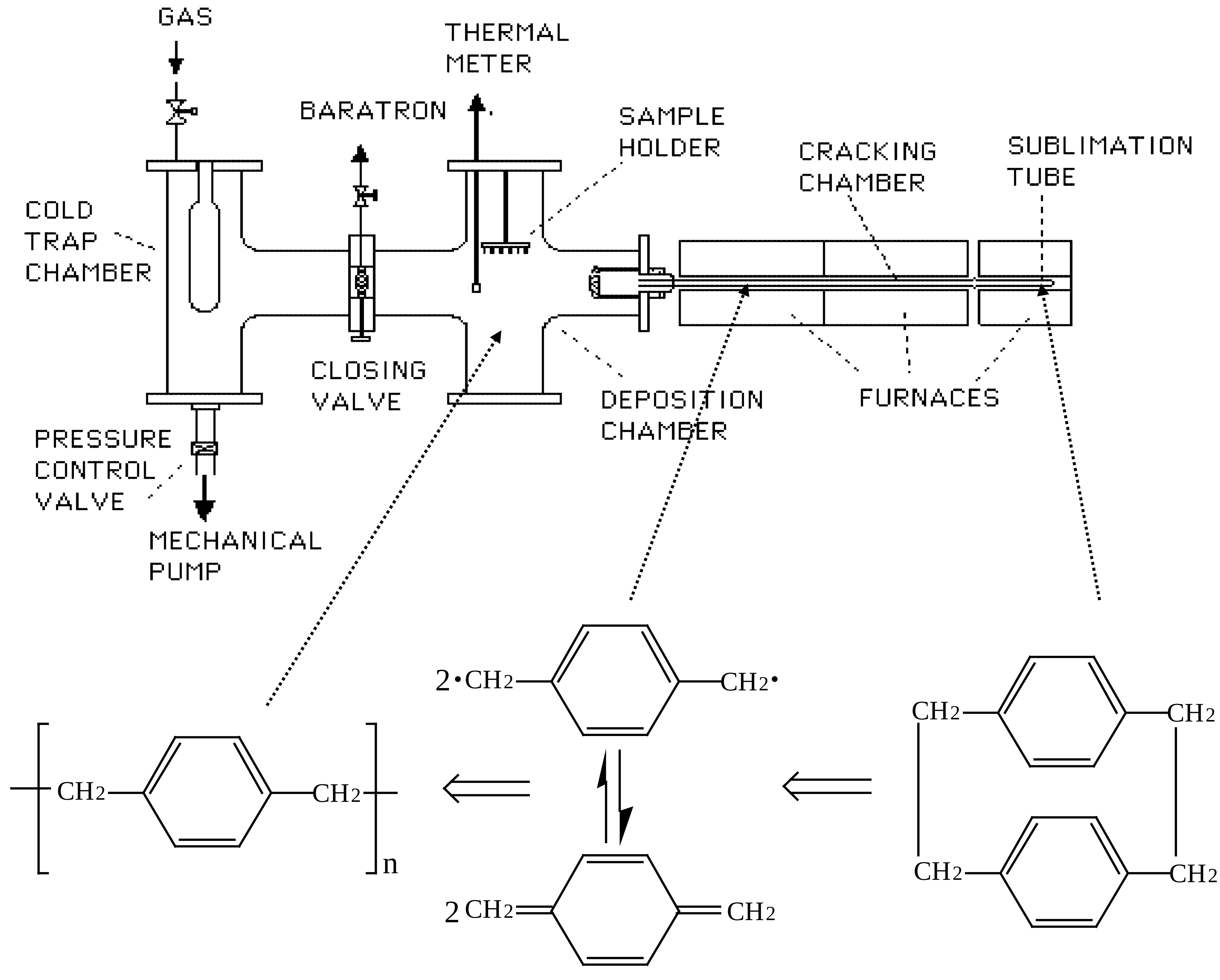
Polymer Formation in Plasma

- Polymerization (conventional, molecular)
- Plasma Polymerization, (atomic)
- Competitive Ablation and Polymerization (CAP)
- Plasma Sensitivity of Elements
- DC Discharge Polymerization
- Field Effects
- Influence of Wall Contamination

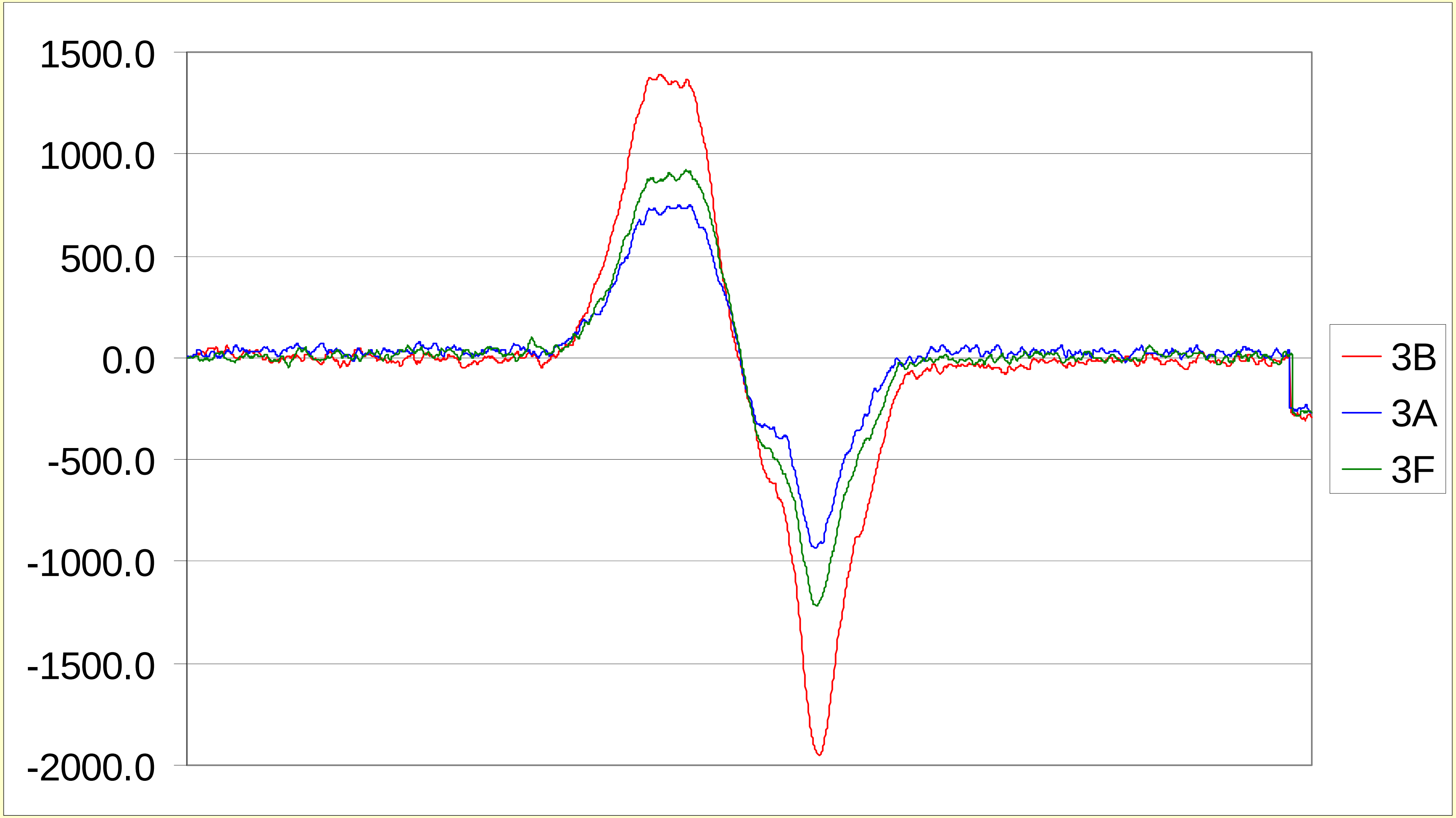
Processes that yield solid deposition from gas phase

- Thermal Activation
  - Chemical Vapor Deposition (CVD)
  - Hot Wire CVD
  - Parylene Polymerization*
- Plasma Activation
  - Plasma Enhanced CVD (PECVD)
  - Plasma Assisted CVD (PACVD)
  - Plasma CVD or Plasma Polymerization*

- * Large amount of free radicals are found in the deposition.


GAS
THERMAL METER
BARATRON
SAMPLE HOLDER
CRACKING CHAMBER
SUBLIMATION TUBE
COLD TRAP CHAMBER
CLOSING VALVE
DEPOSITION CHAMBER
FURNACES
PRESSURE CONTROL VALVE
MECHANICAL PUMP
2•CH2 CH2•
2 CH2 CH2
CH2 CH2
CH2 CH2
CH2 CH2
n

Trapped free radicals (dangling bonds) in plasma polymer



Two major mechanisms of polymerization

Chain-Growth Polymerization

Step-growth Polymerization

Molecular Polymerization

Need specific chemical structures

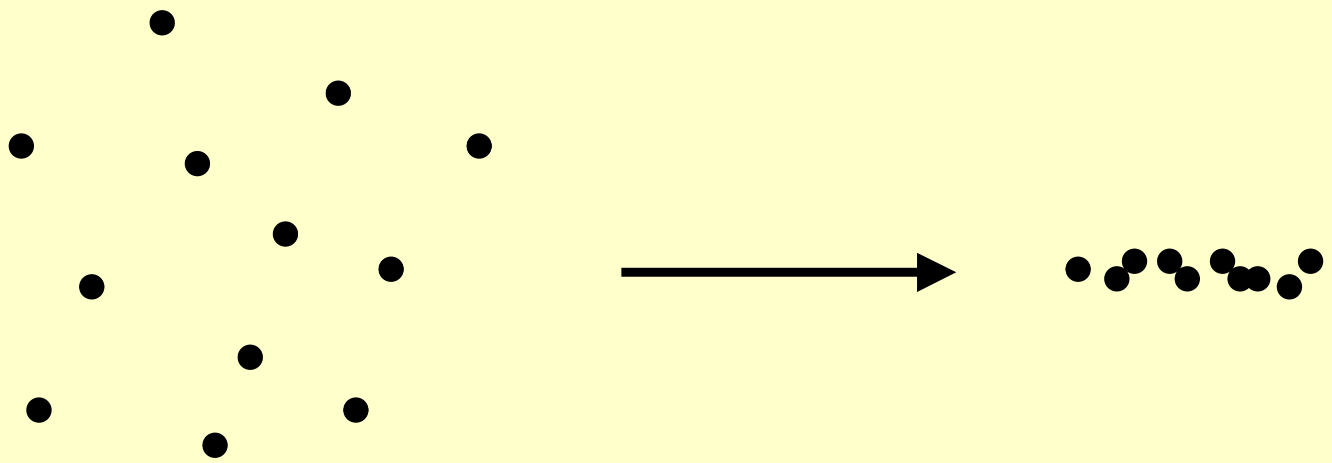
Building Blocks are monomer molecules

Free Radical Chain-Growth Polymerization

Initiation	$I\bullet$ + M	$\longrightarrow$	$IM\bullet$
Propagation	$IM\bullet$ + M	$\longrightarrow$	$IMM\bullet$
	$IM_n\bullet$ + M	$\longrightarrow$	$RM_{(n+1)}\bullet$
Termination	$IM_n\bullet$ + $IM_m\bullet$	$\longrightarrow$	$IM_{(n+m)}I$

No free radical in the product polymer

2 free radicals and 10,000 monomers yields a polymer with the degree of polymerization 10,000



$$\Delta F = \Delta H - T\,\Delta S$$

$$S = k \ln \Omega$$

$-T\,\Delta S$ term is positive for polymerization

ΔH is limited by the difference of bond energies

Polymerization does not proceed in gas phase

Too many free radicals are formed in plasma, and very small amount of monomer exist in plasma phase.

The degree of polymerization decreases inversely proportional to the concentration of the initiator.

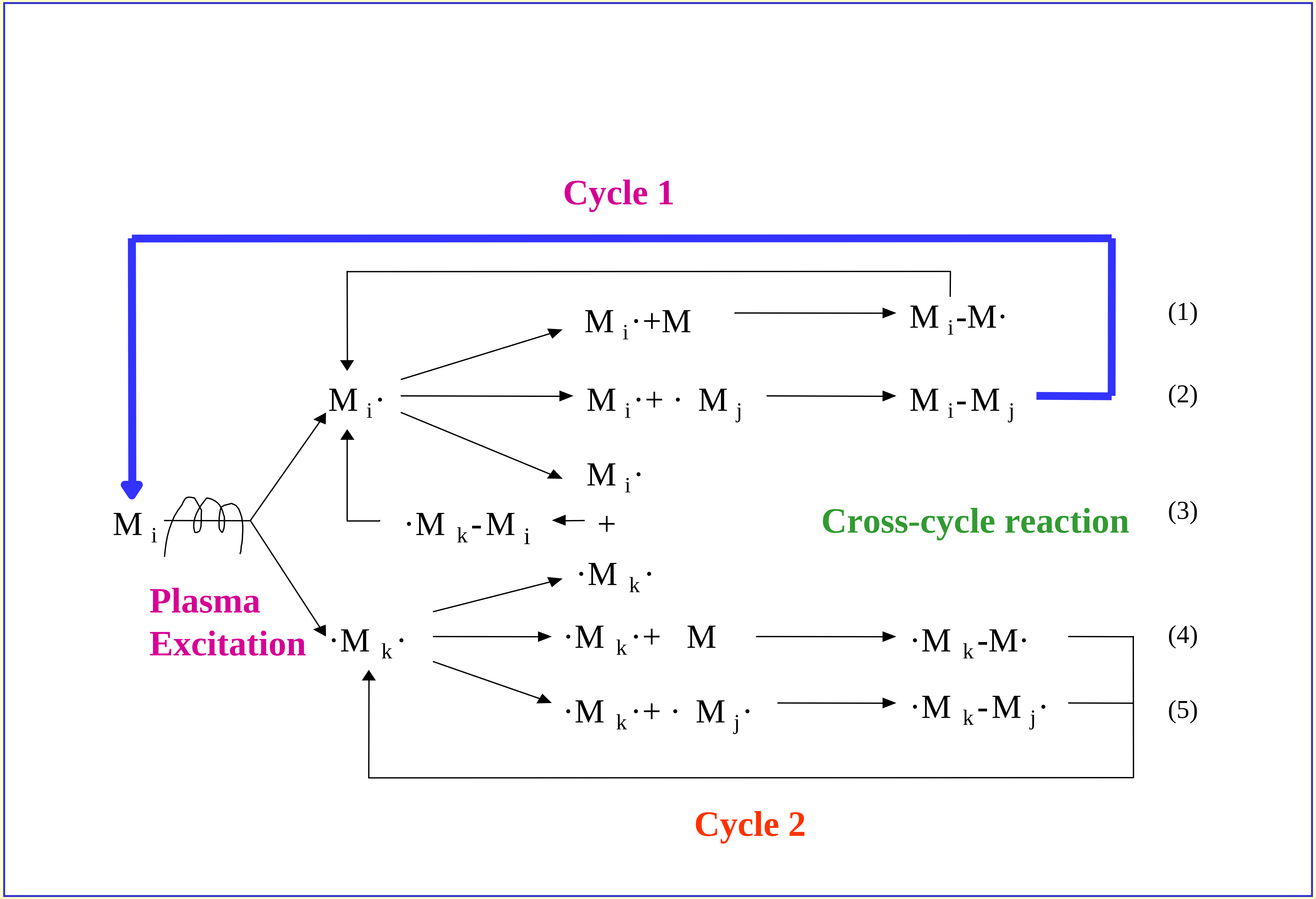
A great number of free radicals exist in plasma polymers.

→ **Plasma polymers are formed by coupling of free radicals.**

Not by the free radical chain growth polymerization

→ **What is the mechanism of plasma polymerization?**

Rapid Step-Growth Polymerization (RSGP) Mechanism



Plasma Polymerization

- **“Atomic” Polymerization**
  - No specific chemical structure is necessary.
- Fragmentation of monomer molecule
- Scrambling of atoms
- Building Blocks are not the original monomer molecule, but atoms liberated by the fragmentation of monomer molecule.
- Characteristic deposition rate for each element
- Key parameter is W/FM in J/kg.
  - W is wattage, F is volume flow rate, and M is molecular weight.

Typical Operational Range of Plasma Polymerization

- W/FM 10 MJ/kg – 10 GJ/kg
- F & W depends on the volume of reactor
  - 100 Liter reactor
    - 1 – 10 sccm
    - 5 – 100 watts
  - The increase of F has the same effect as the decrease of W, and vise versa.
- Current density in DC polymerization
  - Less than 1 mA/cm^2, V 0.5 – 1.5 kV

Input Energy & Bond Energy

- Input energy is given by W/FM in J/kg.
- Specific bond energy of a molecule, which could be defined as $\Phi = \Sigma$(bond energy)/M, is given also in J/kg.
  - Ethylene 80 MJ//kg
  - Tetrafluoroethylene 26 MJ/kg
- When W/FM exceeds ~ 20 times Φ, plasma polymerization becomes a typical **atomic** polymerization, and the molecular structures play little role in determining the characteristics of plasma polymers.

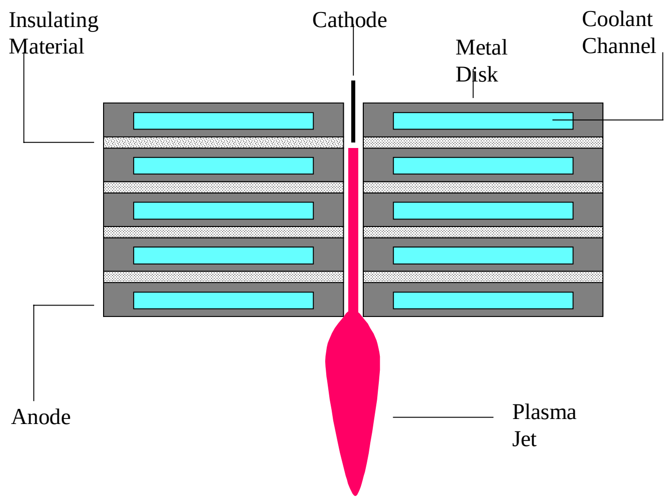
Contrast of Polymer Characteristics

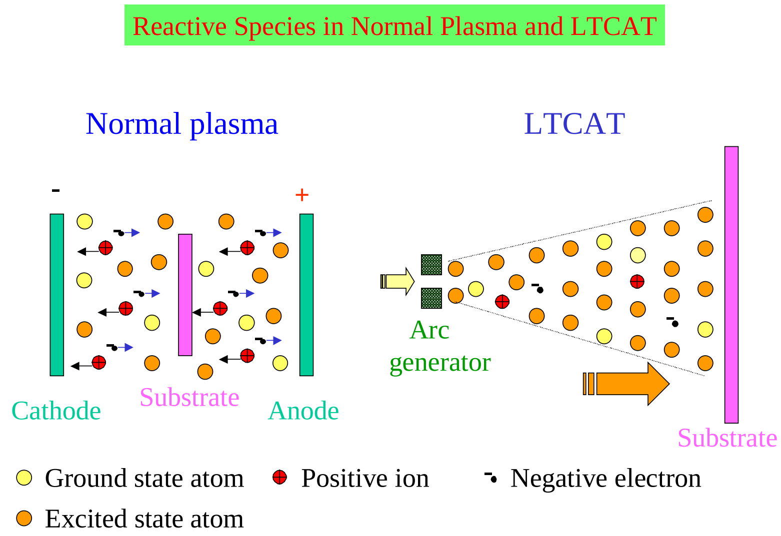
- **Conventional free-radical polymerization**
  - **Free-radical chain-growth polymerization**
    - **Linear polymer with no dangling bonds**
    - **Soluble and fusible**
    - **Positive temperature dependence of polymerization**
    - **Semi-crystalline**
- **Plasma polymerization**
  - **Free-radical recombination step-growth polymerization**
    - **Tight three dimensional network with dangling bonds**
    - **Insoluble & infusible**
    - **Negative temperature dependence of deposition/polymerization**
    - **Amorphous C-H, Si-H, Si-C-H, etc.**

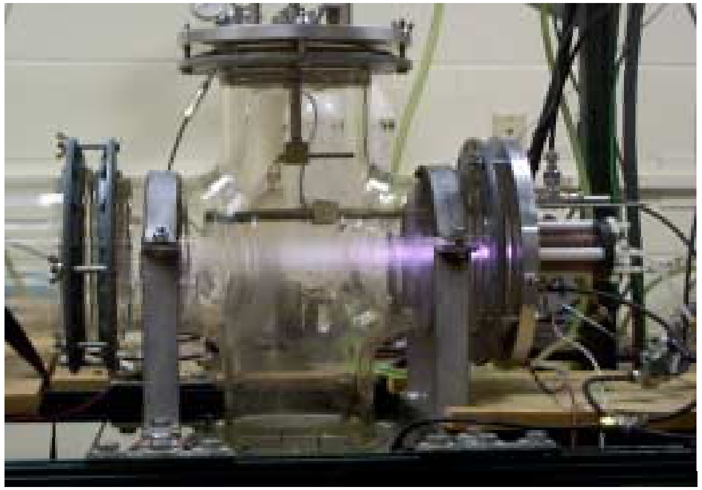
Electronegativity Values for Some Elements

H			
2.1			
C	N	O	F
2.5	3.0	3.5	4.0
Si	P	S	Cl
1.8	2.1	2.5	3.0

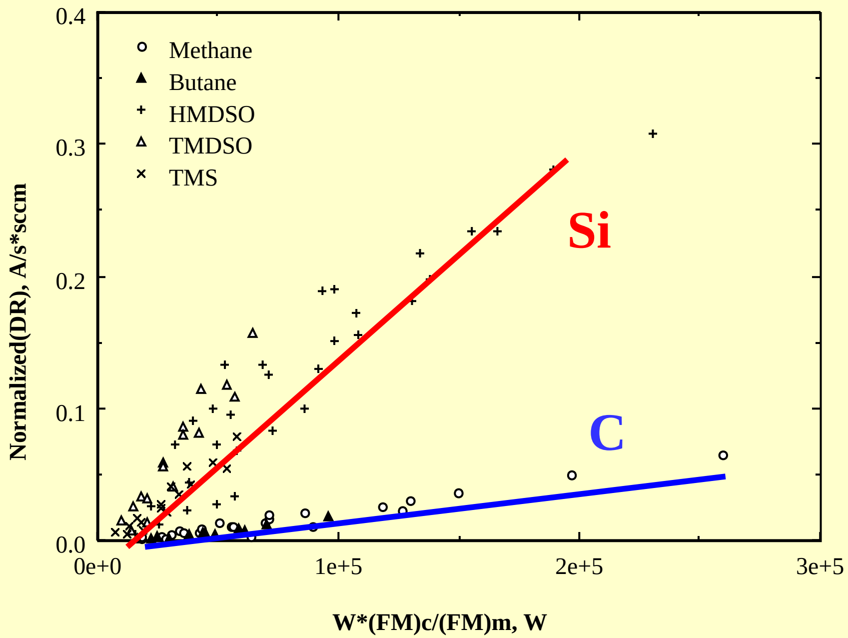
Each Element Has Its Own Characteristic Polymerization Rate

