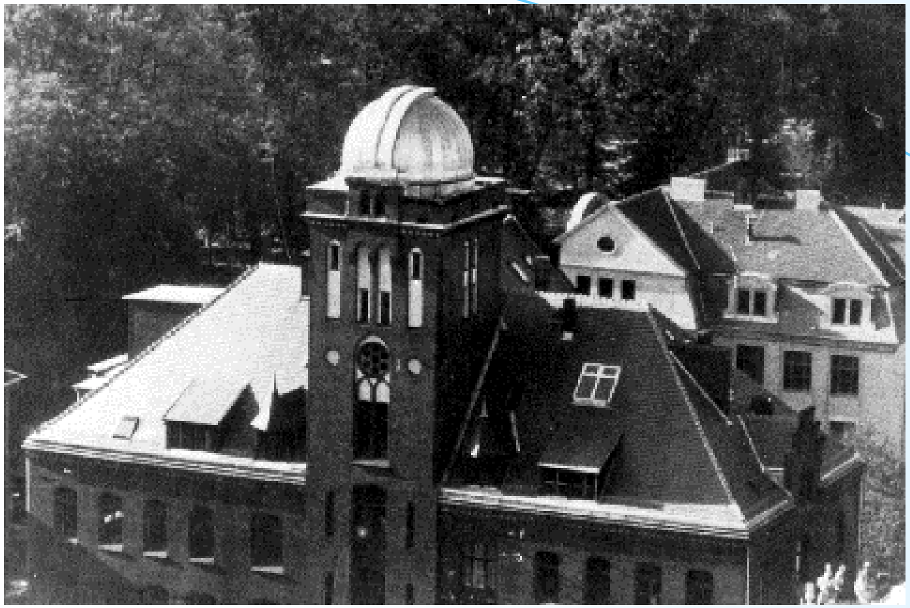
- Interstellare Gas- und Staub-wolken (99:1)
- Staubscheiben in den Galaxien (galaktische Ebene, Spiralarme)
- Zirkumstellare Staubscheiben und Jets
- Sternenstaub

- Staub als ,,Katalysator''
- Diagnostik von Staubbanden (Kohlenstoff, Silikate, Eis)

↓

,,Laboratoriums-Astrophysik"

M42 Aufnahme vom 20.11.1995, HST

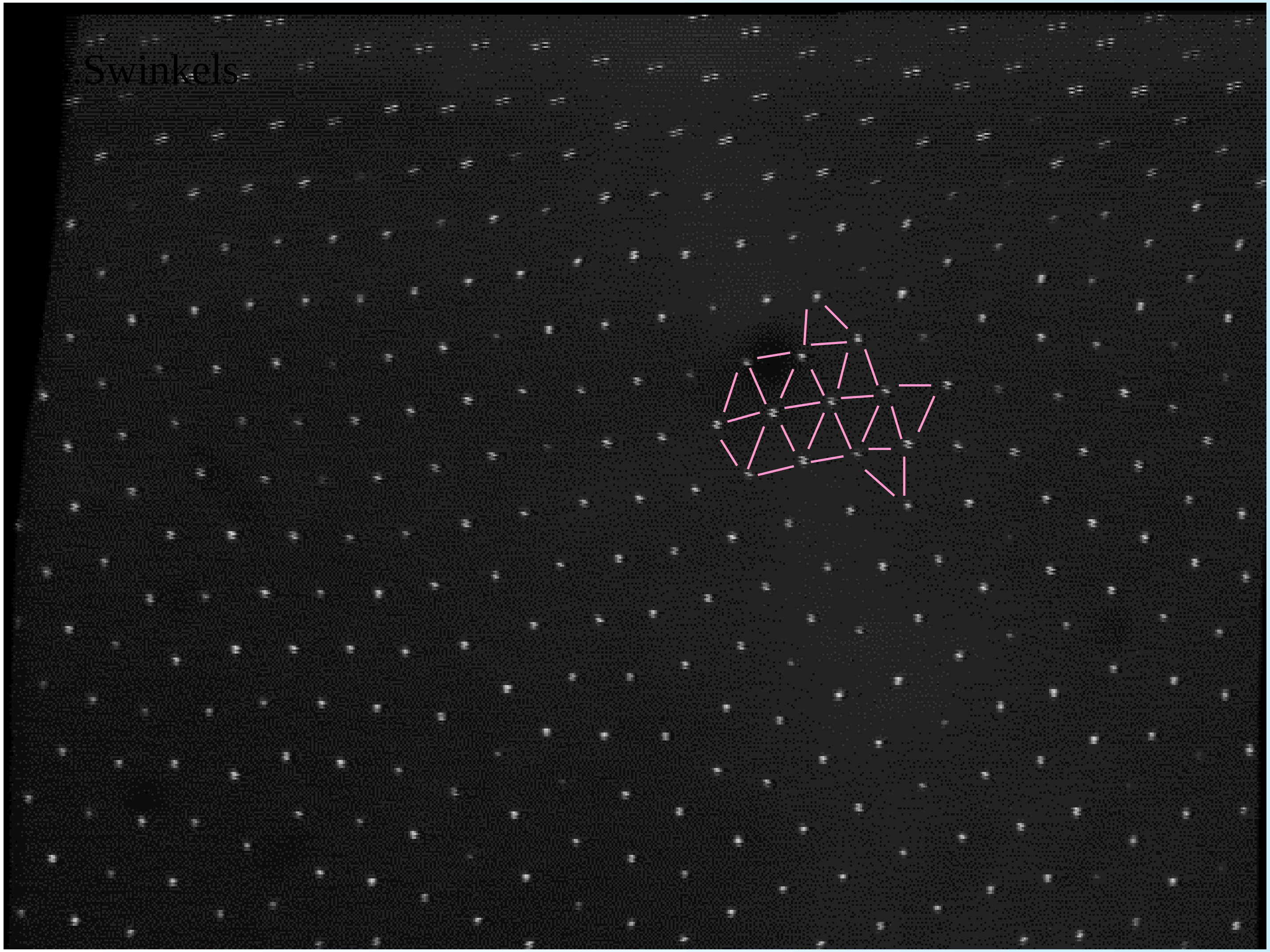


Institut für Physik
Universität Greifswald

Komet Hale Bopp, 03/1997

Greifswalder Sternwarte e.V

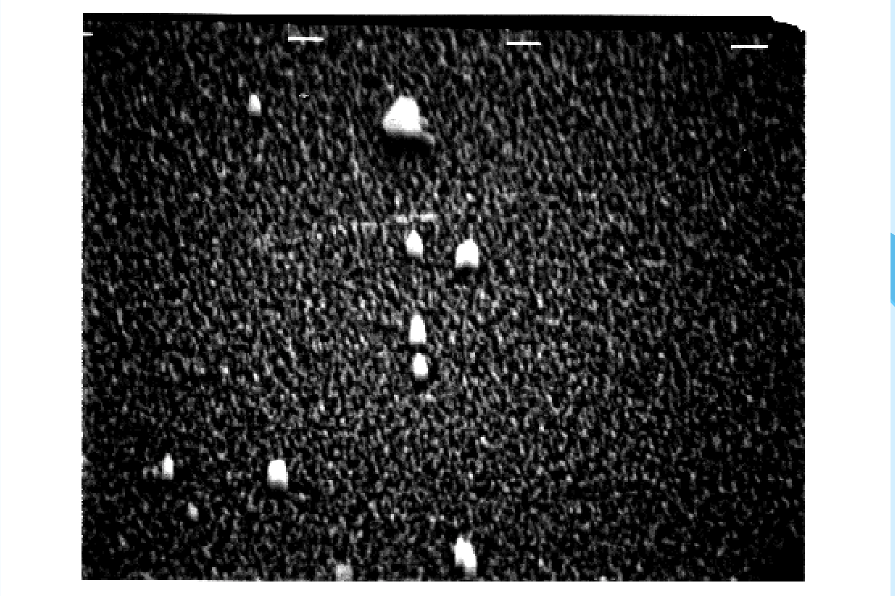
example : plasma crystal



MF - particles (14µm), RF-plasma (Krypton)

2. Störende Einflüsse beim µ-Processing

„ ... Dust ist one of the main problems for the semiconductor industry."



Si-Oberfläche
nach Plasmaätzen

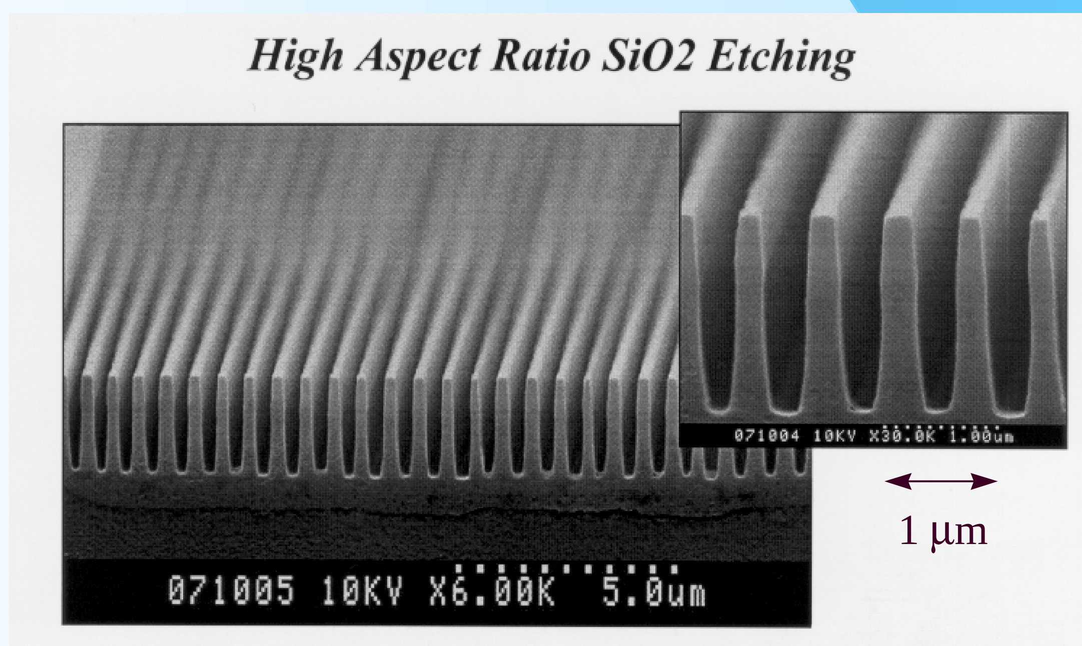
- Verunreinigungen führen zu erheblichen Funktionsstörungen bzw. zum Ausfall von µ-Strukturen („Dreckeffekte")
- Problematik vor allem in ICP-Prozessen, wo elektrostatische Felder im Vergleich zum RIE viel kleiner sind

$\longrightarrow$ Partikeln können viel leichter auf Oberfläche gelangen (Kräftebilanz !)

- Partikelbildung ist stark von Prozessführung (Ätzen, Polymerisation) und Prozessbedingungen abhängig

Zielvorgaben der National Semiconductor Technology Roadmap :

	1997	2012
Transistor / µP	~ 10^7	~ 10^9
Prozesse	350	600
Wafer - Größe	200mm	450mm
Strukturgröße	250nm	50nm
Killer - Partikel	> 120nm	> 20nm
Lebensdauer eines Prozesses	~ 3 Jahre	



Oxford - Instruments

Formation and modification of powder particles

past : dusty plasmas = disturbing side effect
present : dust / powder in plasmas = object of investigation

- modification of nano- and microdisperse powder particles in plasma
  - **applications and perspectives :**
    - film deposition (hard coatings)
    - treatment of flue gas, aerosols, flames
    - chemical catalysis (large specific surface area)
    - improvement of optical, mecahnical, and thermal properties of small particles (pigments, coatings)
    - corrosive protection of magnetic metal particles
    - diffusion barriers for pharmaceutic powders
    - etc. etc.

Tailoring of desired particle functionality may include the geometrical shape as well as chemical, electrical, and optical behaviour.

- Deposition of thin surrounding films (Al) on powder particles (Fe) by magnetron sputtering, during their confinement in an RF-plasma

Interaction plasma - dust

(charging and trapping of powder particles in a plasma)

starting point : particles (mono-disperse, spherical, R, ρ) are injected into RF-plasma (Maxwell, U_{pl}, n_e, T_e, $\lambda_D >> R$, d_{sheath})

⇨ **charging of particles**

---

assumption : OML, Maxwell-distribution, $\Phi_S < 0 < U_{pl}$, $U_{bias} = U_{pl} - \Phi_S$

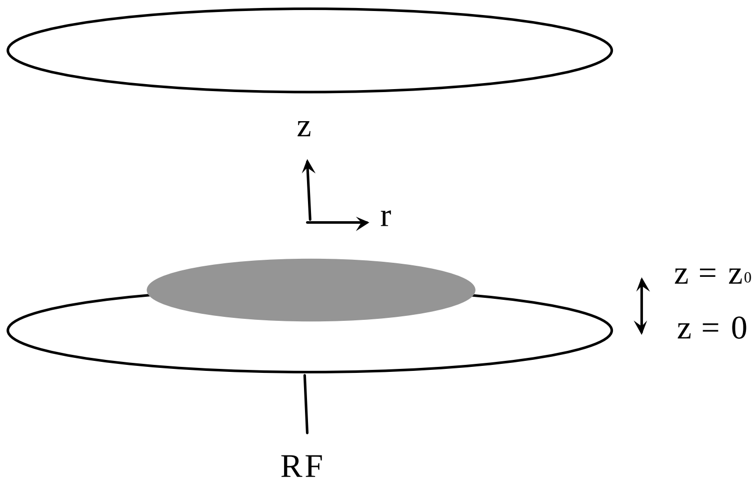
fluxes of charge carriers : $I_e = I_{0e}\exp(-eU_{bias}/kT_e)$, $I_i = I_{0i}(1+z_i eU_{bias}/kT_e)$

charge of a particle : $dQ/dt = \Sigma I_x$, $Q(t) = CU_{bias}(t) = 4\pi\varepsilon_0 R U_{bias}(t)$

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

$<\Phi_S(t)>$, $<Q(t)>$, τ

Plasma - powder - interaction



$$\mathbf{F_g \sim \rho R^3 \sim 3.5\cdot 10^{-13}N}$$ gravitational

$$F_n \sim \eta_{eff}(v_{gas} - v)R \sim R^2 v_{gas} \sim 2.5\cdot 10^{-14}N$$ neutral drag

$$F_i \sim j_i R^2 v_i \sim 1.5\cdot 10^{-14}N$$ ion drag

$$\mathbf{F_{el} \sim ER \sim 3\cdot 10^{-13}N}$$ electrostatic

$$F_{th} \sim \kappa dT/dz \sim R^2 dT/dz \sim 1\cdot 10^{-14}N$$ thermophoretic

$$F_{ph} \sim (Q_{abs}+Q_{streu})I\,R^2 \sim 0$$ photophoretic

experiment :

