SEERS in Sampling Mode – A Tool to Investigate Dynamics in Pulsed R.F.-Plasma

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* Introduction - pulsed r.f.-plasma for polymerisation

* Task - SEERS in sampling for time resolved investigations

* Influence of external parameters on pulsed plasma

* Influence of disturbances

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Introduction

A pulsed r.f.-plasma was used to produce polymer coatings by plasma polymerisation of different monomers.

A continuous low-pressure plasma of glow discharge generates fragments of monomer molecules, which are required to generate a polymerisation on the sample surface. The mechanism can be characterised as an "atomic polymerisation" (H. Yasuda) or as "polyrecombination of radicals". (VUV radiation and collision by high energetic particles produce further destruction on the surface.)
A dense network of hydrocarbon with no or low similarity to the primarily used monomer structure is formed.

Using delay times between short r.f.-pulses (pulsed plasma mode) non-destroyed monomer molecules can react with radicals, formed at the surface during the previous plasma pulse. Such pulsed plasma produced polymer films are more stable against exposure to air. They exhibit a structure similar to those of classic polymers. The retention of the monomer structure in the formed pulsed plasma polymer layer depends strongly on the used plasma parameters.

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Influence of delay time on the formation of plasma polymerised film

(J.G.Calderon and R.B.Timmons, Macromolecules, Vol.31, 1998, 10, 3216 ff.)

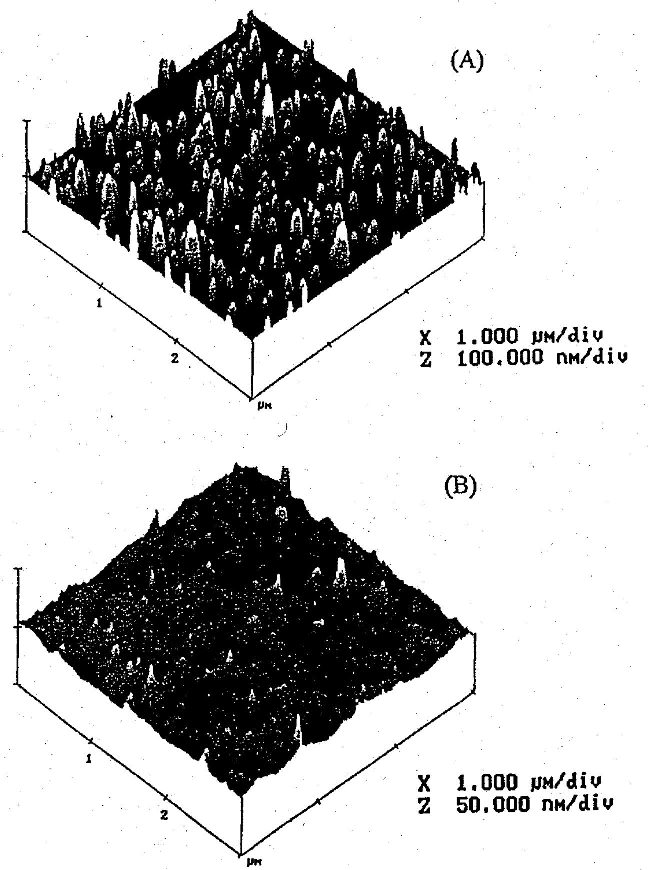
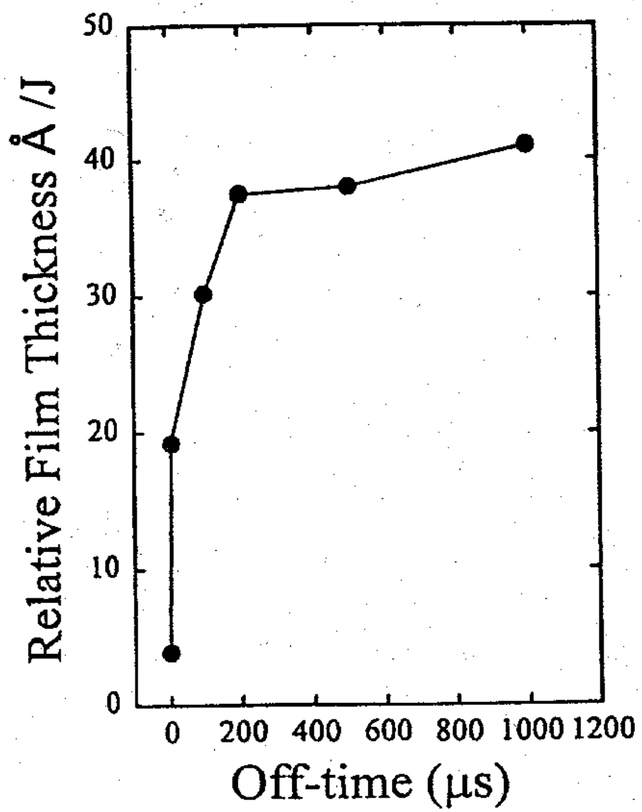
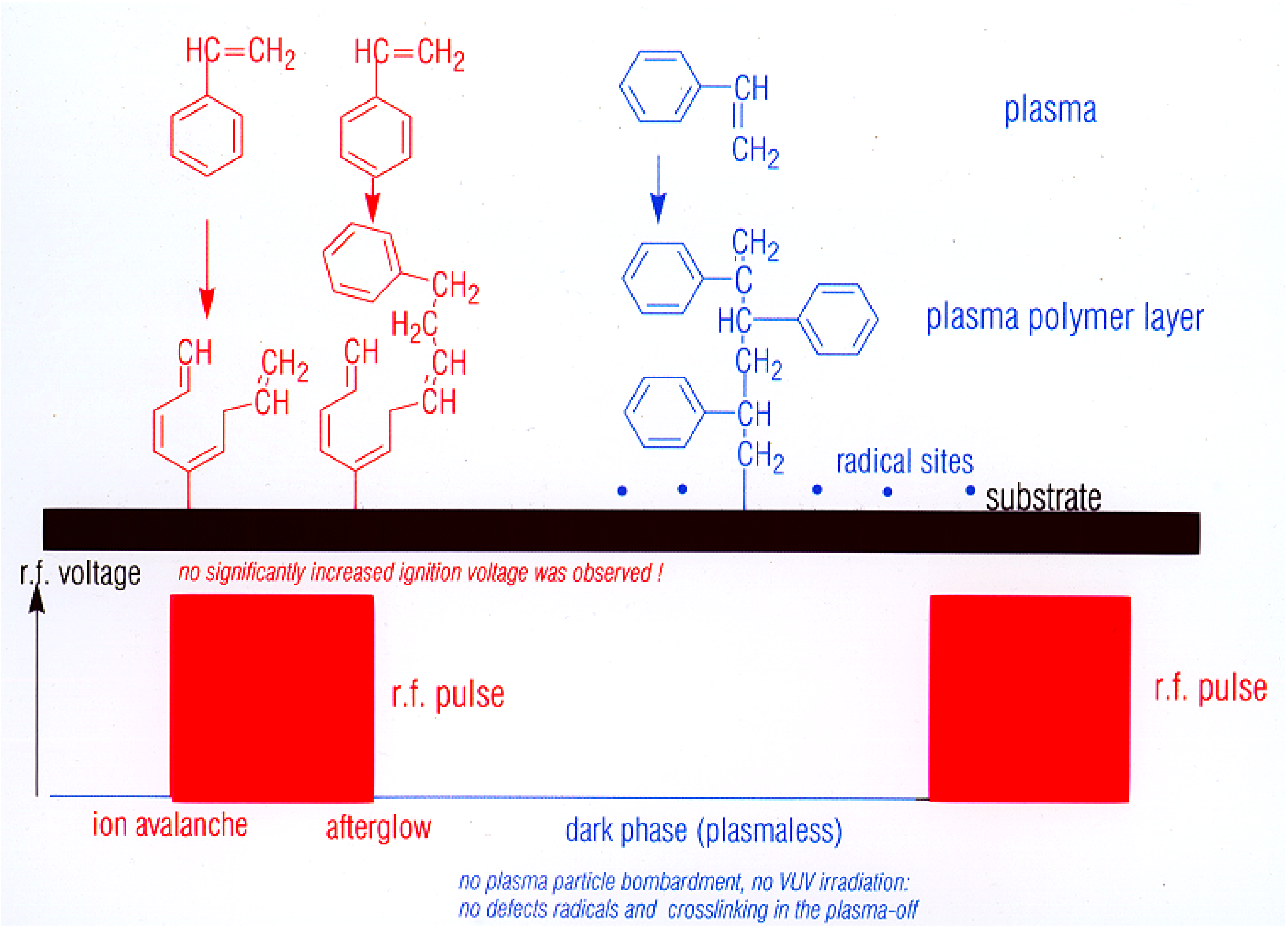