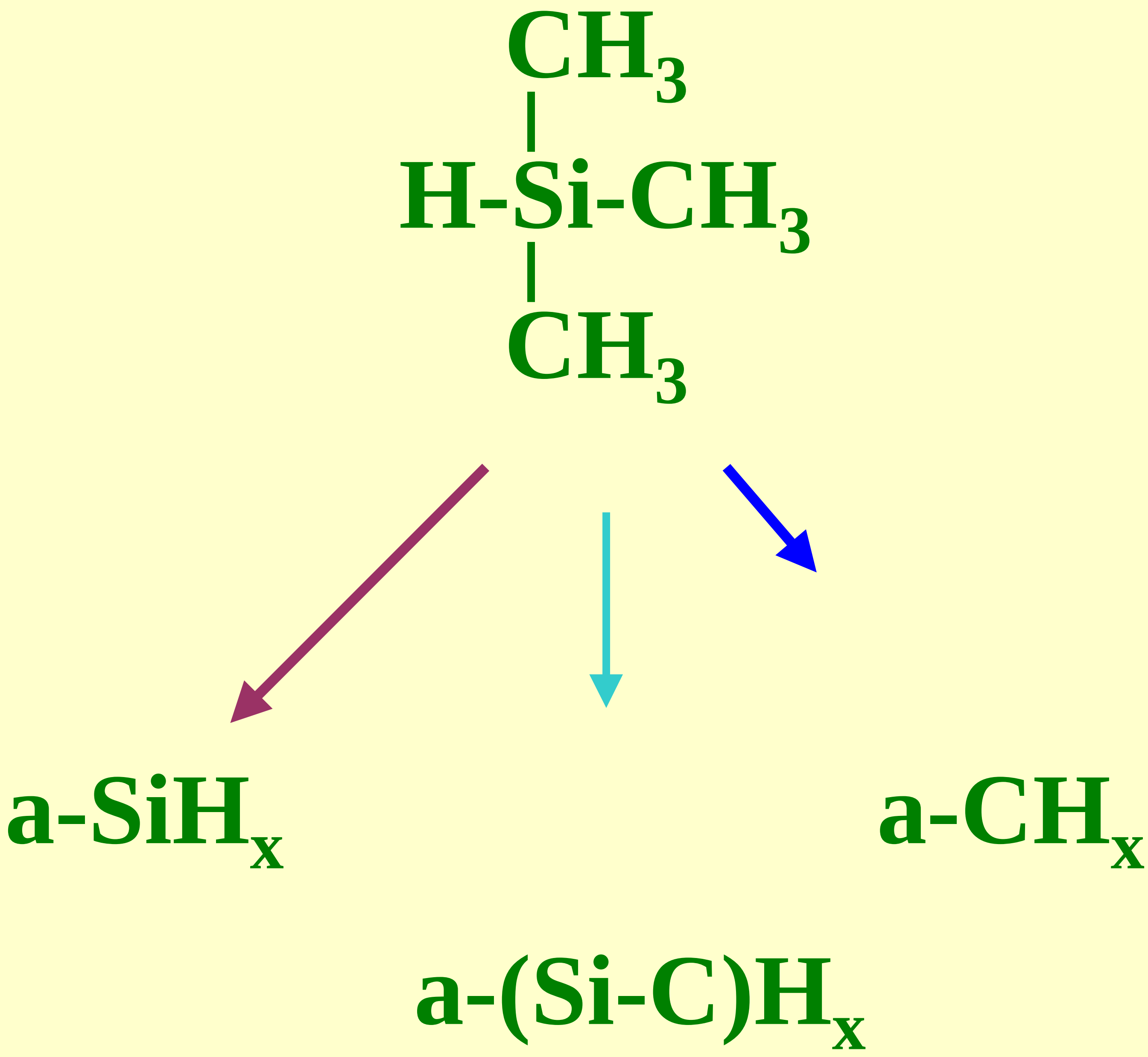




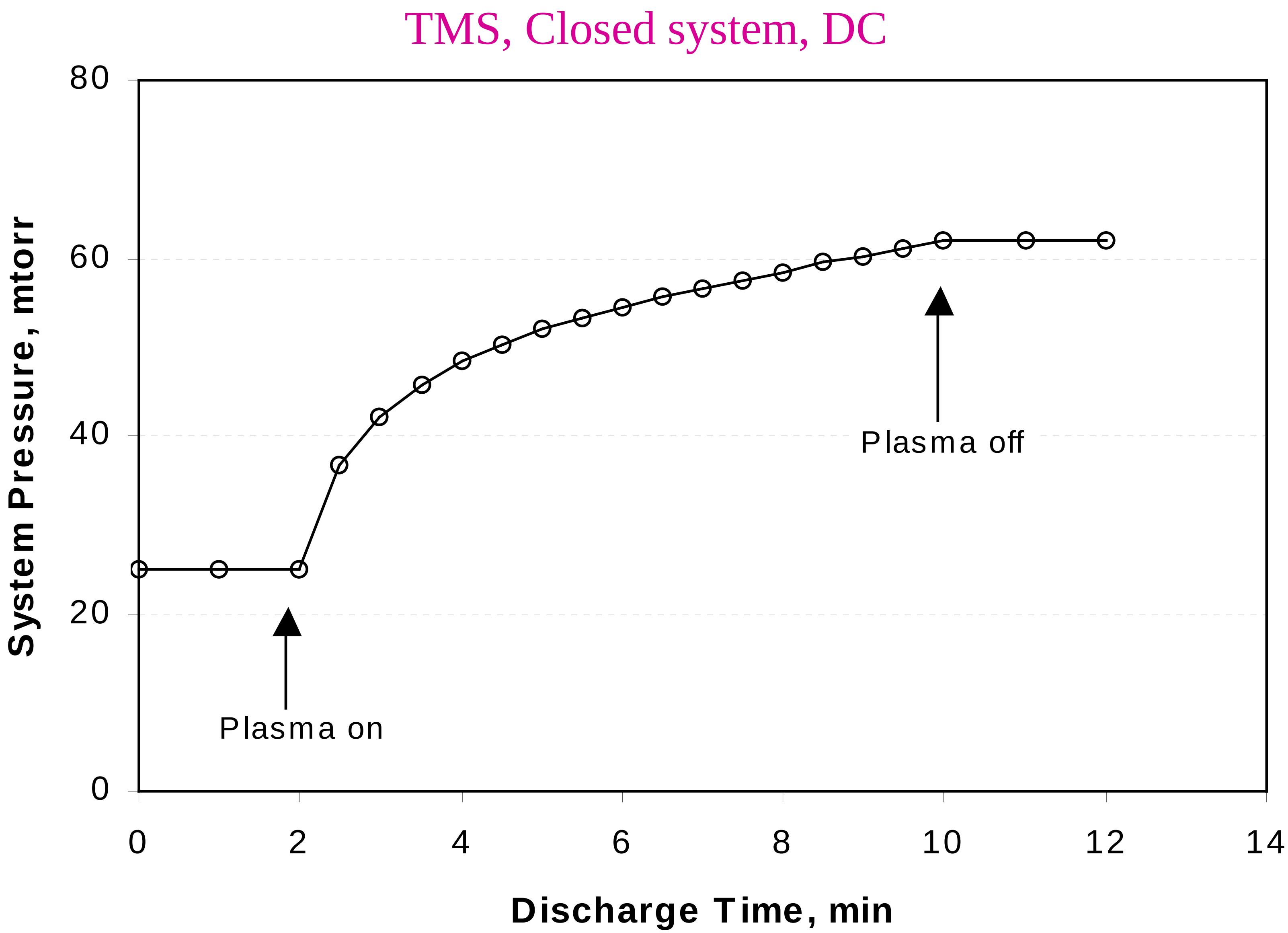


Cascade Arc Reactor

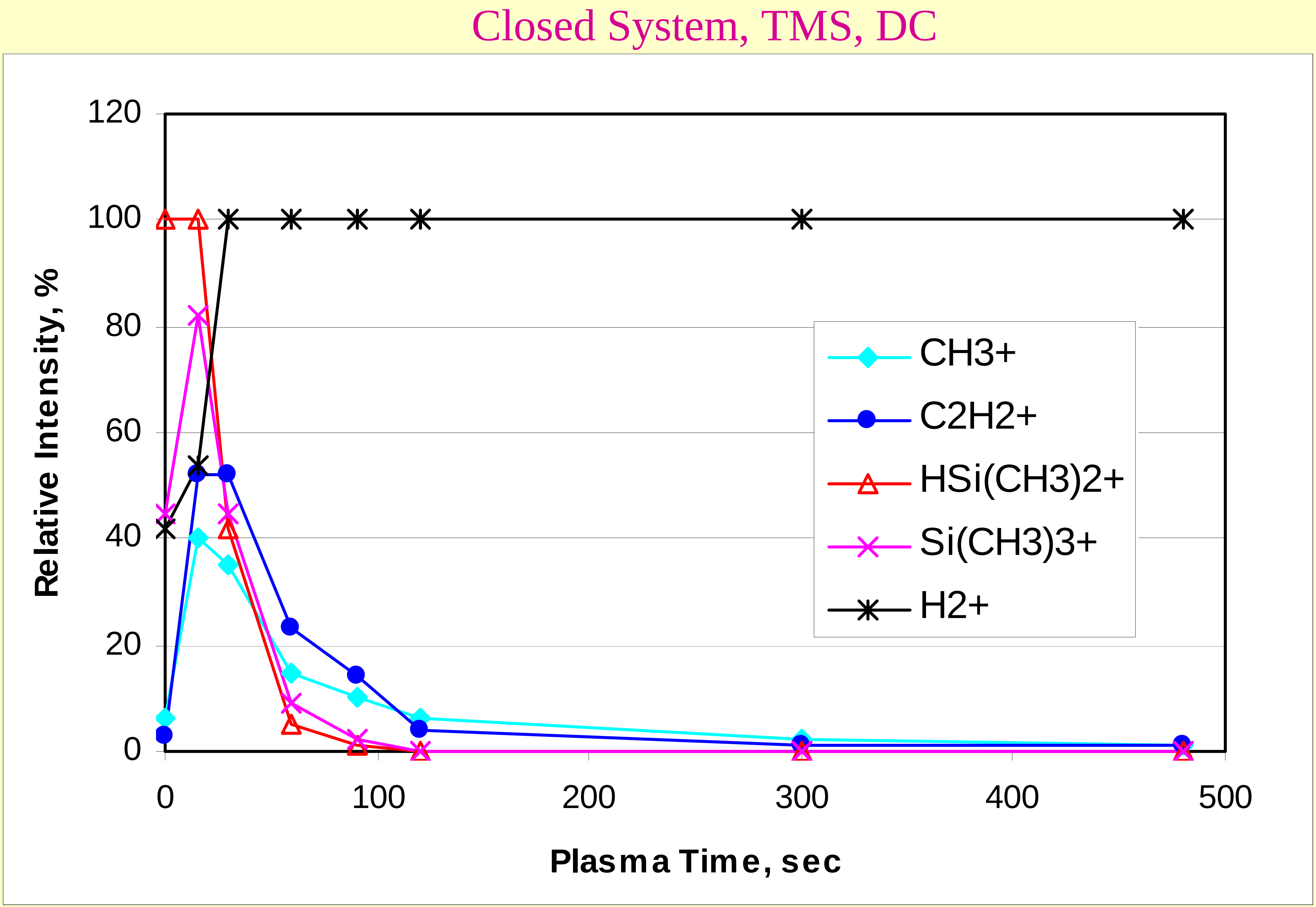



CH3
H-Si-CH3
CH3
a-SiHx
a-CHx
a-(Si-C)Hx

Total number of gaseous species could increase in spite of the deposition of plasma polymers depending on the fragmentation pattern.

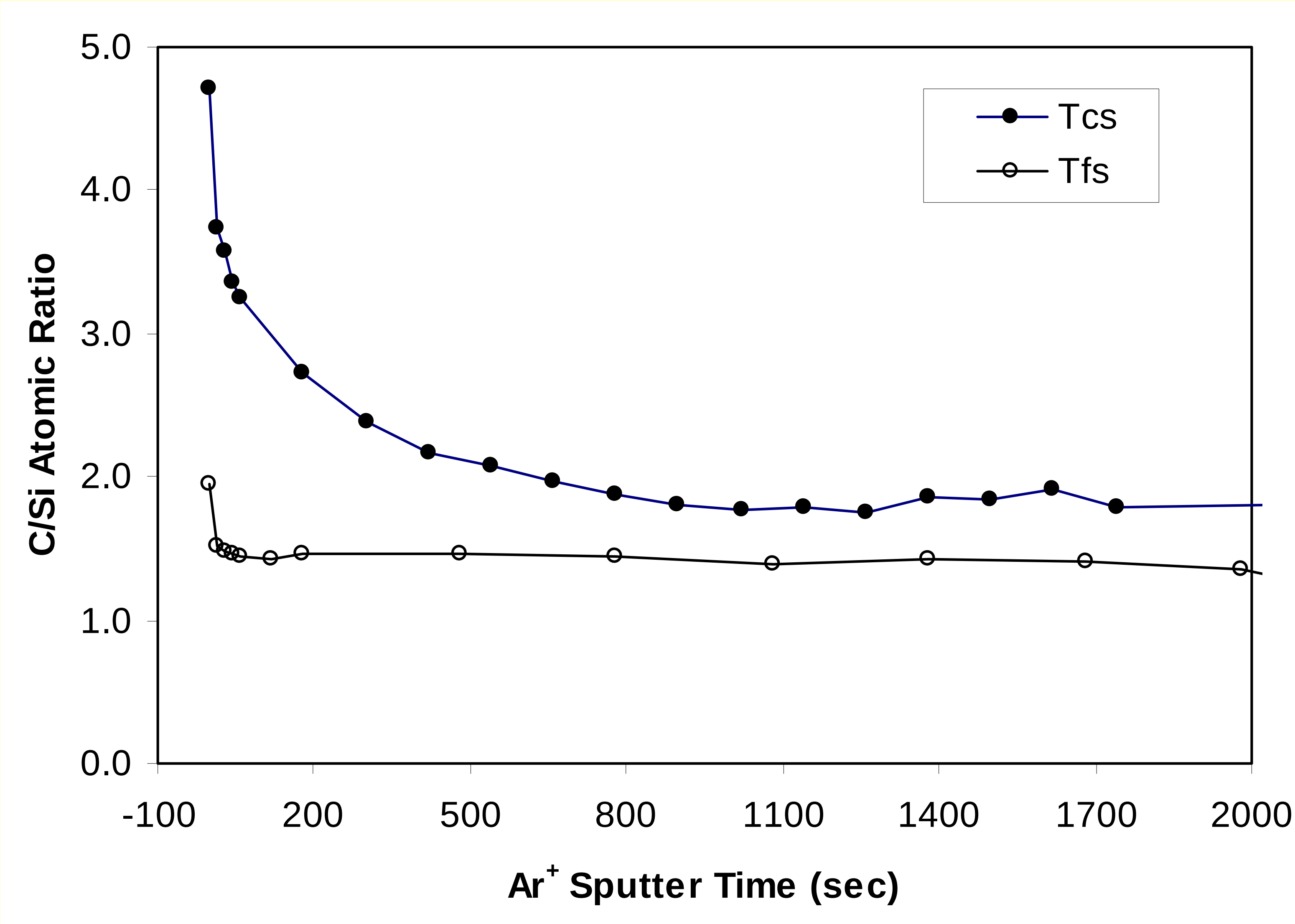


The change of selected RGA peak intensity with plasma time



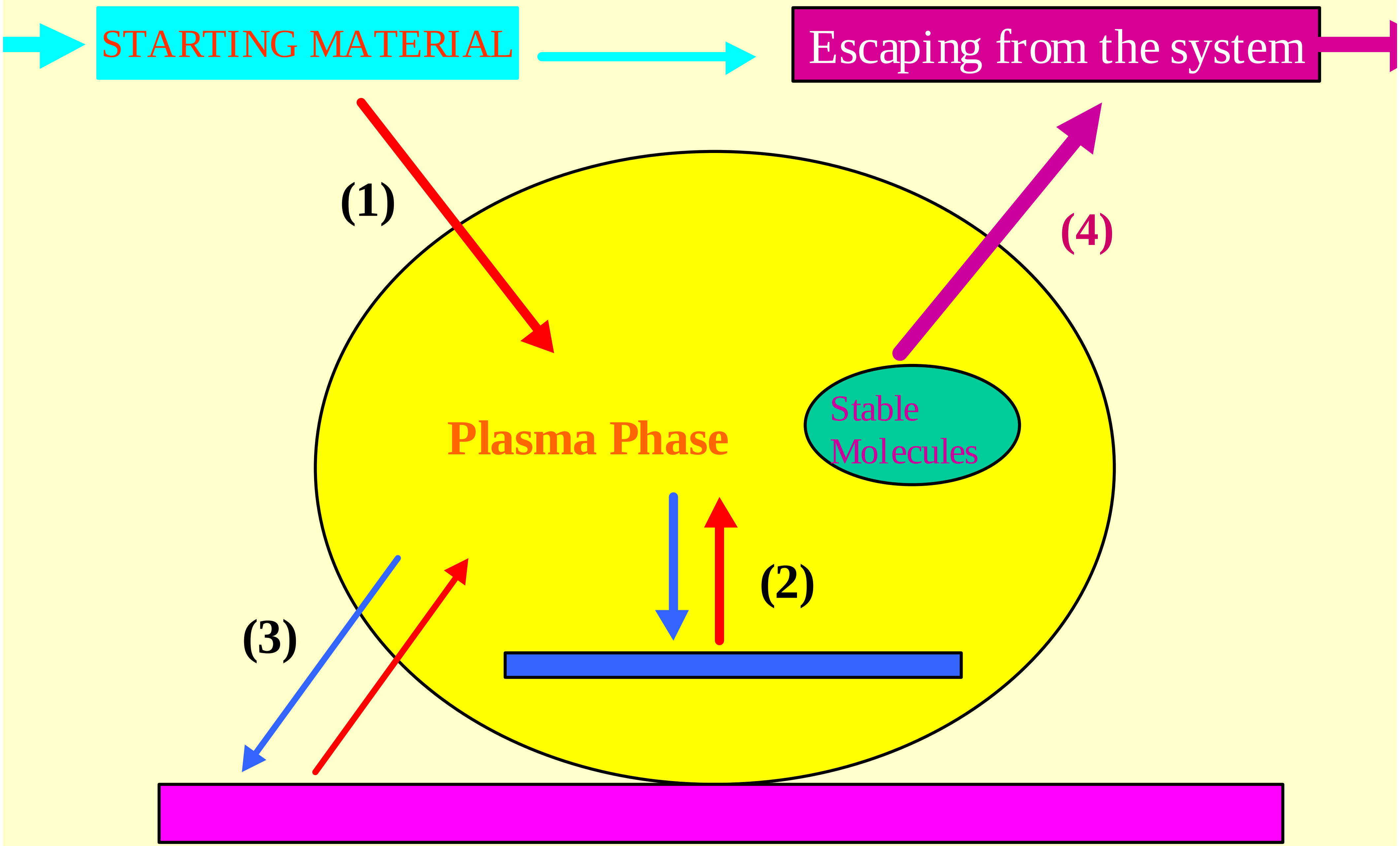
Change of the gas phase species changes the composition of plasma deposition

TMS, DC, Closed system (cs) and Flow system (fs)



Competitive Ablation and Polymerization (CAP) Principle

- Combination of two observations made in two processes aimed to achieve opposing results.
- Formation of polymers of an etching gas (CF_4) in etching of silicon wafer (Kay's group at IBM).
- Weight loss observed in plasma polymerization of C_2F_4 in high energy input domain (Yasuda's group at RTI).
- Ablation and polymerization simultaneously occur in a plasma process, but the respective contribution depends on the conditions of discharge.

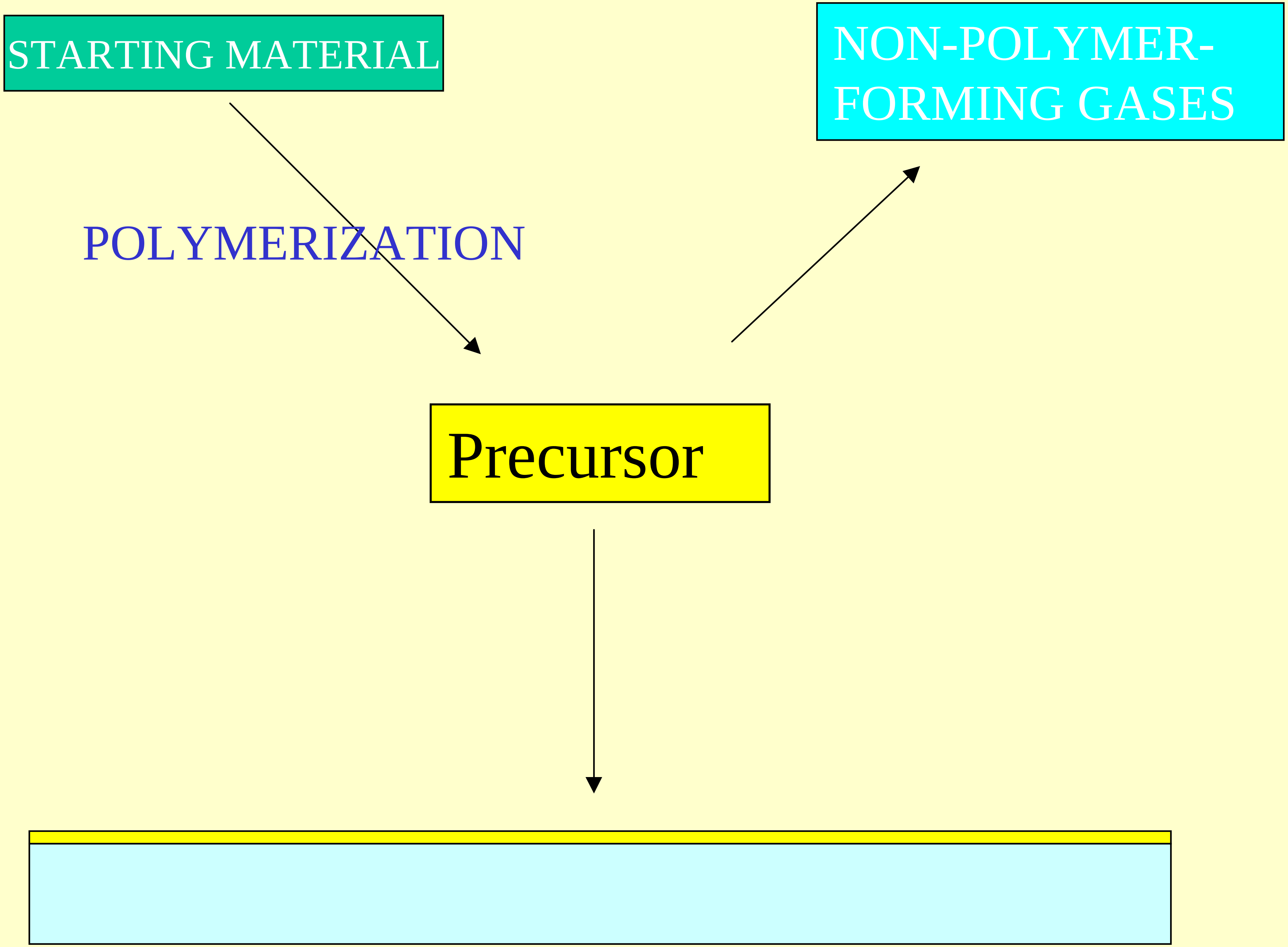

STARTING MATERIAL
Escaping from the system
(1)
(4)
Plasma Phase
Stable
Molecules
(2)
(3)

MONOMER → UNREACTED MONOMER

If Chain-Growth Polymerization could occur in vacuum

The structure of polymer is determined by the structure of the monomer

Plasma Polymerization by Precursor Concept



iN – Out Rule

Fragmentation of molecules in gas phase and also in solid phase, which contact with plasma, follows the rule of thumb of Nitrogen in and Oxygen out.

Oxygen incorporation into a plasma polymer and that into a plasma-treated polymer are largely due to post-plasma reaction of free radicals with oxygen.

Nitrogen has high tendency to be incorporated into a plasma polymer (not in the original forms), and N in a N_2 plasma to the treated polymer.

<u>Post-plasma incorporation of N does not occur</u>. N found in a plasma polymer, of which monomer has no N, is due to contamination of the reactor in which N-containing monomer was used.

Plasma Sensitivity Series of Elements

- Ionization of organic molecules does not follow the same path of ionization of simple atoms.
- Fragmentation of an organic molecules precedes the ionization of fragmented species.
- In-out rule seems to reflect the trends of plasma fragmentation of organic molecules which contain different elements other than C and H.

Types of Monomers for Plasma Polymerization

- **Nearly all organic and organo-metallic compounds polymerize in plasma.**
- Type 1
  - Triple bond, aromatic & hetero aromatic
- Type 2
  - Double bond, cyclic
- Type 3
  - Linear & branched aliphatic
- Type 4
  - Oxygen containing aliphatic

Polymerization characteristics based on the types of monomers

- Polymerization rate
  - Type 1 > Type 2 > Type 3 > Type 4
- Photo-emission
  - Type 4 > Type 3 > Type 2 > Type 1
- Free radicals in polymer substrate
  - Type 4 > Type 3 > Type 2 > Type 1
- Dangling bonds in plasma polymer
  - Type 1 > Type 2 > Type 3 > Type 4

Difference of photo-emission at the same energy input level, 40 kHz, with magnetic enhancement

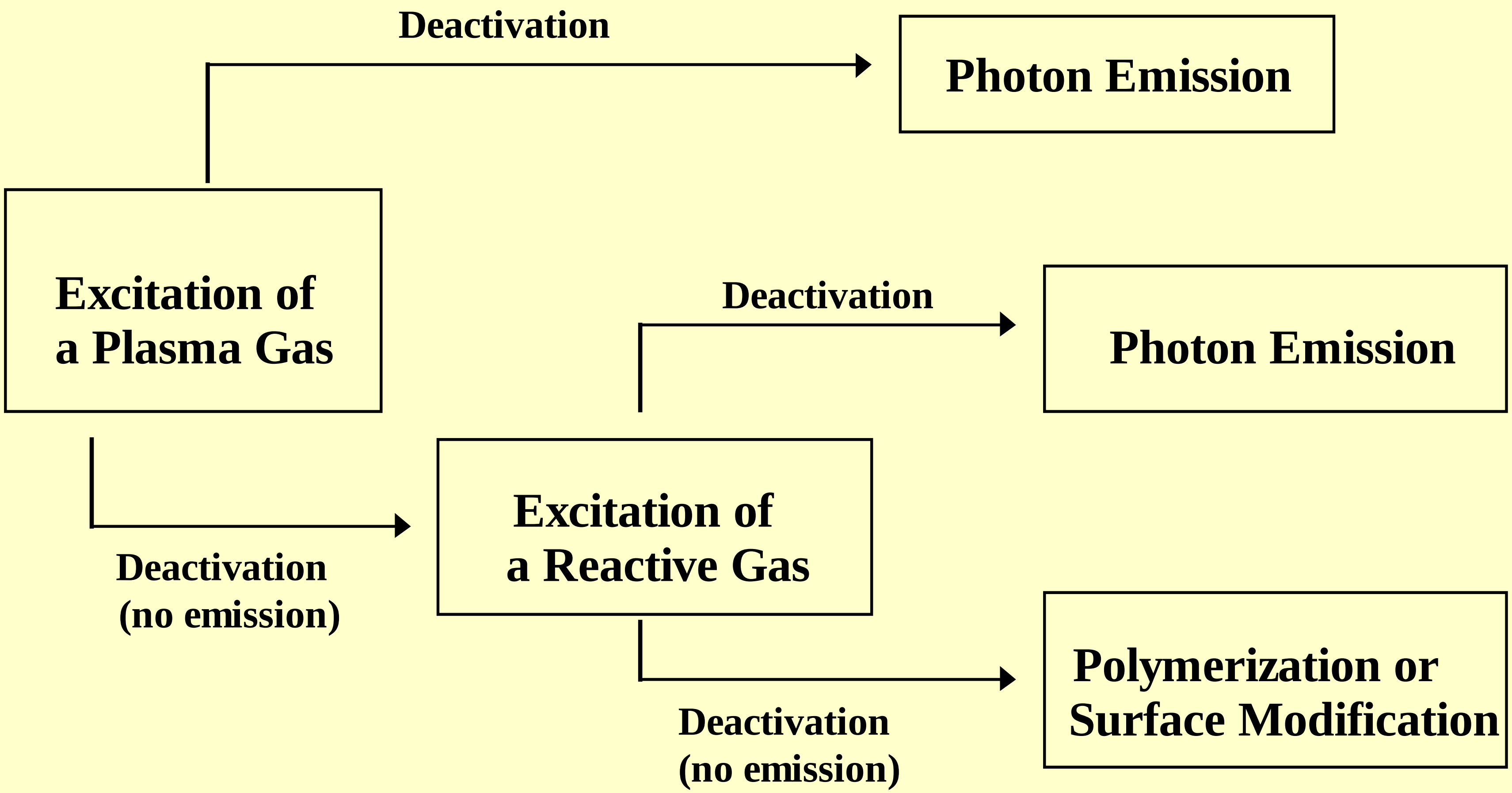
TMS Type 2

W/FM=722MJ/kg

TMS+O_2 Type 4

W/FM=762MJ/kg

Correlation between photon emission and polymerization



Deposition Rates

Local deposition parameters (at a specific place of substrate)

mass deposition rate	k_1 (kg/m^2 s)
thickness growth rate	$k_2 = k_1/\rho$ (m/s)
ρ = specific gravity	(kg/m^3)
specific mass deposition rate	$\mathbf{k_0 = k_1/FM}$ (1/m^2)

mass flow rate corrected deposition rate

In the monomer deficient domain

$$k_1 = k' FM$$

$$k_1/FM = k'$$

F: volume or molar flow rate

M: molecular weight of monomer

In the power deficient domain

$$k_1 = k''W$$

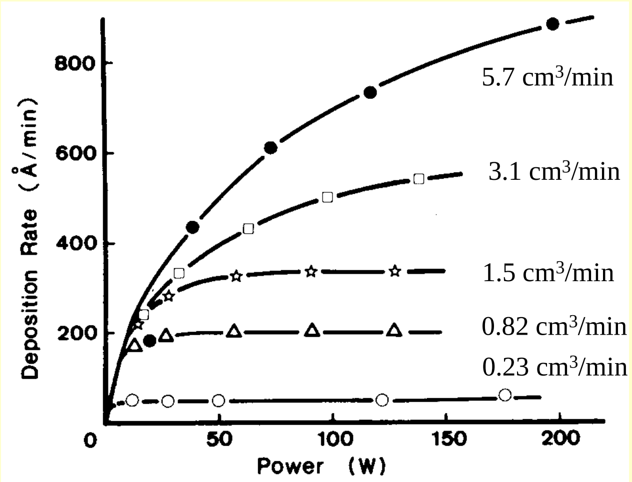
$$k_1/FM = k'' (W/FM)$$

$$k_0 = k_1/FM$$

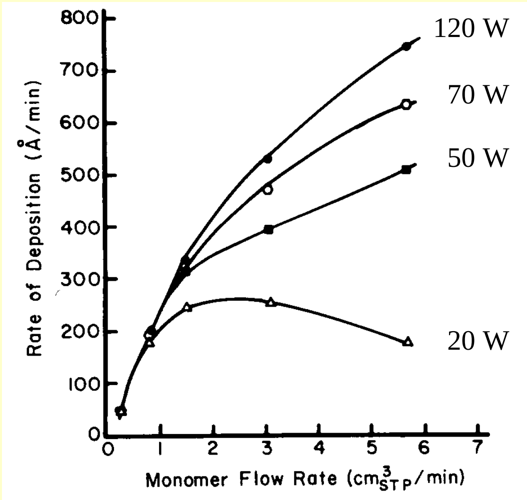
$$k_0 = k'' (W/FM)$$

Deposition rate is independent of pressure

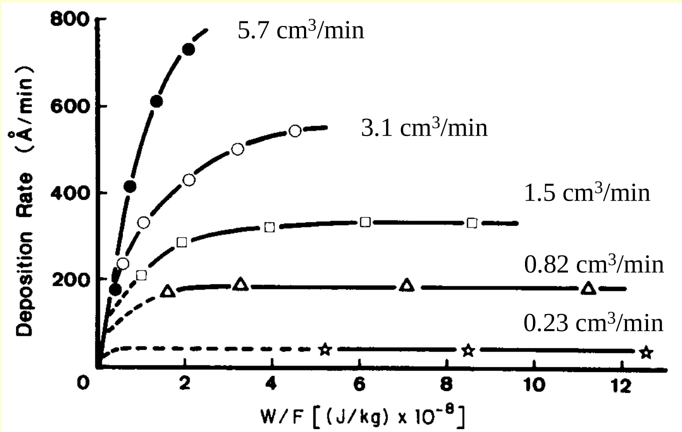
Dependence of deposition rate on operational parameters and domains of plasma polymerization



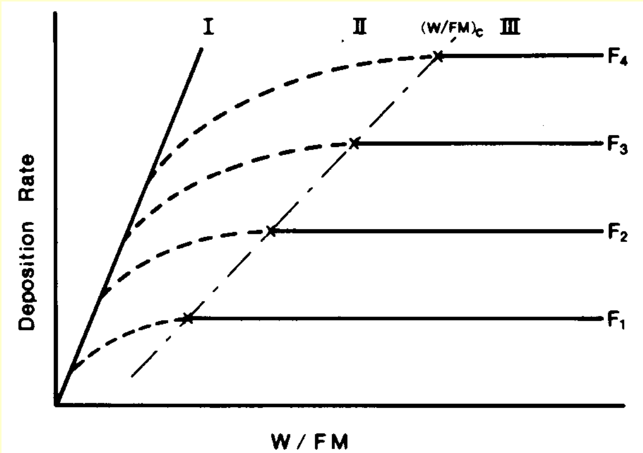
Dependence of deposition rate of plasma polymer of tetramethyldisiloxane on discharge wattage at the flowing monomer flow rates (cm^3/min).