$R = 1\mu m,$

$U_{pl} = 15V, U_{fl} = 3V$

$$m = 3.5\cdot 10^{-14}kg$$

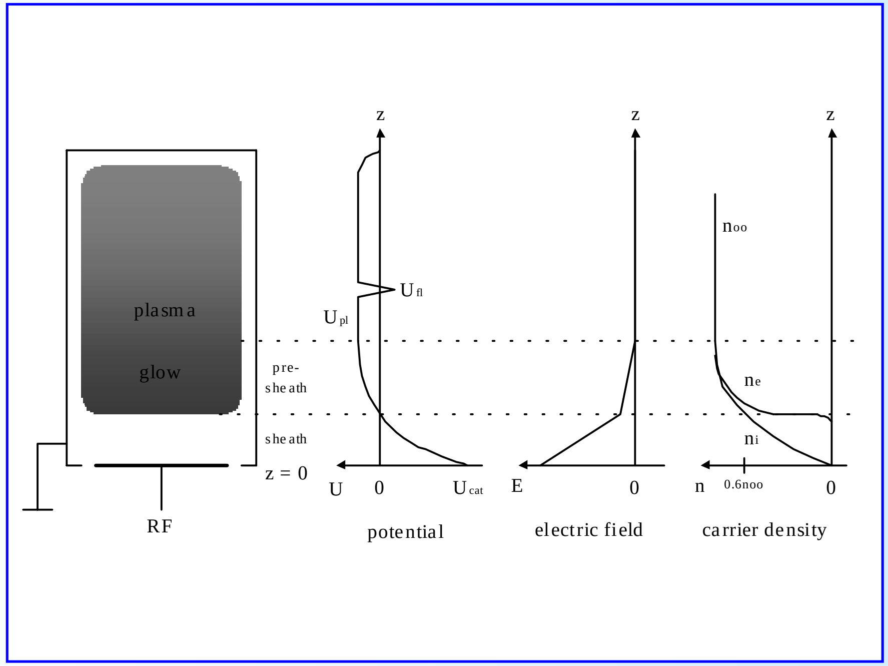
$$Q = C\cdot U = 4\pi\varepsilon_0 R\cdot(U_{fl} - U_{pl}) \approx 7000$$

$$F_g = mg = 3.5\cdot 10^{-13}N$$

$$F_g = F_{el} = QE(z_0) = 3.5\cdot 10^{-13}N$$

$$\rightarrow E(z_0) = 300V/m$$

Plasma characterization by particle probing



$$\nabla^2 V = -\frac{dE}{dz} = \frac{\rho}{\varepsilon_0} = \frac{e_0}{\varepsilon_0}(n_e - n_i)$$

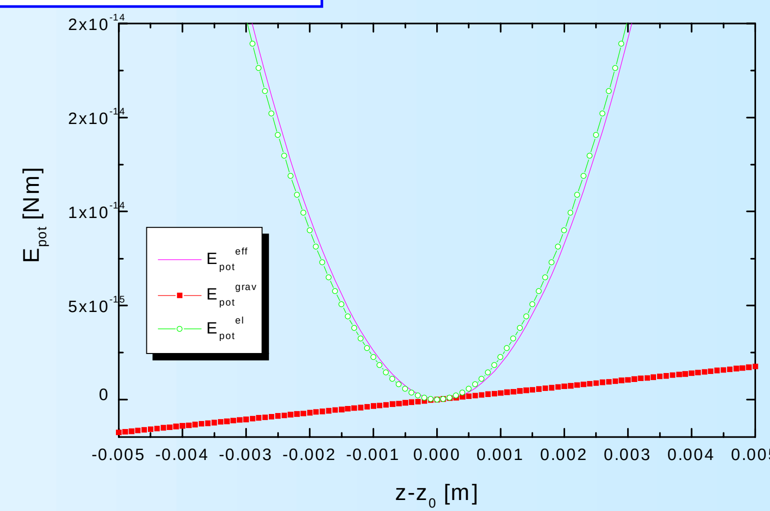
$$E(z) = \frac{e_0}{\varepsilon_0} n_i (z - z_0)$$

$$E_{pot}^{el}(z) = \frac{Ze_0^2 n_i}{2\varepsilon_0}(z - z_0)^2$$

$$E_{pot}^{grav}(z) = mg(z - z_0)$$

$$E_{pot}^{eff}(z) = mg(z - z_0) - \frac{Ze_0^2 n_i}{2\varepsilon_0}(z - z_0)^2$$

effective potential



Modification of particles in plasmas

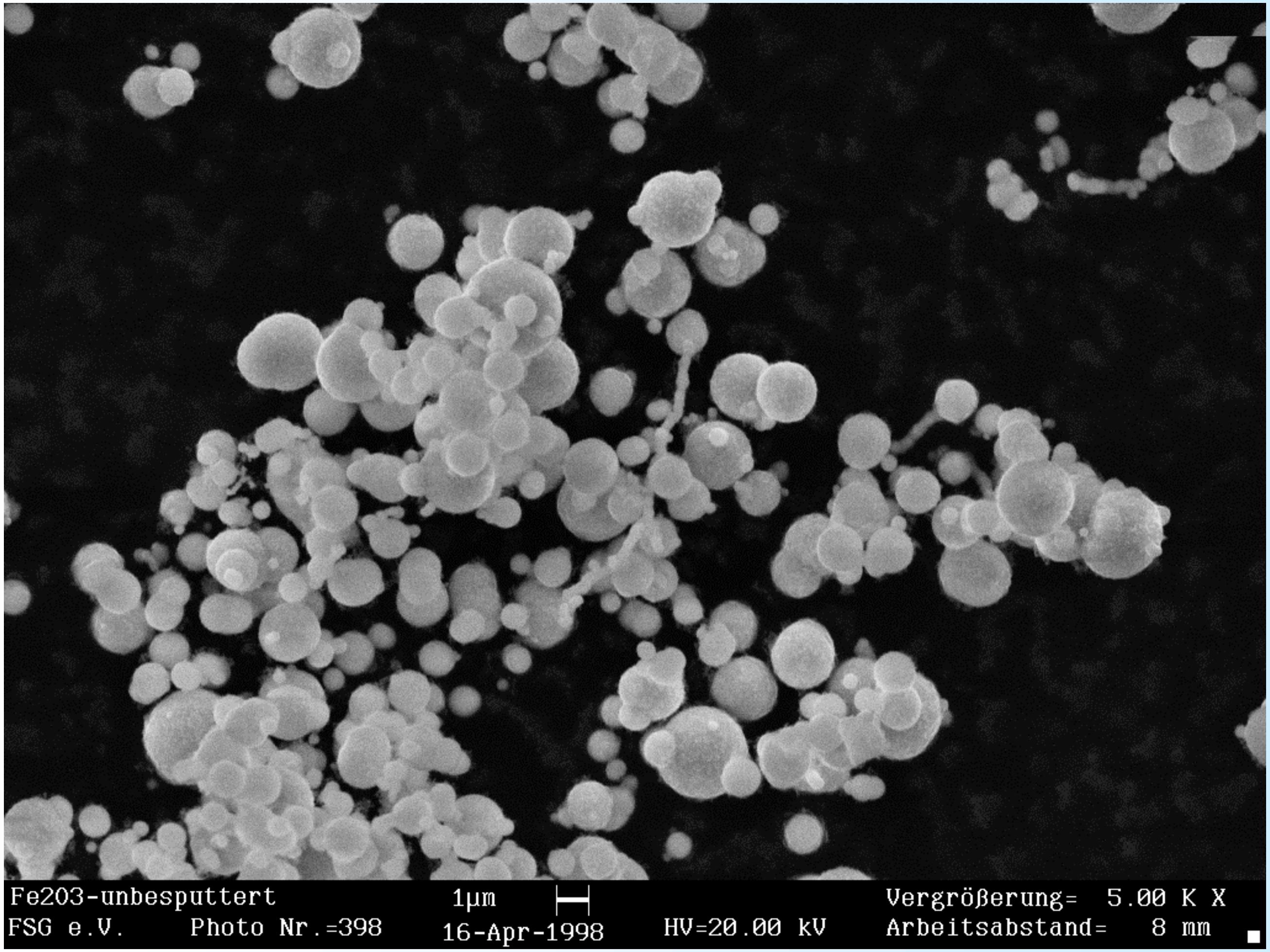
goal : „tailoring" of powder particles with desired surface properties
(geometrical, chemical, optical, elektrical, ...)

here : coating of microdisperse particles (~µm) like MF, SiO_2, c-Fe
with thin metal films (~100nm) (Cu, Ti, Al) or polymer layers
by an RF-discharge (charging and confinement)
and DC-magnetron sputtering, thermal evaporation
or RF-plasma polymerization (modification, coating)

possible ? functionality ? efficient ? etc. ?

example : c-Fe powder particles, untreated

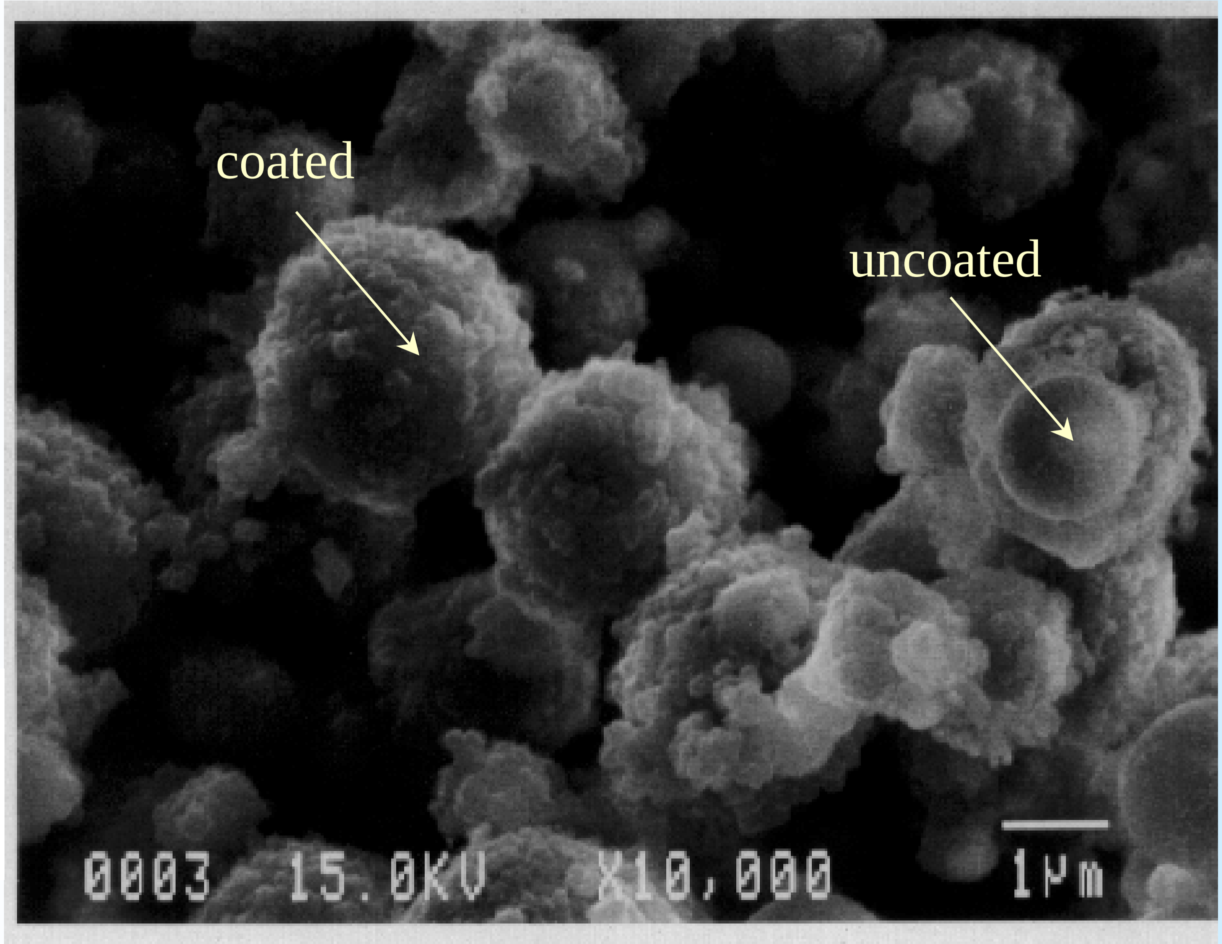
SEM



- spherical
- rather smooth surface
- strongly adhesive
- size distribution

example : c-Fe powder particles, coated with Al

SEM



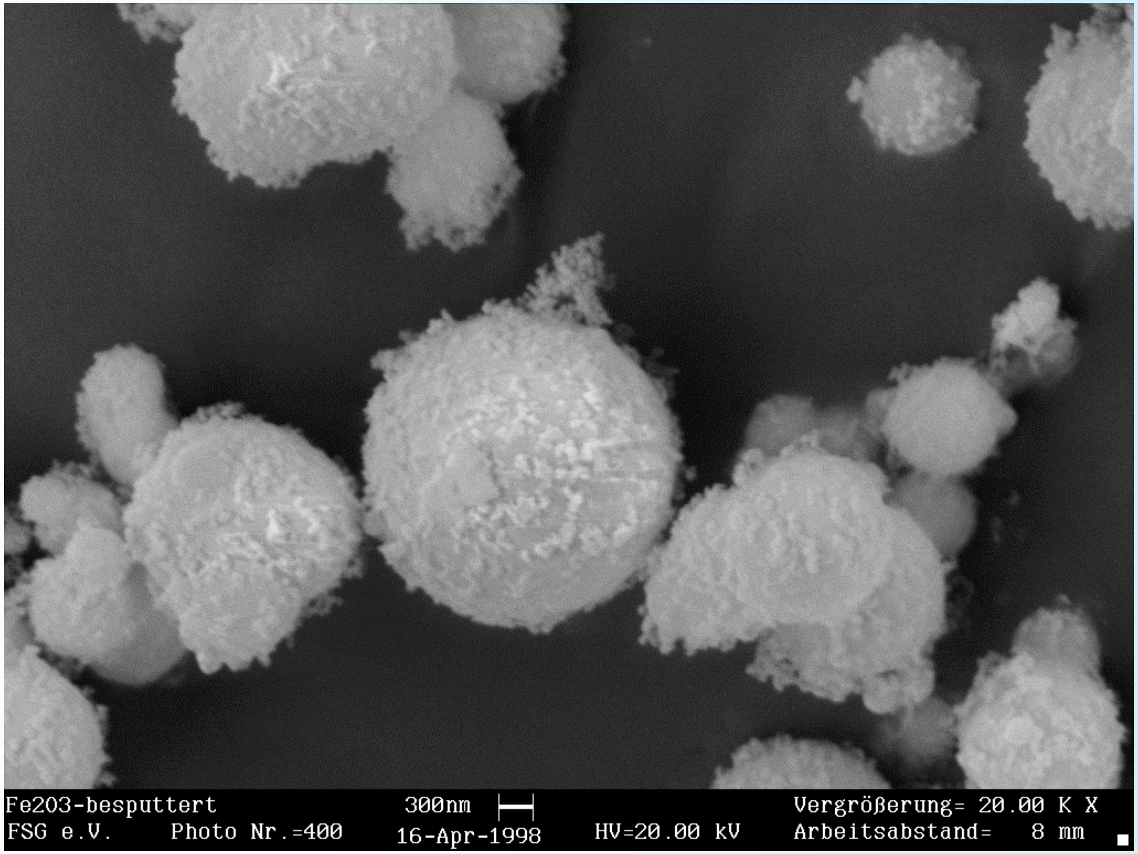
Kersten,H., Schmetz,P., Kroesen,G.M.W., Surface and Coatings Technology 108-109(1998), 507.