Figure 6. Surface morphology of films obtained at two different pulsed plasma duty cycles but constant peak power: (A) 10/50 μs, 200 W; (B) 10/1000 μs, 200 W. Note the change in vertical (i.e., *Z* scale) resolution employed.



Acryloyl chloride

Proposed mechanism of the pulsed plasma polymerisation of styrene



Problem

To solve the problems of
- more reproducibility,
- better structure and
- stability of plasma polymerised films

and to
- optimise the plasma polymerisation process for various monomers

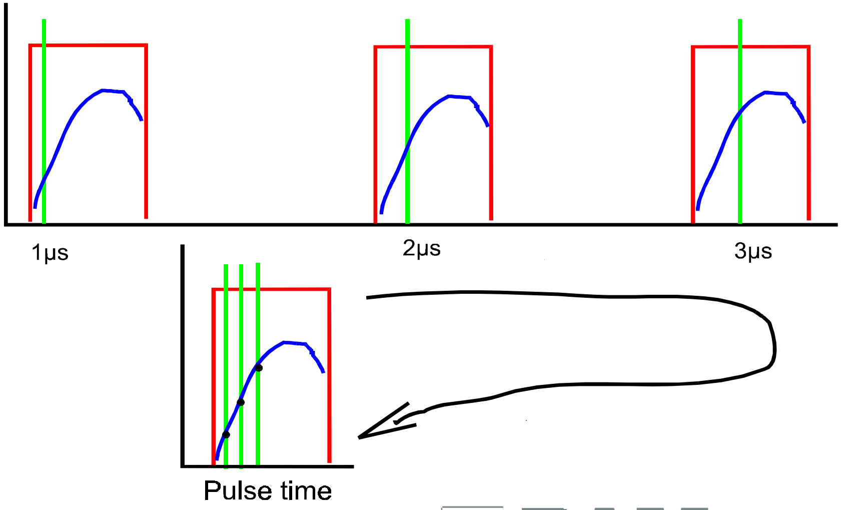
there is interest to study the real behaviour of ionising molecules in the short plasma pulse, as possible resolved in time.

Method

In contrary to Langmuir probes and optical methods the SEERS method has the benefit to be **not influenced** by continuously coating of the reactor walls.

Calculated parameters of **electron density n_e** and **electron collusion rate ny_e** should correspond to generation of free radicals necessary for further chemical reactions.

Data acquisition time of **less than 1 µs** for one measurement by the "Hercules" (ASI Berlin) allows to realise a sampling regime. With the modified apparatus we are able to investigate the real behaviour of the **time resolved parameters** within the r.f.-pulse.



