Plasma parameters - time resolved investigations down to 1µs inside cyclic pulses of pulsed r.f.-plasma by modified SEERS

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

* Task - principle of Self Excited Electron Plasma Resonance Spectroscopy (SEERS) and of time equivalent sampling

* Influence of external parameters on pulsed plasma

* Influence of disturbances

VIth International Workshop on Plasma-Based Ion Implantation (PBII - 2001), June 26-28, 2001 - Grenoble, France
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.

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.
Proposed mechanism of the pulsed plasma polymerisation of styrene

[Diagram showing the proposed mechanism with chemical structures and labels for plasma, plasma polymer layer, radical sites, substrate, r.f. voltage, ion avalanche, afterglow, dark phase (plasmaless)]

- No significantly increased ignition voltage was observed.
- No plasma particle bombardment, no VUV irradiation.
- No defects, radicals, and crosslinking in the plasma-off.
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.

Film deposition on chamber walls and sensor should not influence on the measurement.

Self Excited Electron Resonance Spectroscopy
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.

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Theory of Hercules

SEERS is based on the nonlinearity of the space charge sheath at the rf-electrode, which provides harmonics with the modulated sheath width and high-frequency oscillations in the bulk plasma.

Using a hydrodynamic approach for the plasma body, the inert mass of the electrons can be treated as an inductance and the collisions with neutrals (including power dissipation in the expanding sheath) as a resistance. Taking into account the capacitive behavior of the space charge sheath, the plasma can be regarded as a damped oscillation circuit. The nonlinear sheath capacitance excites the plasma by causing damped oscillations close to the geometric resonance frequency which lies well below the plasma frequency (Langmuir frequency). For asymmetrical discharges the current is known to be the sum of a saw tooth shaped part plus a damped oscillation.

SEERS allows to determine simultaneously the volume averaged

- electron density  
  \[ \tilde{n} = \frac{1}{v} \left( \int_{v} n^{-1} dV \right)^{-1} \]

- electron collision rate  
  \[ \tilde{v} = \frac{\tilde{n}}{v} \int_{v} \frac{dV}{n} \]

- power dissipated in plasma body  
  \[ P_p = \frac{U_b v \omega A_0}{4 \kappa_e (1 - \tilde{\eta})^2} \frac{m_e e_0}{\epsilon} \]

Using a fast numerical algorithm the plasma monitoring system Hercules provides a temporal resolution better than half a second and performs SEERS measurements automatically. The peak voltage of the substrate was measured by using a capacitive voltage divider. Hercules used a special sensor. The measured discharge current signal is converted using a fast ADC (analog/digital converter) with a bandwidth of 500 MHz and a sampling rate of 2 GS/s.

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Data acquisition time of less than 1 μs for one measurement by the "Hercules" (ASI Berlin) allows to realise a sampling regime with continuous shift of trigger delay.

With the modified apparatus we are able to investigate the real behaviour of the time resolved parameters within the r.f.-pulse.

Method of equivalent time sampling

Calculated parameters of electron density \( n_e \) and electron collision rate \( v_e \) should correspond to generation of free radicals necessary for further chemical reactions.
Plasma development in a 25µsec r.f.-pulse

Nitrogen 5Pa 25W 10kHz
Influence of gas flow
Nitrogen, 5 Pa, 10kHz-25µsec 20W

15 sccm

45 sccm
Influence of chamber pressure
Nitrogen, 45sccm, 10kHz-25µsec 20W

5Pa

10Pa

16Pa
Influence of r.f.-power
Nitrogen, 30 sccm, 5 Pa, 10 kHz-25 µsec

5 W  
20 W  
60 W

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In the diagram, the influence of r.f.-power on the electron density $n_e$ is shown for different power levels (5 W, 20 W, and 60 W) with nitrogen as the working gas. The data is presented in a log-log scale for a time $t$ ranging from 0 to 20 µs. The graphs illustrate the changes in $n_e$ and $v_e$ (electron mobility) over time, with distinct markers indicating specific data points. The x-axis represents time in microseconds, while the y-axis represents the electron density $n_e$ and electron mobility $v_e$ in logarithmic scale.
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

25 µsec 10kHz 20(28)W
100 µsec 1kHz 20(23)W

nye [1/s], ne [1/cm³]

power: nominal (indicated in pulsed mode)
Pulse variation with power and delay time
oxygene, 5 Pa, 30sccm

Offset voltage discharges with increasing delay time
Long delay time requires an higher amplitude (power voltage) to ignite r.f.-plasma
after ~50 µs Offset has established
Reproducibility of plasma parameters

oxygen, 5 Pa, T= 3000µs (333Hz) 100W, Pulse-on time variation
Influence of gas flow disturbance
ethylene, 5 Pa, 10kHz-25μsec 20W
Styrene in pulsed plasma at pressure variation

5.5(14) Pa 20 sccm, 15(24) W 10 kHz 25 µsec


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
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)
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 extreme pulse and delay time variations the plasma behaviour depends also from power supply regulation and shows a more complex behaviour.

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 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.