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

⇨ each particle is surrounded by a compact layer

⇨ change of optical properties

example : c-Fe powder particles, partly coated with Al



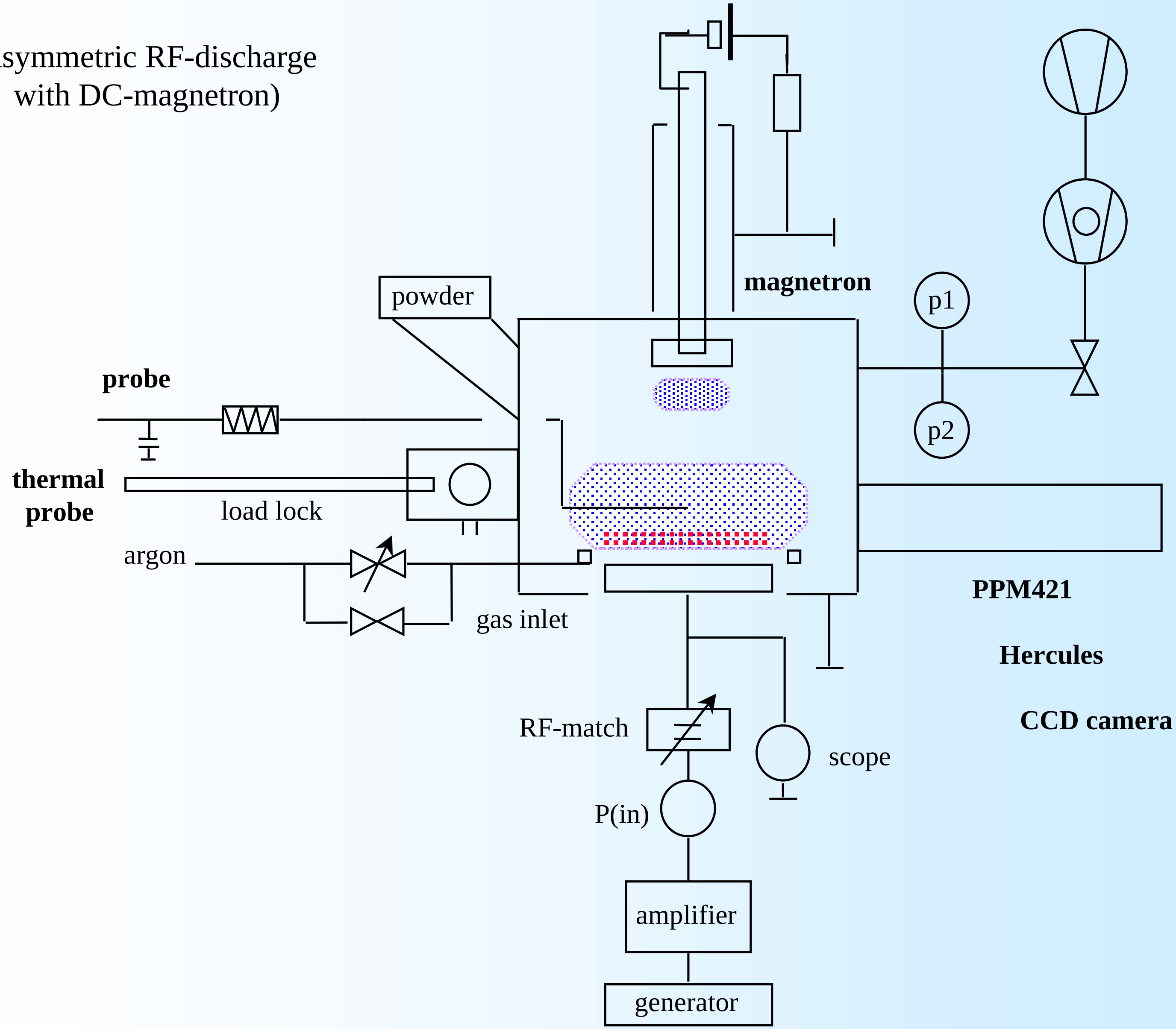
deposition of Al (< 50nm) onto particles

⇨ islands on each particle

⇨ change of chemical properties (catalysis)

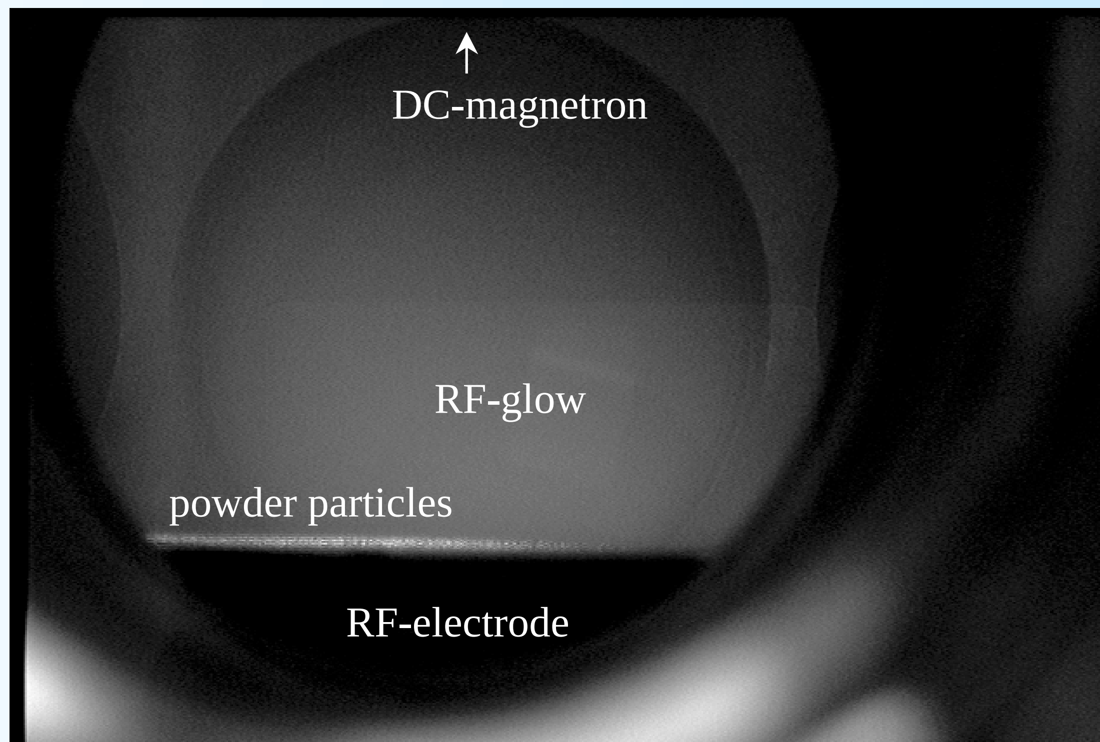
Experimental setup

(asymmetric RF-discharge
with DC-magnetron)



RF + powder particles

particles are charged and confined in RF-plasma (Ar)



RF + powder + magnetron

coating of particles with metal during their confinement by DC-magnetron sputtering

Experimetal conditions

RF activated region (charging, trapping) :

- RF plasma : 13.56 MHz)
- gas : Ar, Ar+O_2
- pressure : $5 \cdot 10^{-3} \ldots 10^{-1}$ mbar
- RF-voltage : 100 … 400 V
- power : 5 … 30 W
- power density : 0.05 … 0.25W/cm^{-2}

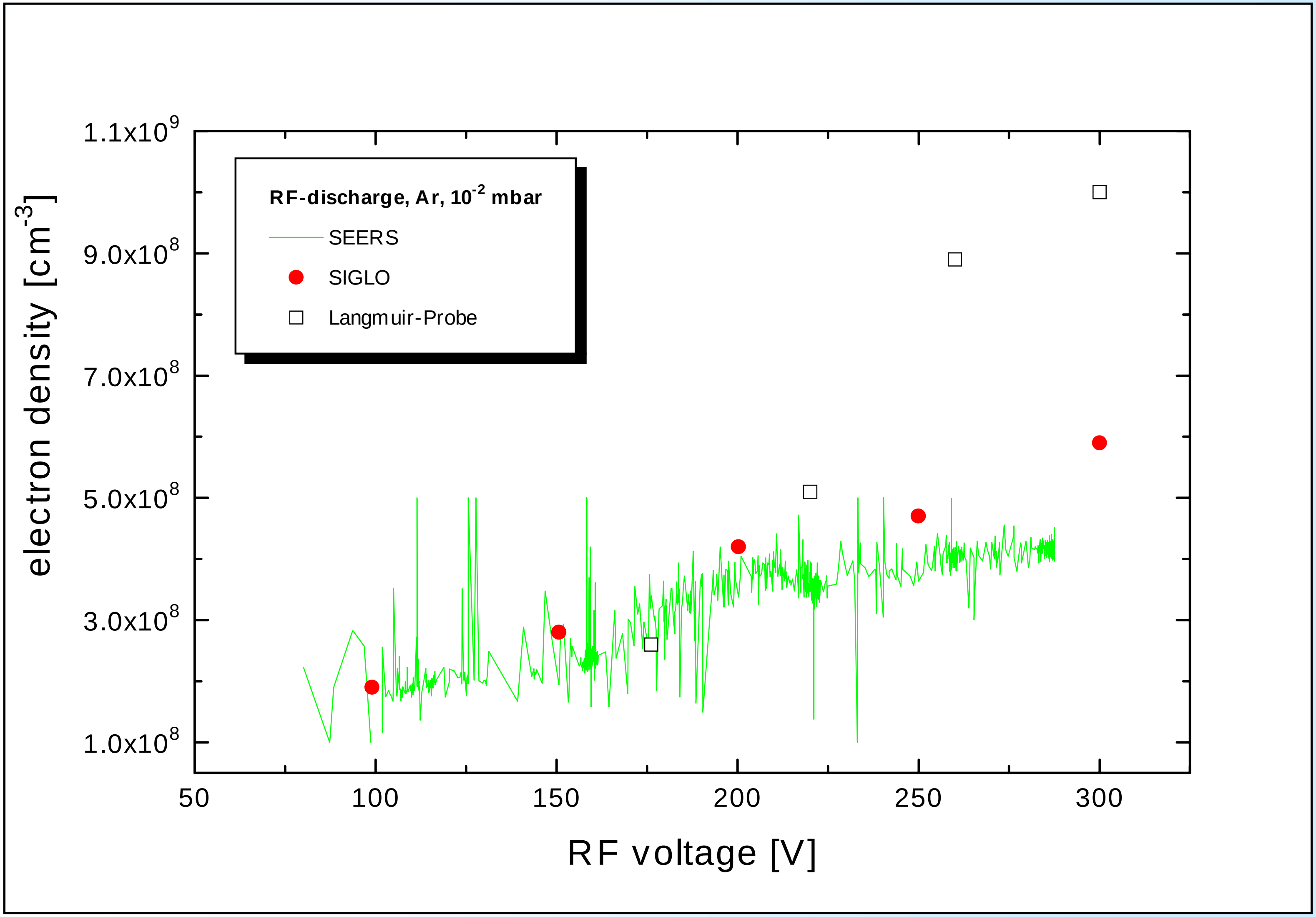
Magnetron source region (coating) :

- voltage : 250 … 450 V
- current : 0.02 … 0.23 A
- power : 5 … 100 W
- power density : 1 … 20 W/cm^{-2}
- pressure : $10^{-3} \ldots 10^{-1}$ mbar
- distance : 2 … 15 cm

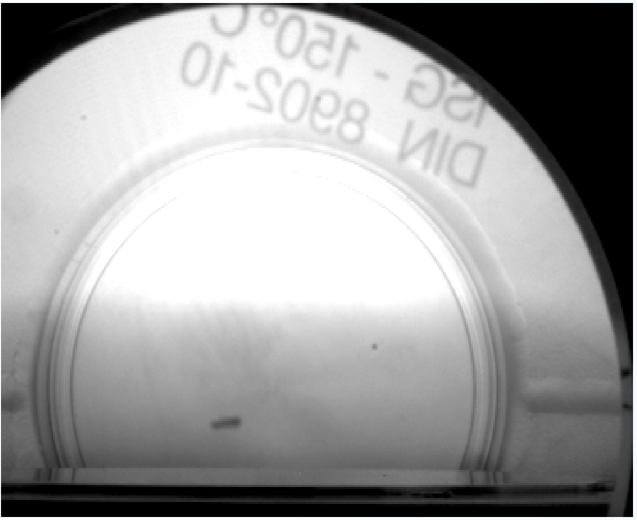
Diagnostics

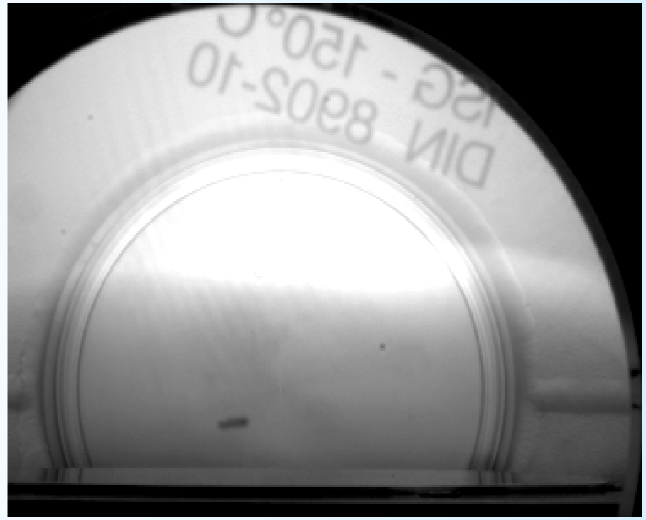
plasma	• Langmuir probes	→	V_{pl}, $V_{fl,}$ EEDF, n_e, kT_e
	• SEERS	→	n_e
	• energy resolved MS	→	IEDF, NEDF, n_i, n_n
	• macroscopic parameter	→	I,V,d_{sh}
	• DL absorption and CCD photometry	→	excited species
powder in plasma	• CCD photometry	→	particle distribution
	• micro-calorimetry	→	energy influx
	• LF-excitation	→	particle charge
	• MIE-scattering	→	particle density, state
particles (substrates)	• SEM, AFM	→	particle size, morphology
	• XPS, EDX	→	surface composition
	• XRD	→	surface structure

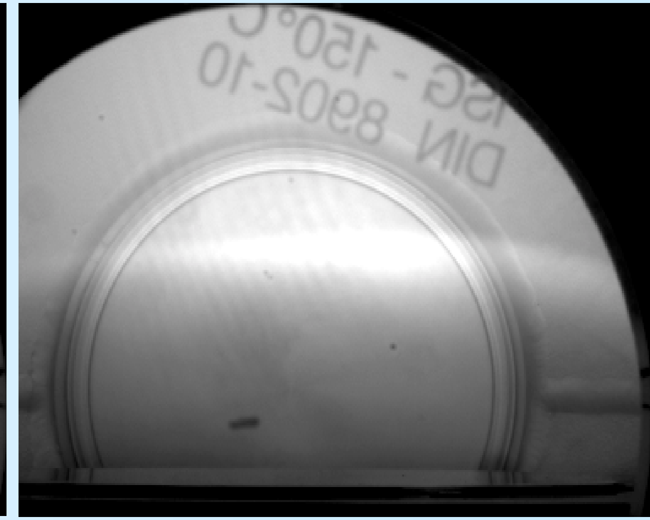
electron component in RF-plasma (probe, SEERS, SIGLO)