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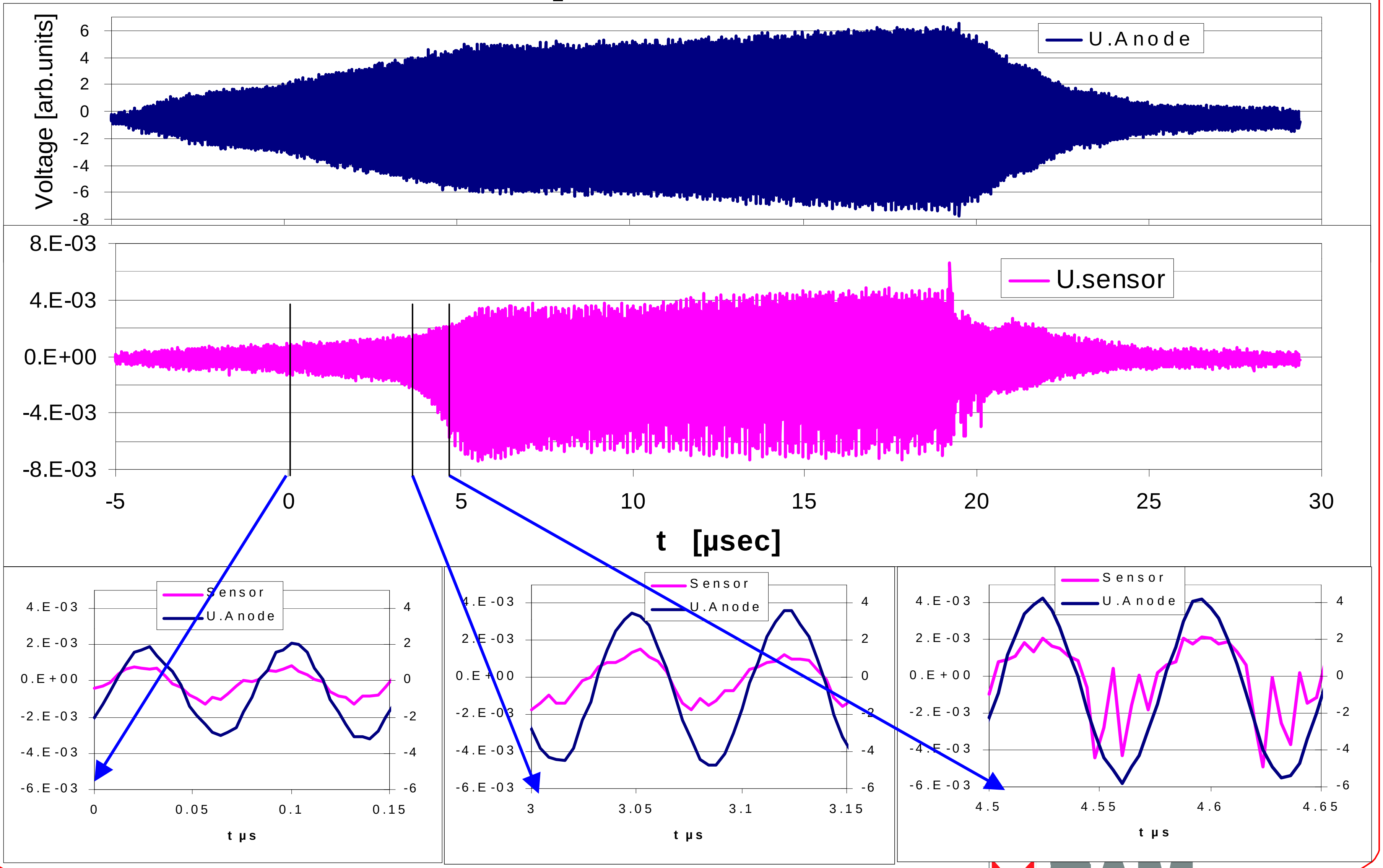
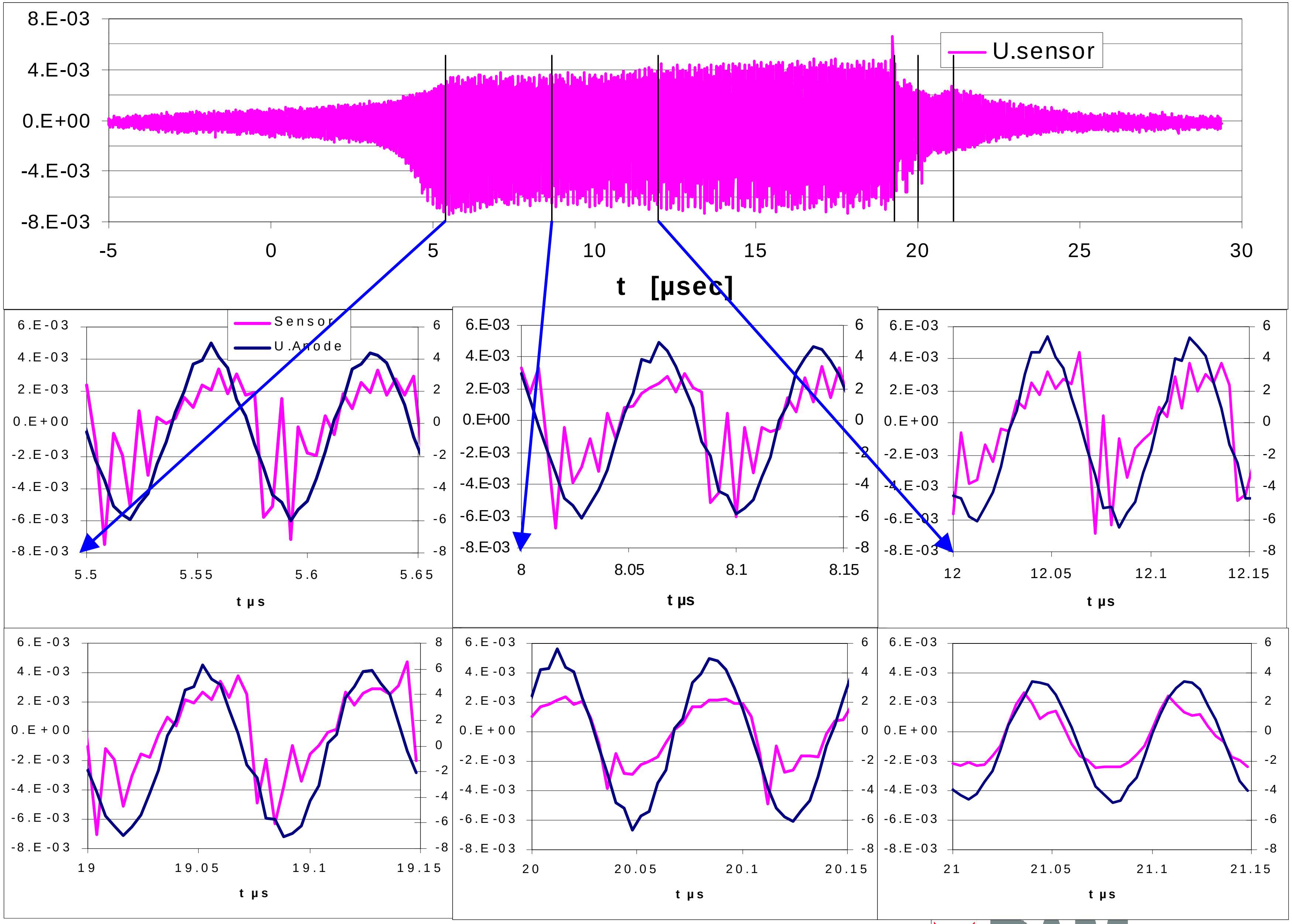
Plasma development in a 25µsec r.f.-pulse