Dependence of deposition rate of the plasma polymer of tetramethyldisiloxane on discharge power at a fixed flow rate

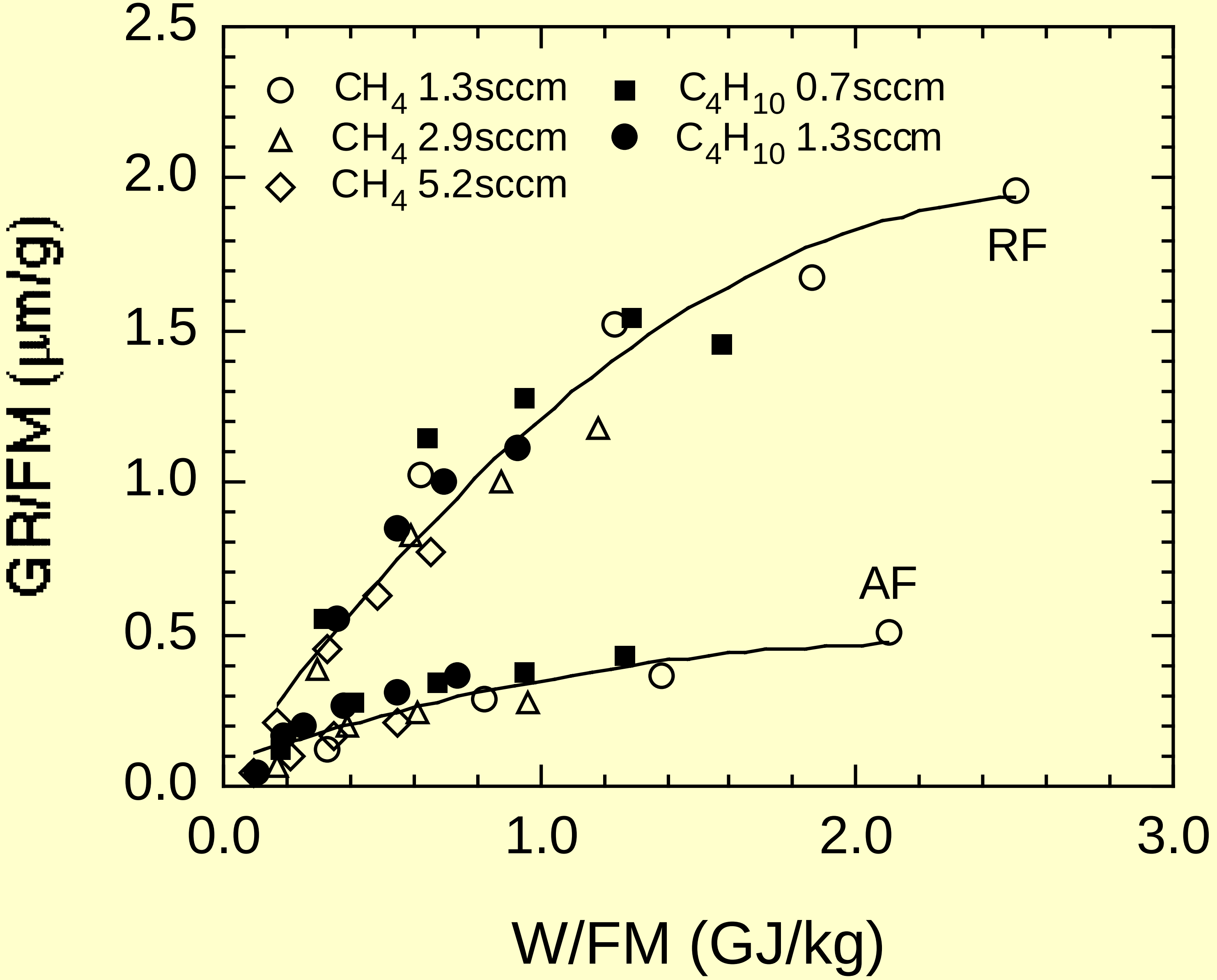


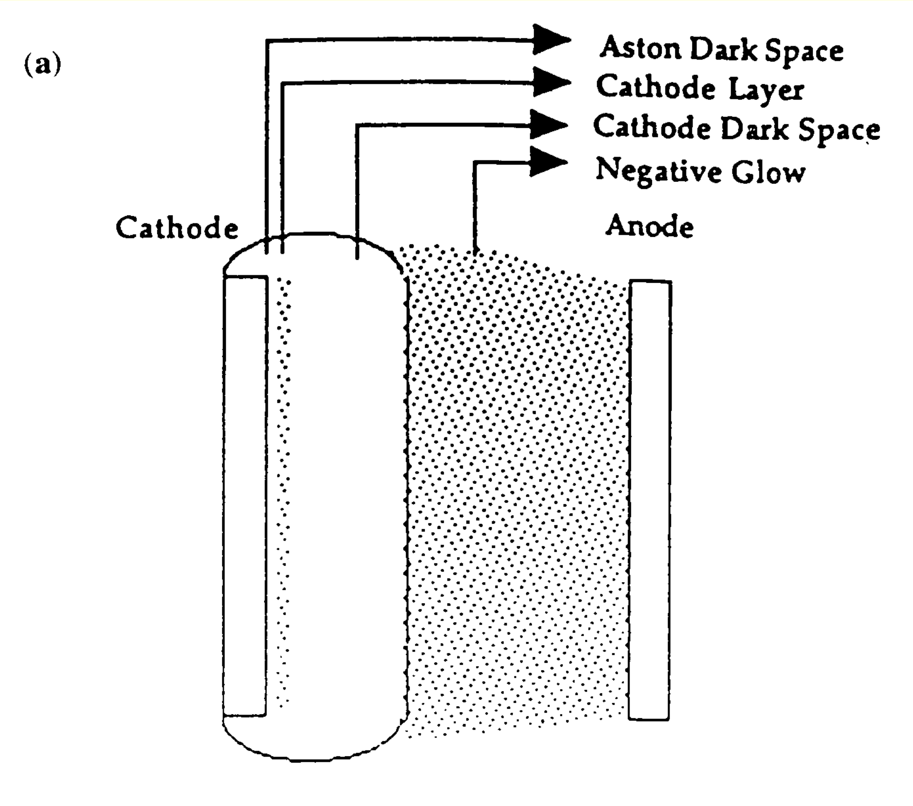
Dependence of deposition rate of the plasma polymer of tetramethyldisiloxane on W/FM at different flow rates

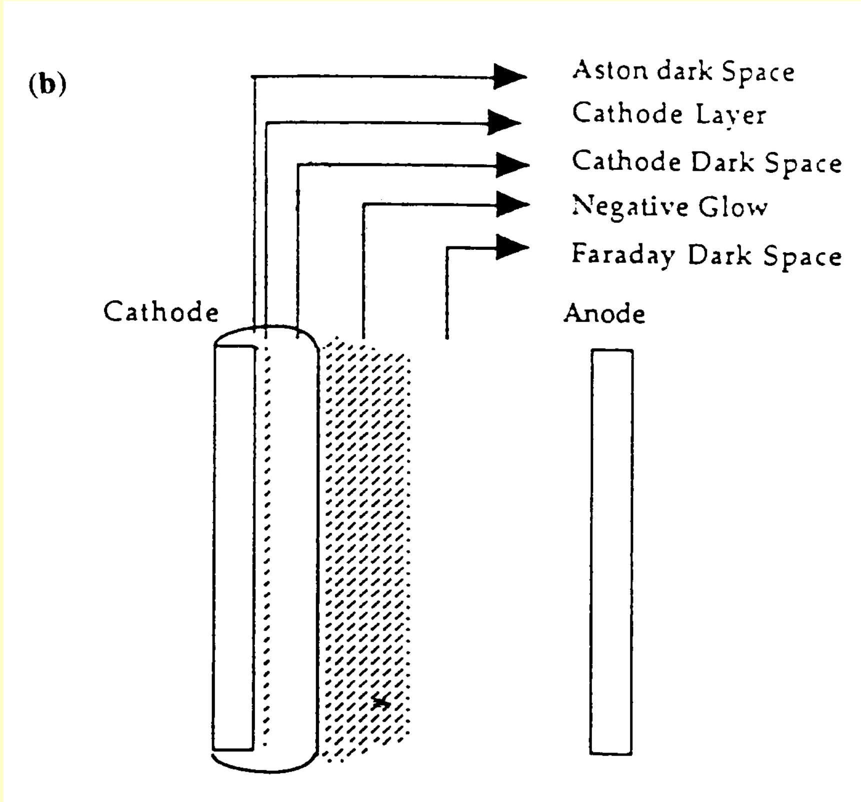


Dependence of plasma polymerization domains on deposition rate and W/FM at various flow rates.

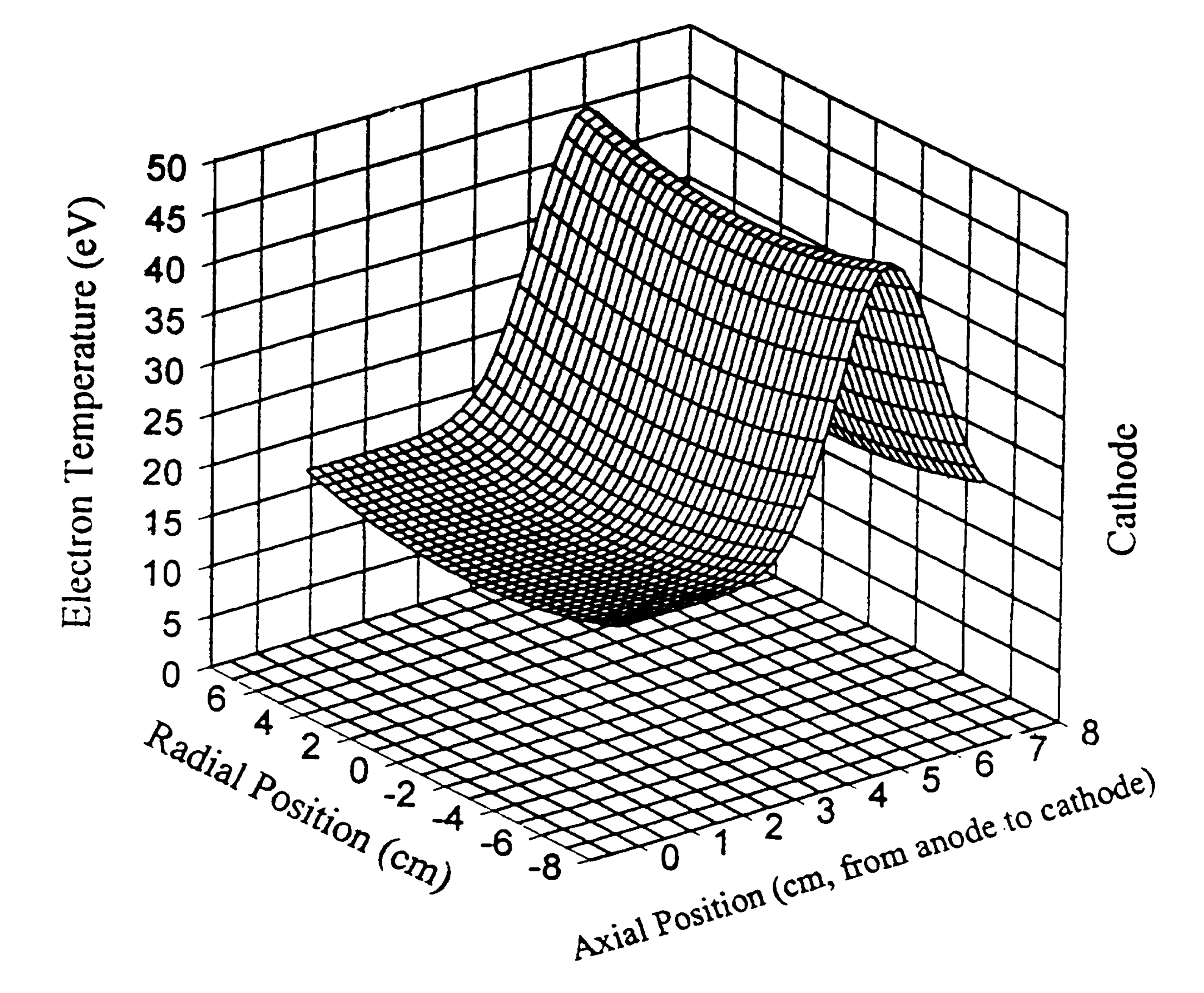
Deposition characteristics in glow discharge, in energy deficient domain



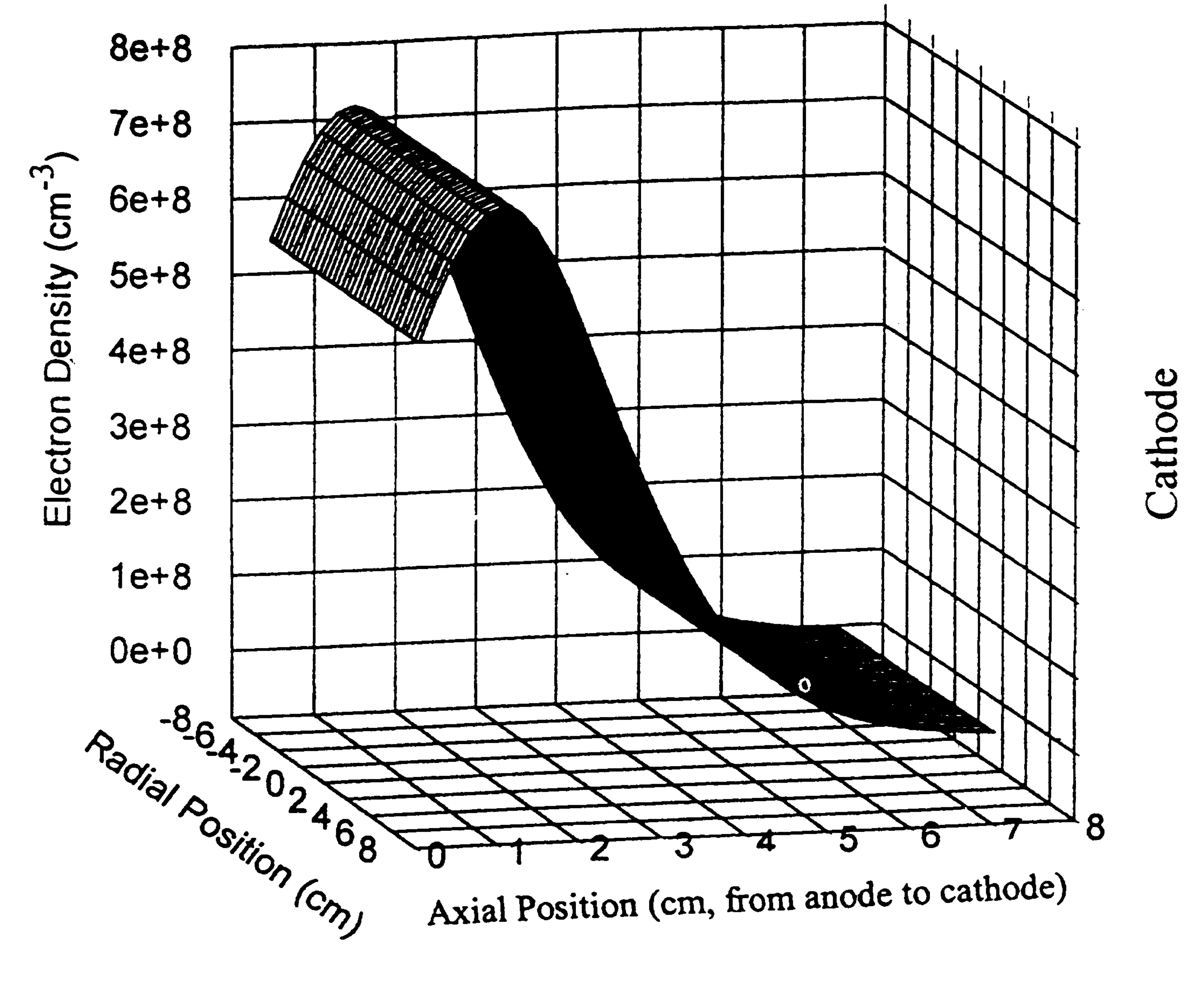




Schematic presentation of D.C. glow discharge in a plasma polymerization reactor, (a) System pressure < 6.66 Pa (50 mTorr), (b) > 13.33 Pa (100 mTorr).

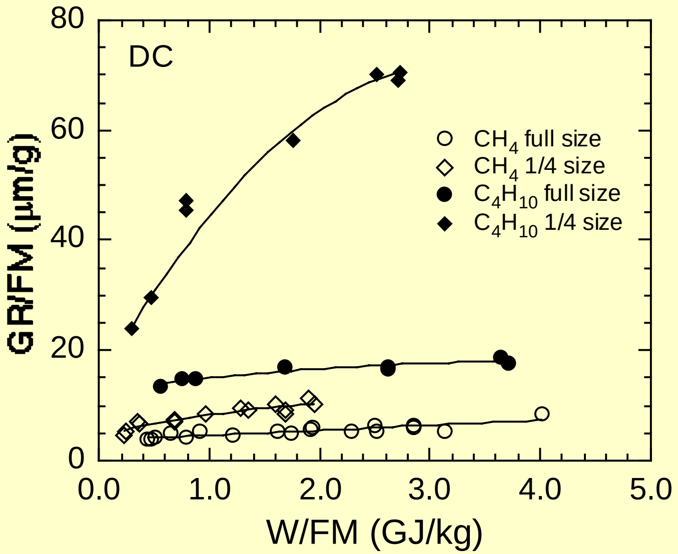


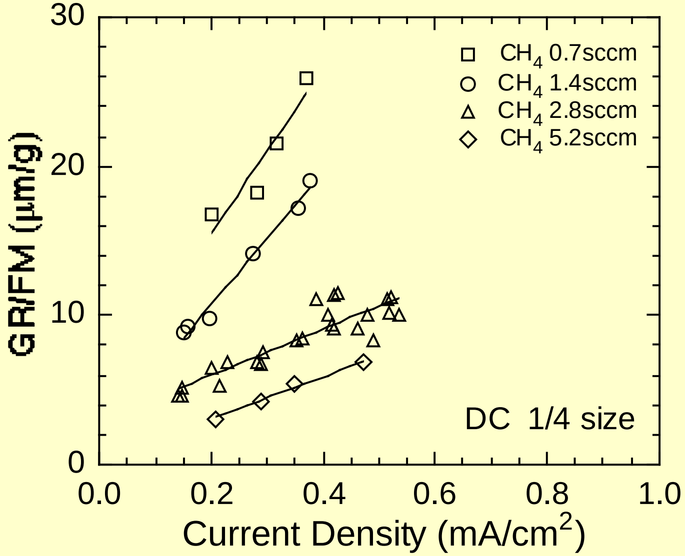
Distribution profile of electron temperature in an argon D.C. glow discharge in a plasma polymerization reactor

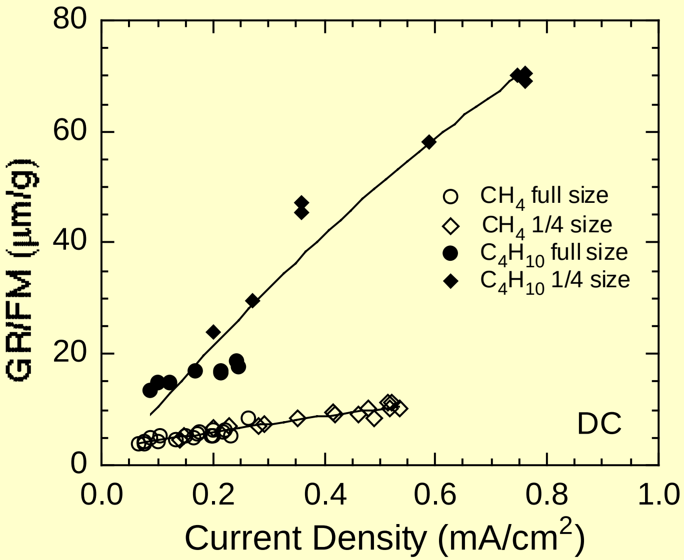


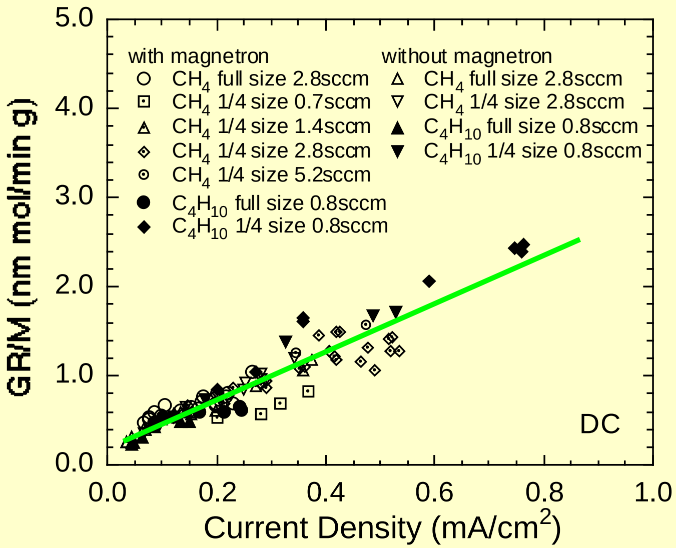
Distribution profile of electron density in an argon D.C. glow discharge in a plasma polymerization reactor

Dependence of DC cathodic polymerization on operational parameters









Cathodic polymerization

(deposition on the cathode surface)

$$k_1/[CM] = k_c[I]$$

[I] : current density

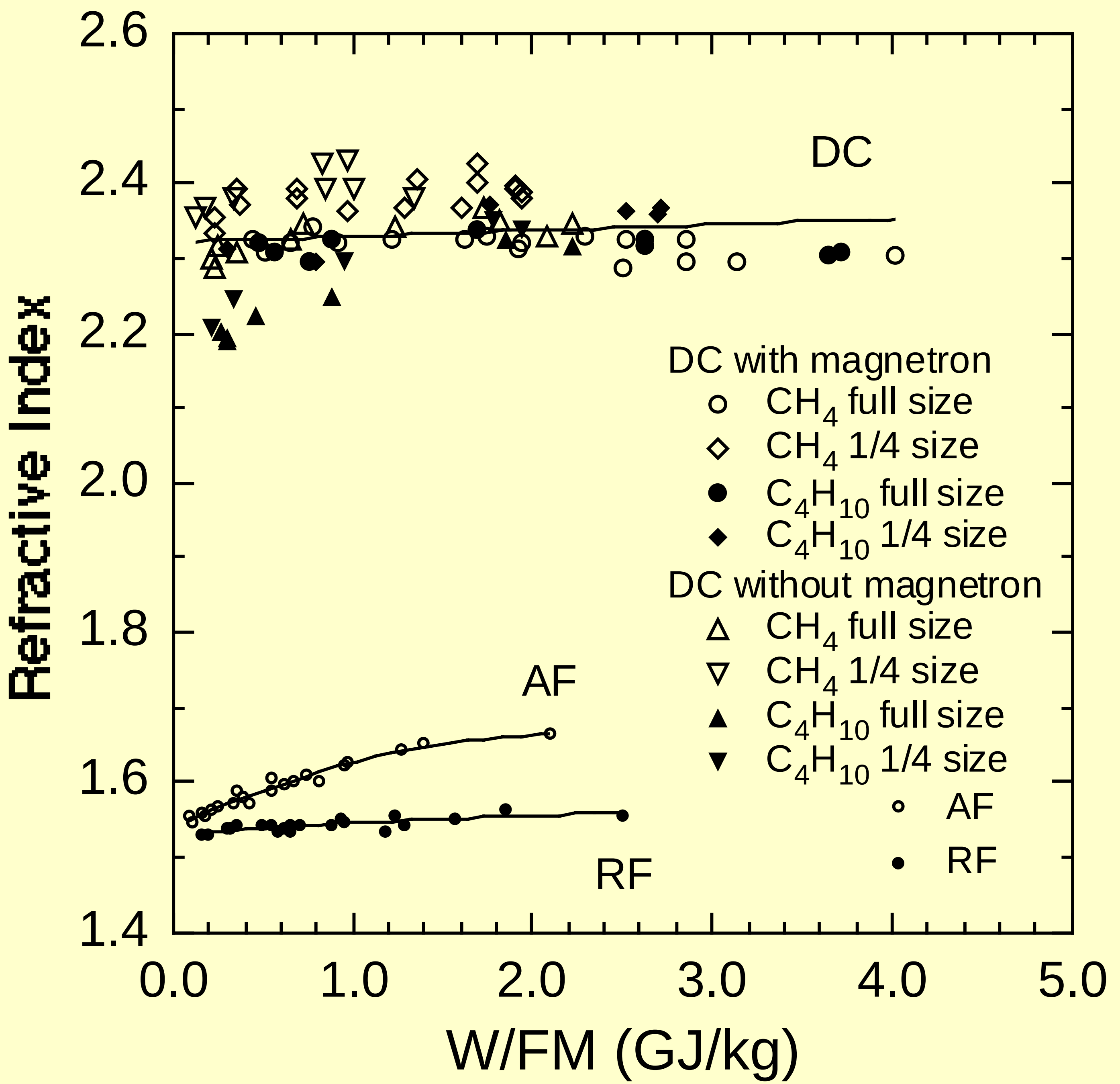
$$k_1 = k_c[I][CM]$$

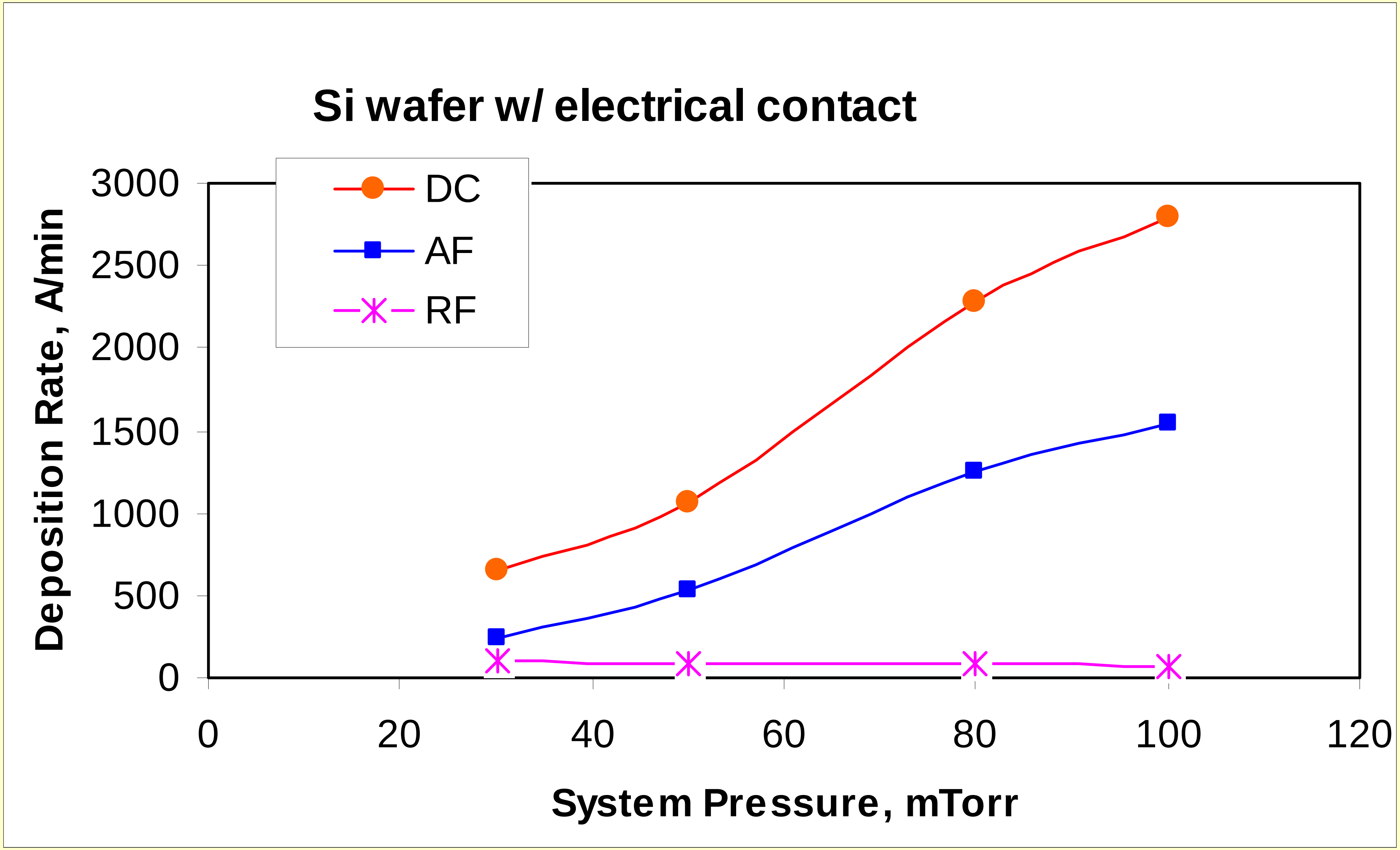
[CM] : mass concentration

$$k_1 = k'_c[I]\,p$$

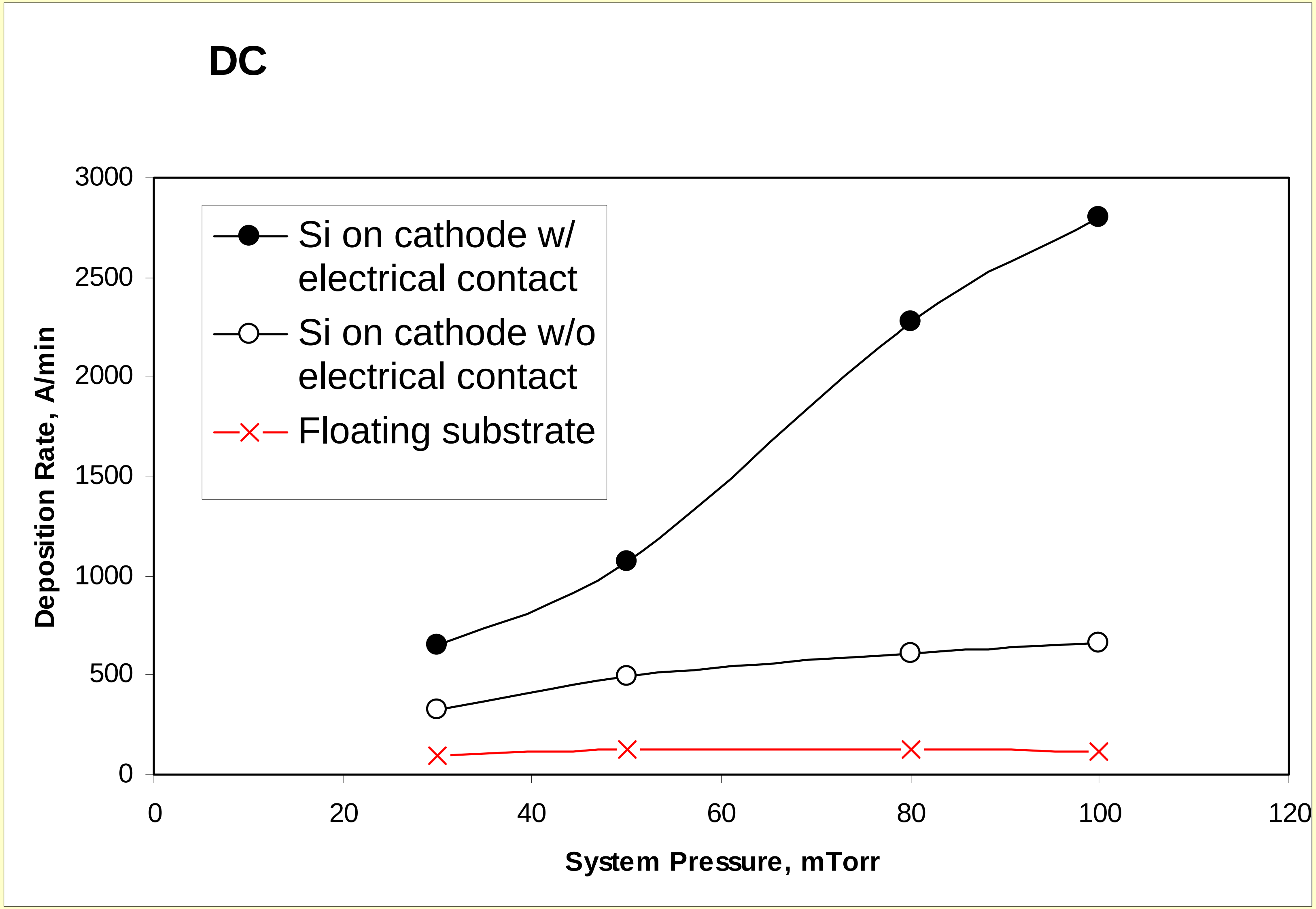
p : system pressure

Deposition rate is dependent on pressure and independent of flow rate.