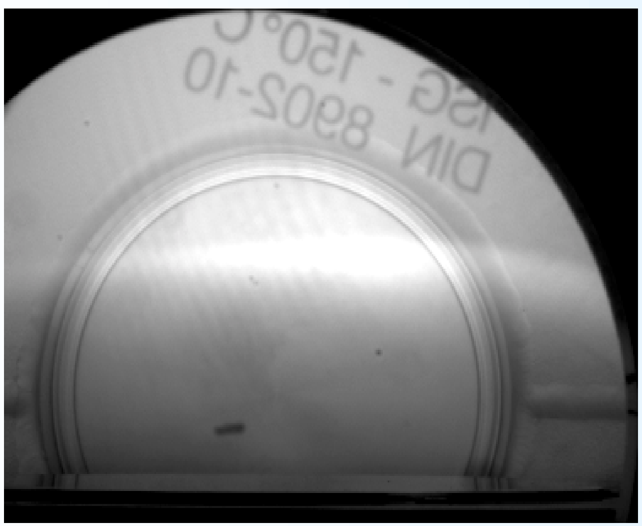
determination of sheath thickness

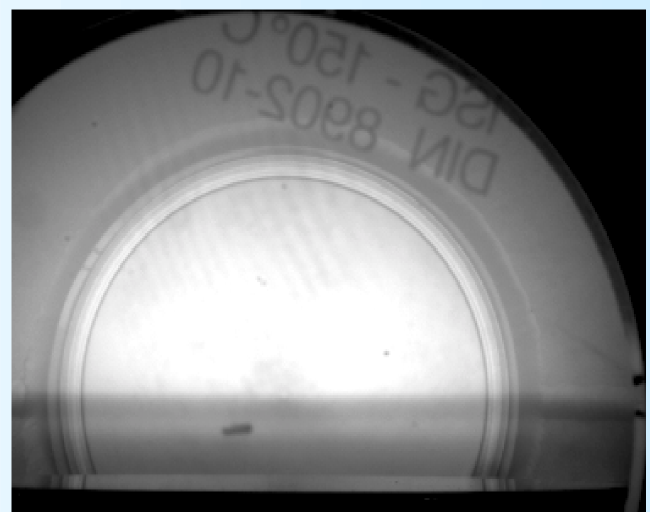






argon, 0.005mbar, 10W 30W 50W





argon, 50W 0.005mbar 0.01mbar

determination of sheath thickness

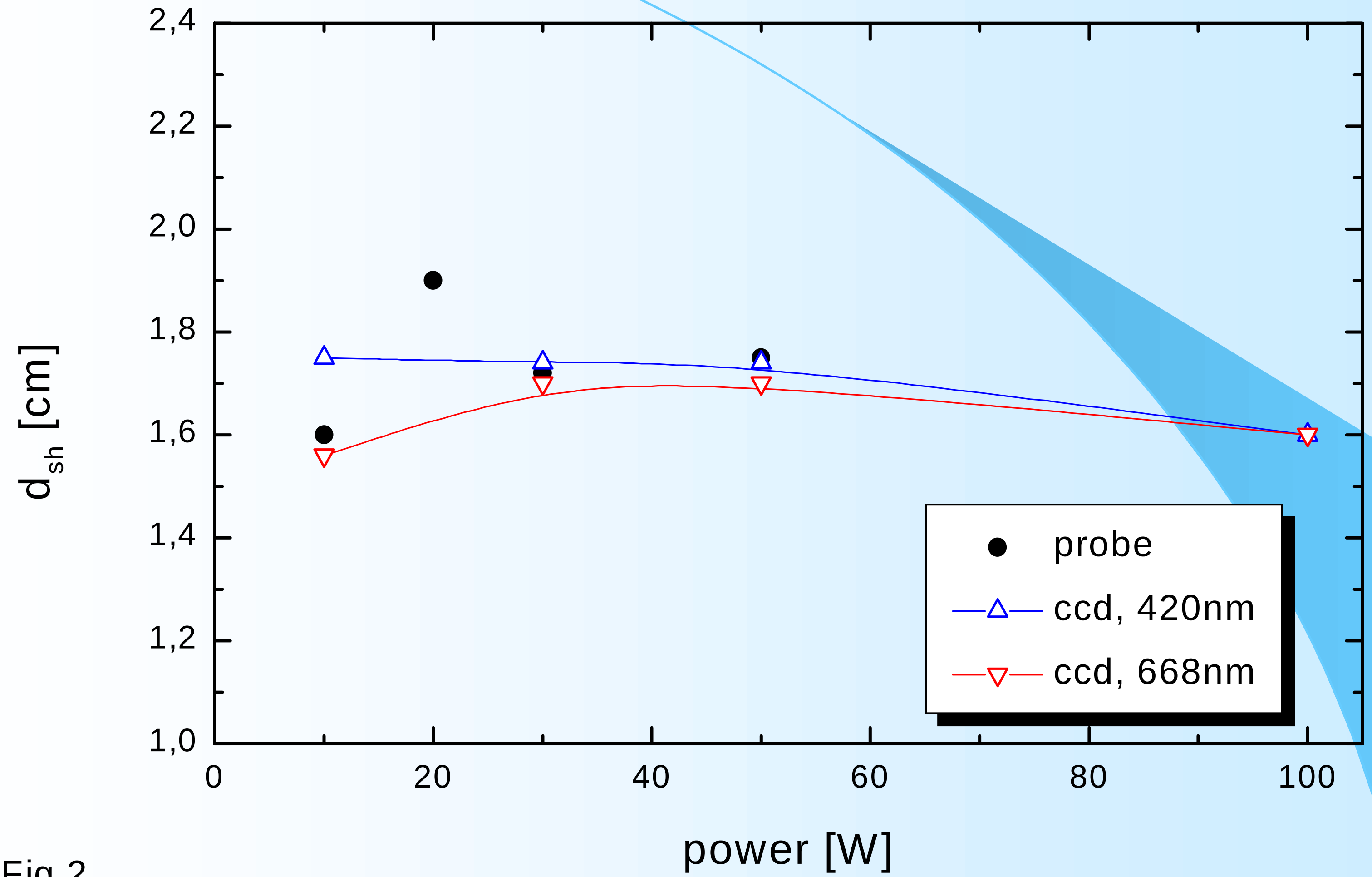
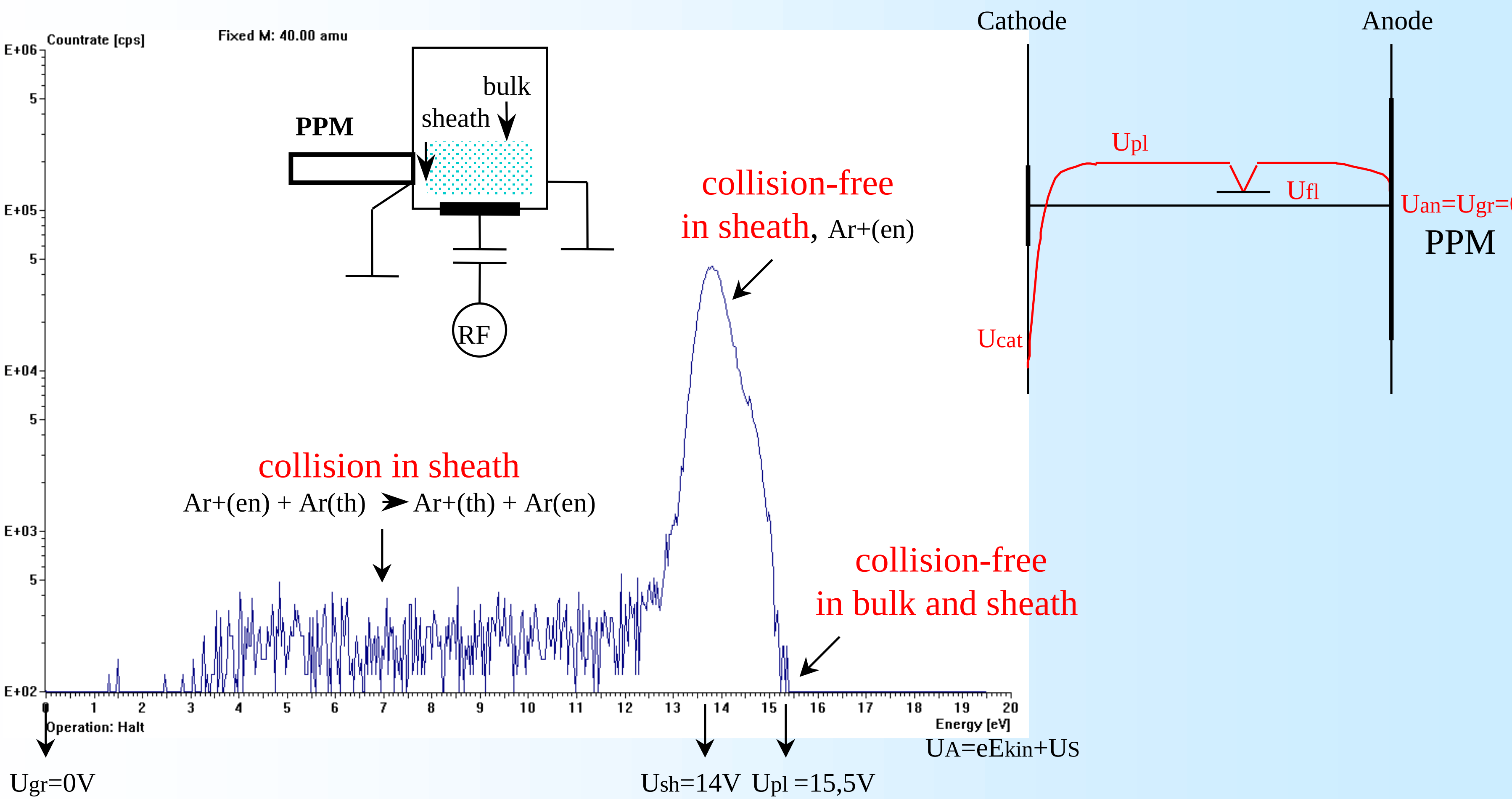
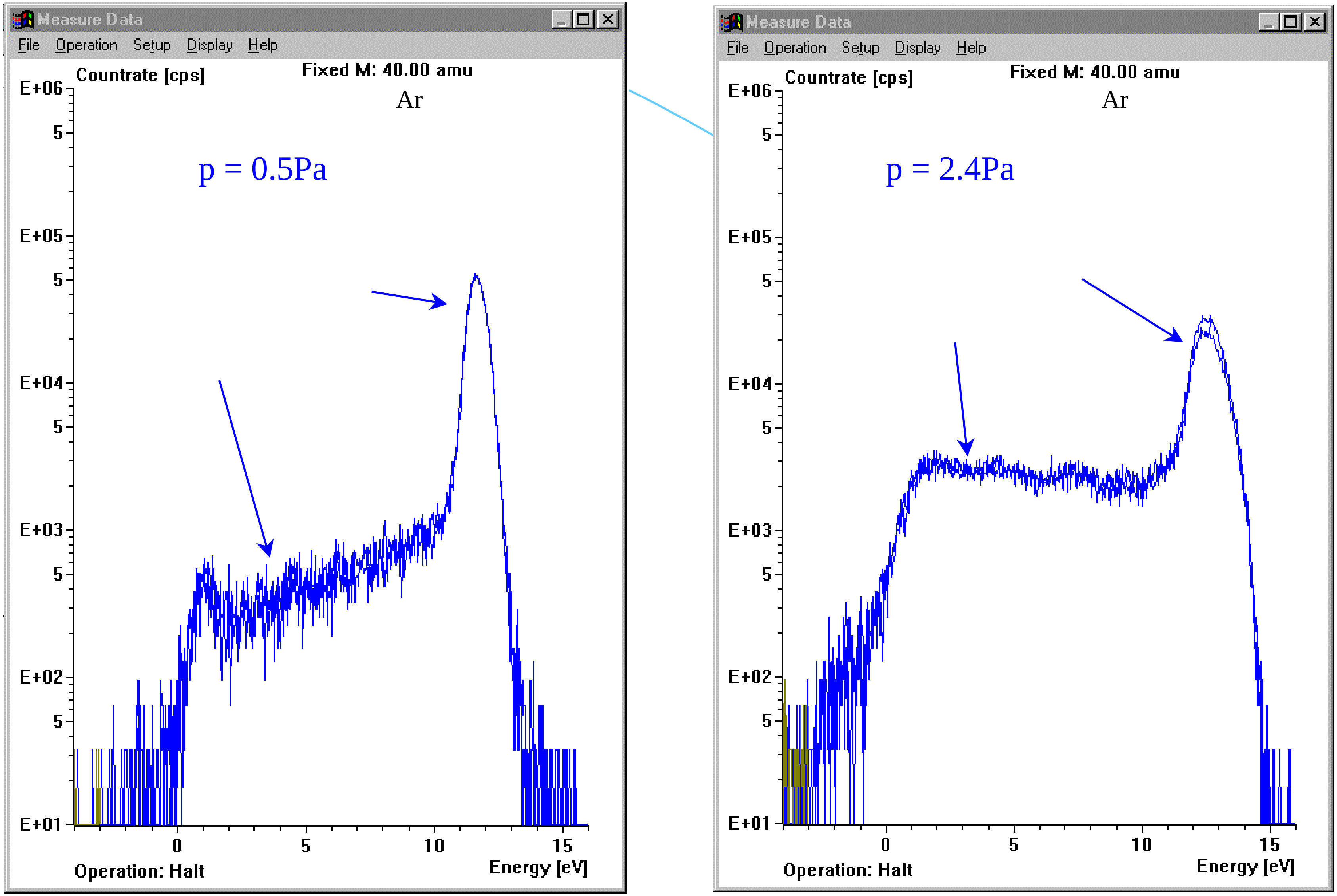