N_2 5Pa 25W 10kHz




U.sensor
t [µsec]
Sensor
U.Anode
t µs
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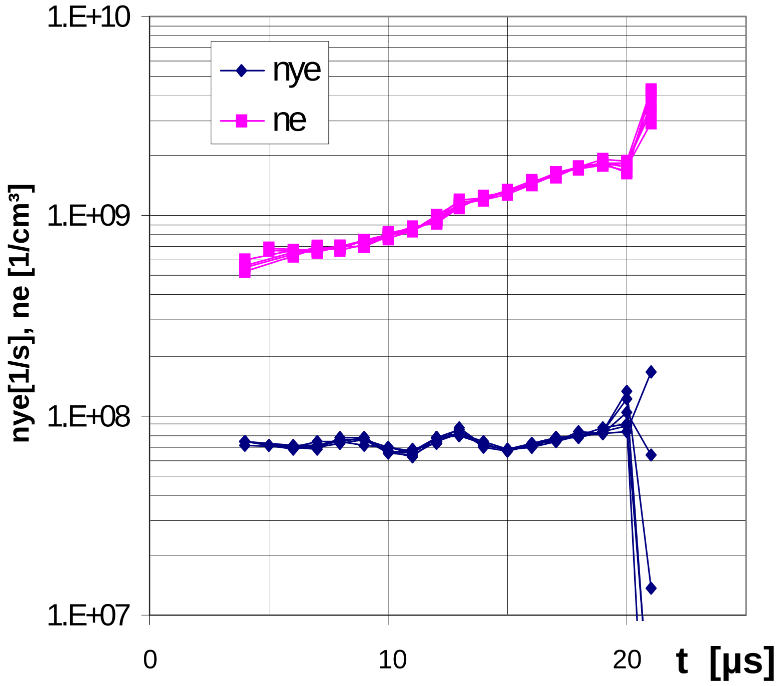
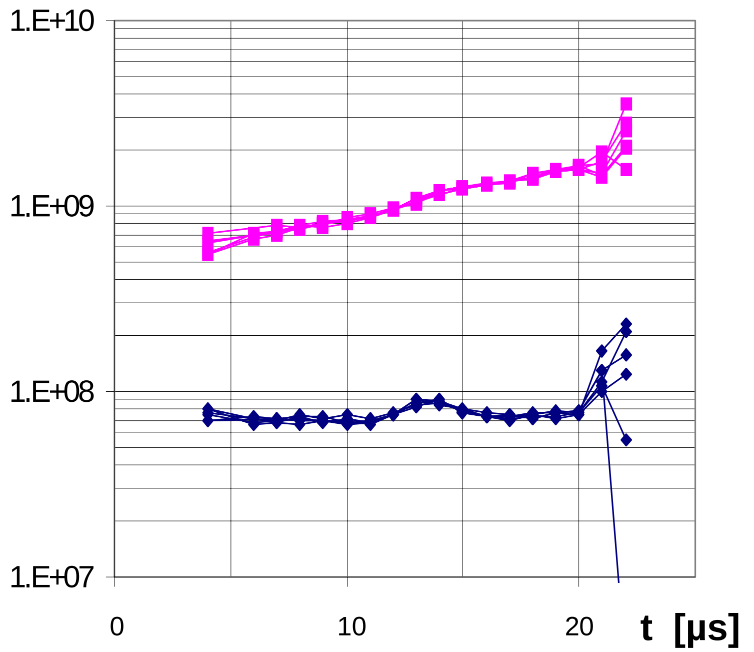
Influence of gas flow