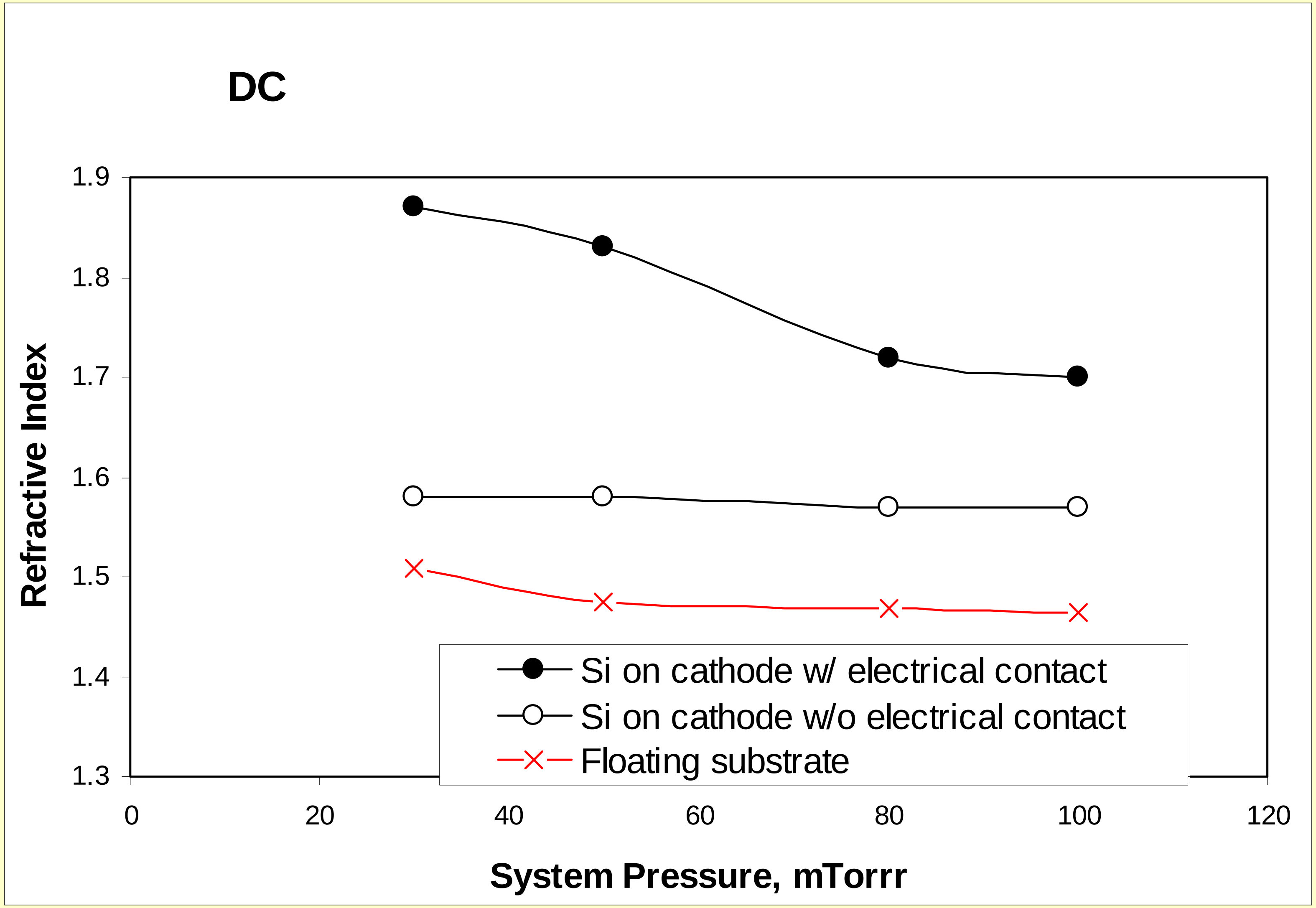

2.6
2.4
2.2
2.0
1.8
1.6
1.4
Refractive Index
0.0
1.0
2.0
3.0
4.0
5.0
W/FM (GJ/kg)
DC
AF
RF
DC with magnetron
CH_4 full size
CH_4 1/4 size
C_4H_{10} full size
C_4H_{10} 1/4 size
DC without magnetron
CH_4 full size
CH_4 1/4 size
C_4H_{10} full size
C_4H_{10} 1/4 size
AF
RF



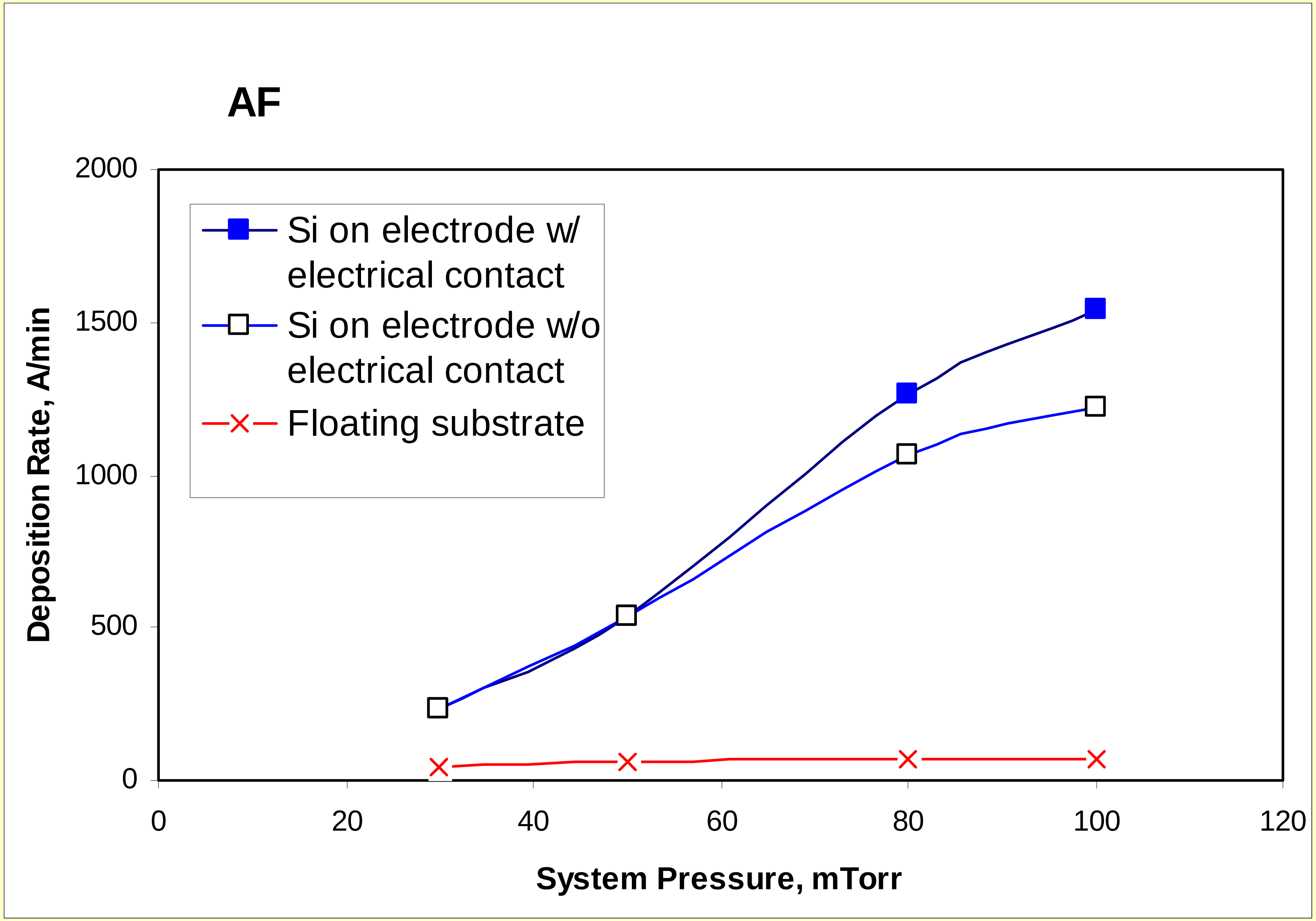
The system pressure dependence of deposition rate of TMS on Si wafer with electrical contact to the substrate as powered electrode in DC cathodic polymerization, AF (40 kHz) and RF (13.5 MHz) plasma polymerization processes. Plasma conditions are 1 sccm TMS, 5 W power input.



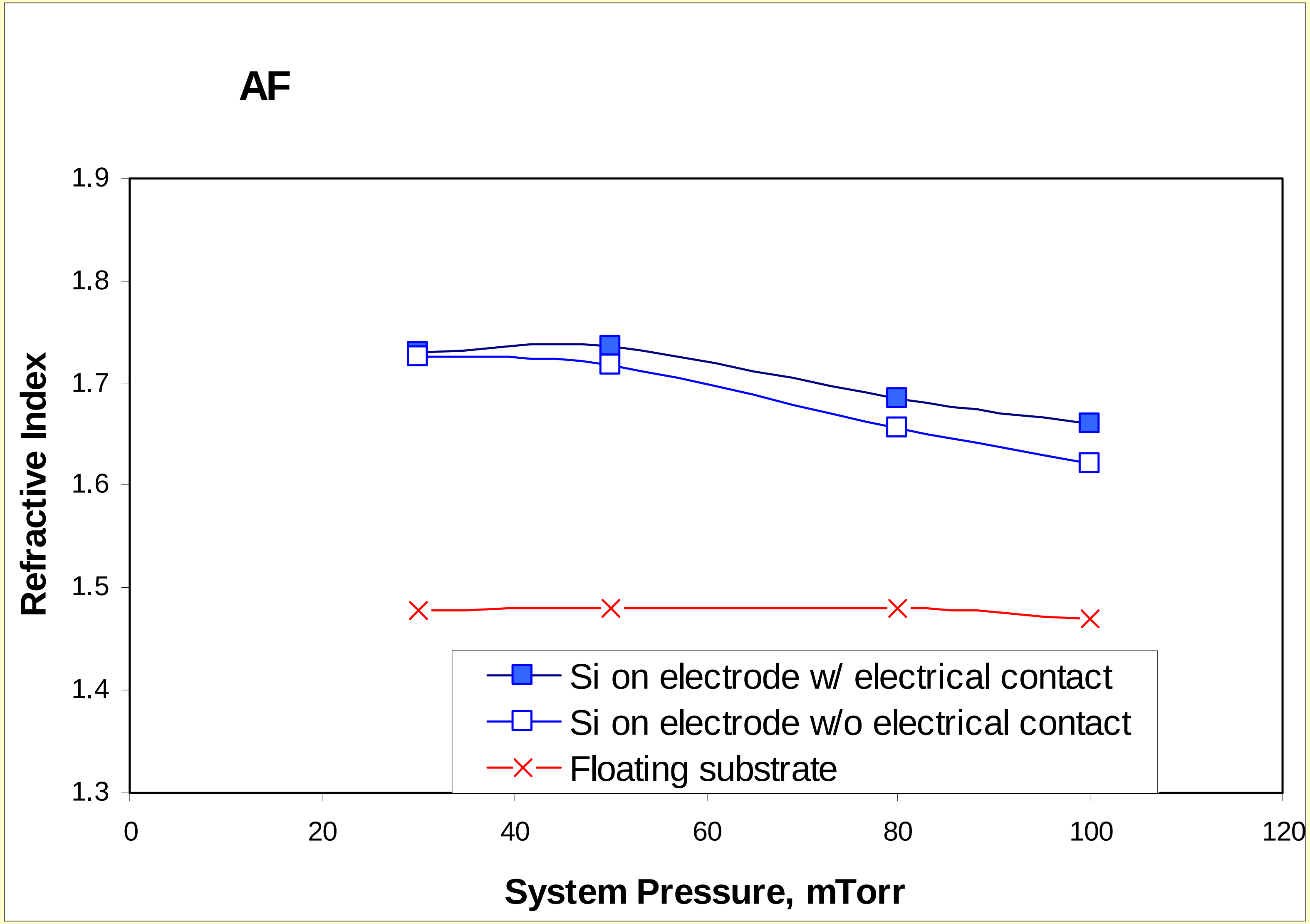
The system pressure dependence of deposition rate of TMS on Si wafer with electrical contact and without electrical contact to **powered electrode or floating substrate** in DC cathodic glow discharge polymerization,. Plasma conditions are 1 sccm TMS, 5 W power input.



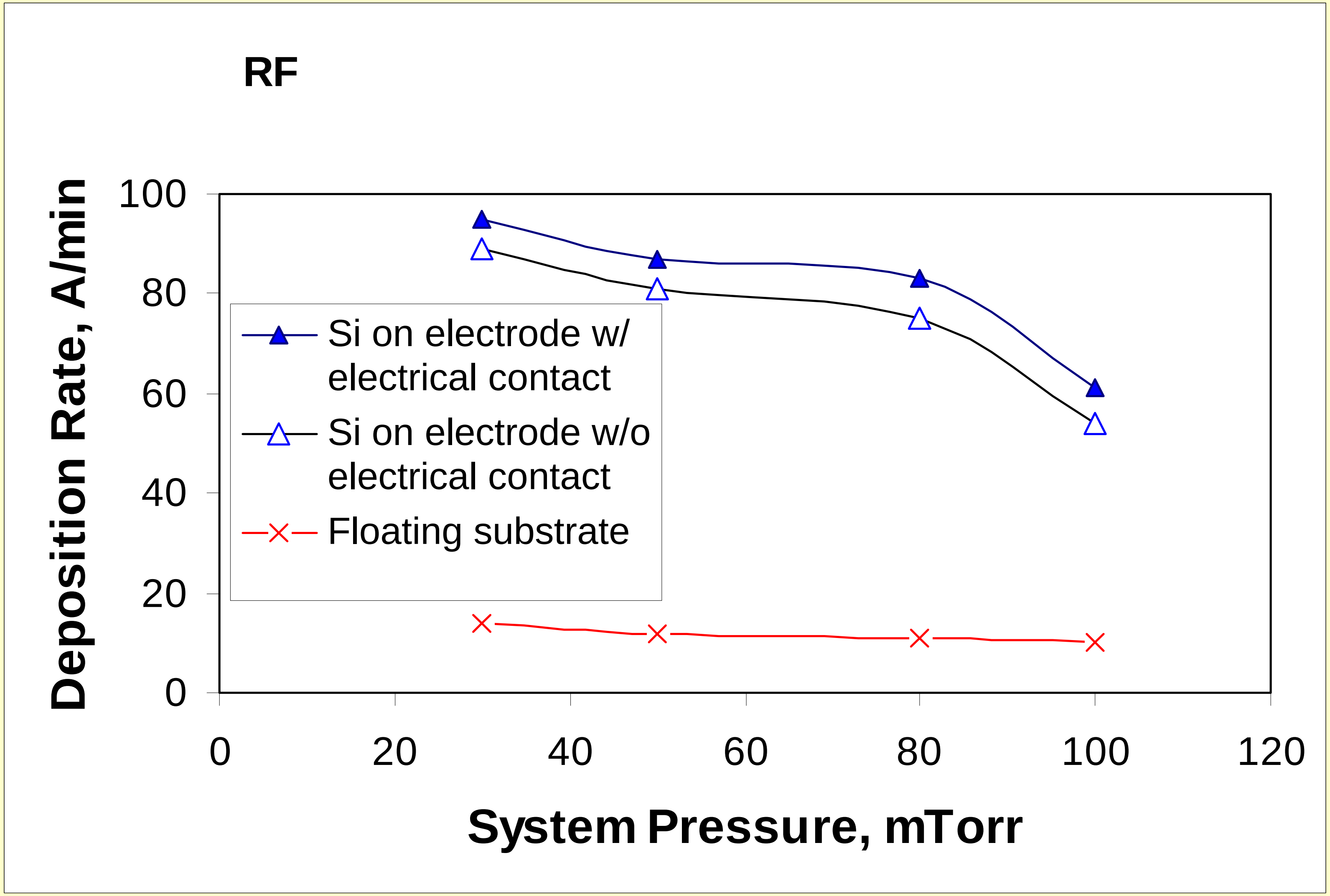
The system pressure dependence of refractive index of TMS on Si wafer with electrical contact and without electrical contact to **powered electrode or floating substrate** in DC cathodic glow discharge polymerization,. Plasma conditions are 1 sccm TMS, 5 W power input.



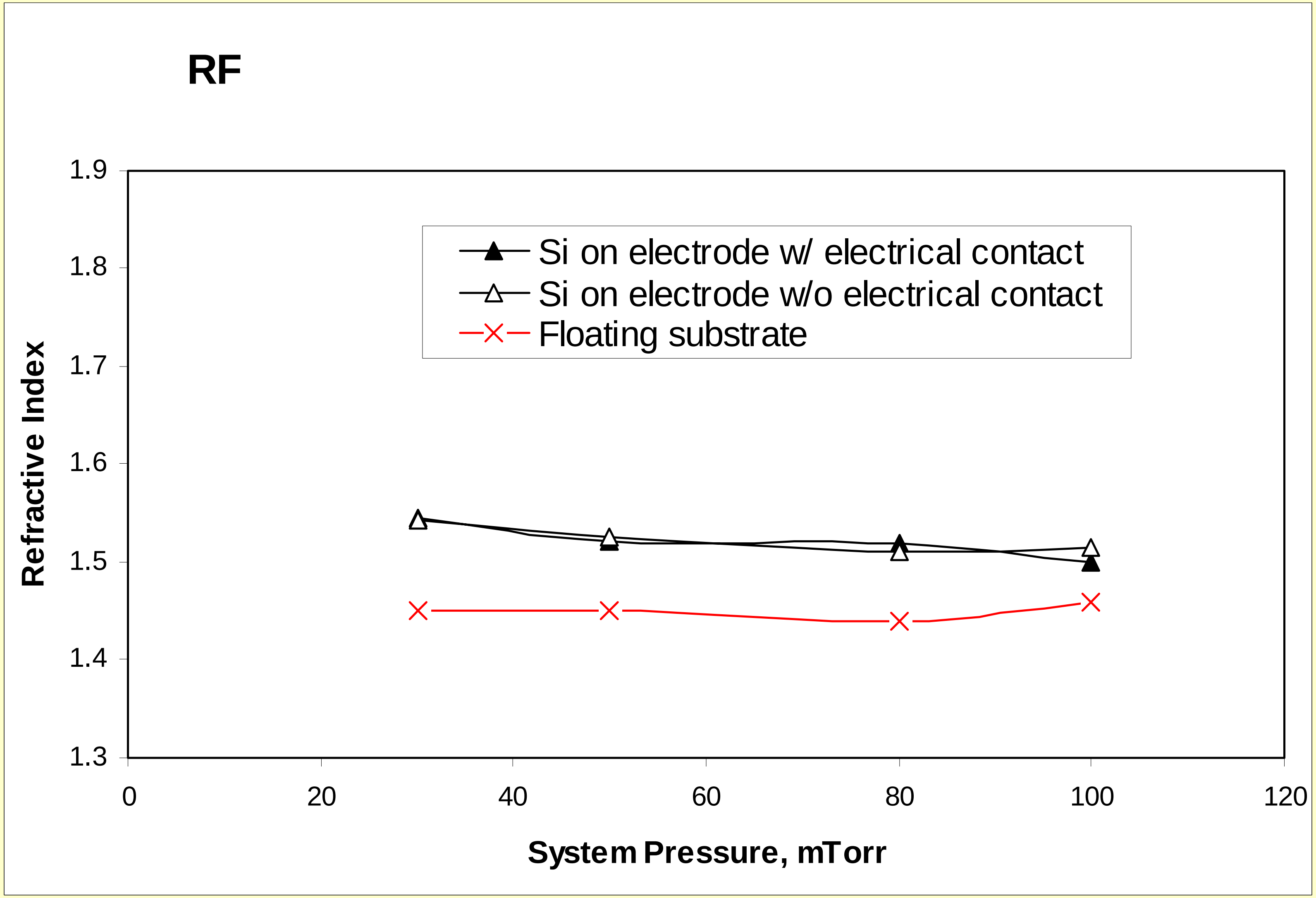
The system pressure dependence of deposition rate of TMS on Si wafer with electrical contact and without electrical contact to **powered electrode or floating substrate** in AF plasma polymerization processes. Plasma conditions are 1 sccm TMS, 5 W power input.



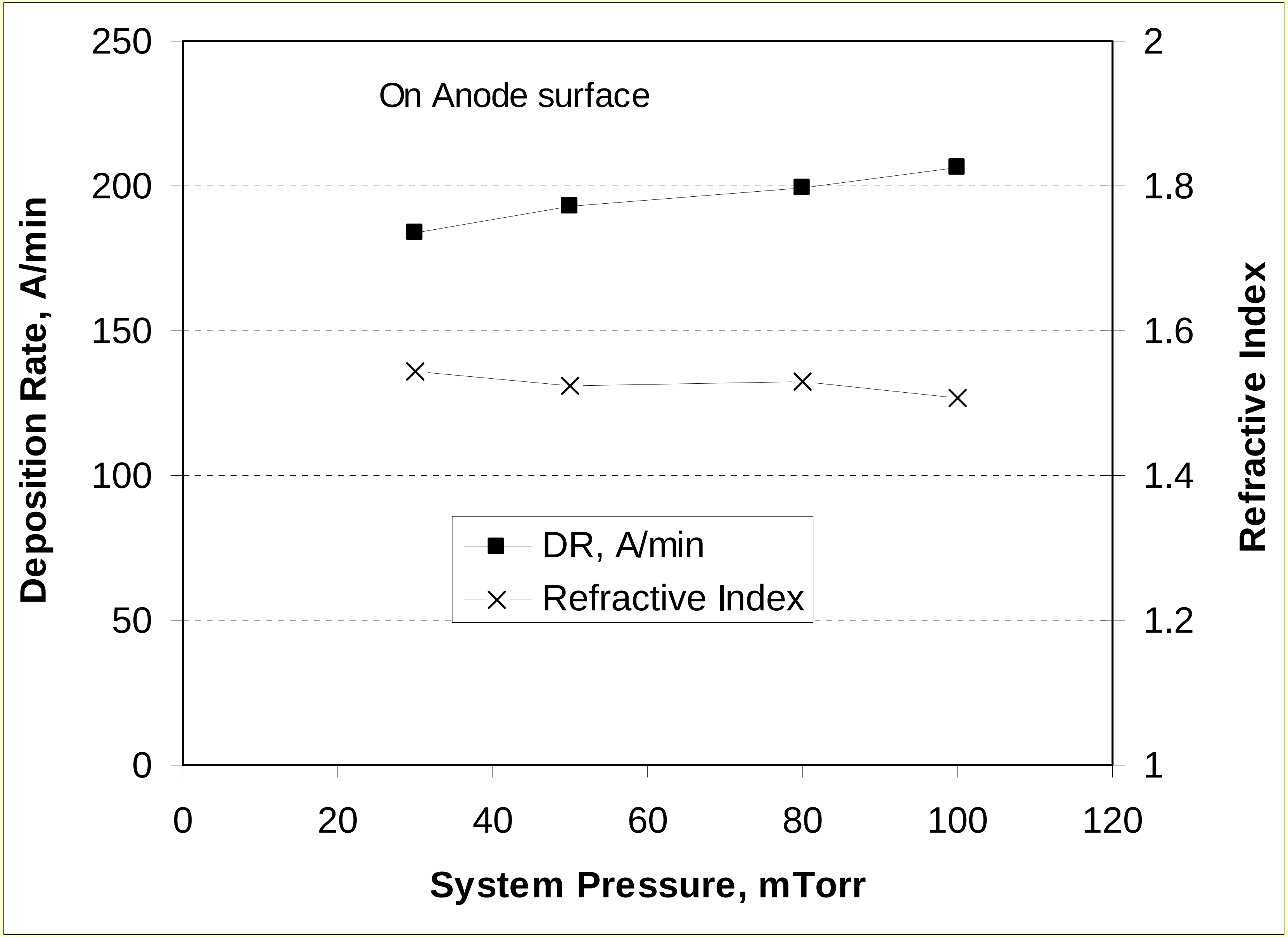
The system pressure dependence of refractive index of TMS on Si wafer with electrical contact and without electrical contact to **powered electrode or floating substrate** in AF plasma polymerization processes. Plasma conditions are 1 sccm TMS, 5 W power input.



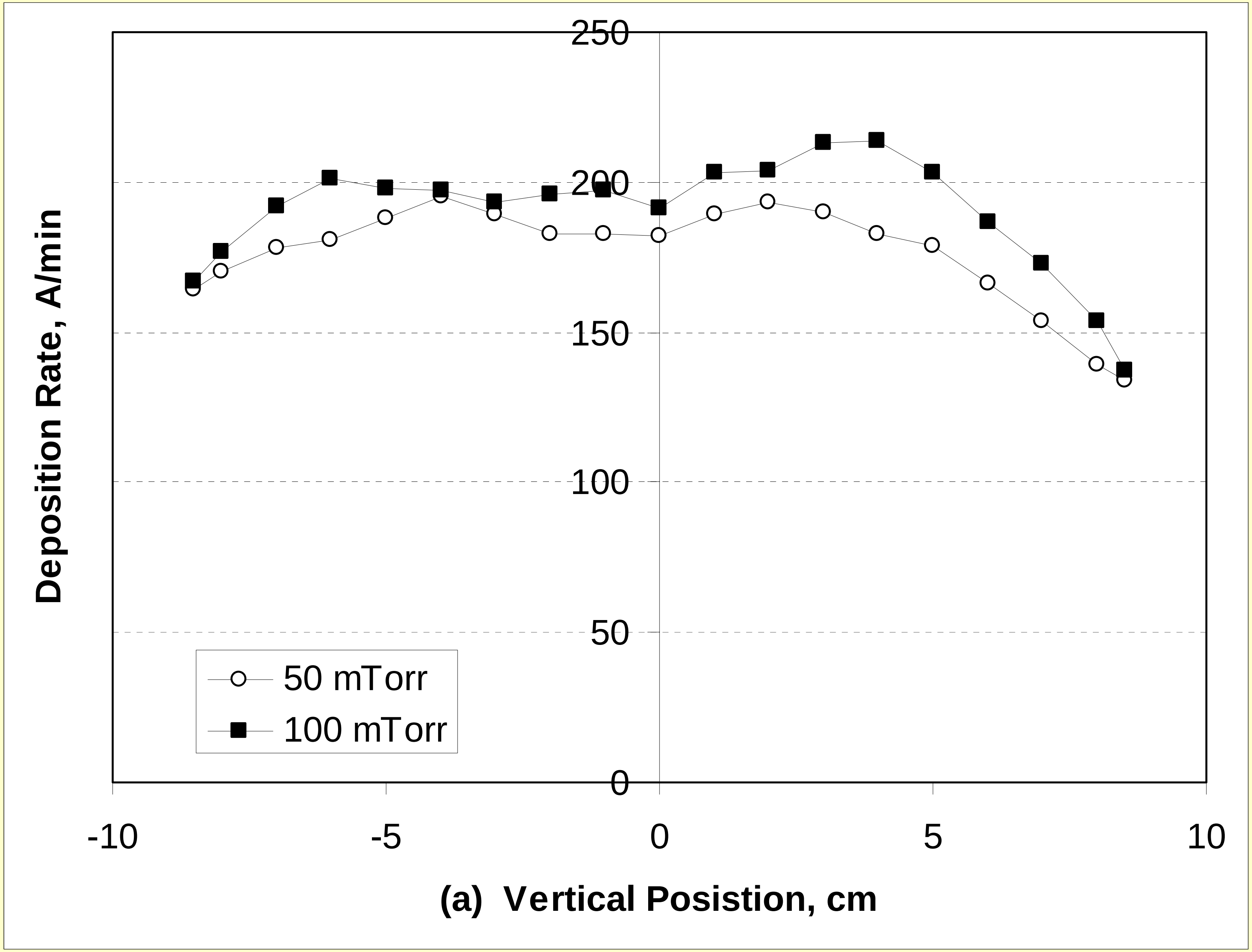
The system pressure dependence of deposition rate of TMS on Si wafer with electrical contact and without electrical contact to **powered electrode or floating substrate** in RF plasma polymerization processes. Plasma conditions are 1 sccm TMS, 5 W power input.