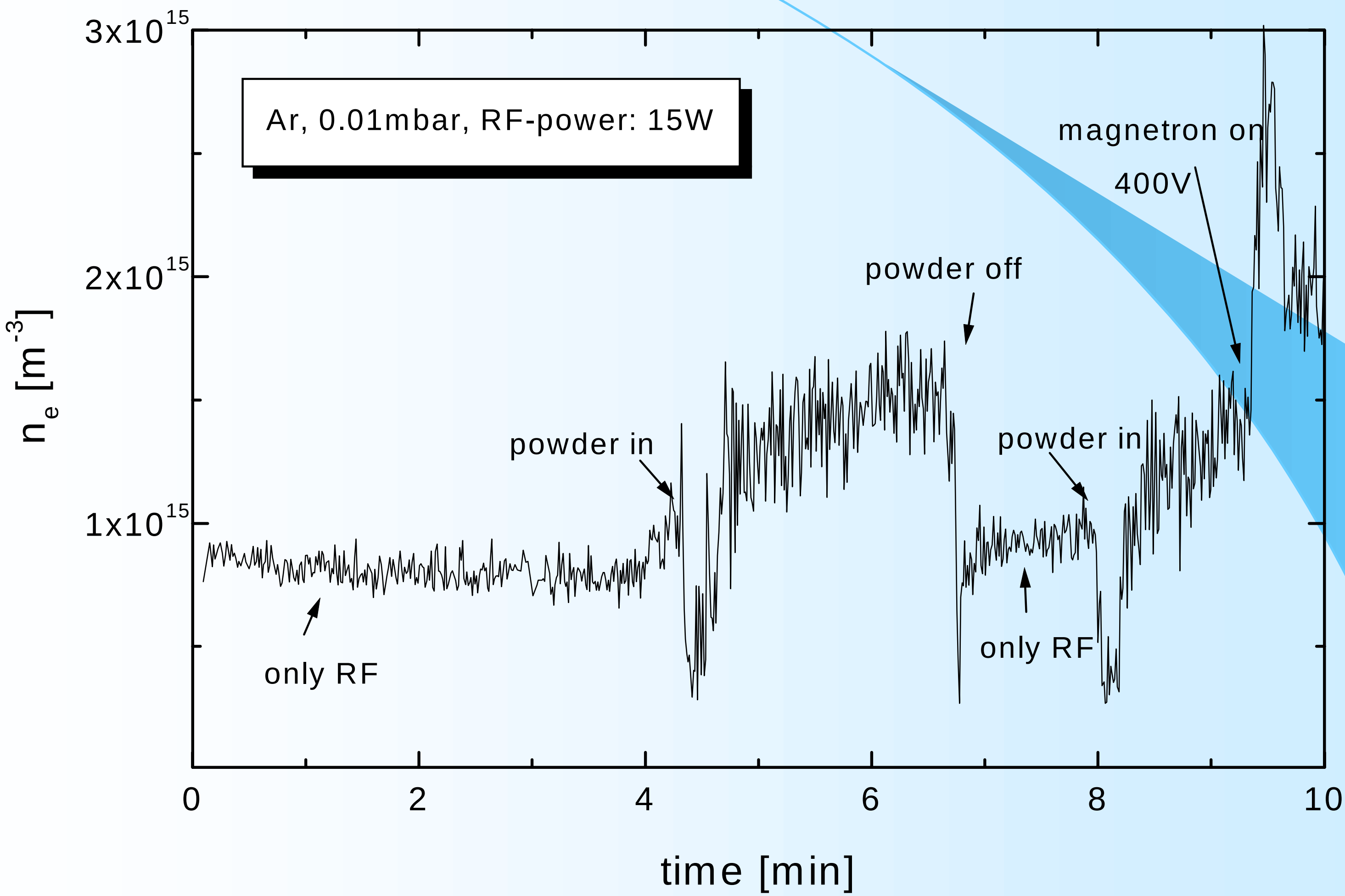
Fig.2

ion species in RF-plasma (PPM)



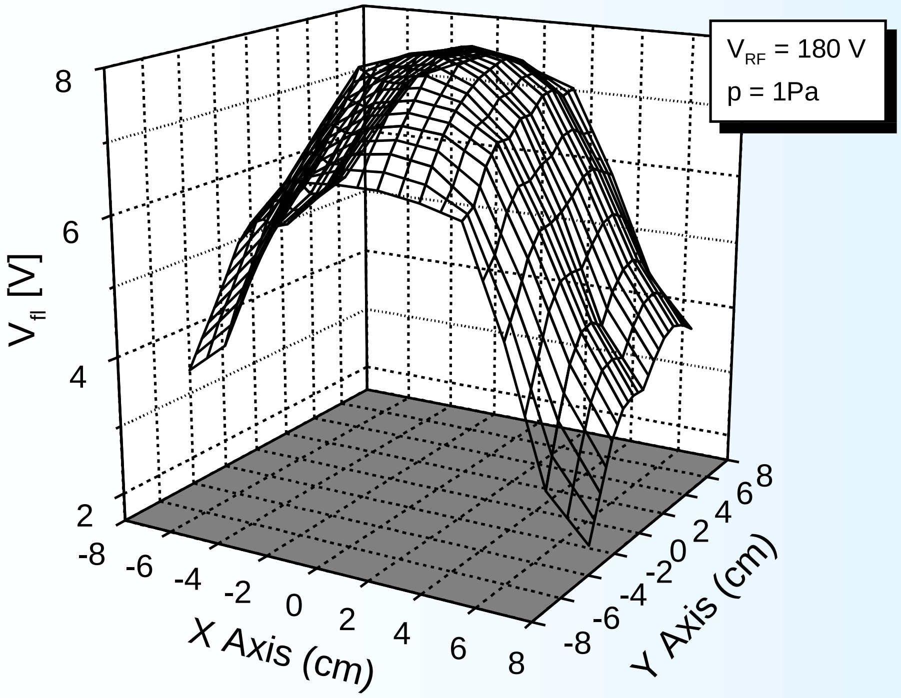


more low-energetic ions due to more collisions at higher pressure

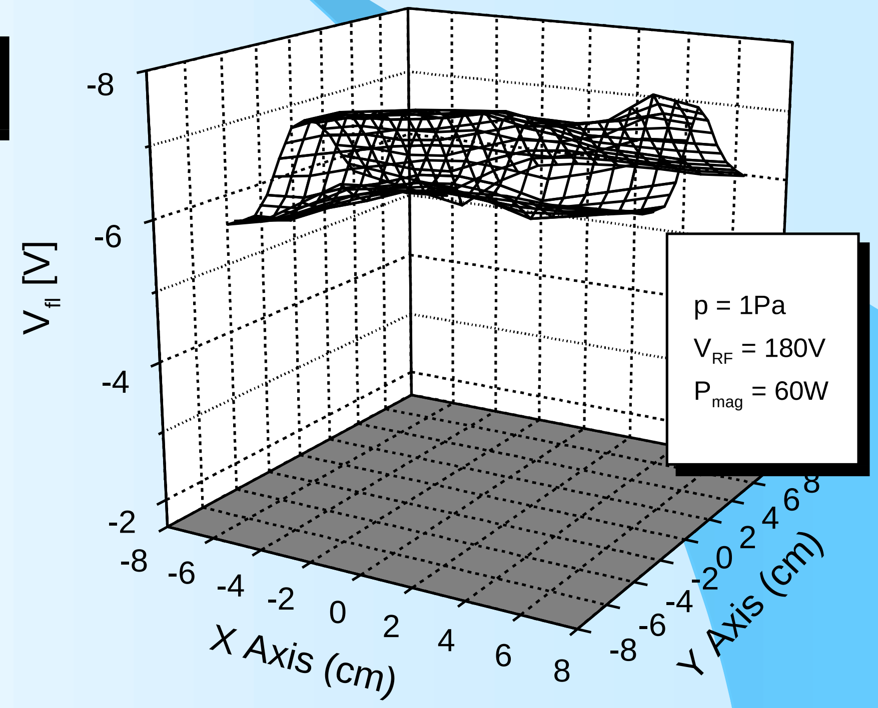

Ar, 0.01mbar, RF-power: 15W
magnetron on
400V
powder off
powder in
powder in
only RF
only RF
3x10^15
2x10^15
1x10^15
n_e [m^-3]
0
2
4
6
8
10
time [min]

Änderung des Floatingpotentials beim Magnetronbetrieb

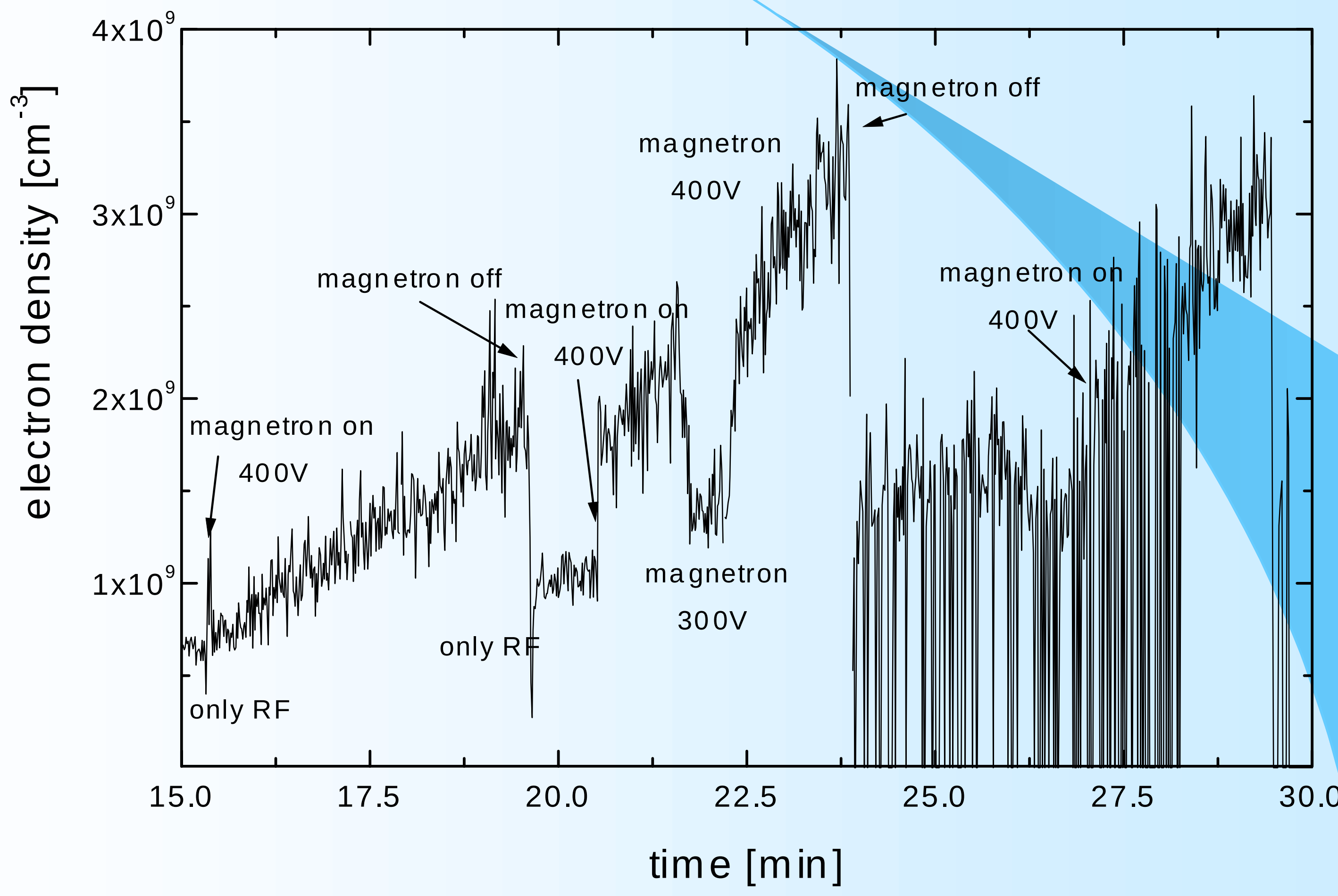
only RF plasma



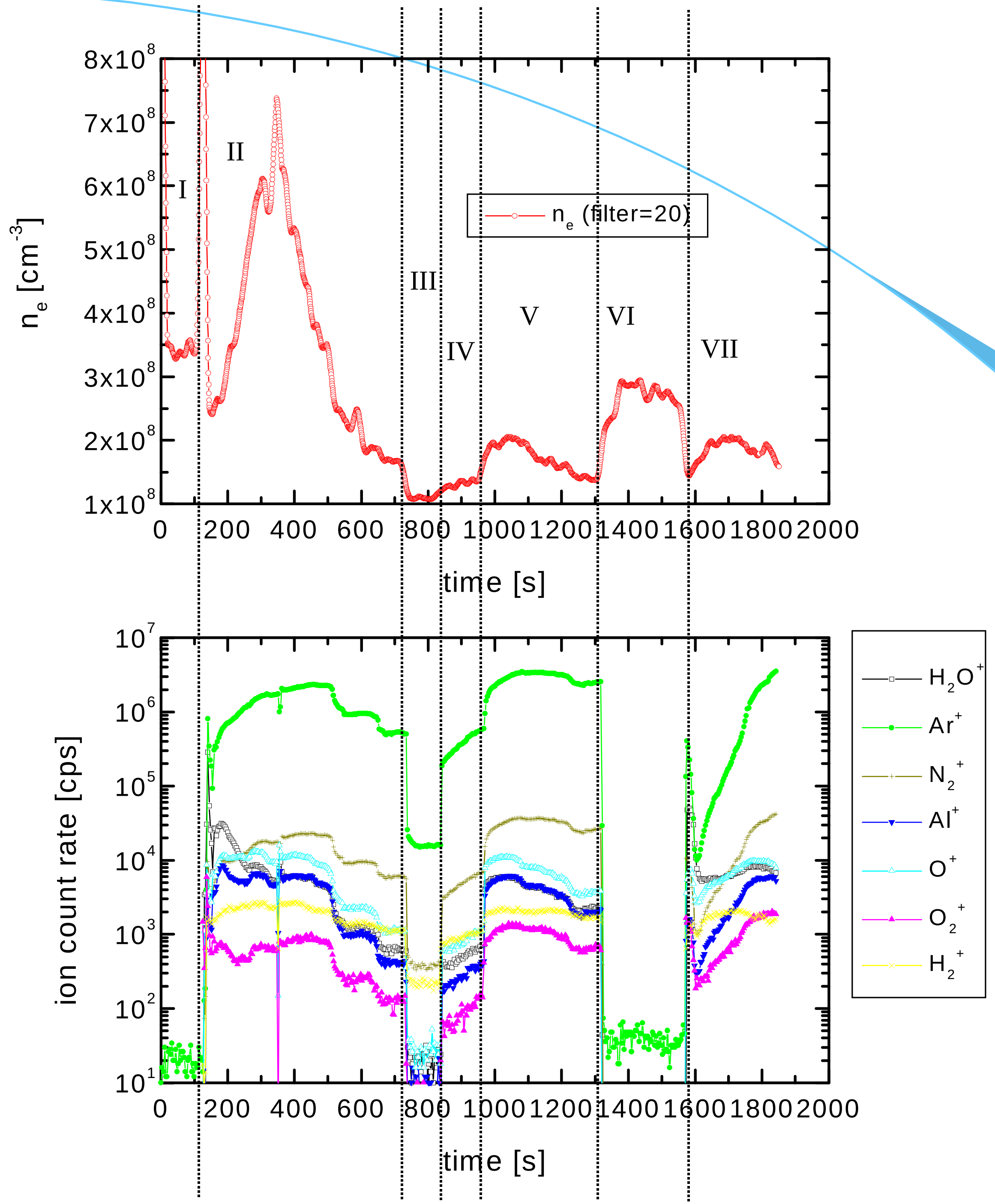
RF plasma *and* DC-magnetron discharge



Electron density in substrate region



Electron density



Ar, 1Pa, Vrf=185V
+ magnetron

I only RF

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

III magnetron lower: 500V, 36mA

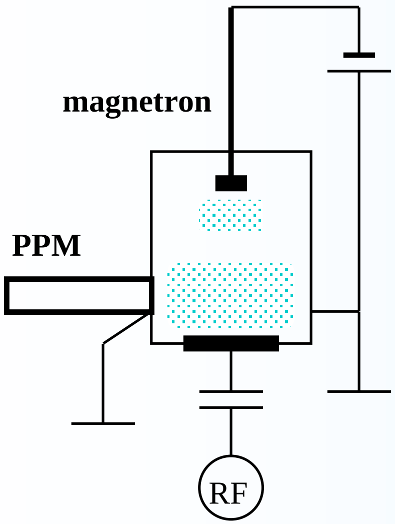
IV magnetron higher: 540V, 42mA

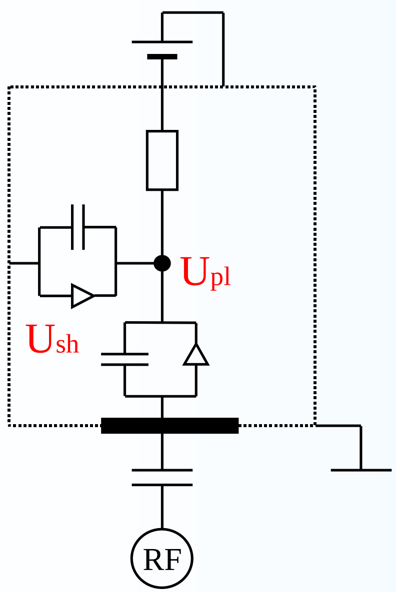
V magnetron higher: 585V … 595V
50mA … 46mA