Nitrogen, 5 Pa, 10kHz-25µsec 20W

15 sccm

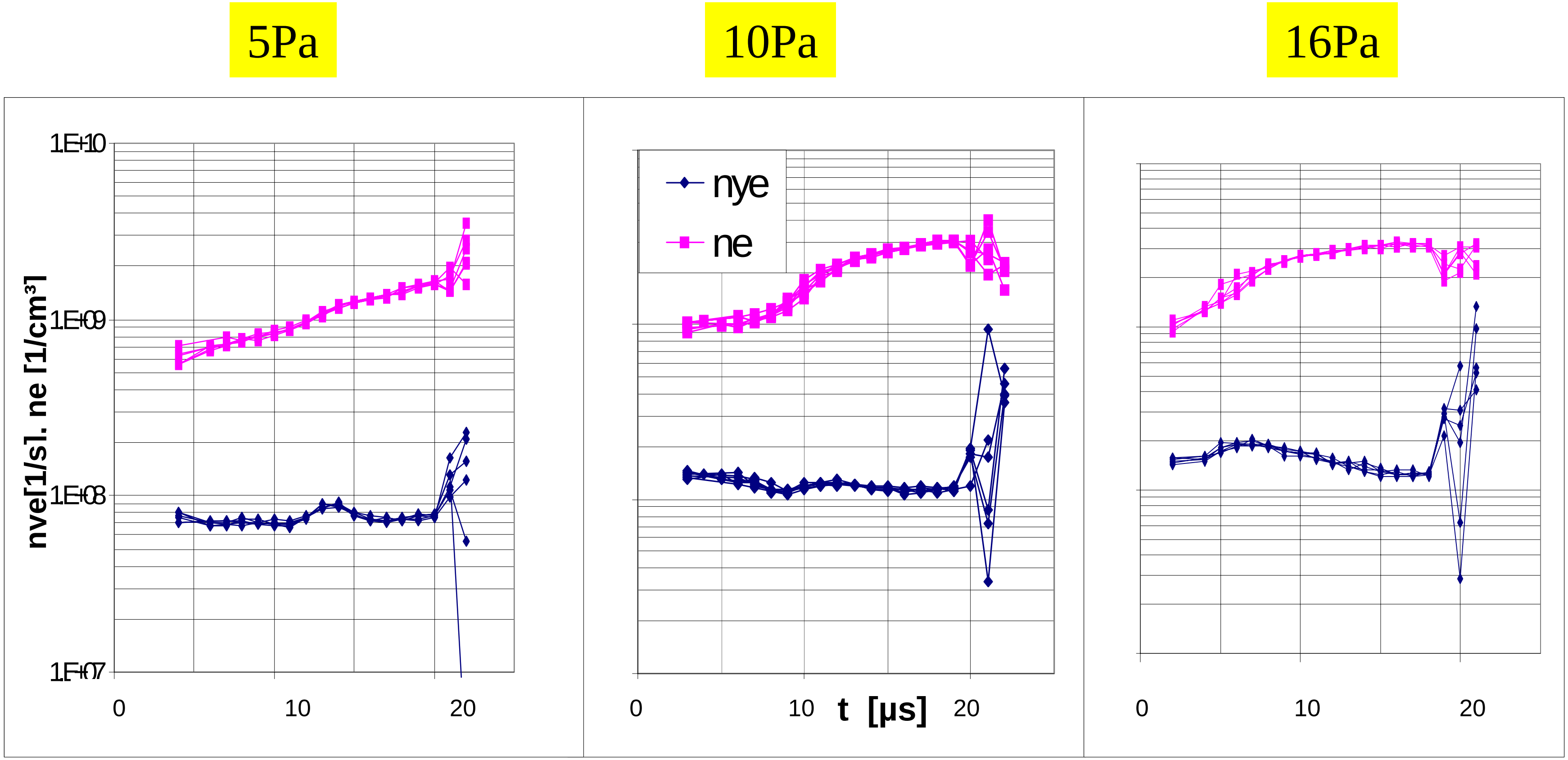
45 sccm





Influence of chamber pressure

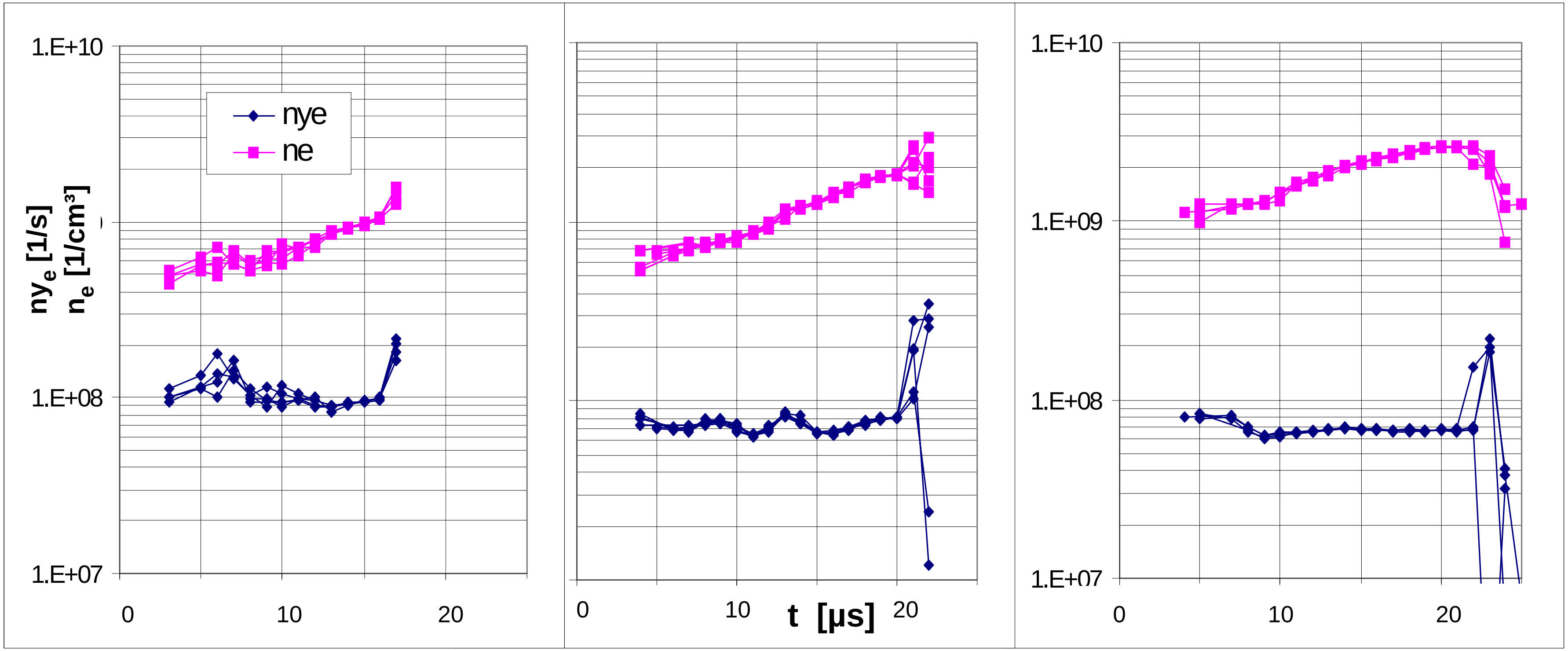
Nitrogen, 45sccm, 10kHz-25µsec 20W



Influence of r.f.-power

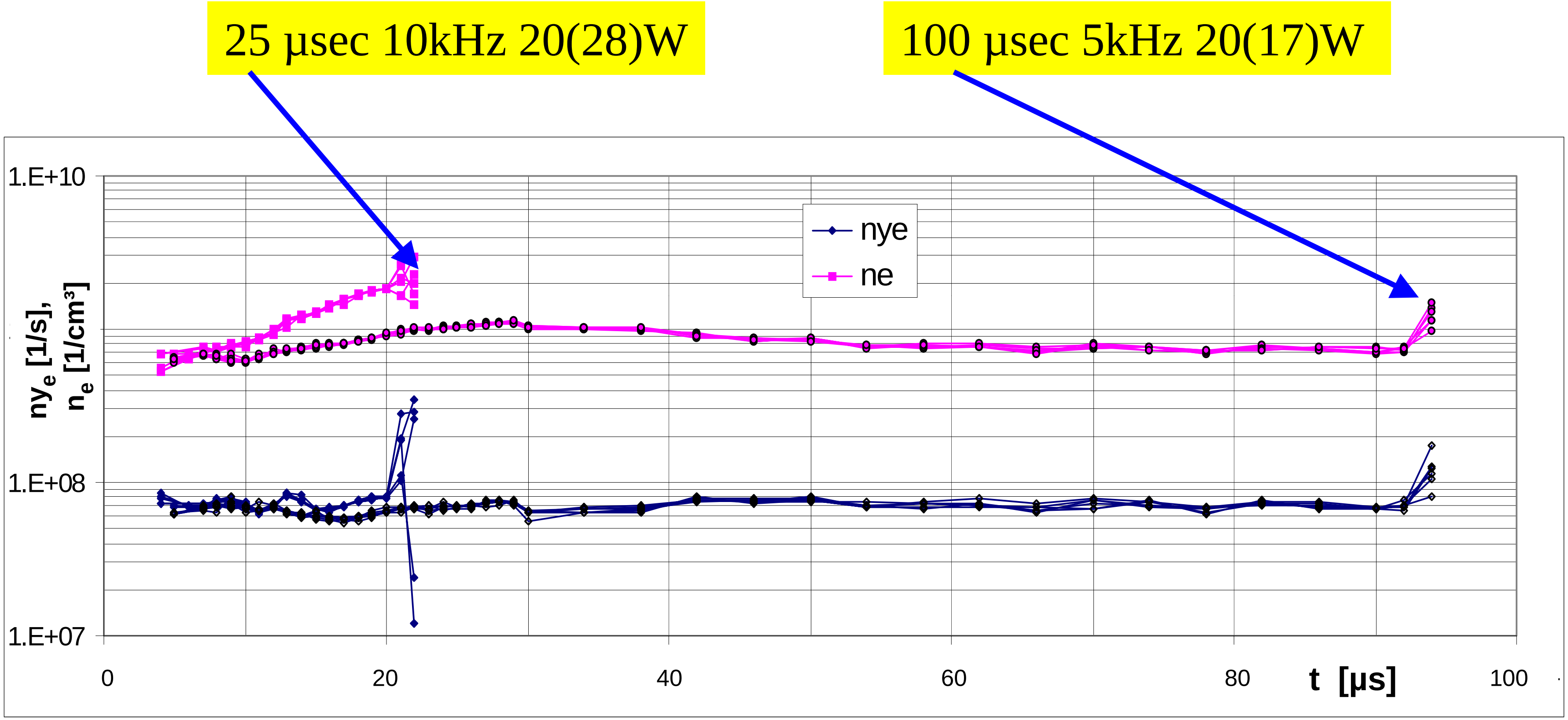
Nitrogen, 30 sccm, 5 Pa, 10kHz-25µsec

5 W | 20 W | 60 W