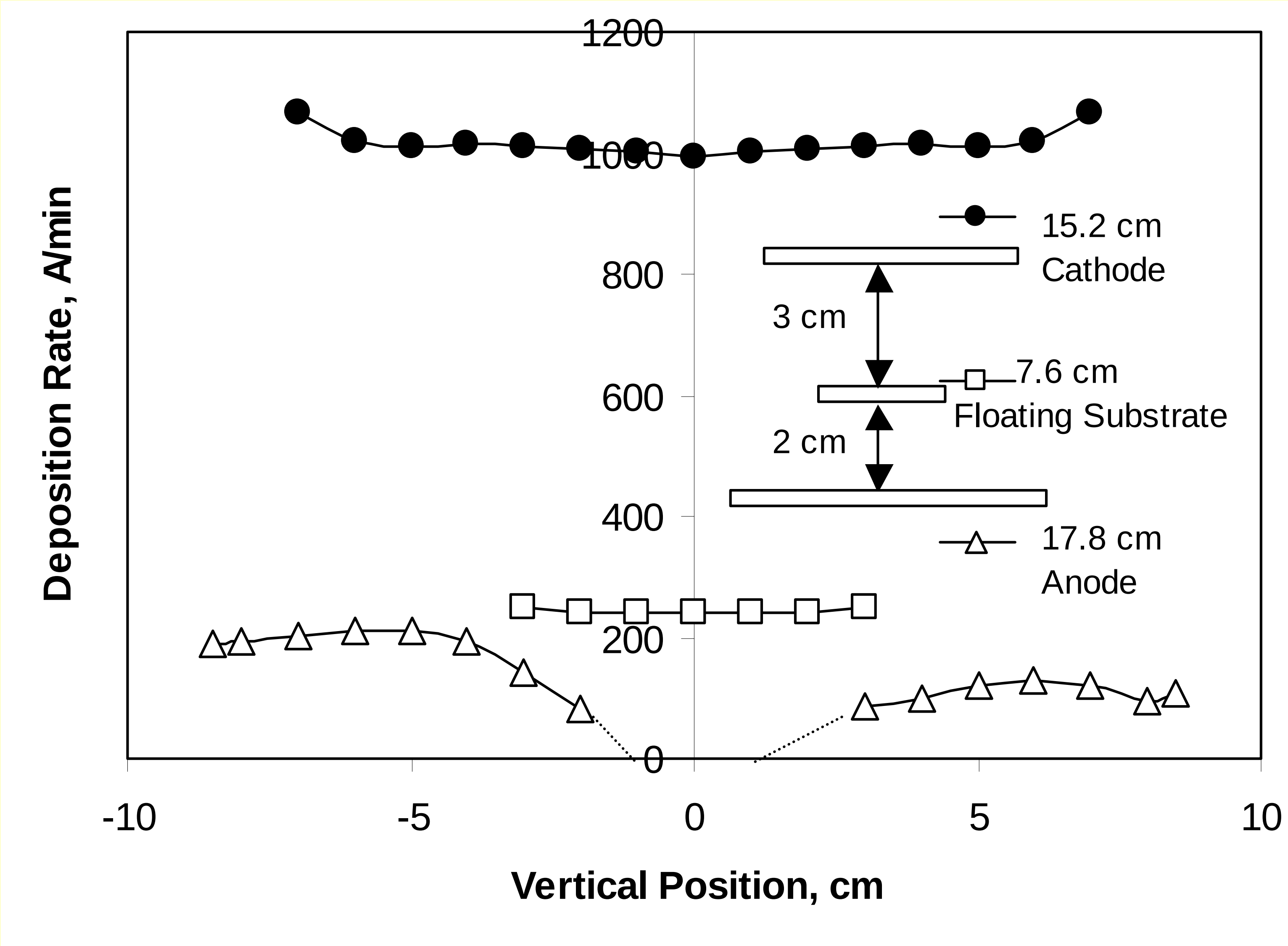
The system pressure dependence of refractive index of TMS on Si wafer with electrical contact and without electrical contact to **powered electrode or floating substrate** in RF plasma polymerization processes. Plasma conditions are 1 sccm TMS, 5 W power input.



The pressure dependence of plasma polymer deposition rate and Refractive index in TMS DC polymerization (on anode). Conditions are 1sccm TMS, DC 5 W.

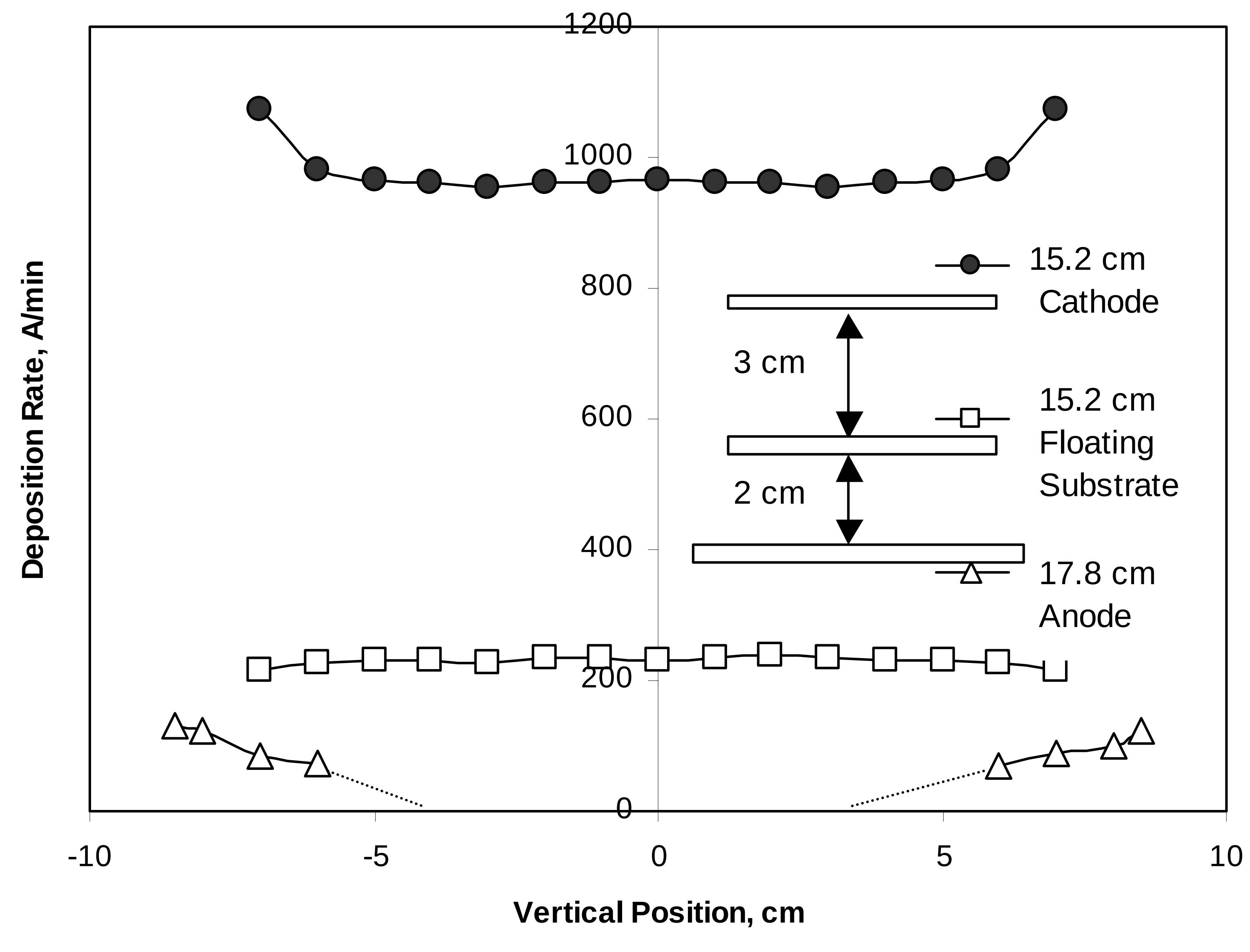


The plasma polymer deposition profile on anode surface in TMS DC cathodic polymerization. Conditions are 1sccm TMS, DC 5 W.



1/2 piece of Al panel in front of Anode

The effect of the floating panels positioned in front of the anode on the deposition rate on Anode surface and Cathode surface in DC cathodic polymerization.
Conditions are: 1 sccm TMS, 50 mTorr, DC 5 W, d = 100 mm.



1 whole piece of Al panel in front of Anode

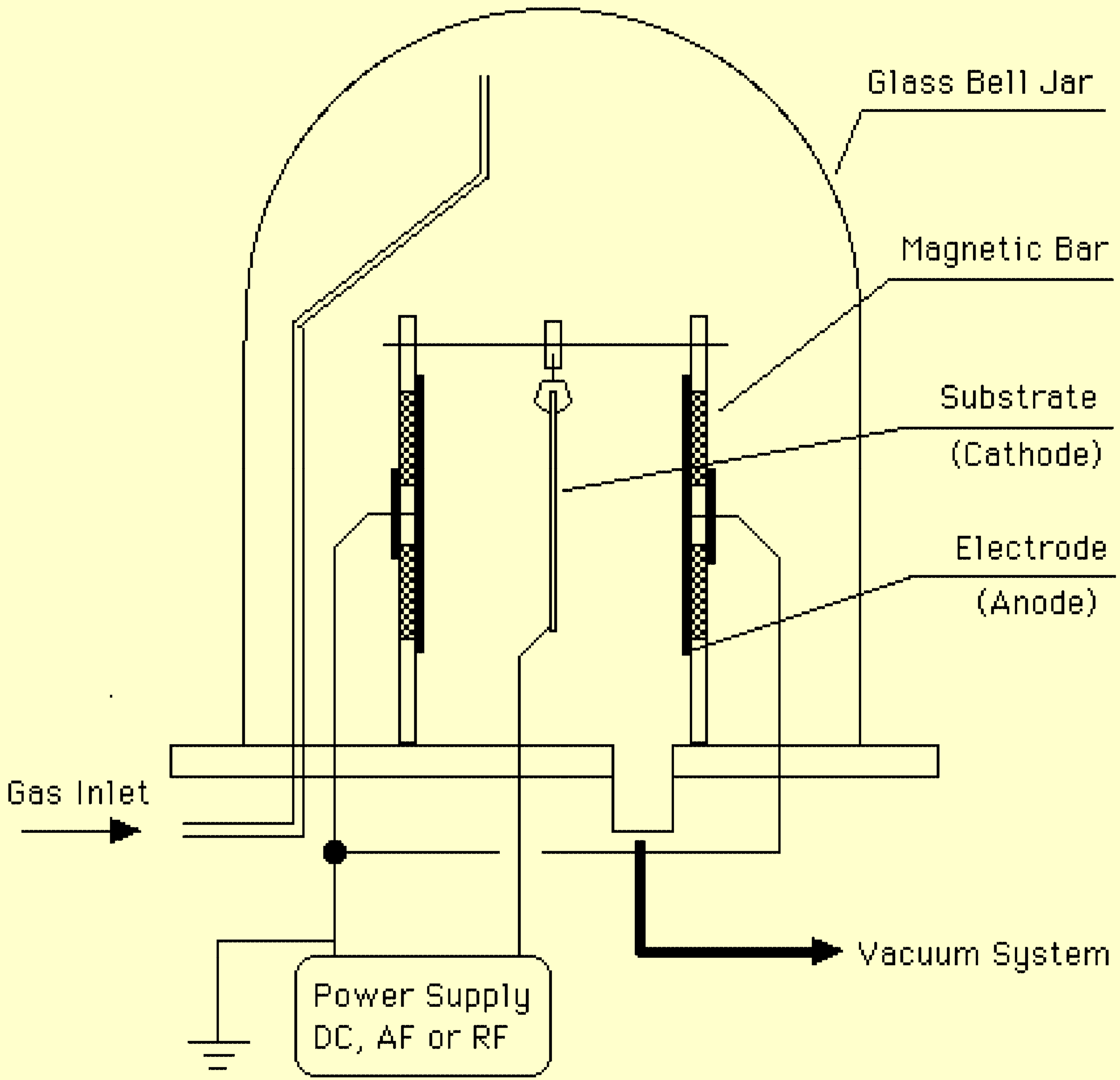
The effect of the floating panels positioned in front of the anode on the deposition rate on Anode surface and Cathode surface in DC cathodic polymerization.
Conditions are: 1 sccm TMS, 50 mTorr, DC 5 W, d = 100 mm.

Dark polymerization in cathode region & plasma polymerization in the negative glow

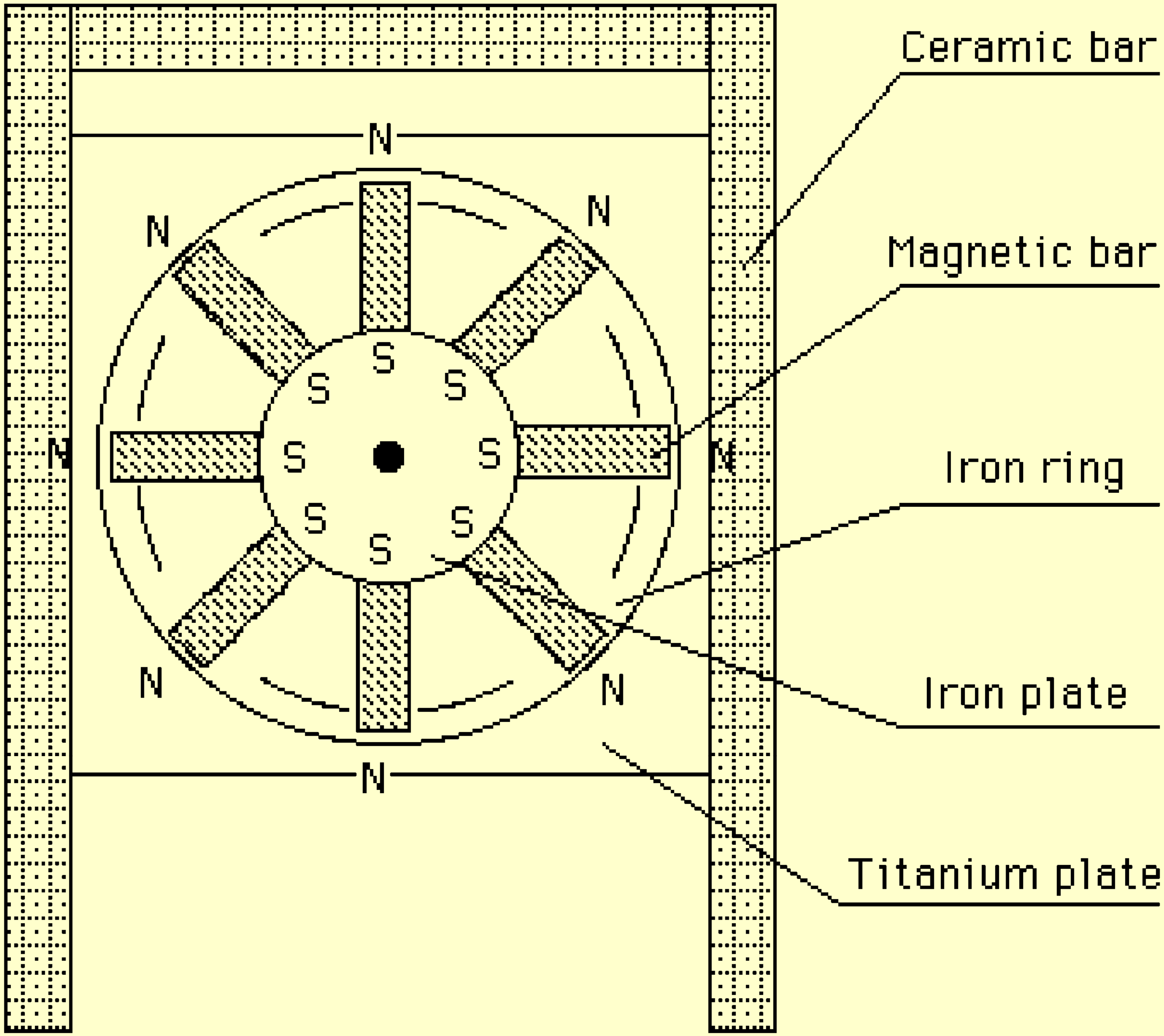
- **Dark polymerization (on the cathode surface)**
  - Much faster polymerization
  - Yields film with high refractive index
  - Deposition rate is pressure-dependent.
- **Glow discharge polymerization (on floating surface)**
  - Slower polymerization
  - Yields film with lower refractive index
  - Deposition rate is flow-rate dependent (pressure-independent)
- **Anode is a passive surface, which collects the same glow polymers.**

Effect of Electrical Field

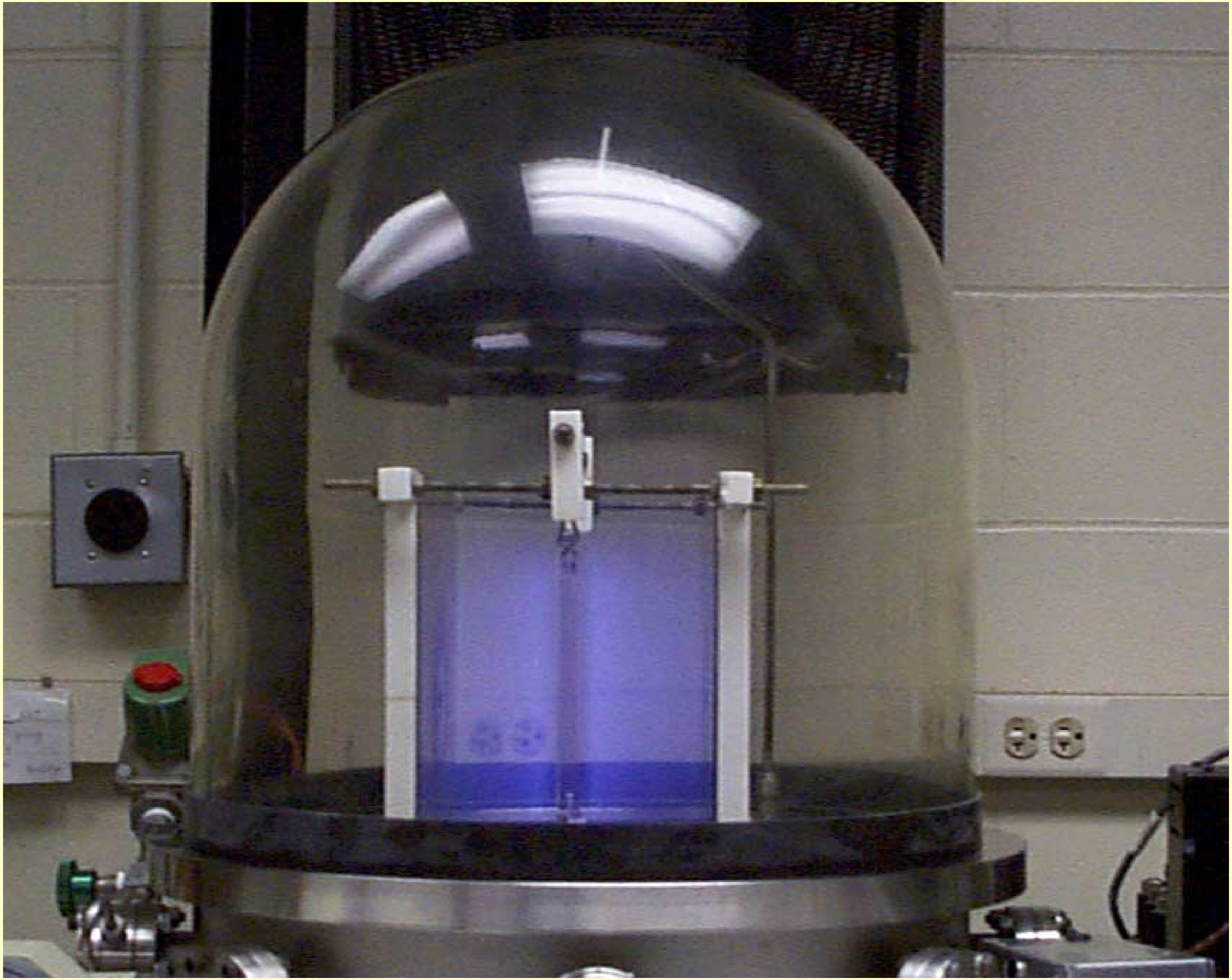
- Edge effect
  - Sputtering by Ar plasma
  - Deposition on the cathode surface
- Un-balanced surface areas of cathode and anode
  - Deposition rate onto a small cathode or powered electrode is higher.
- Effect of magnetic confinement
  - Reduce the edge effect on sputtering
  - Over correct the edge-effect in the depositon



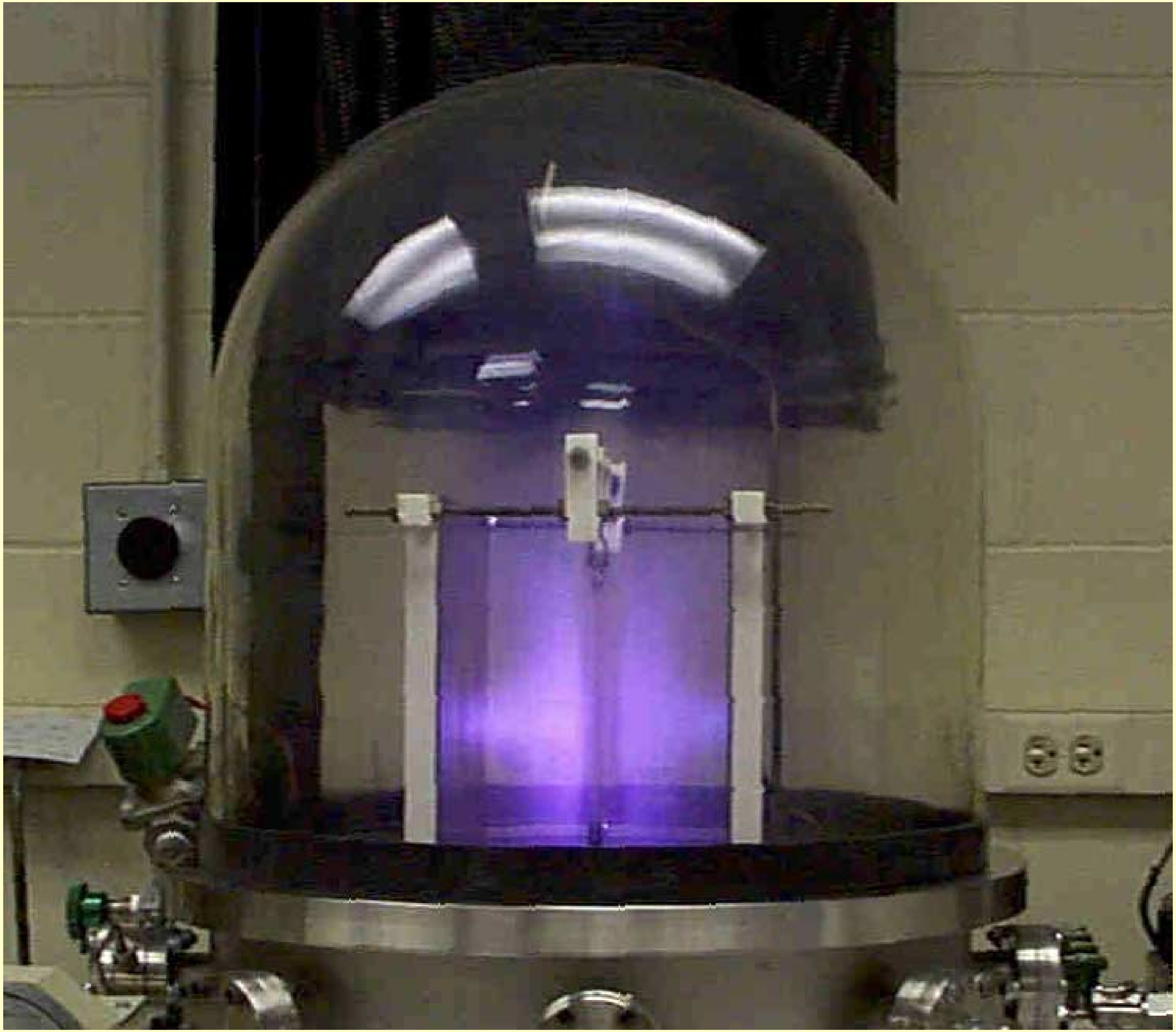
Schematic diagram of bell jar reactor system