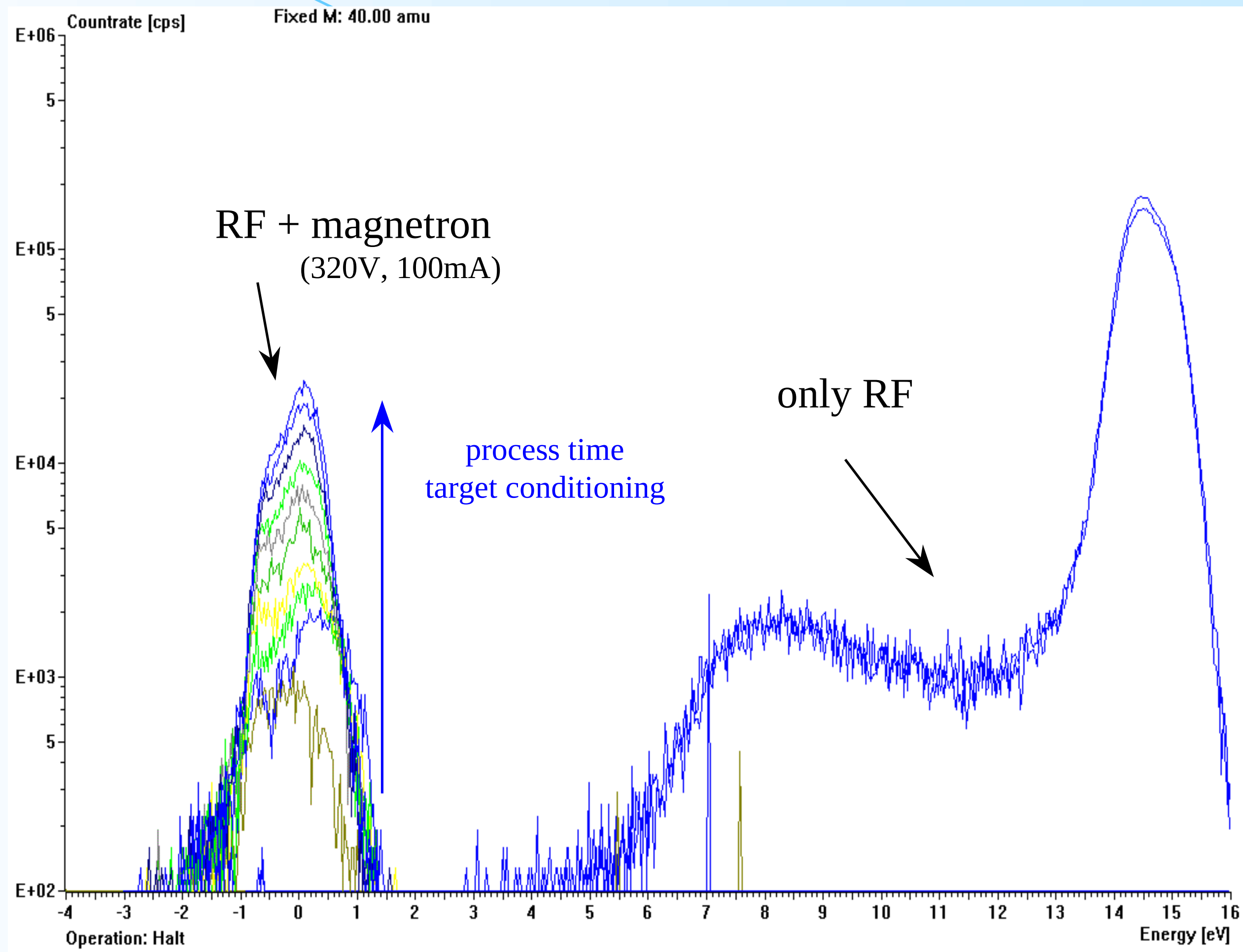
VI magnetron off: only RF

VII magnetron on: 590V, 48mA

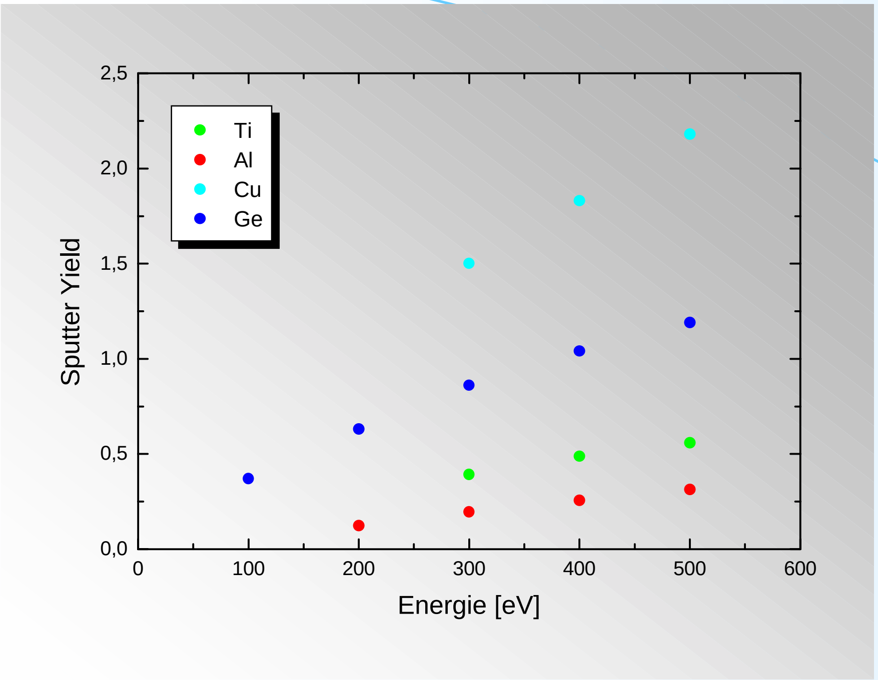
effect of DC magnetron on IED: ions (Ar, 1Pa, 170V_{rf})

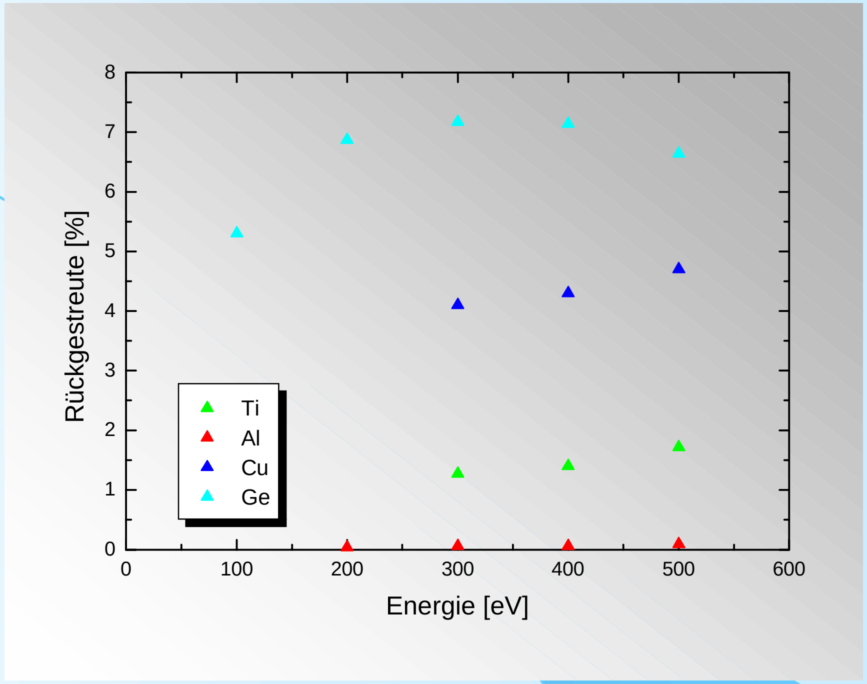


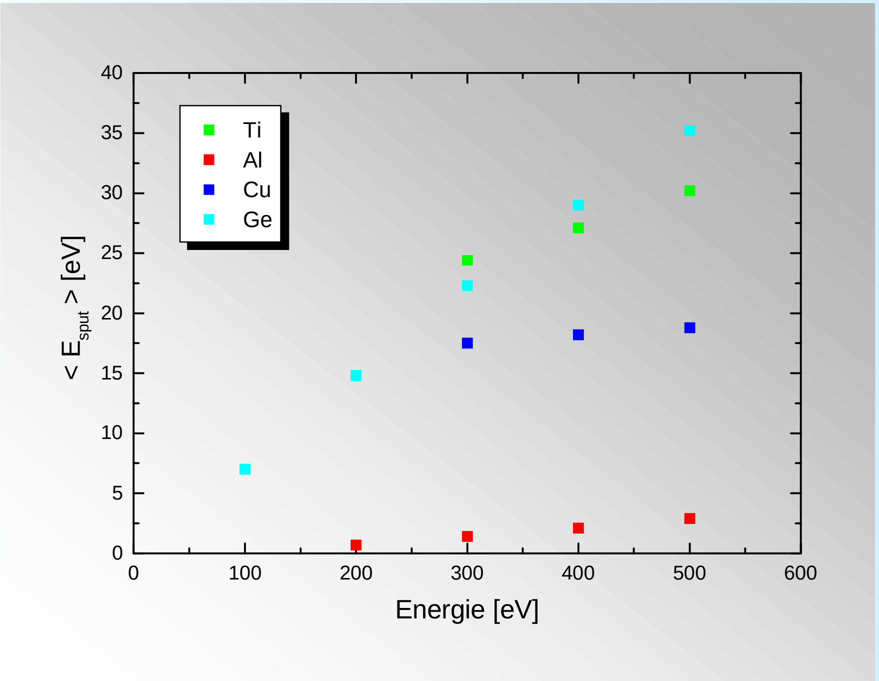




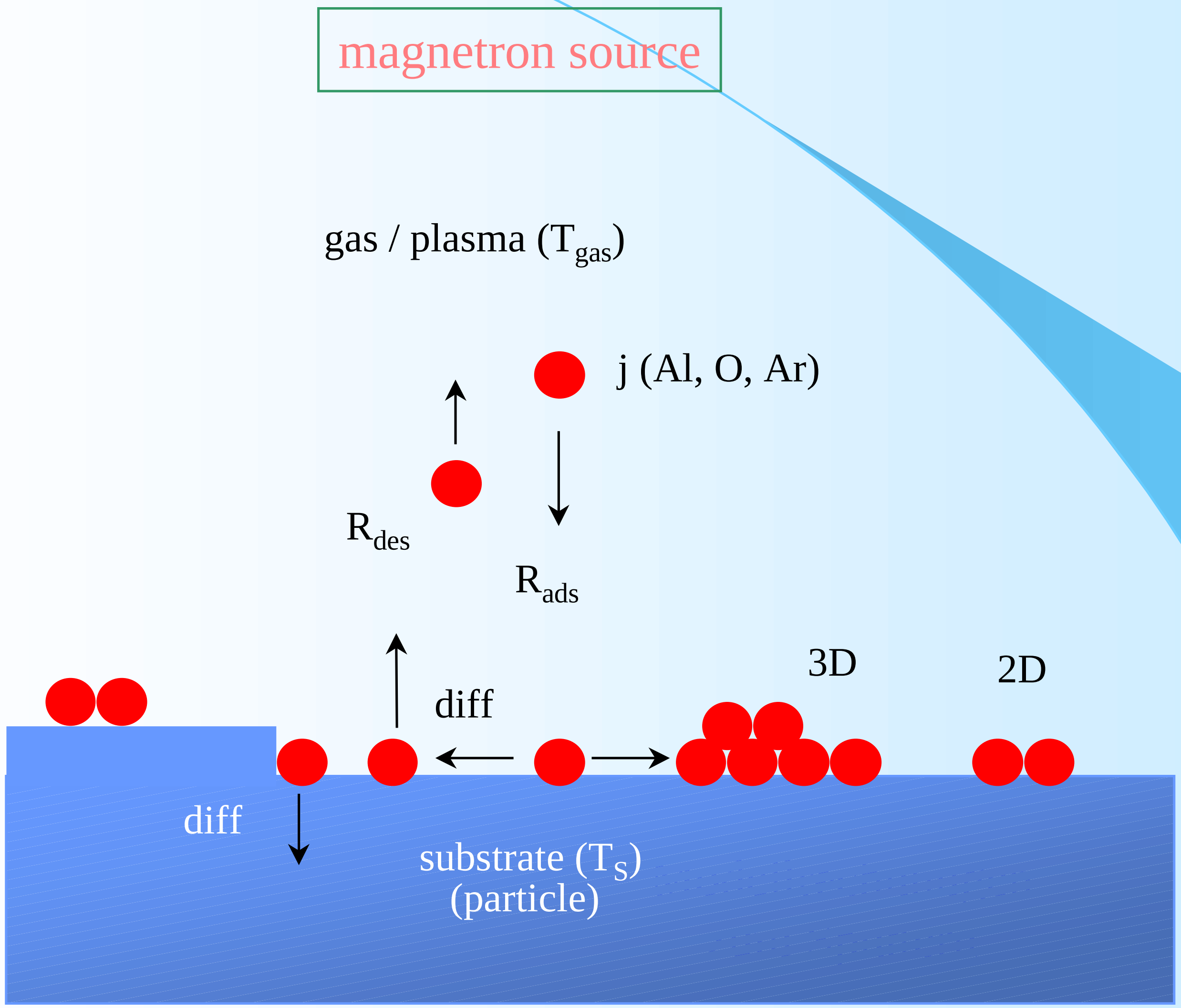
magnetron has drastic influence on U_{pl} and U_{sh}