Influence of pulse time

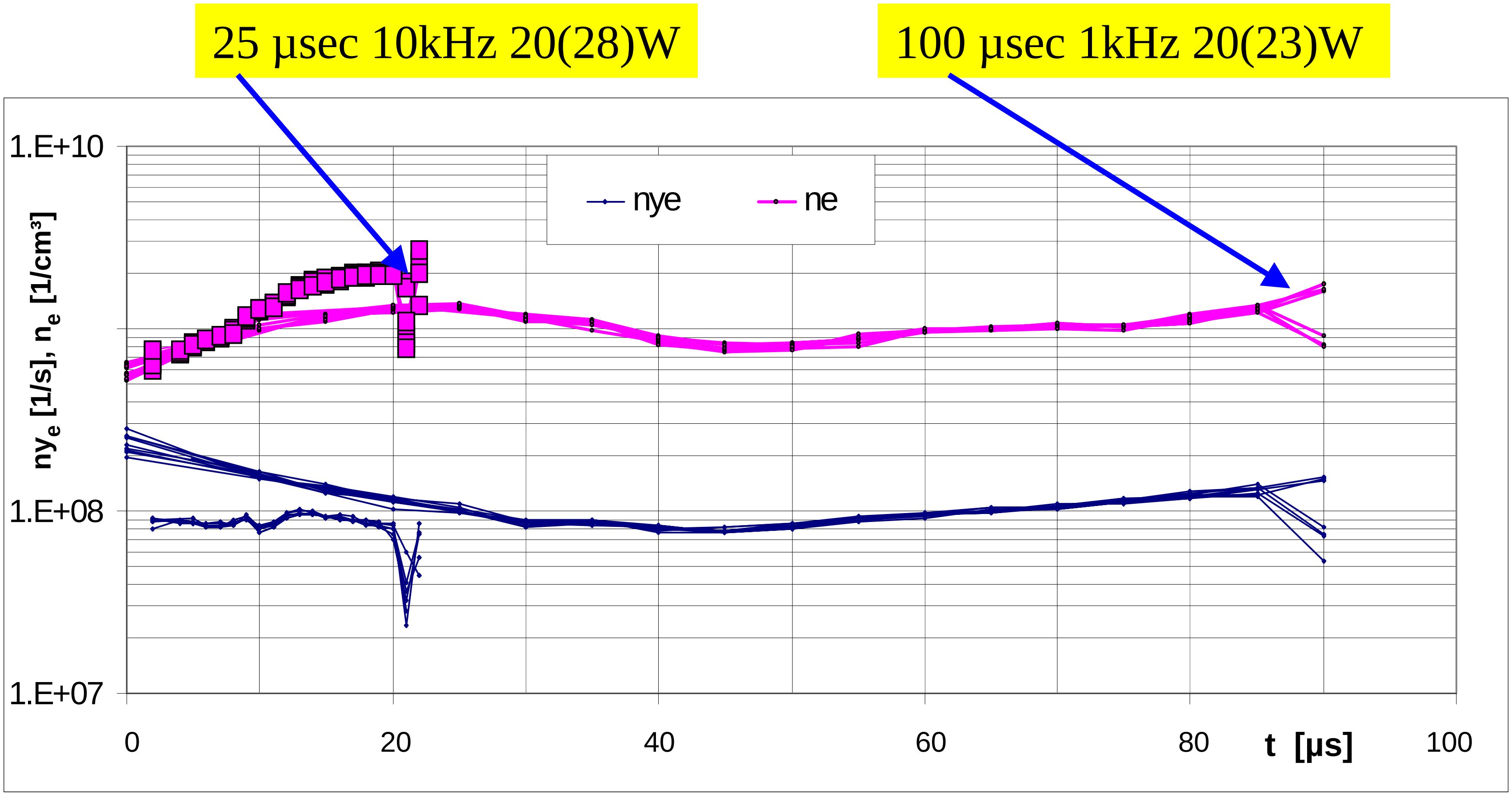
Nitrogen, 5 Pa, 30sccm, 20W



power: nominal (indicated in pulsed mode)

Influence of pulse time

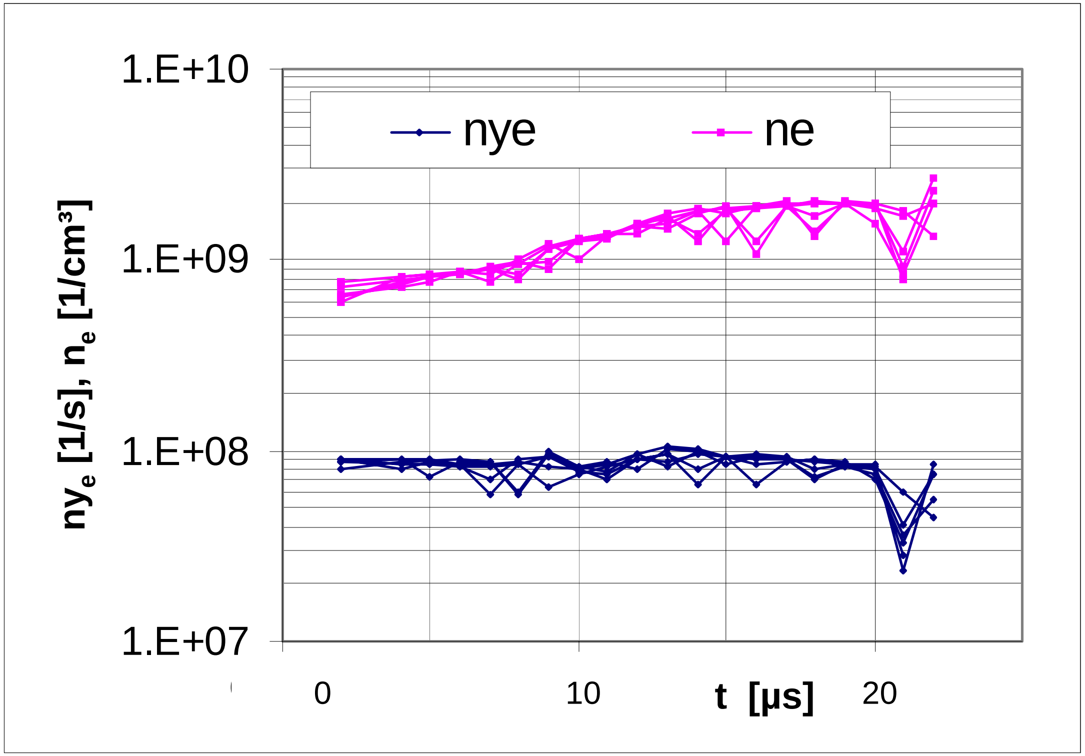
Ethylene, 4-6 Pa, 30sccm, 20W



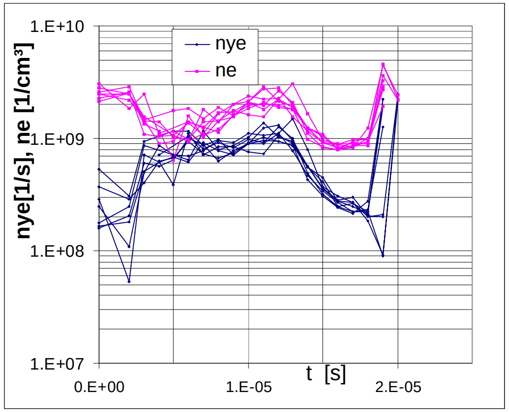
power: nominal (indicated in pulsed mode)