Structure of anode magnetron electrode

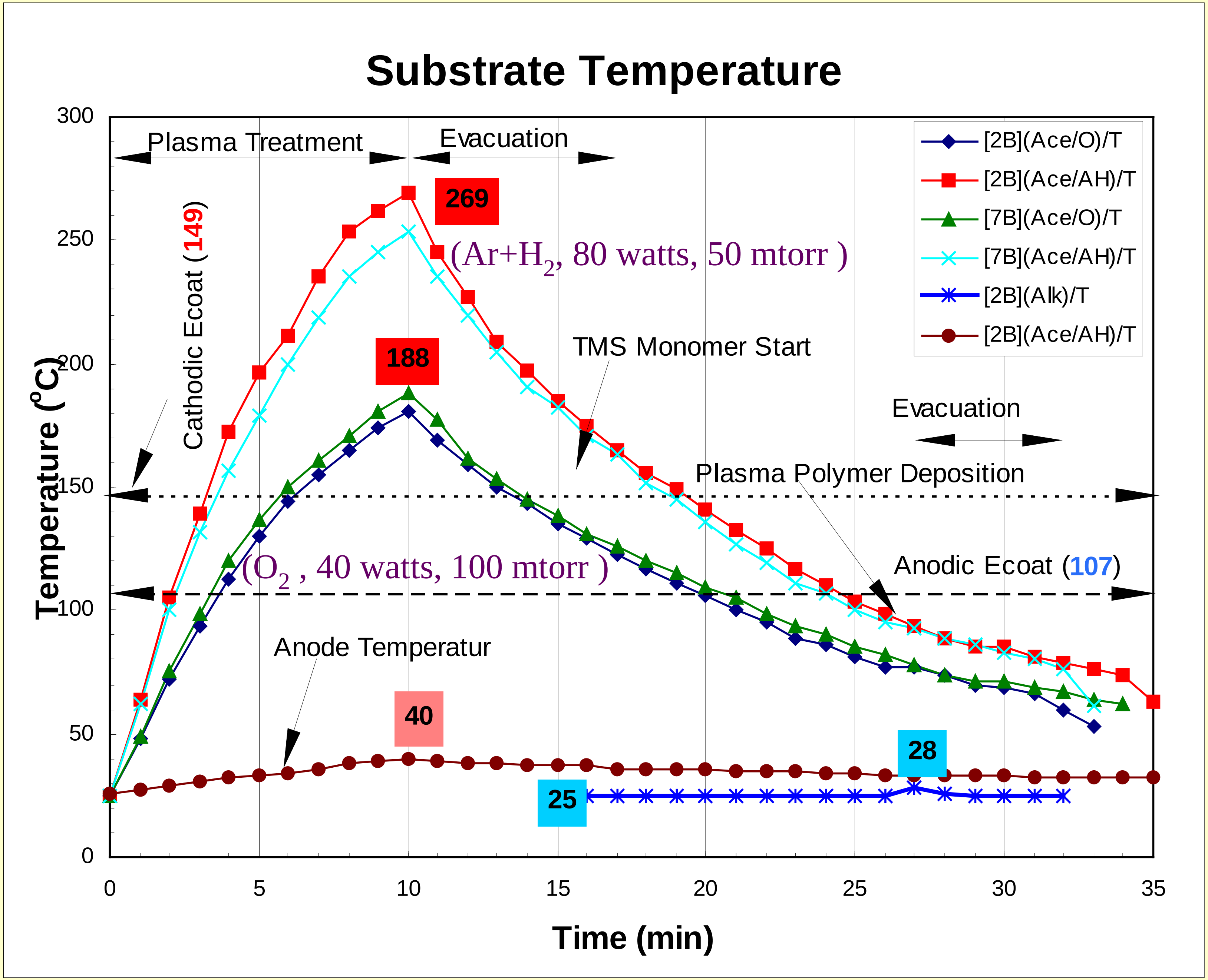


Oxygen DC plasma without magnetron enhancement

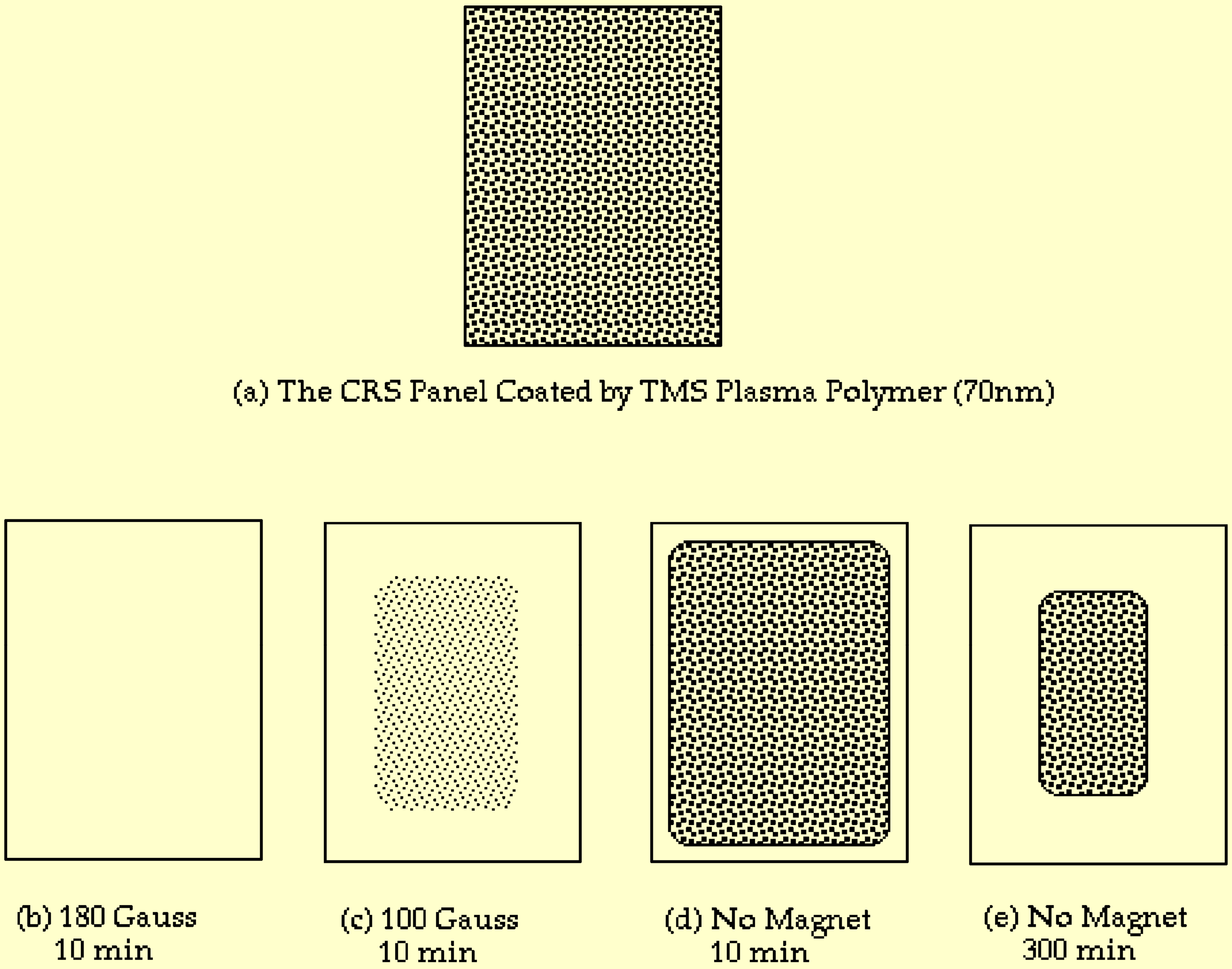


Oxygen DC plasma with anode magnetron

Temperature of cathode (substrate) & anode

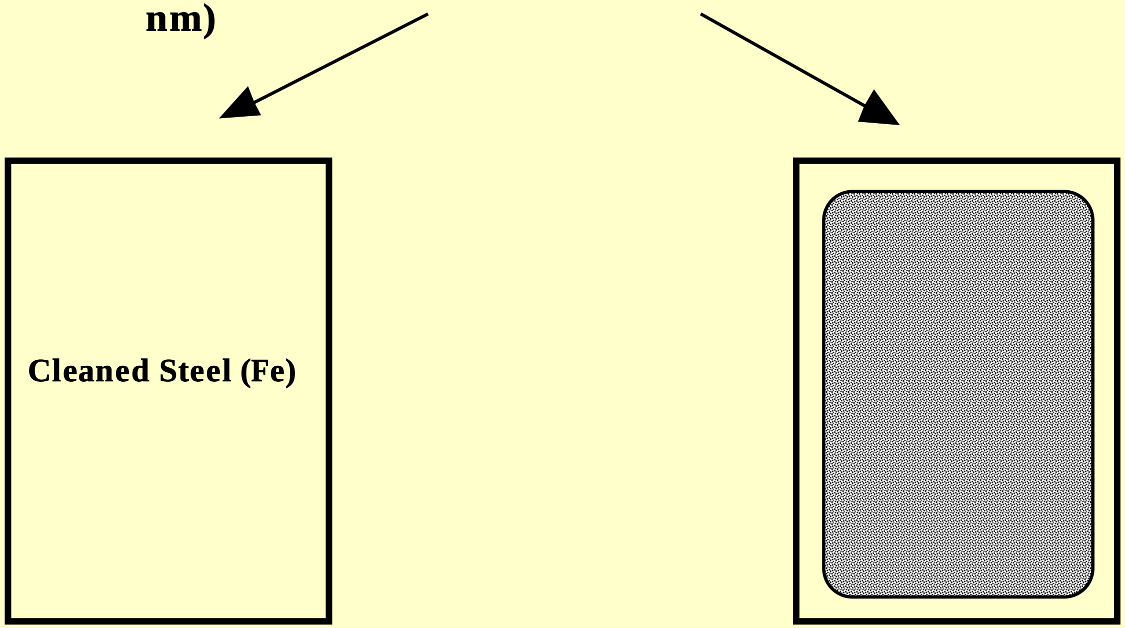


Sputter Cleaning of Cathode Coated with TMS Plasma Polymer



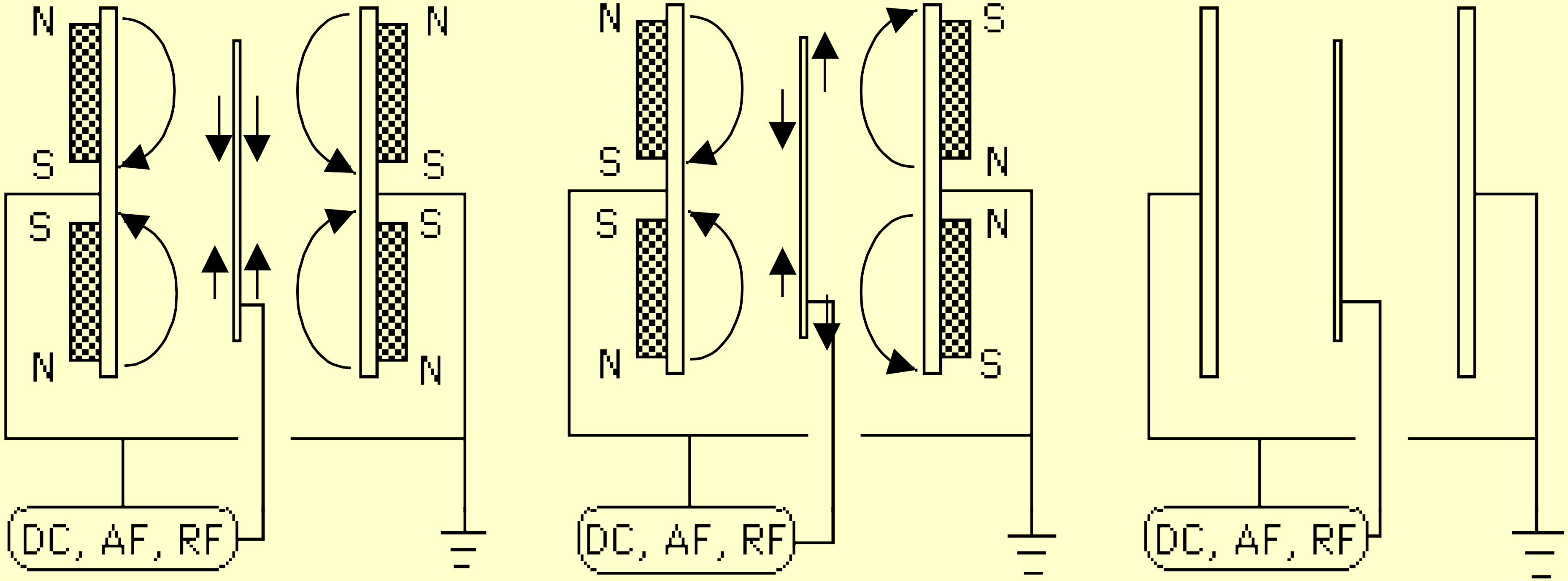
Sputter Cleaning of Cathode Coated with TMS Plasma Polymer

(a): The CRS Panel Coated by TMS Plasma (70 nm)



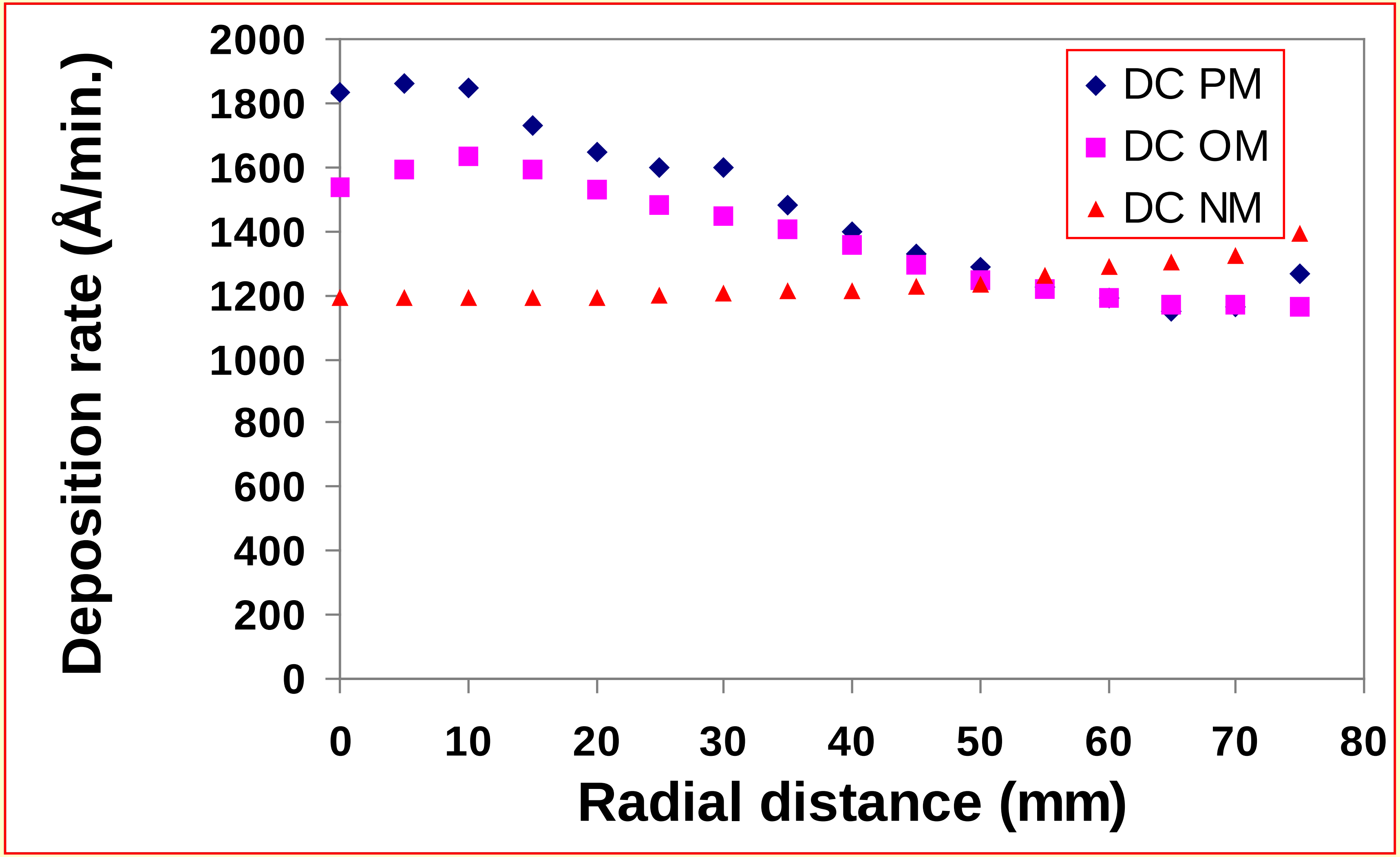
(b): Interelectrode distance of 50 mm or 75 mm

(c): Interelectrode distance of 100 mm to 175 mm

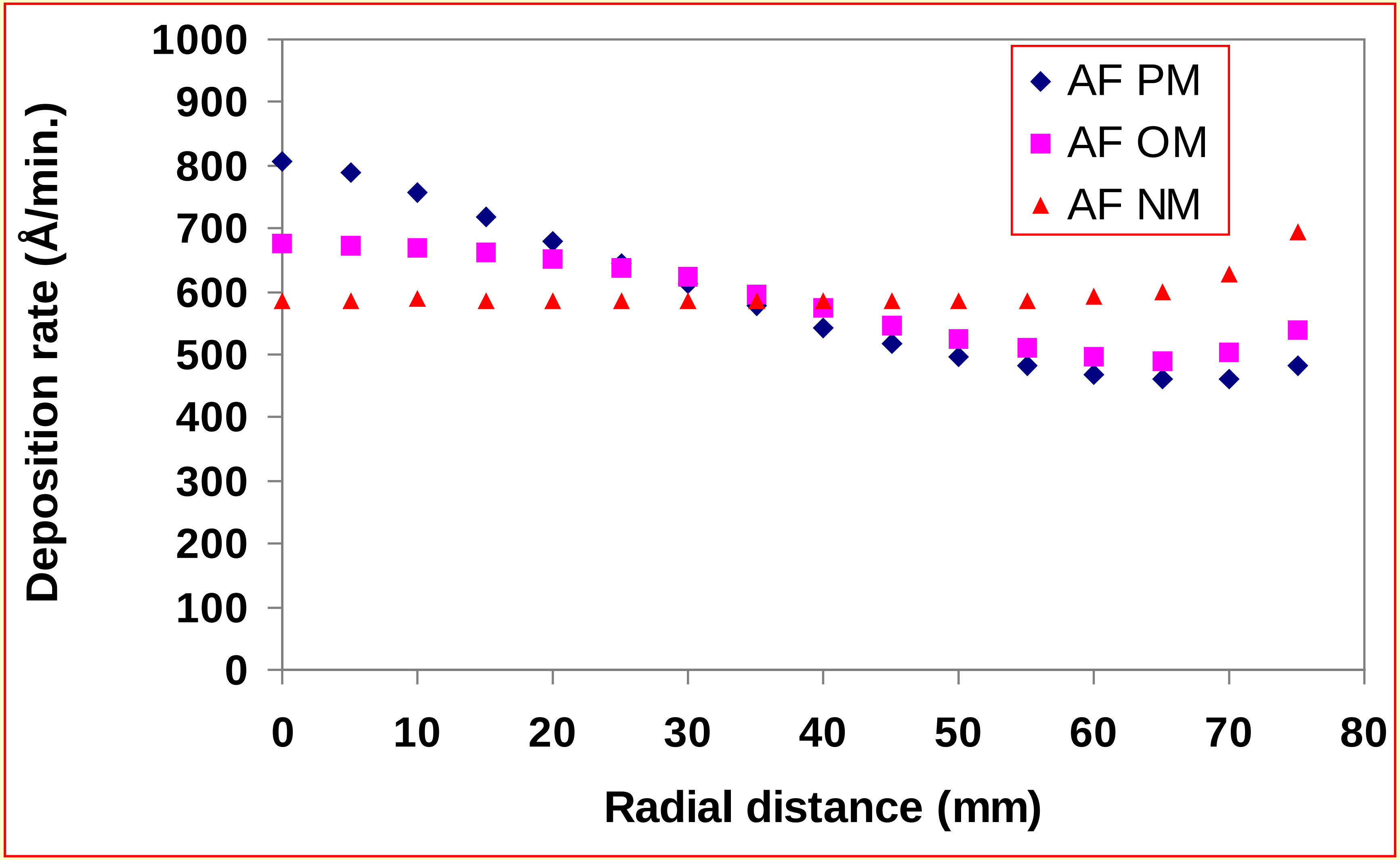


Schematic diagram of different magnetic field configuration.

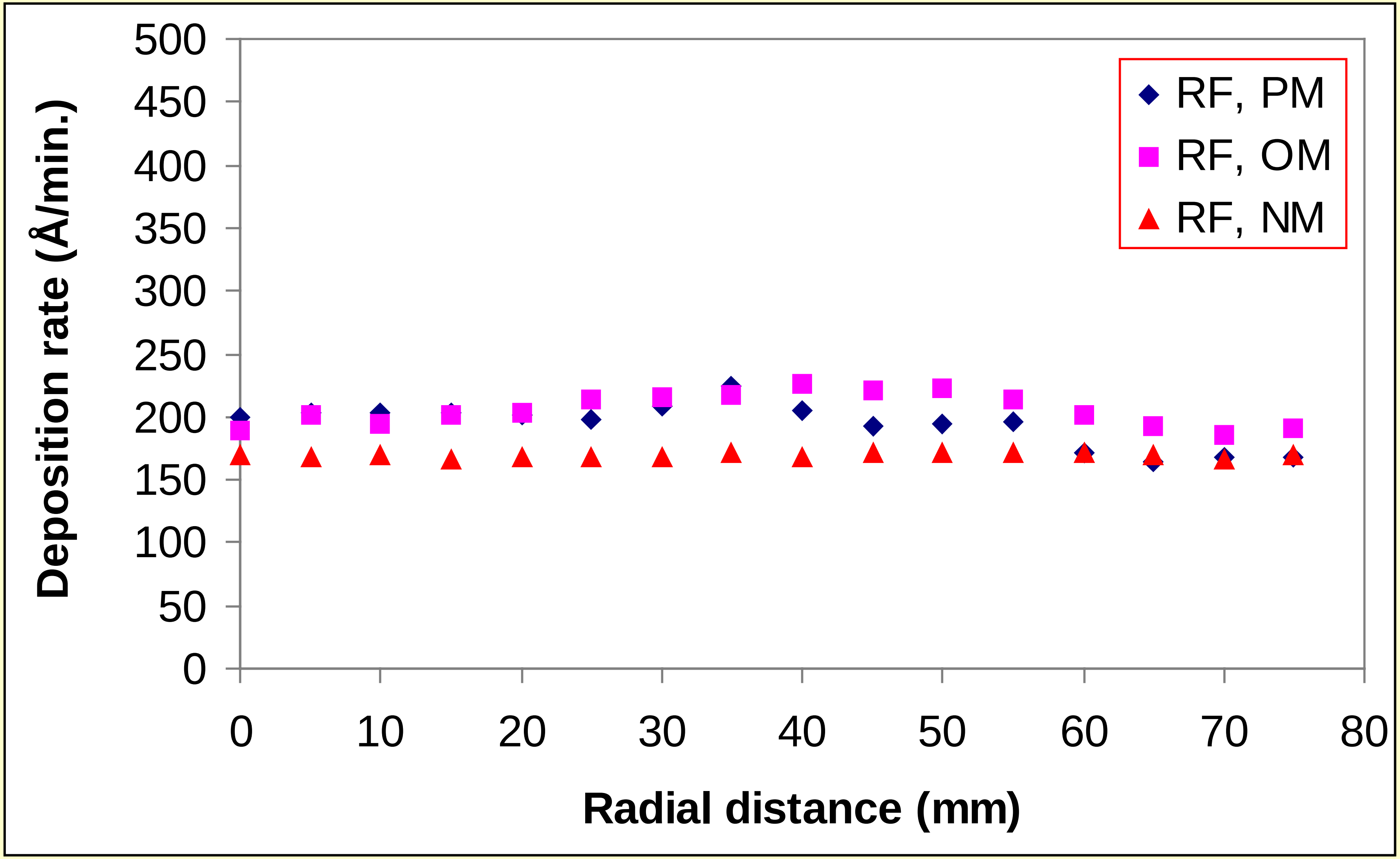
- parallel magnetic field configuration (PM),
- (b) opposite magnetic field configuration (OM) and
- (c) no magnetron on the backside of anode electrodes.



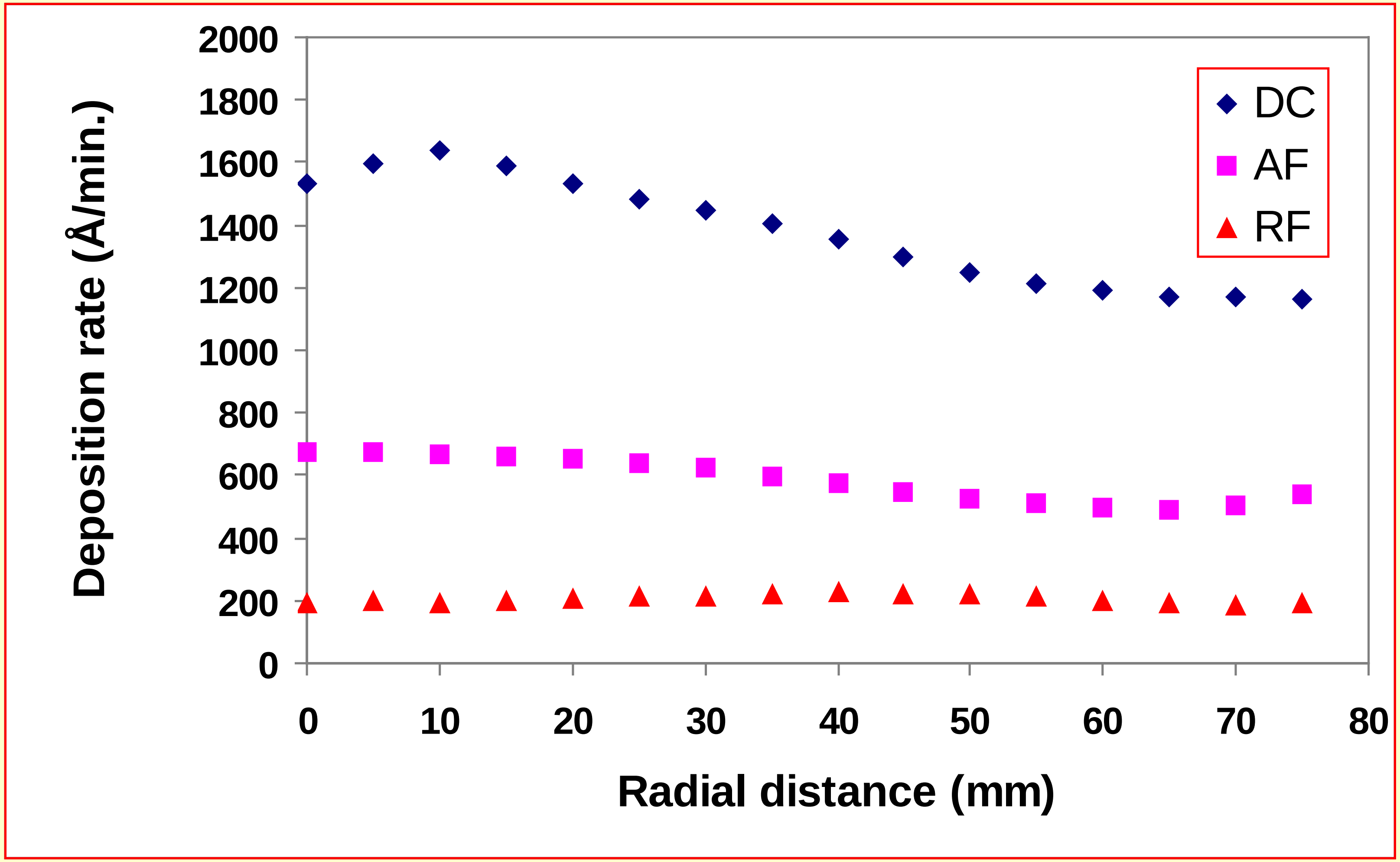
Dependence of the deposition rate distribution on the magnetic field configuration (DC, TMS, 5 w, 50 mtorr, d=100 mm, 1 sccm)



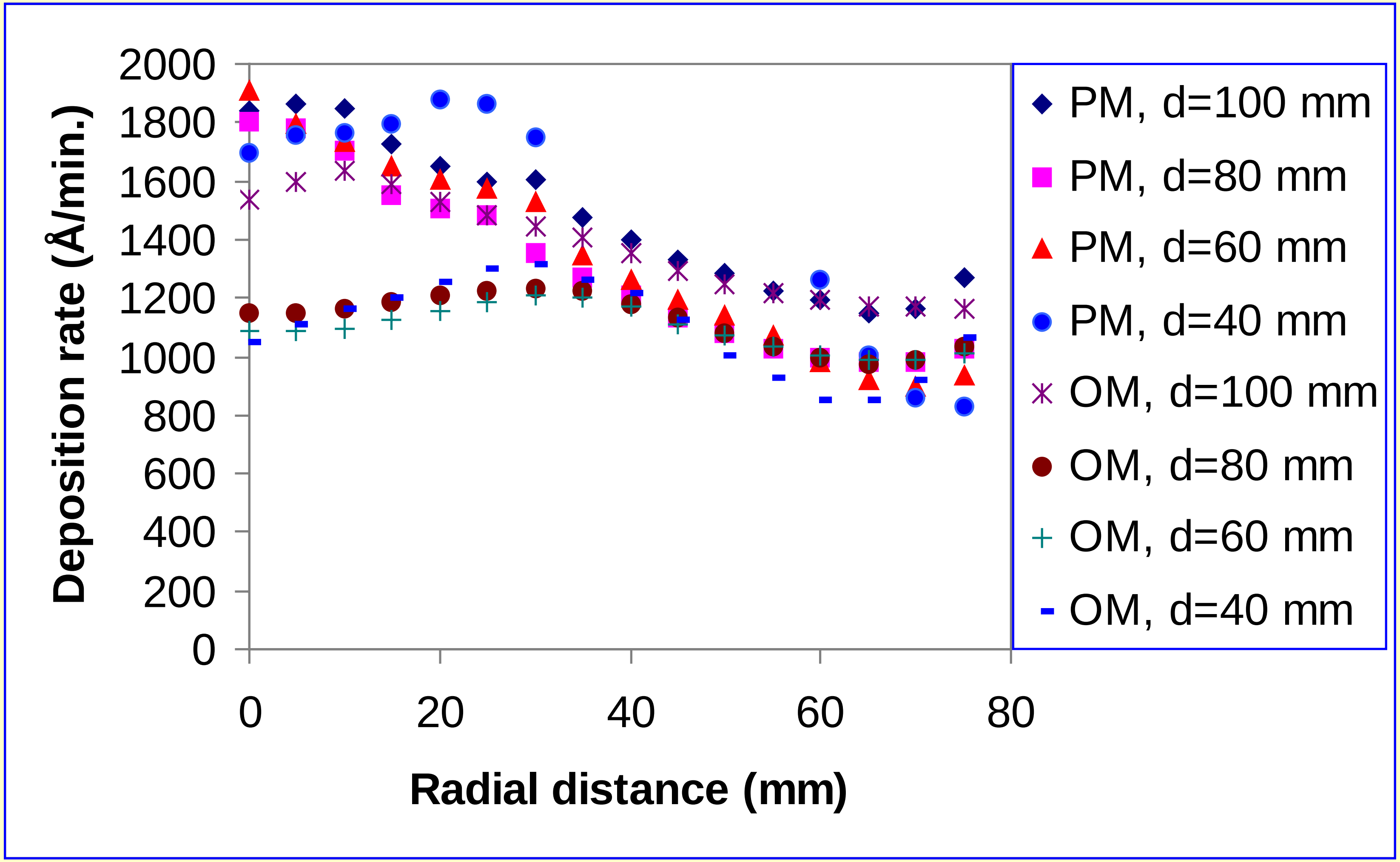
Dependence of the deposition rate distribution on the magnetic field configuration (AF, TMS, 5 w, 50 mtorr, d=100 mm, 1 sccm)