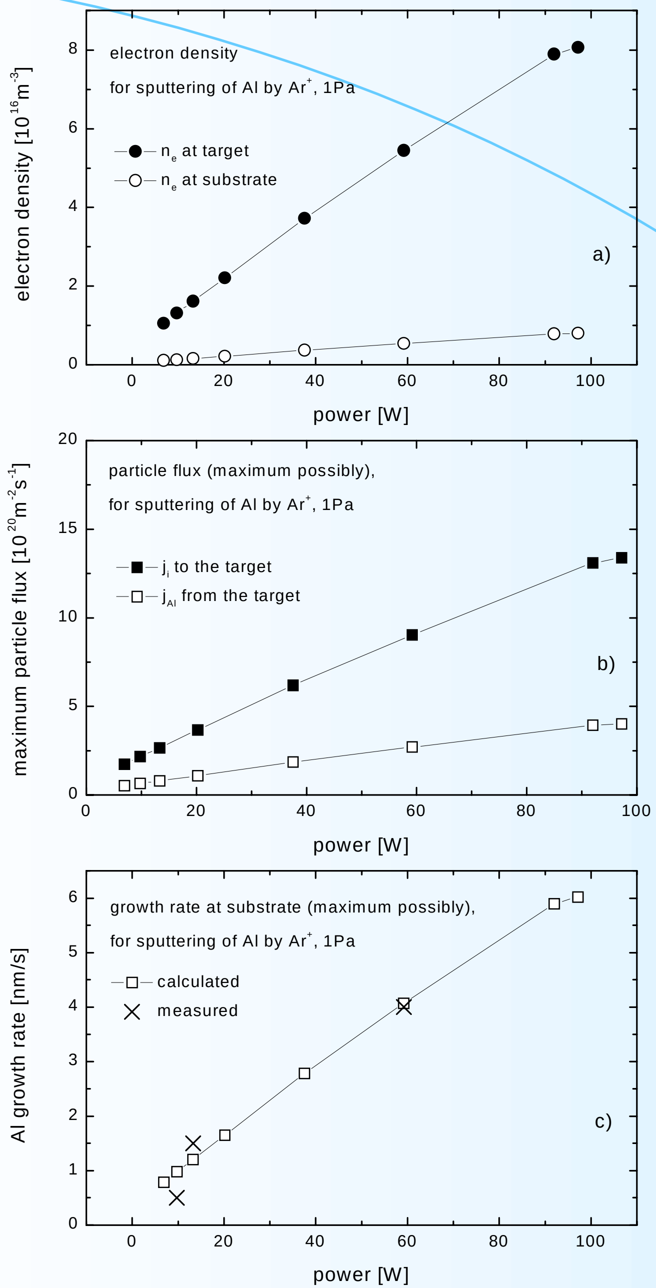




Modellrechnungen zum Sputtern (TRIM)



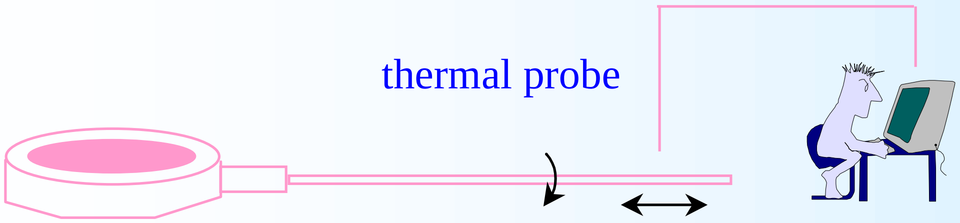
magnetron source
gas / plasma (T_{gas})
j (Al, O, Ar)
R_{des}
R_{ads}
diff
3D
2D
diff
substrate (T_S)
(particle)



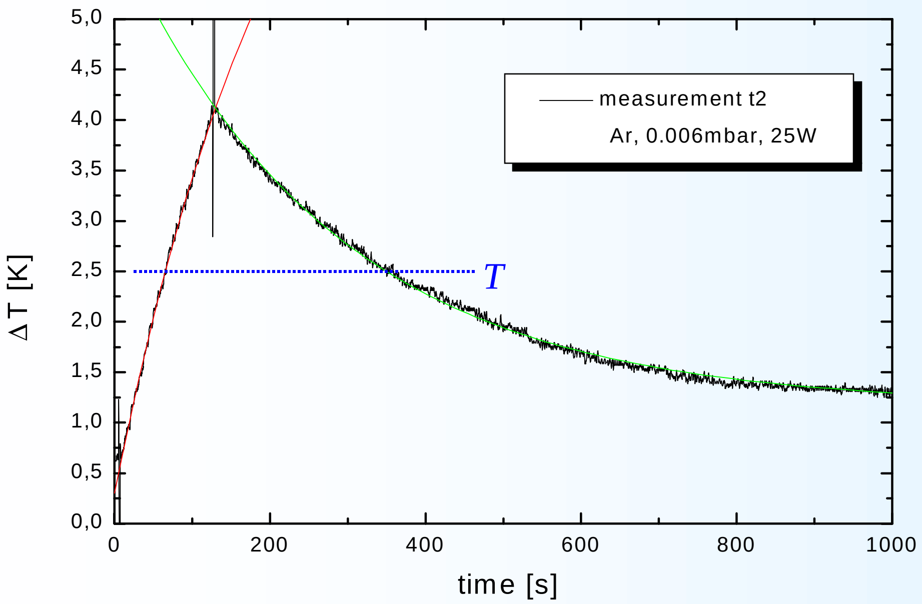
electron density
for sputtering of Al by Ar+, 1Pa
ne at target
ne at substrate
a)
electron density [10^16 m^-3]
power [W]
particle flux (maximum possibly),
for sputtering of Al by Ar+, 1Pa
ji to the target
jAl from the target
b)
maximum particle flux [10^20 m^-2 s^-1]
power [W]
growth rate at substrate (maximum possibly),
for sputtering of Al by Ar+, 1Pa
calculated
measured
c)
Al growth rate [nm/s]
power [W]

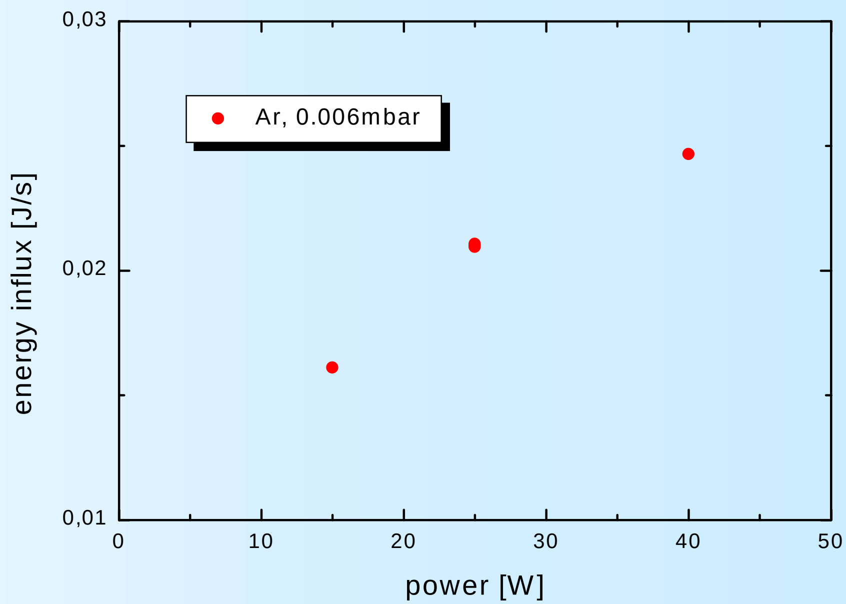
Fig.4

measurement of energy fluxes to the substrates

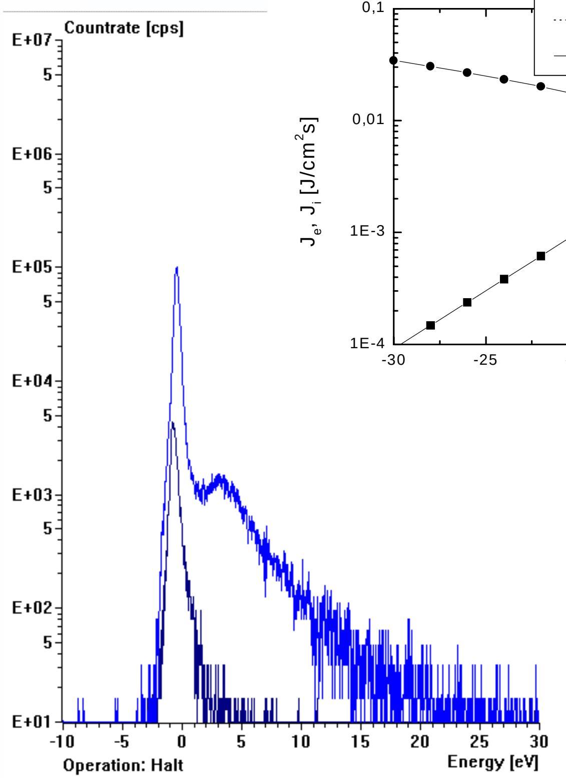


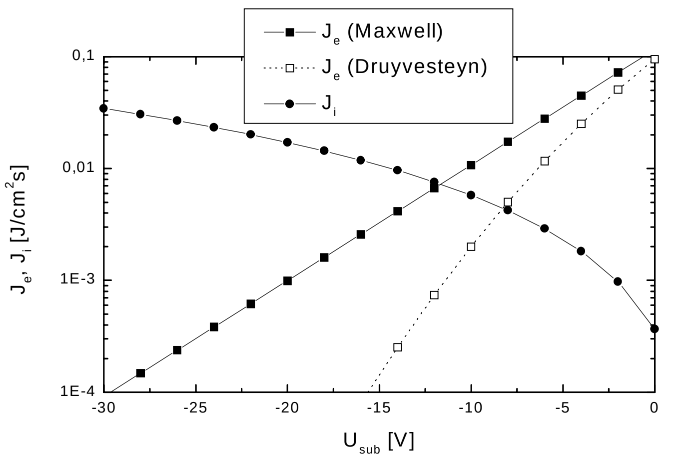
energy influx $\sim [(dT/dt)_{heat} - (dT/dt)_{cool}]_T$





energy fluxes to the substrates at thin film deposition





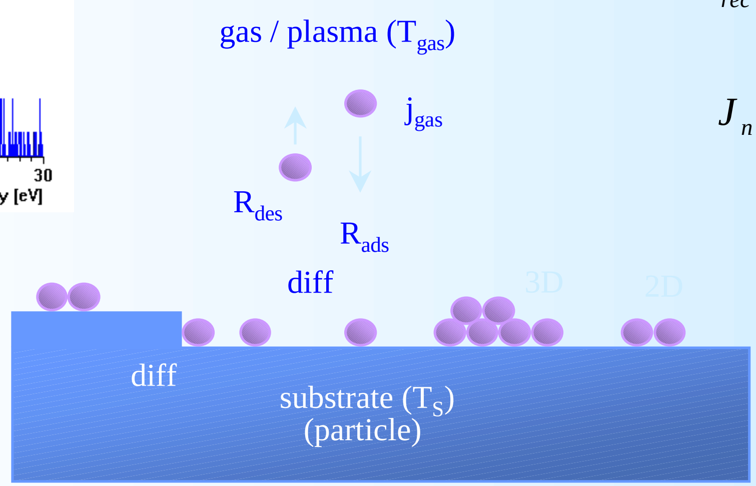
$$J_c = q_c \cdot \rho \cdot R_{dep} = j_{Al} \cdot E_c$$

$$J_e = n_e \sqrt{\frac{kT_e}{2\pi m_e}} \exp\left\{-\frac{e_0 U_{bias}}{kT_e}\right\} \cdot 2kT_e$$

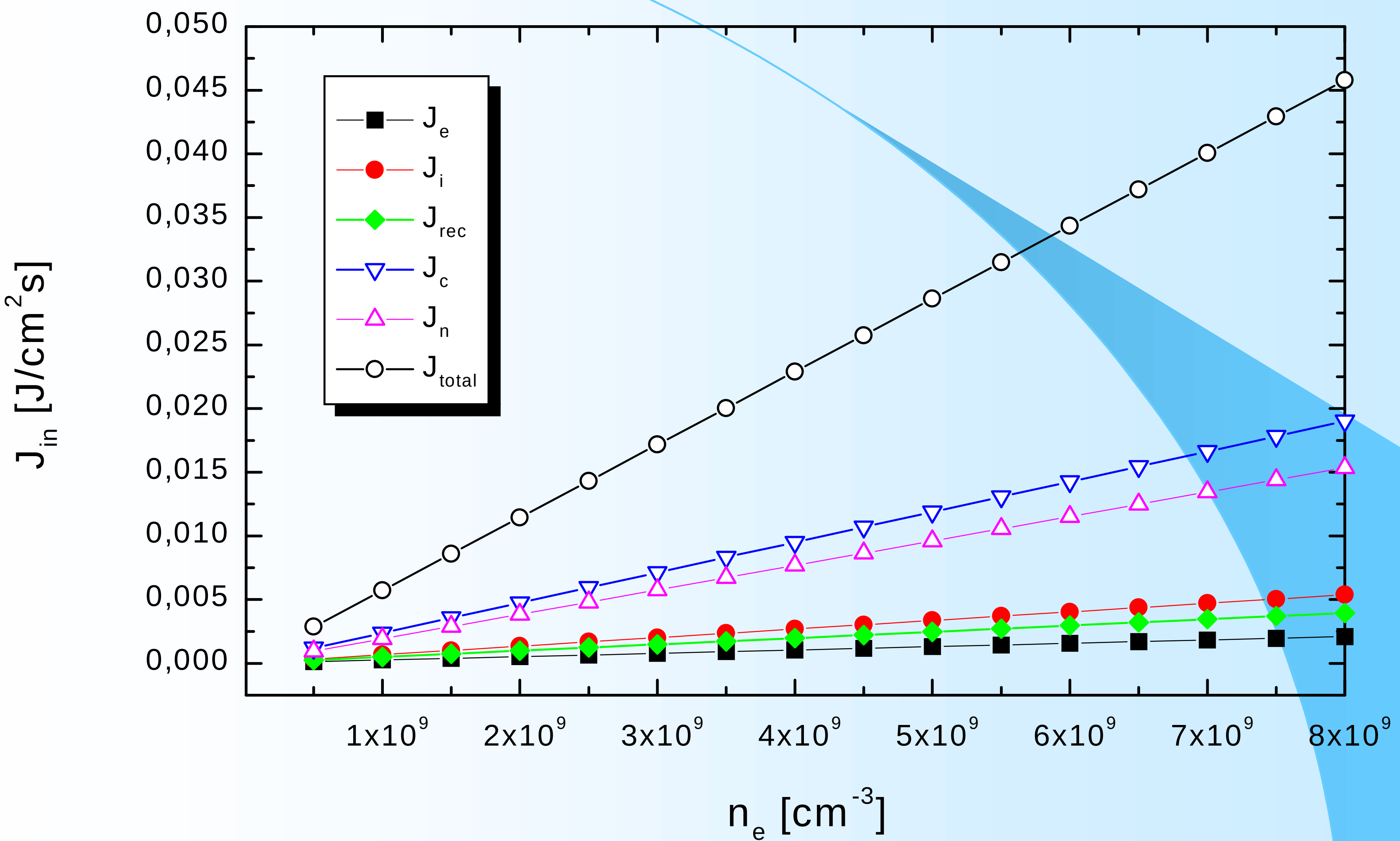
$$J_i = n_e \sqrt{\frac{kT_e}{m_i}} \exp\{-0.5\} \cdot e_0 U_{bias}$$

$$J_{rec} = j_e \cdot E_i$$

$$J_n = j_{Al} \cdot E_n = R_{dep} \frac{N_A \rho}{M} \cdot E_n$$

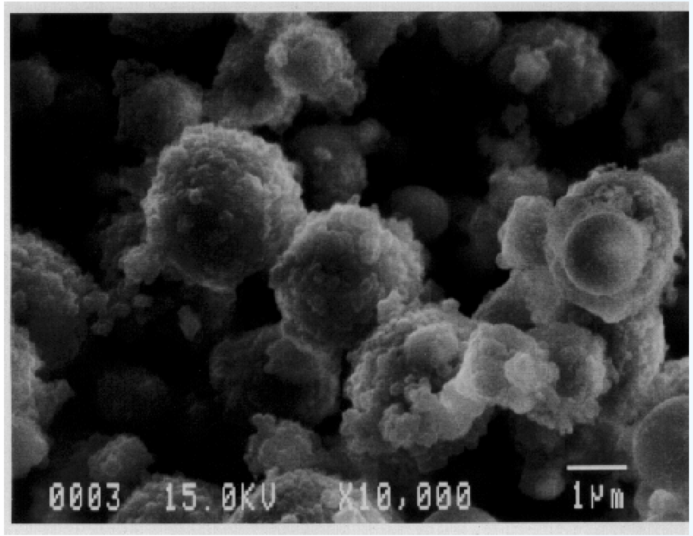


Kersten,H., Kroesen,G.M.W.,Hippler,R.,
Thin Solid Films 332(1998), 282.