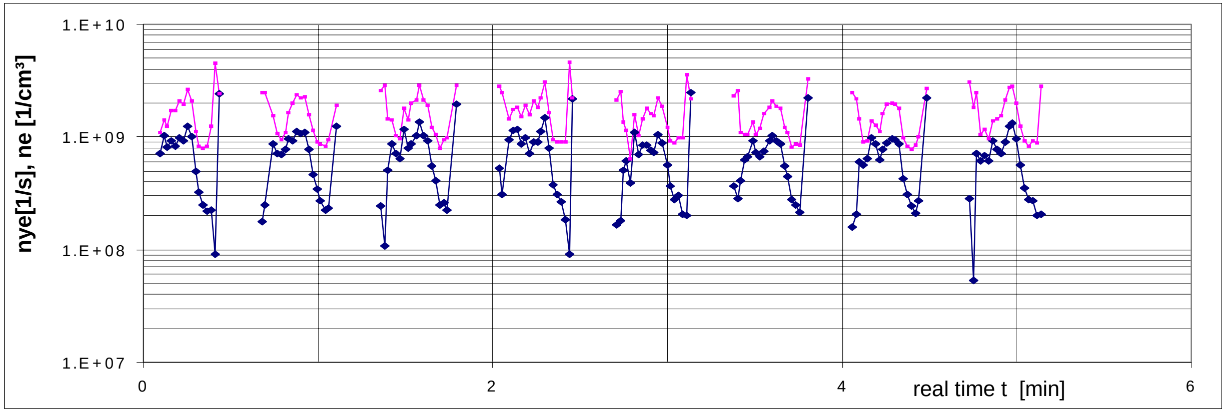
Influence of gas flow disturbance

ethylene, 5 Pa, 10kHz-25µsec 20W

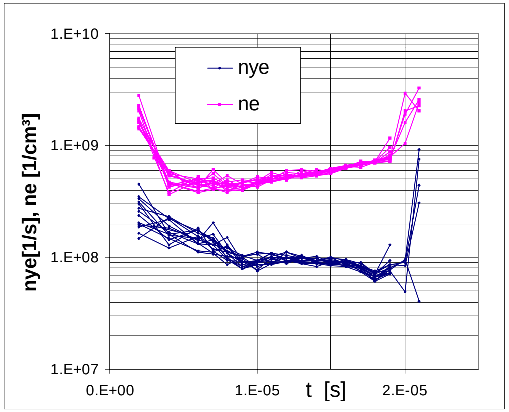


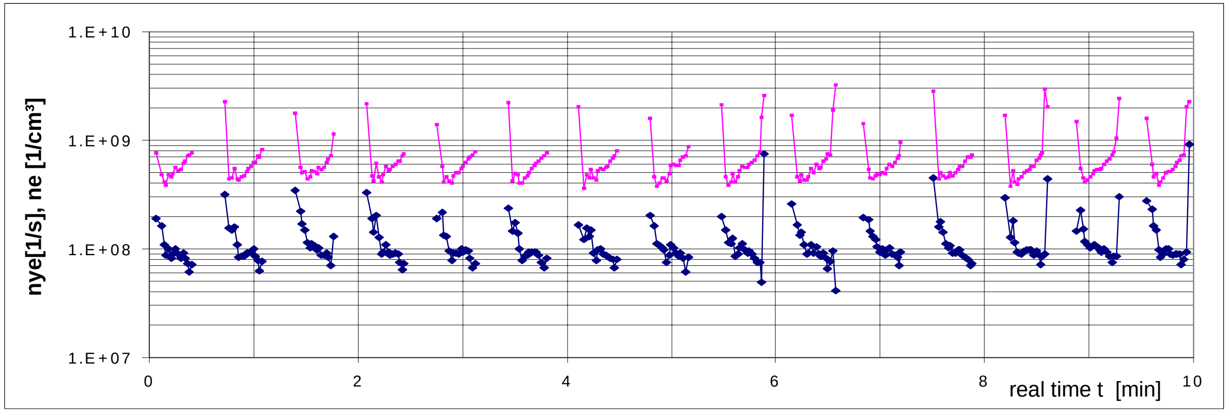
Styrene in pulsed plasma at pressure variation