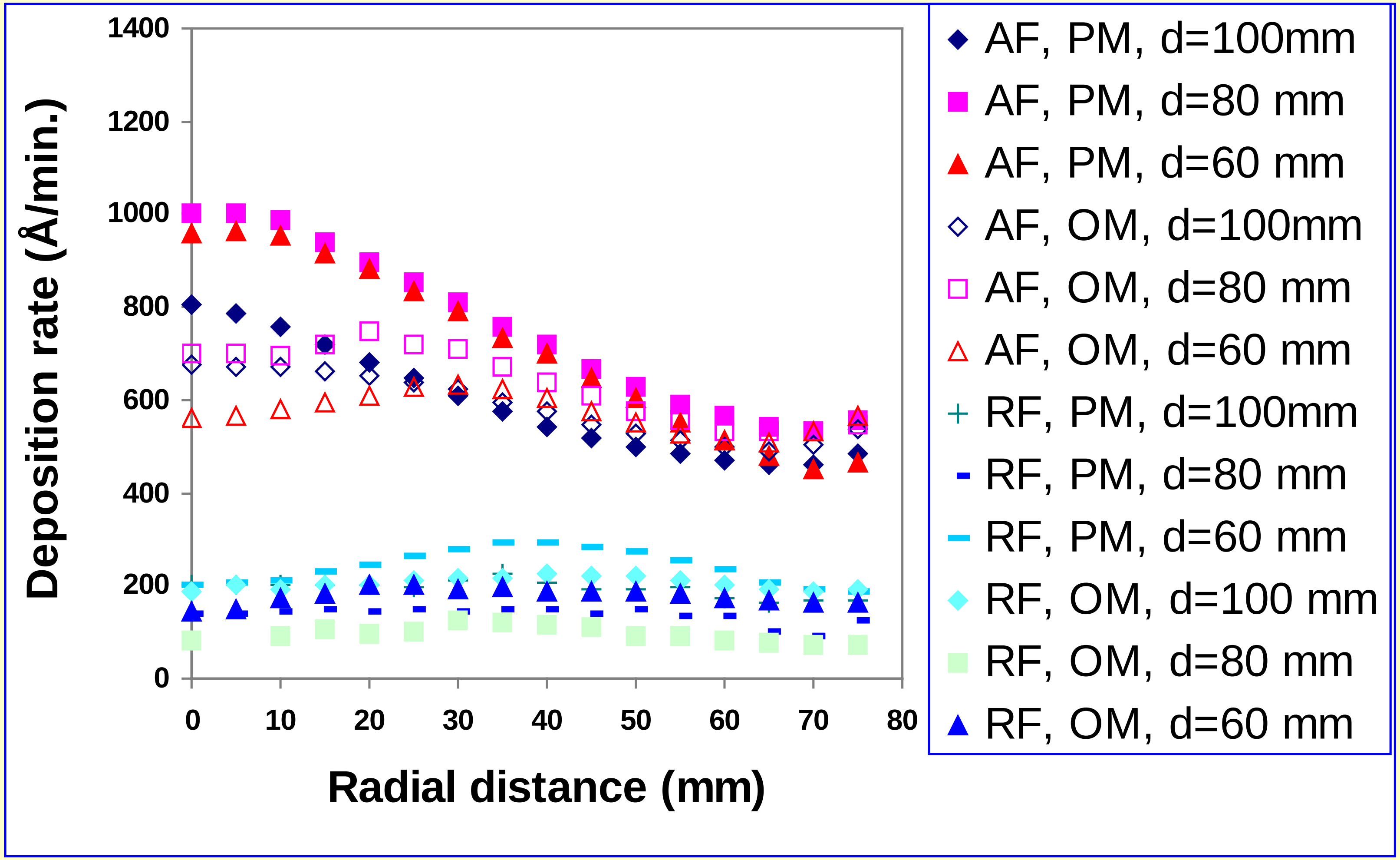
dependence of the deposition rate distribution on the magnetic field configuration (RF, 5 w, 50 mtorr, d=100 mm, 1 sccm)



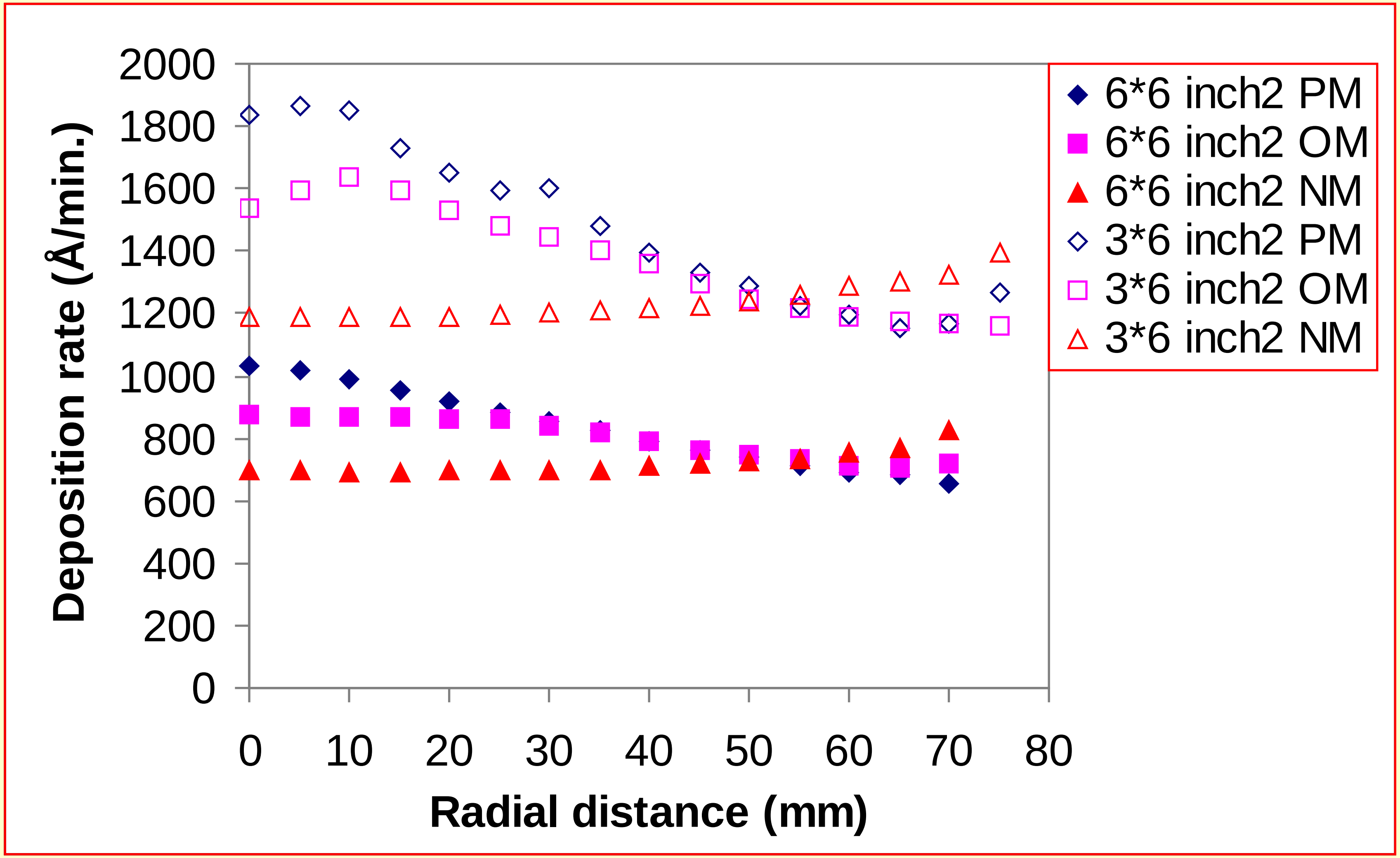
Dependence of deposition rate on power supplies
(OM, TMS, 50 mtorr, 1 sccm, 5 w, d = 100 mm)



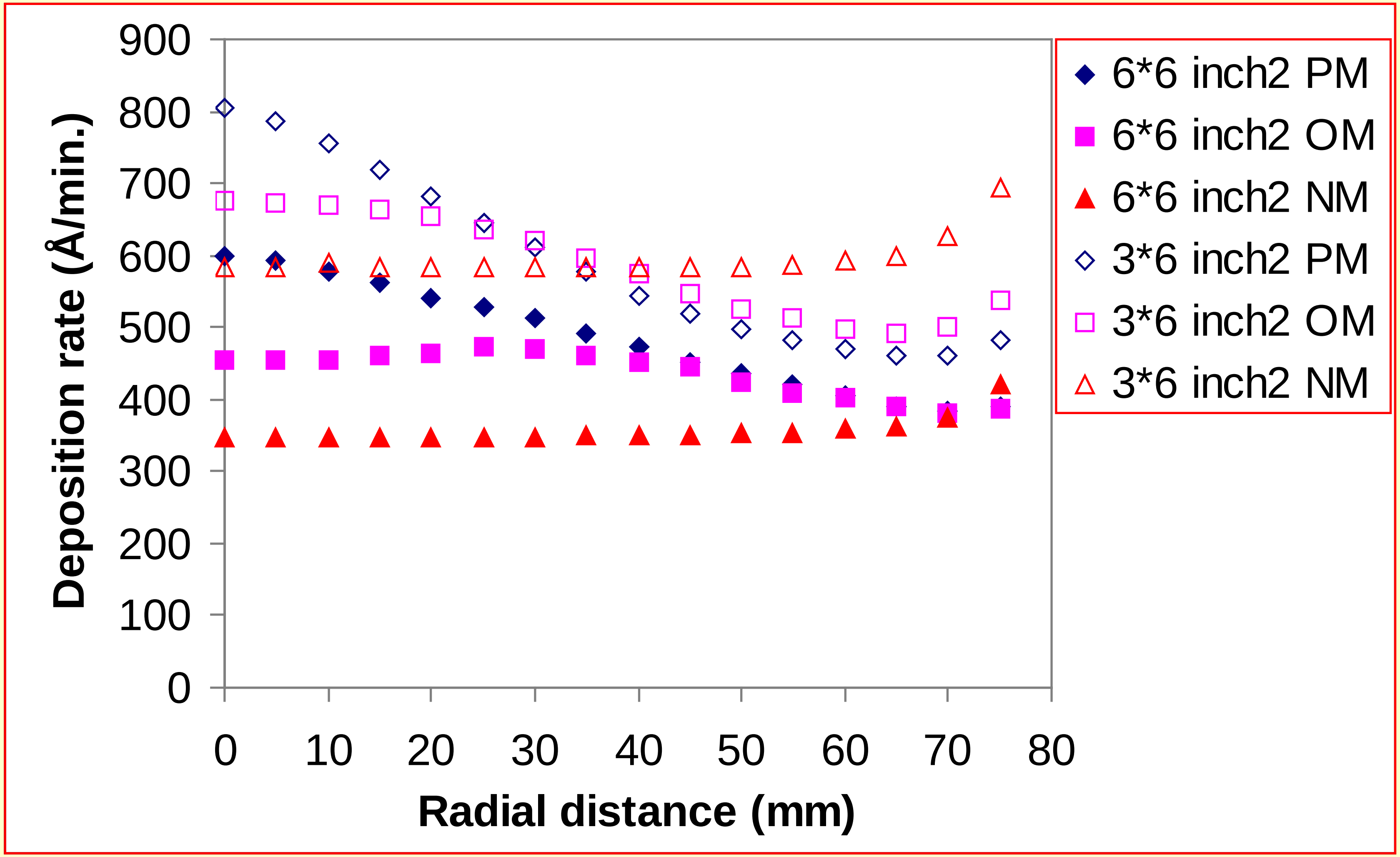
The influence of electrode distance on the deposition rate
(DC. TMS, 50 mtorr, 1 sccm, 5 w)



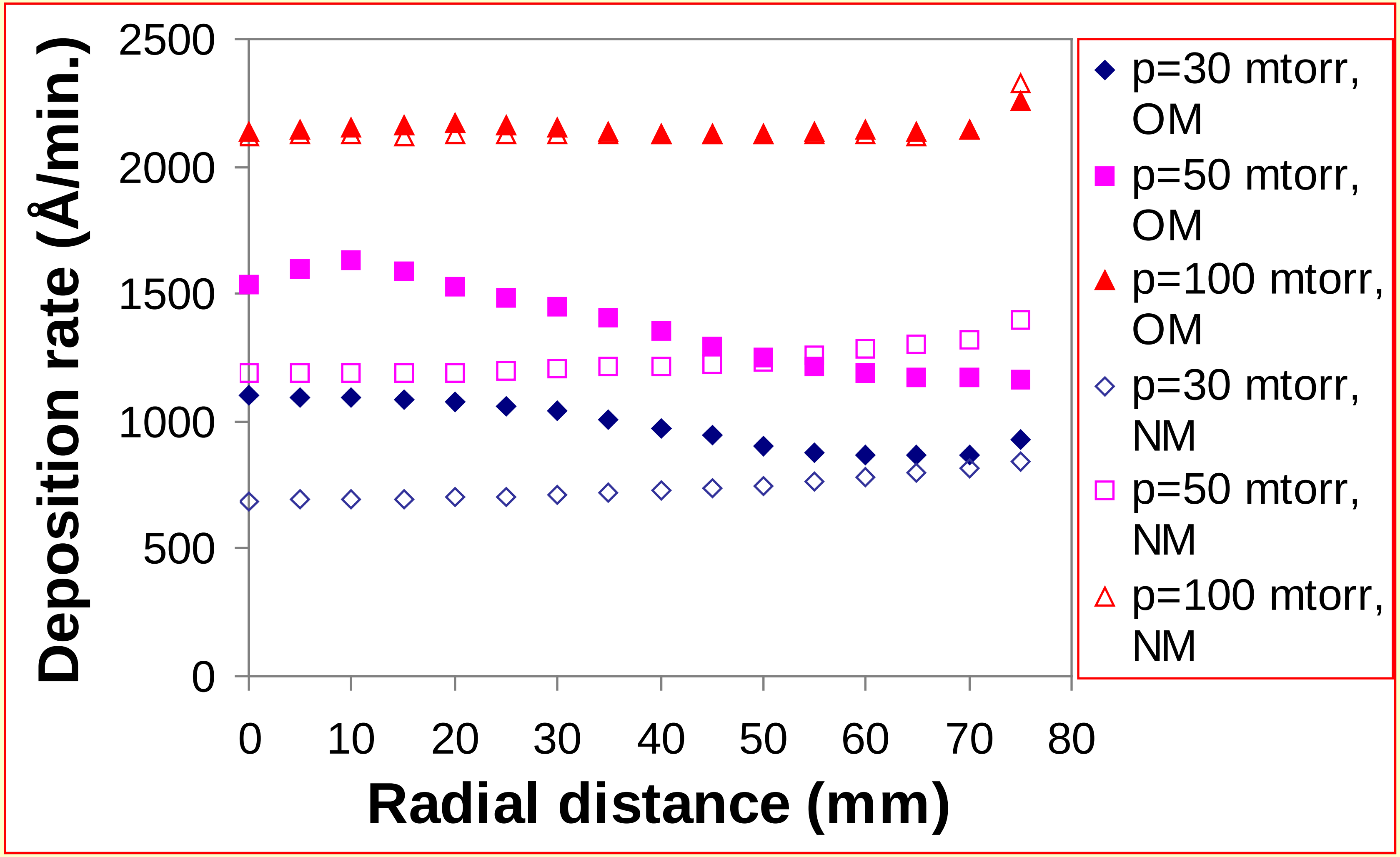
The influence of electrode distance on the deposition rate
(AF or RF, TMS, 50 mtorr, 1 sccm, 5 w)



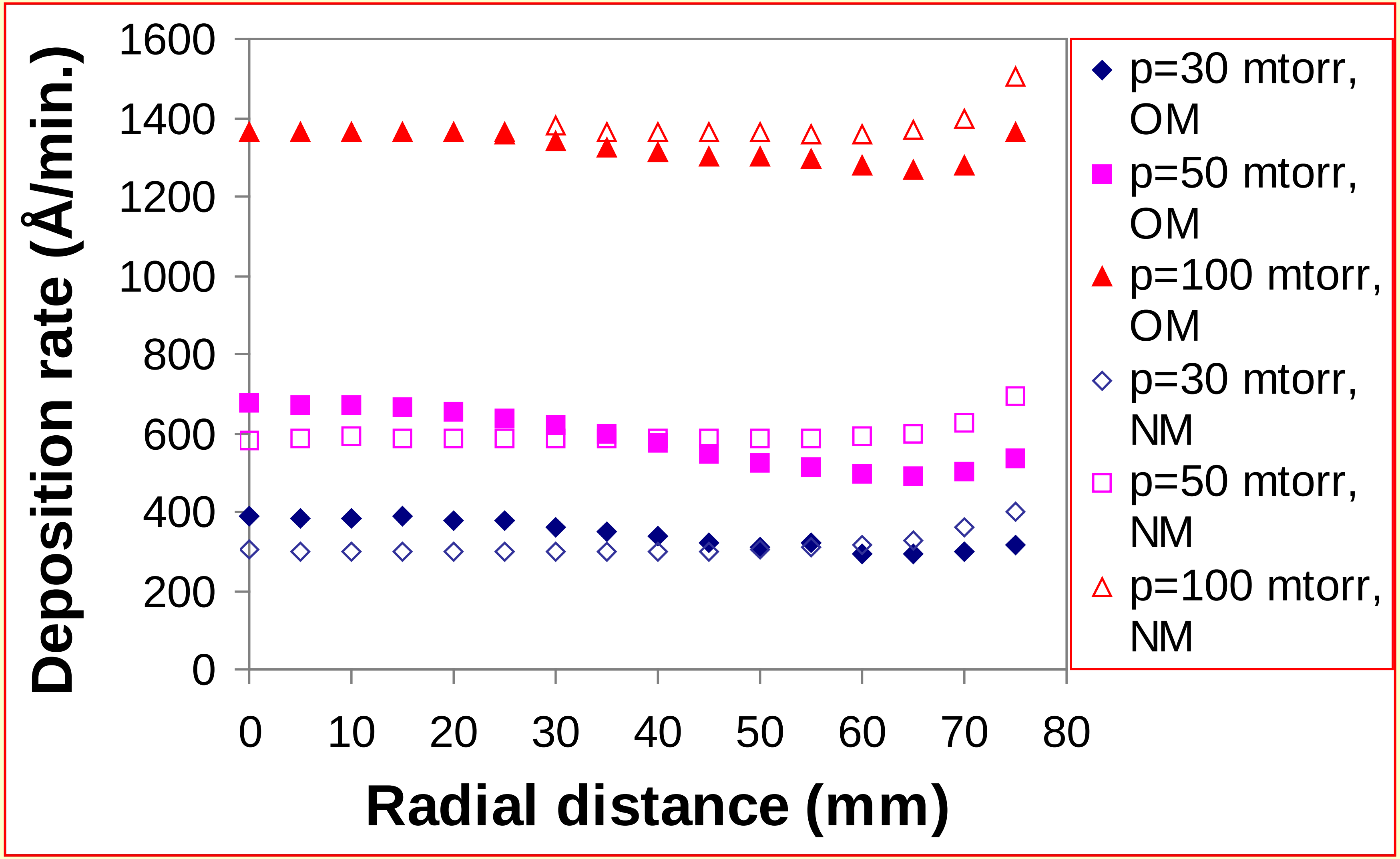
The influence of substrate area on the deposition rate
(DC, TMS, 50 mtorr, 1 sccm, 5 W)



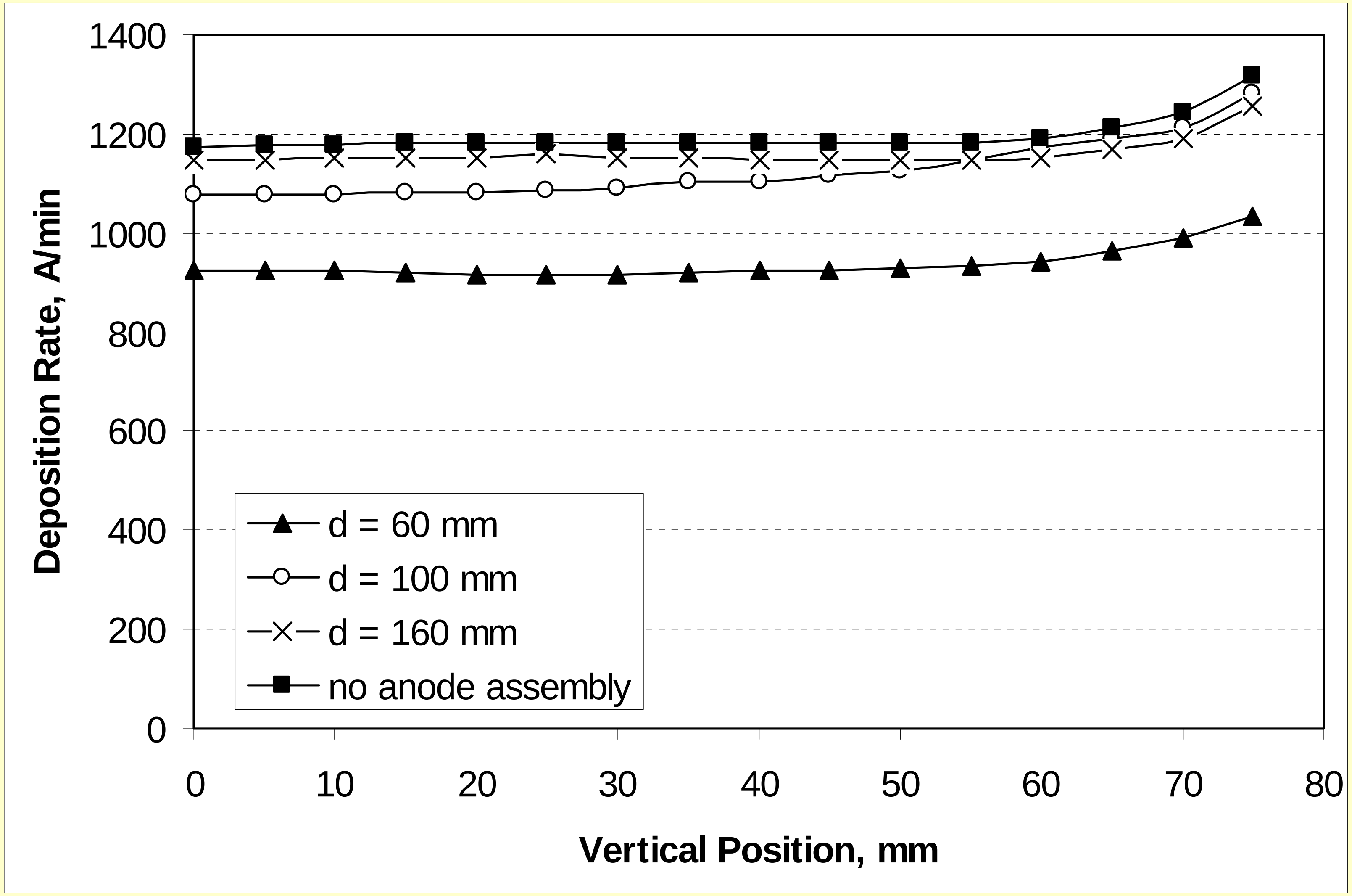
The influence of substrate area on the deposition rate
(AF, TMS, 50 mtorr, 1 sccm, 5 W)



Dependence of deposition rate distribution on system pressure
DC glow discharge (TMS, 5 W, d=100 mm, 1 sccm)



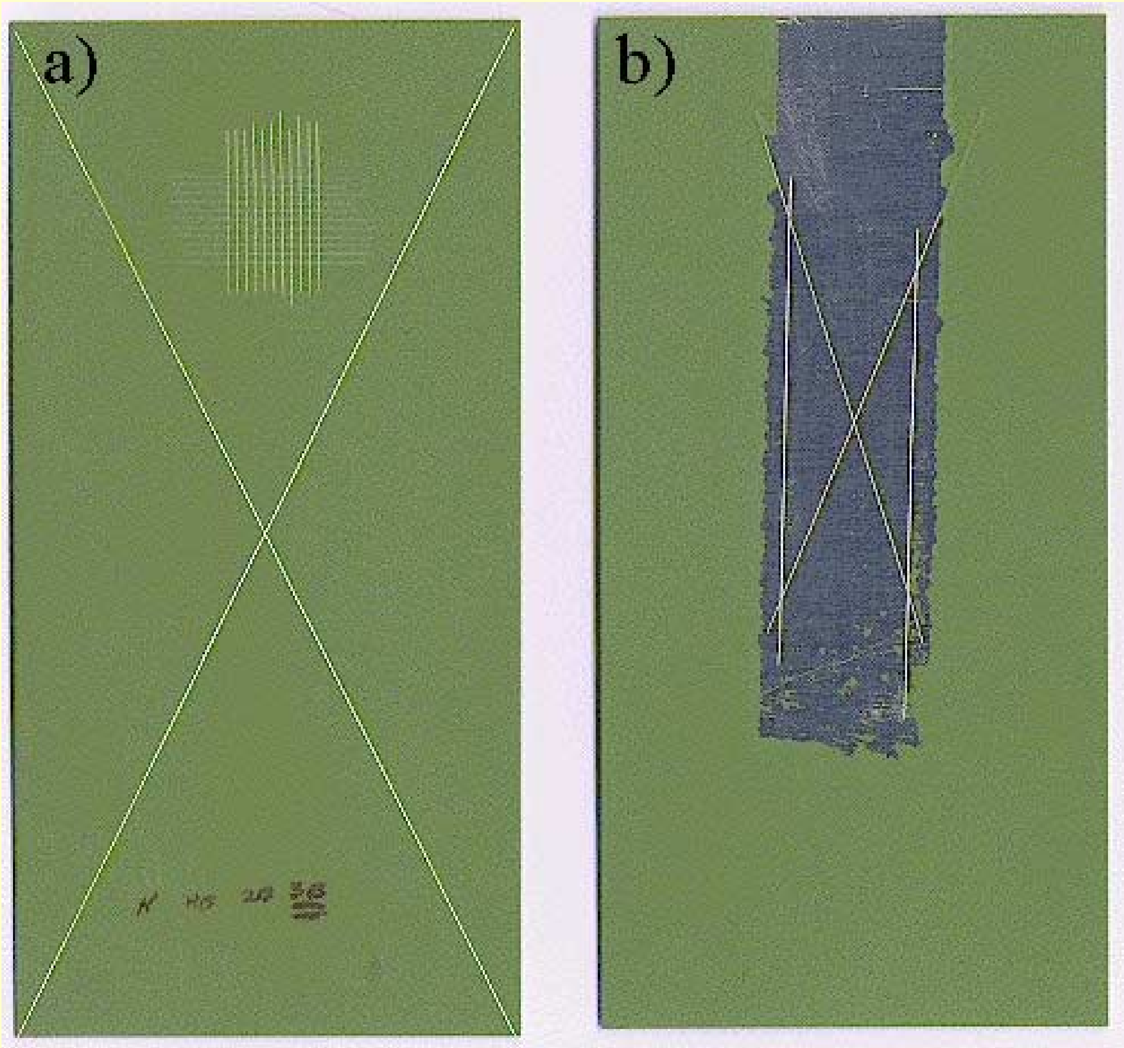
dependence of deposition rate distribution on system pressure
AF glow discharge (TMS, 5 W, d=100 mtorr, 1 sccm).



The influence of electrode distance on the deposition rate on **Cathode surface** in DC cathodic polymerization. Conditions are: 1 sccm TMS, 50 mTorr, DC 5 W, d is the distance between two anodes (the cathode is placed in the middle of the two anodes).

Effect of Wall Contamination

- Because of CAP principle, wall contamination could change the deposition pattern.
- Elements with high electro negativity in the wall contamination cause the most pronounced change in the deposition.
  - Change from the super adhesion system to no adhesion system caused by F containing wall contaminants.



Scanned image of the surface of two alloy panels showing adhesion failure caused by the omission of O_2 plasma treatment of the substrate prior to plasma film deposition and application of the primer (Deft 44-GN-72 MIL-P-85582 Type I Waterbased Chromated Control Primer). a) Panel after Skydrol LD4® fluid resistance test, which had the O_2 plasma treatment prior to film deposition and primer application. b) Panel after scribed wet (24-hour immersion in tap water) tape test, which had not been treated with the O_2 plasma treatment prior to film deposition and primer application.