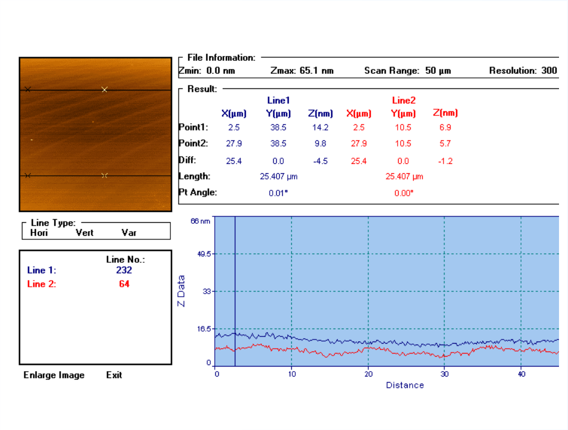


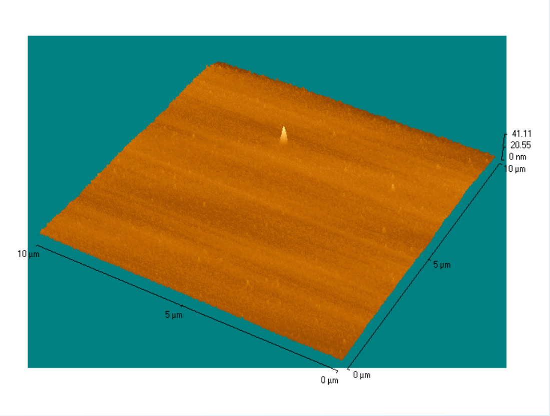
Kersten,H., Kroesen,G.M.W., Hippler,R.
angenommen in Thin Solid Films.

Thermische Bilanz der Substrate infolge des Energieeinstroms manifestiert sich u.a. in der Mikrostruktur



Sputtern von Al
auf Pulverteilchen
(~460...770K)





Sputtern von Al
auf ebene Si - Substrate
(~RT)

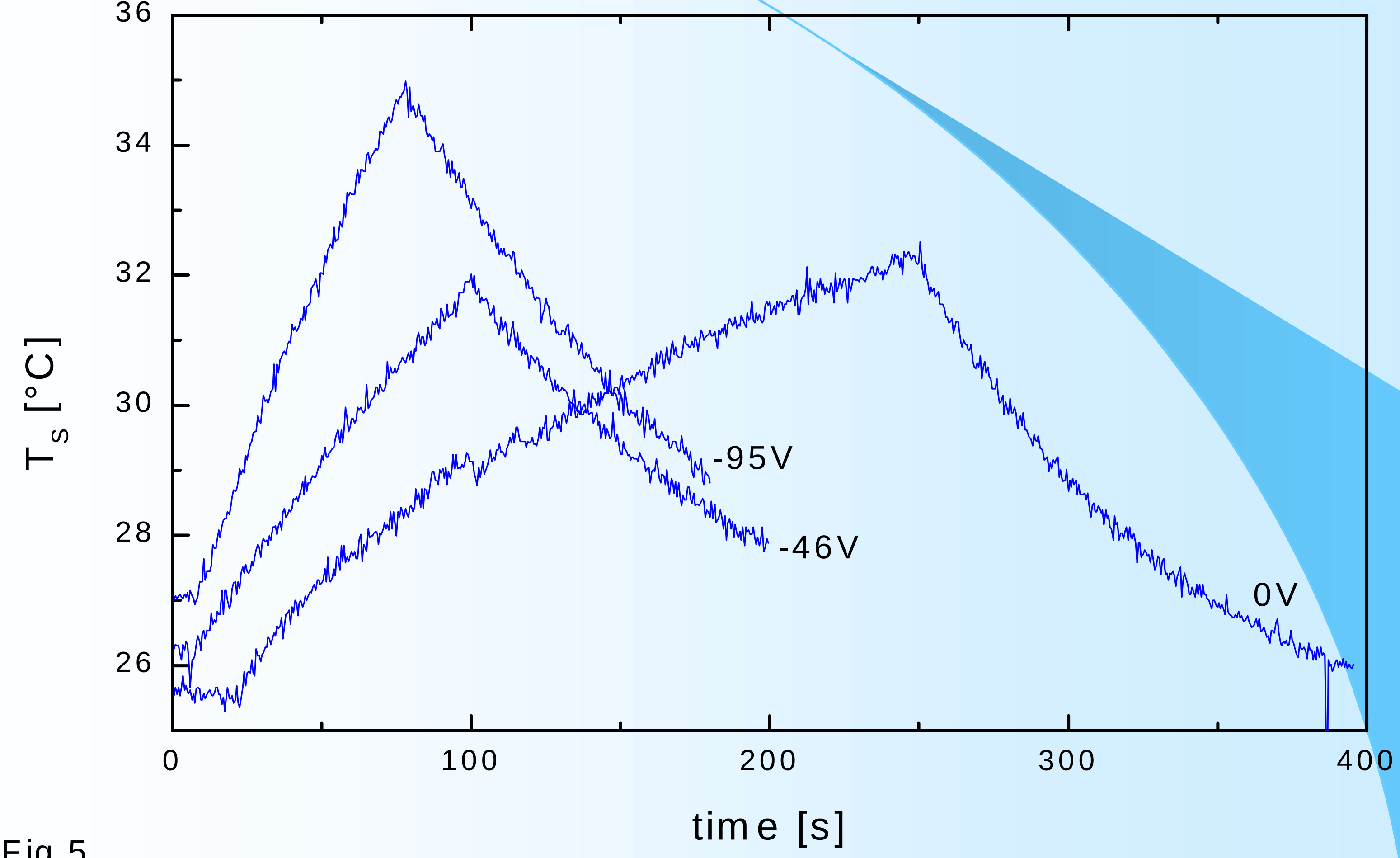


Fig.5

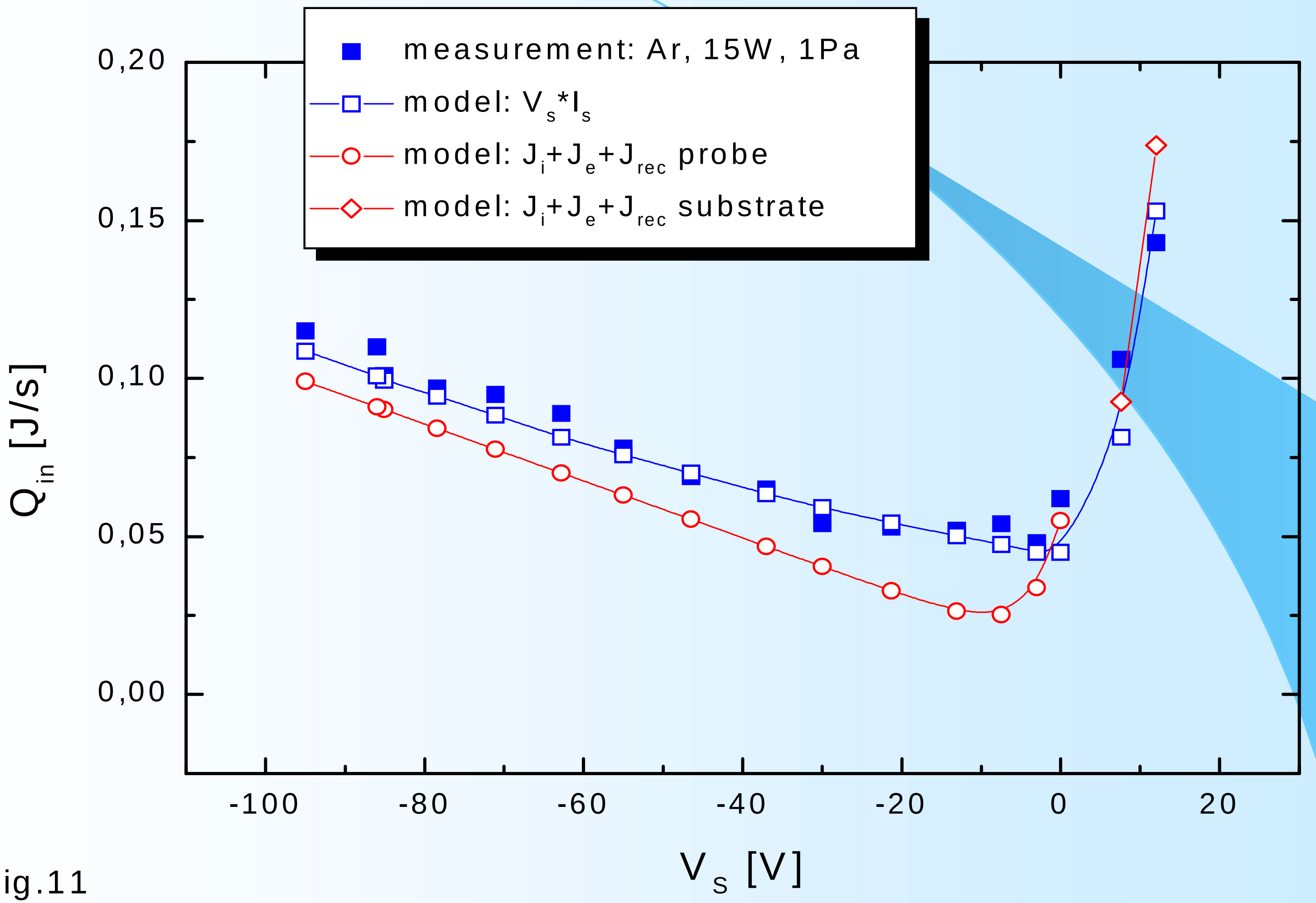

measurement: Ar, 15W, 1Pa
model: V_s*I_s
model: J_i+J_e+J_{rec} probe
model: J_i+J_e+J_{rec} substrate
0,20
0,15
0,10
0,05
0,00
Q_{in} [J/s]
-100
-80
-60
-40
-20
0
20
V_S [V]

Fig.11

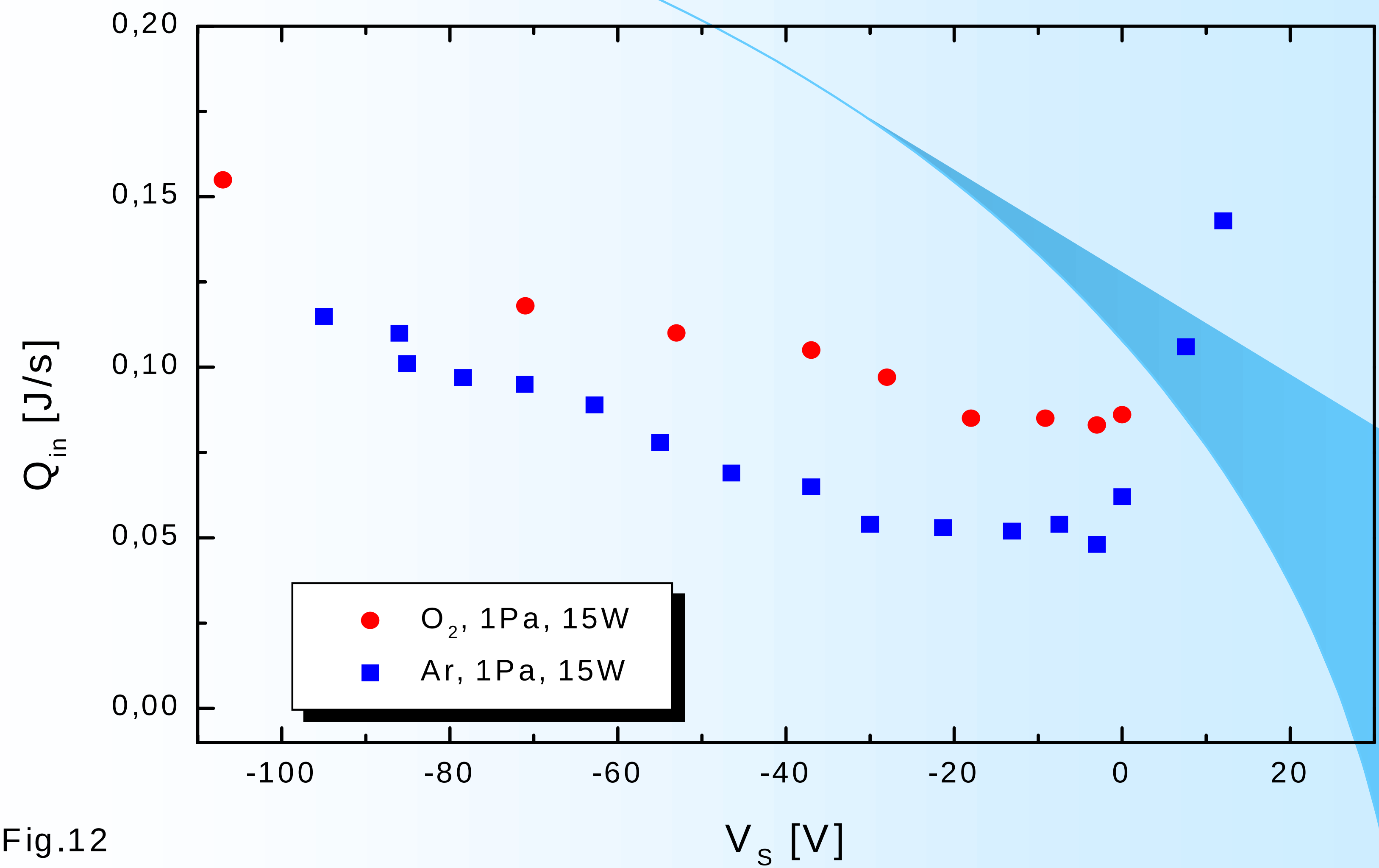

0,20
0,15
0,10
0,05
0,00
Q_{in} [J/s]
O_2, 1Pa, 15W
Ar, 1Pa, 15W
-100
-80
-60
-40
-20
0
20
V_S [V]

Fig.12