5,5(14)Pa 20sccm, 15(24)W 10kHz 25µsec



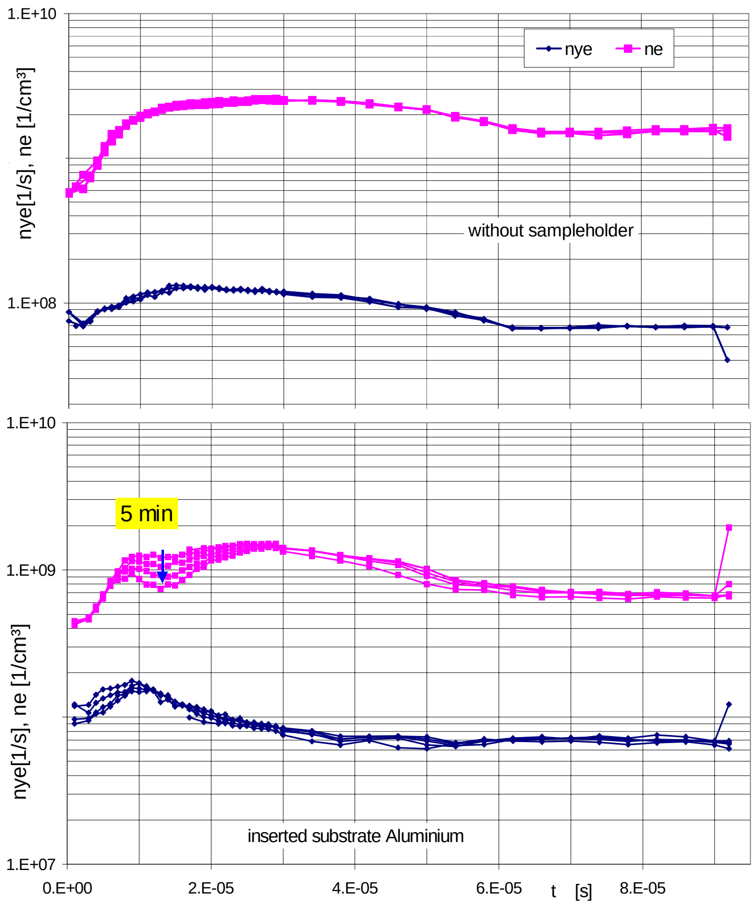


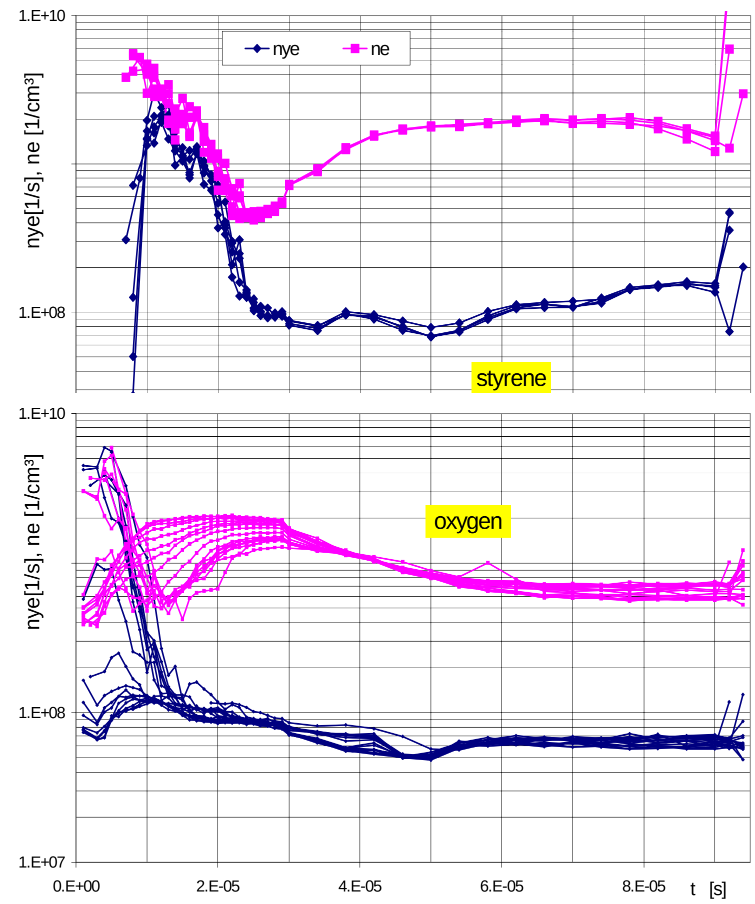
2(5)Pa 20sccm, 15(25)W 10kHz 25µsec

pressure: capacitance gage (Pirani gage)

power: nominal (indicated in pulsed mode)

Influence of chamber conditions and wall contamination

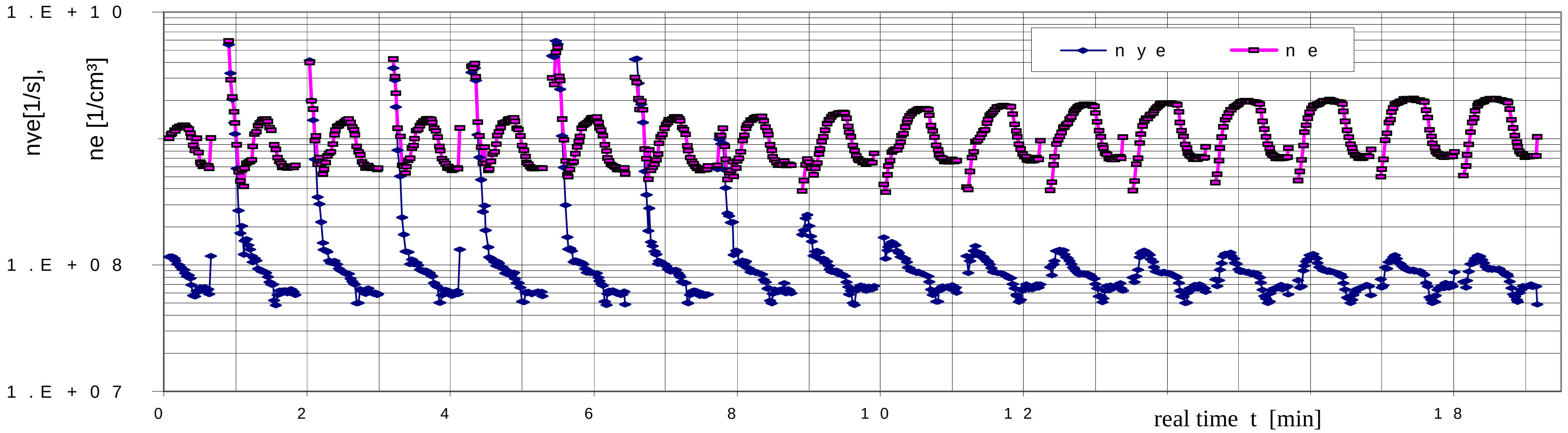




pulsed plasma: 5 min oxygen 5Pa 30sccm 100µsec 1kHz
a) oxygen without sample holder; 20(23)W
b) inserted sample holder with Al substrate; 20(23)W
changes during 5 minutes

pulsed plasma: 5 min 100µsec 1kHz
c) plasma polymerisation of **styrene** 20sccm 20(11)W 2(5)Pa
d) without sample holder as (a); oxygen 5Pa 30sccm 20(28)W
changes during 5 minutes

Oxygen pulsed plasma in styrene contaminated chamber



Calculated parameters of graphic (d) in real time scale (not equidistant relation in pulse time)

Summary

Using a sampled SEERS
the parameters of pulsed r.f.-plasma have been investigated in time resolution.

For nitrogen and oxygen we established an influence of
- input power
- chamber pressure
- time of pulse length

but - no influence of gas flow
(at our conditions)
- no notable differences between nitrogen and oxygen according to comparable atomic properties.

At pulse time variation the amplitude behaviour seems to be more complex and needs further investigation

Pulsed plasma polymerisation conditions show comparable behaviour, but are less stable (suggested chamber contamination).

Using ethylene and styrene we demonstrated the influence of pressure variation or gas flow disturbances .

The method is extreme sensitive to changes in plasma conditions.

The results suggest an essential influence of the chamber wall (and sample and holder surface) isolation on the plasma development in the r.f.- pulse.

The SEERS method is extremely sensitive to changes in plasma conditions and an useful tool to compare plasma conditions.

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