Sequence of processes in the normal operation

Evac./O_2 /TMS /($HFE+H_2$)/ Evac./ O_2 / TMS /($HFE+H_2$)/

New substrate → The first batch

New substrate → The second batch

<u>Sequence of Plasma Polymerization</u>

TMS Plasma/($HFE+H_2$) Plasma

Sequence of processes in the abnormal operation

Evac./TMS /(HFE+H_2)/ Evac./ TMS /(HFE+H_2)/

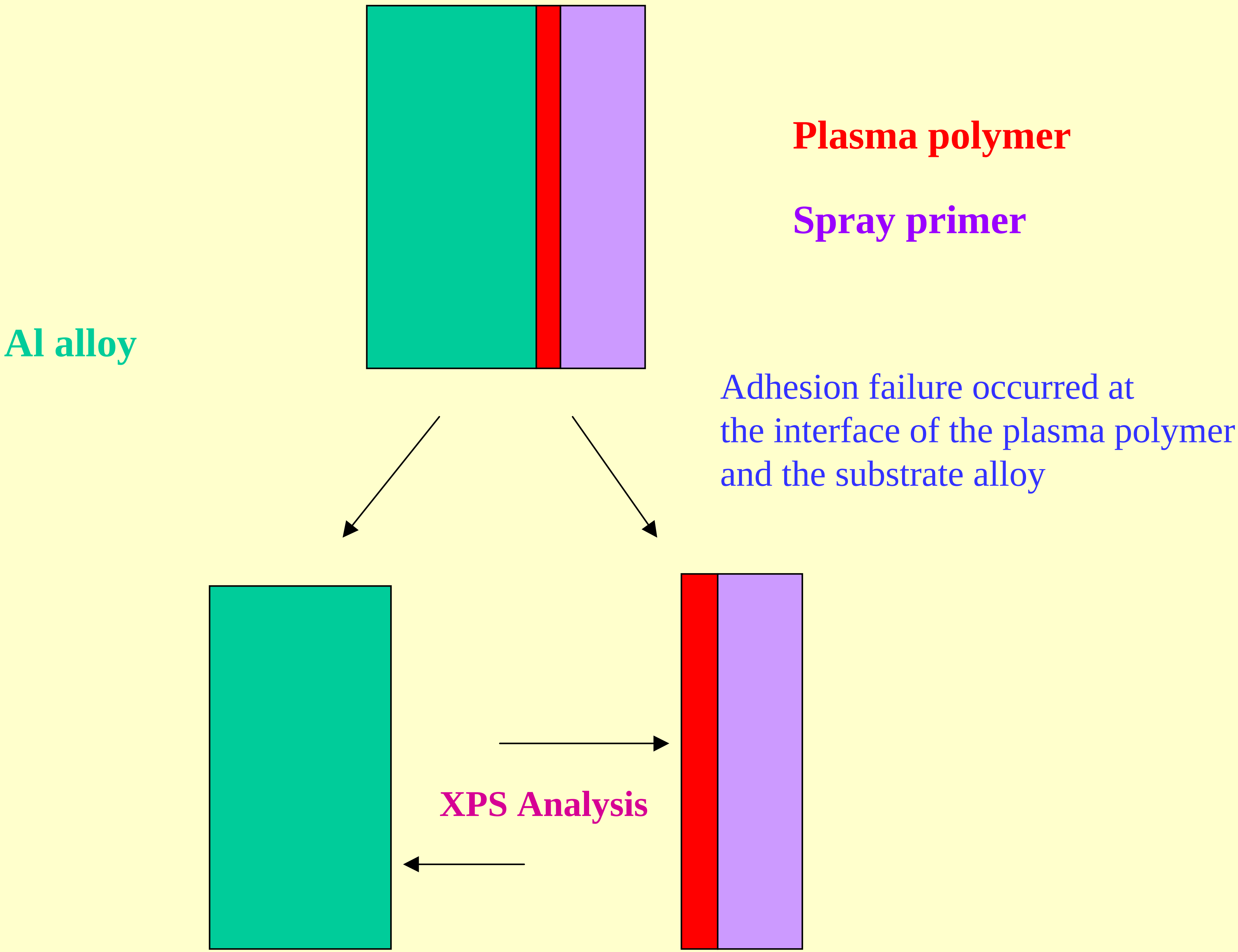
New substrate → **New substrate** →

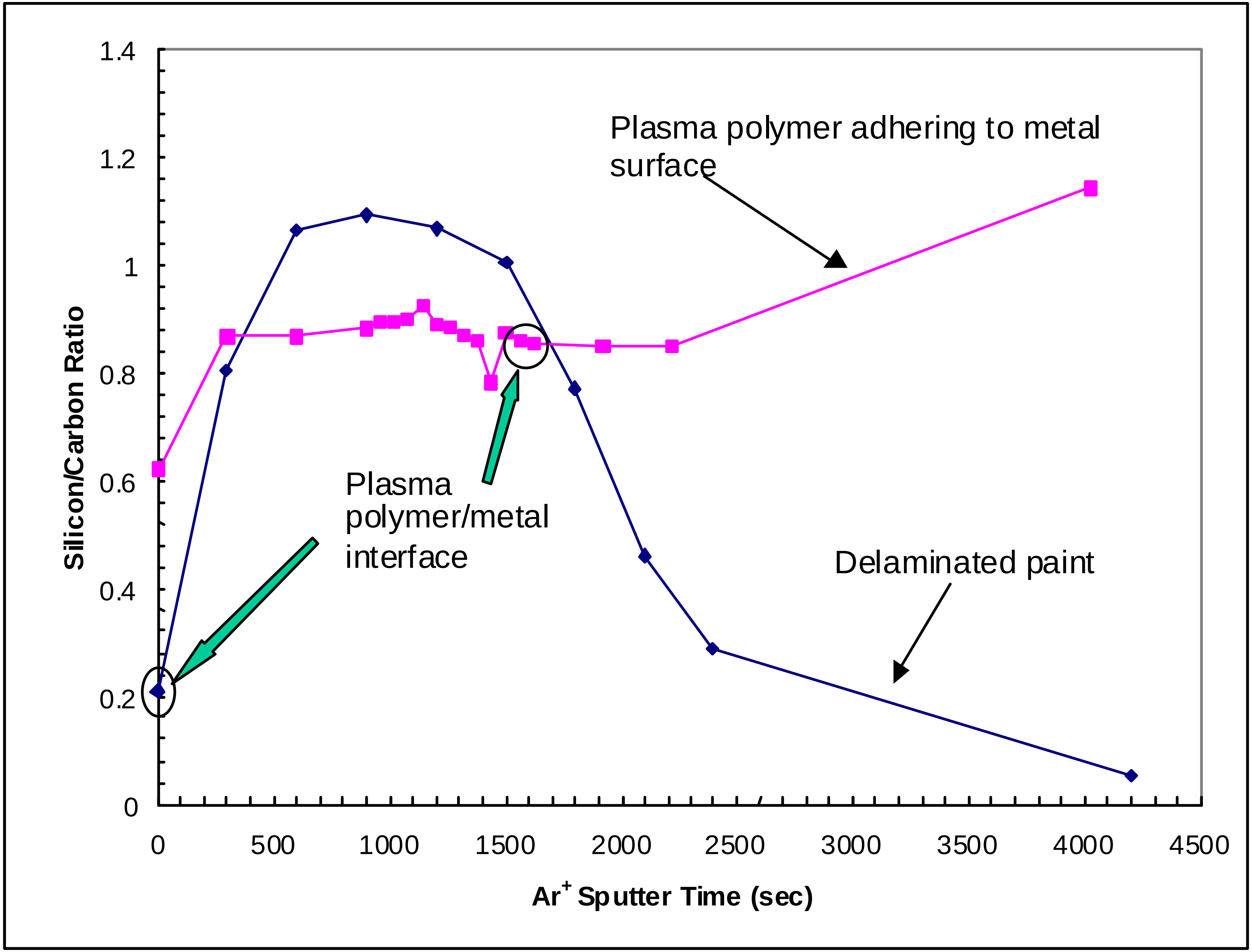
The first batch The second batch

<u>Sequence of Plasma Polymerization</u>

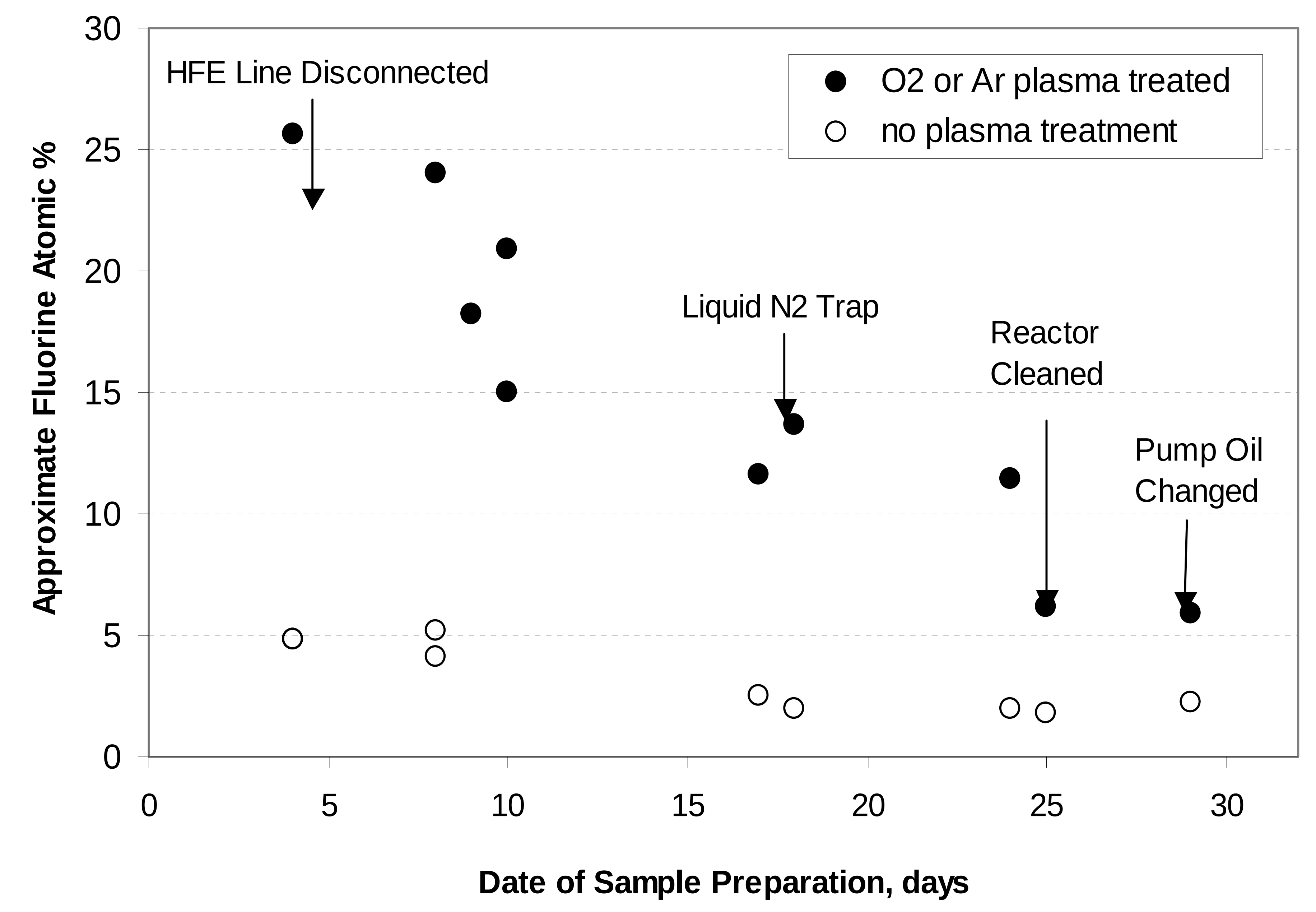
(HFE+H_2) Plasma/TMS Plasma

Previous batch


Plasma polymer
Spray primer
Al alloy
Adhesion failure occurred at
the interface of the plasma polymer
and the substrate alloy
XPS Analysis



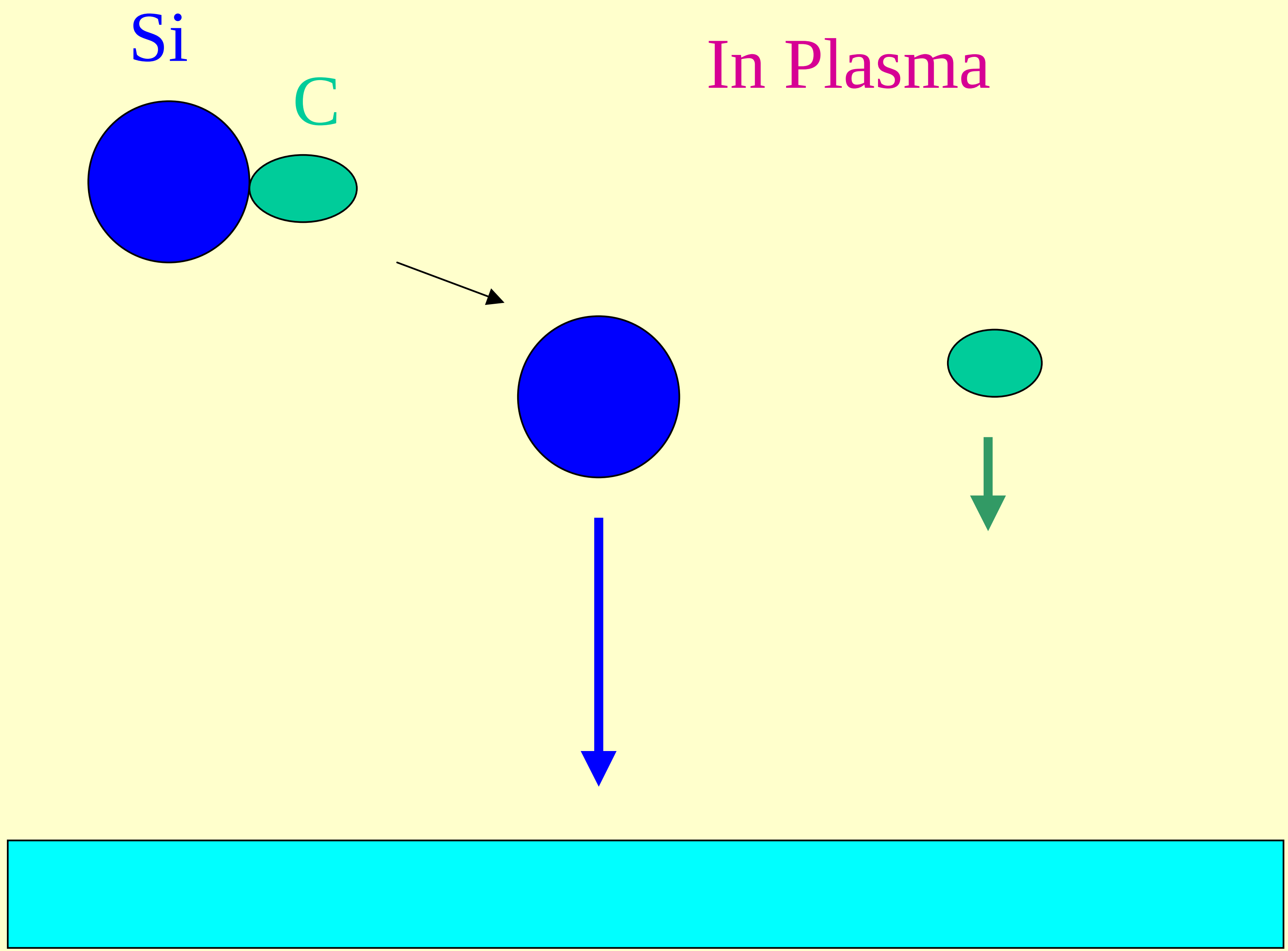
Plasma polymer adhering to metal surface
Plasma polymer/metal interface
Delaminated paint
Silicon/Carbon Ratio
Ar+ Sputter Time (sec)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
0
500
1000
1500
2000
2500
3000
3500
4000
4500



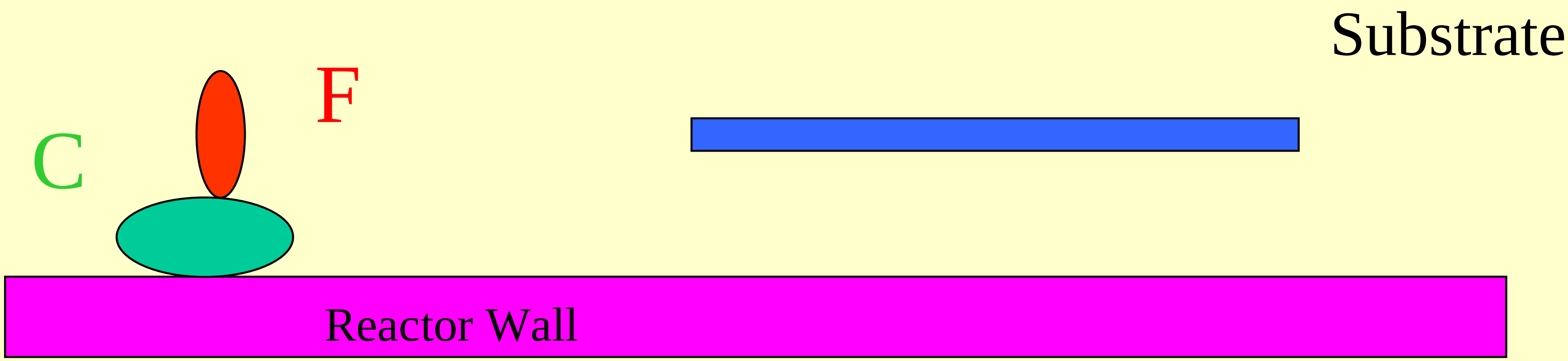
HFE Line Disconnected
O2 or Ar plasma treated
no plasma treatment
Liquid N2 Trap
Reactor Cleaned
Pump Oil Changed
Approximate Fluorine Atomic %
0
5
10
15
20
25
30
Date of Sample Preparation, days

Formation of stable molecules in plasma

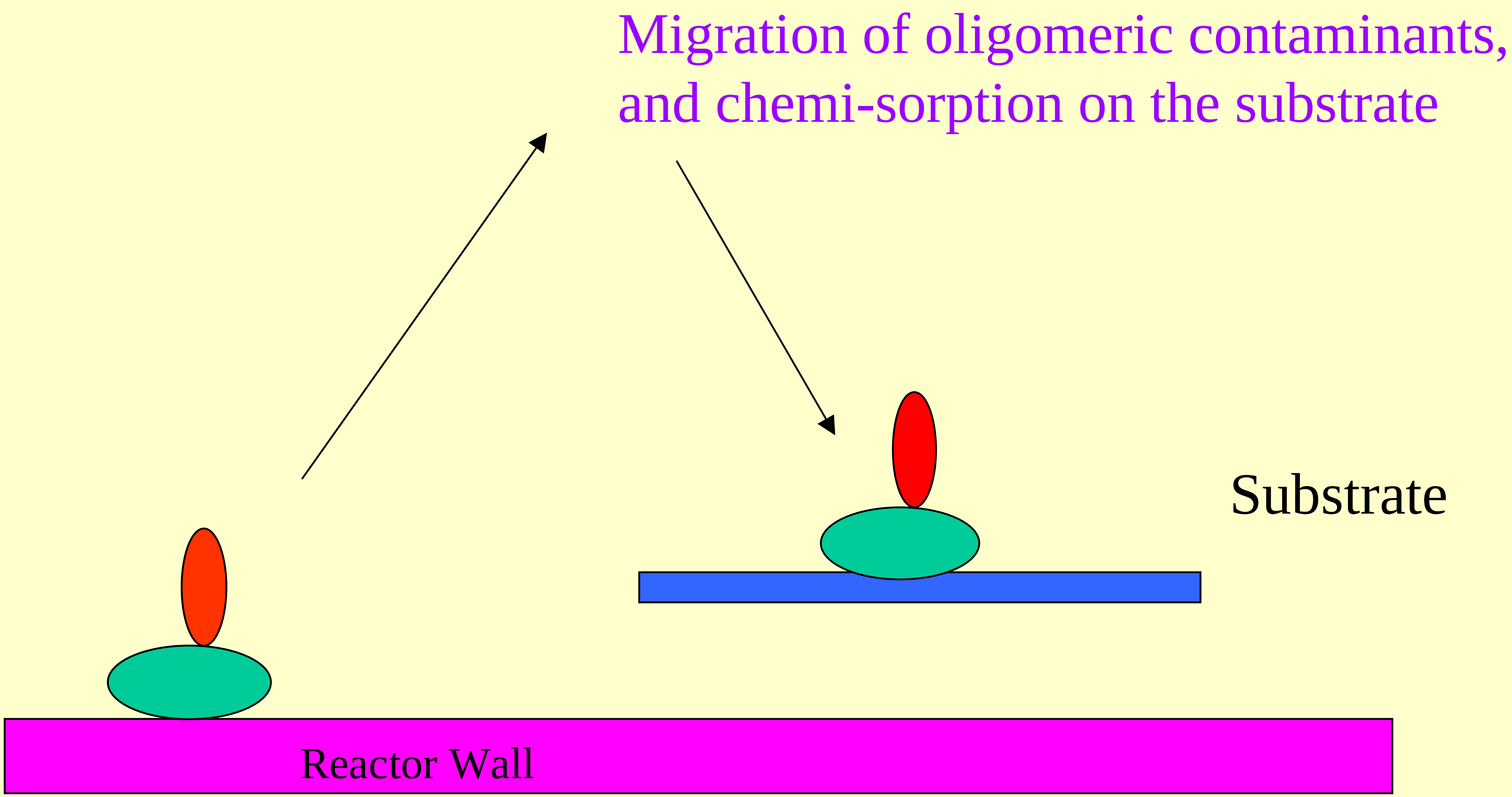
- **Stable molecules escape from the system.**
- **Stable molecules shorten the kinetic-path length of plasma polymerization.**
  - **Increase the oligomer content in plasma polymer.**
  - **Change elemental composition of plasma polymer.**
- **Stable molecules formation change the balance of ablation and polymerization.**
  - **Stable molecules formation such as SiF_4 is the basis for plasma etching of silicon, and HF for polymerization of etching gas.**
  - **Depending the source of element to form stable molecules, adhesion and/or barrier characteristics of plasma polymer could be completely damaged.**

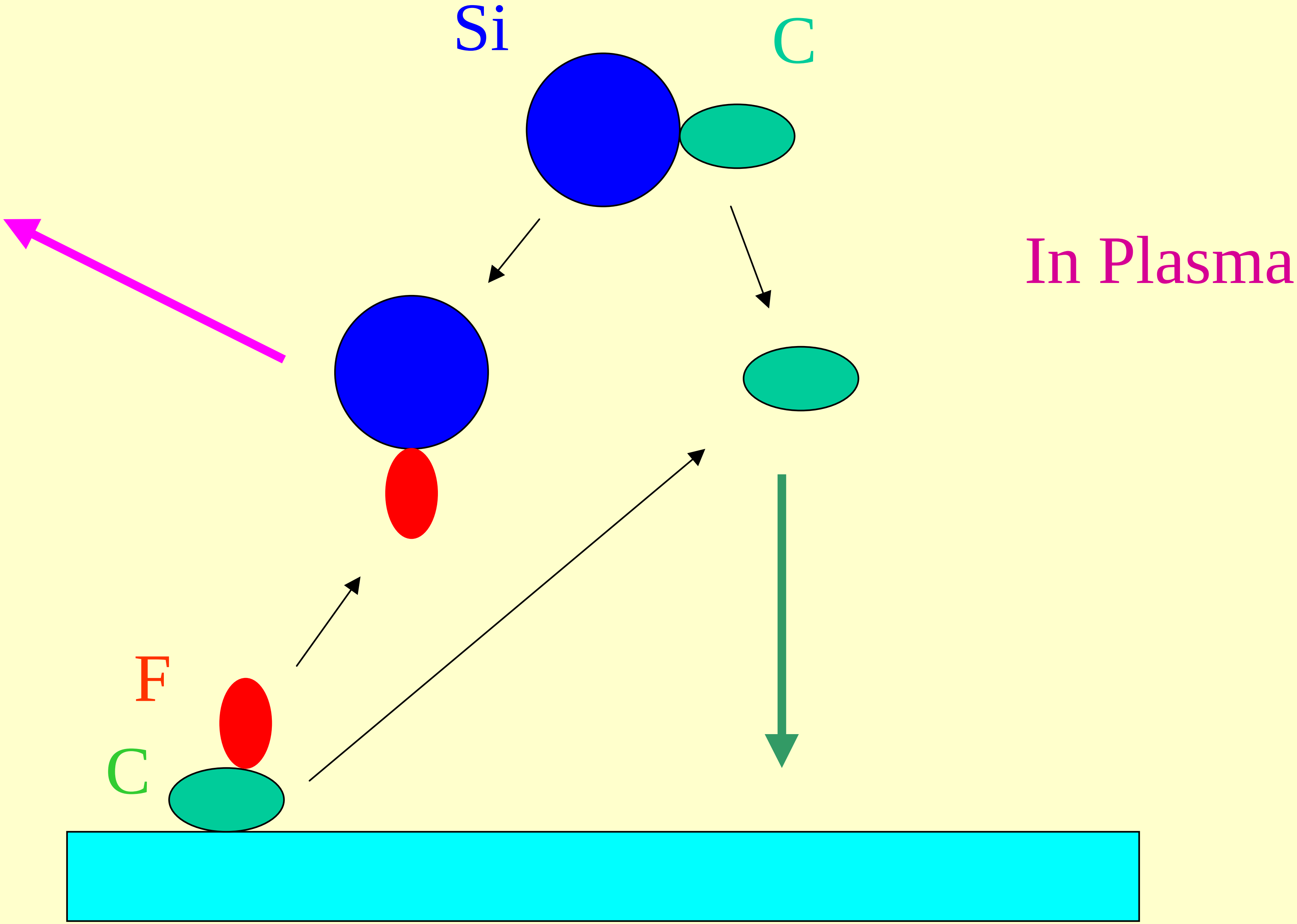

Si
C
In Plasma

Placing a new substrate in a contaminated reactor

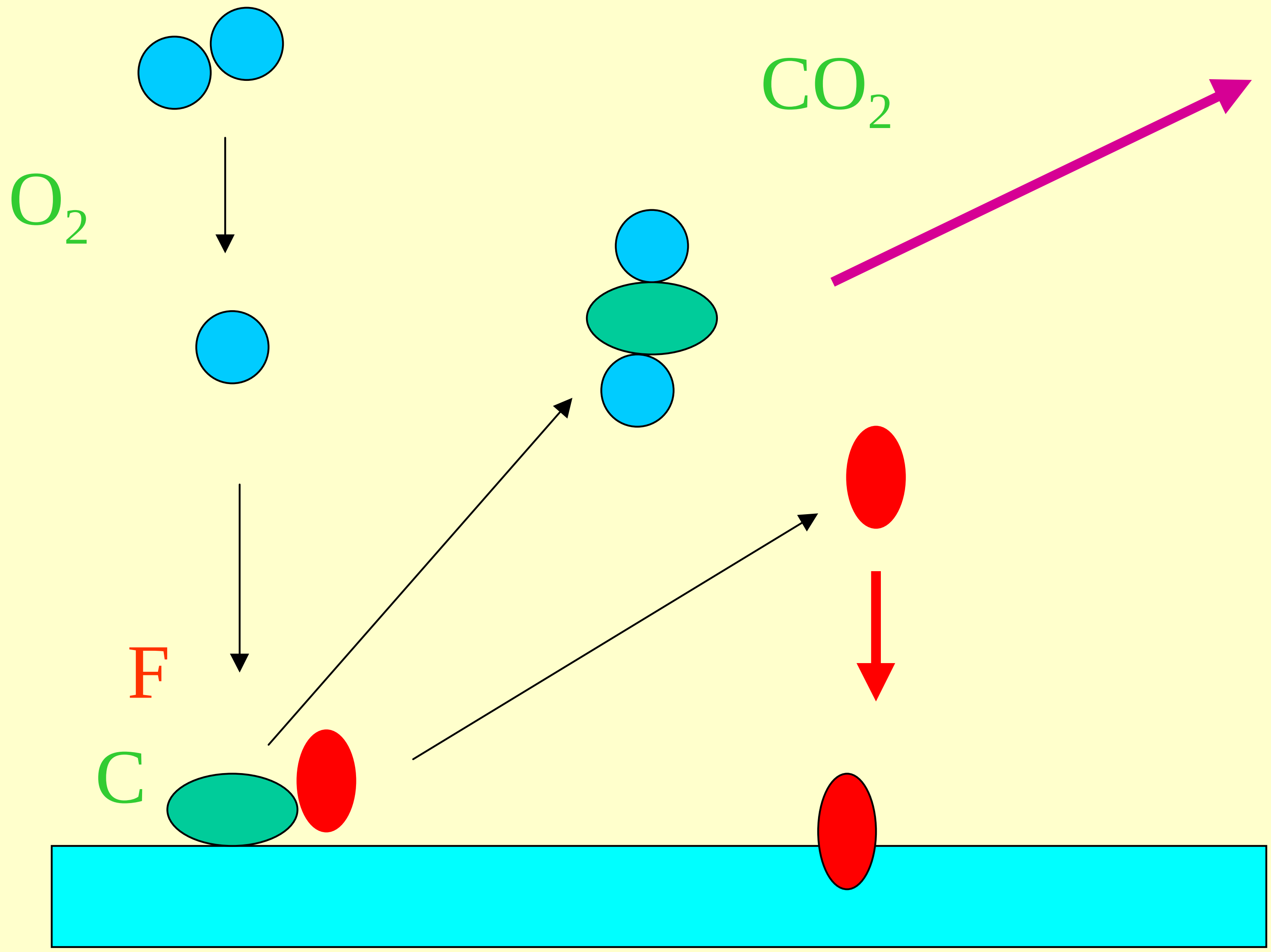


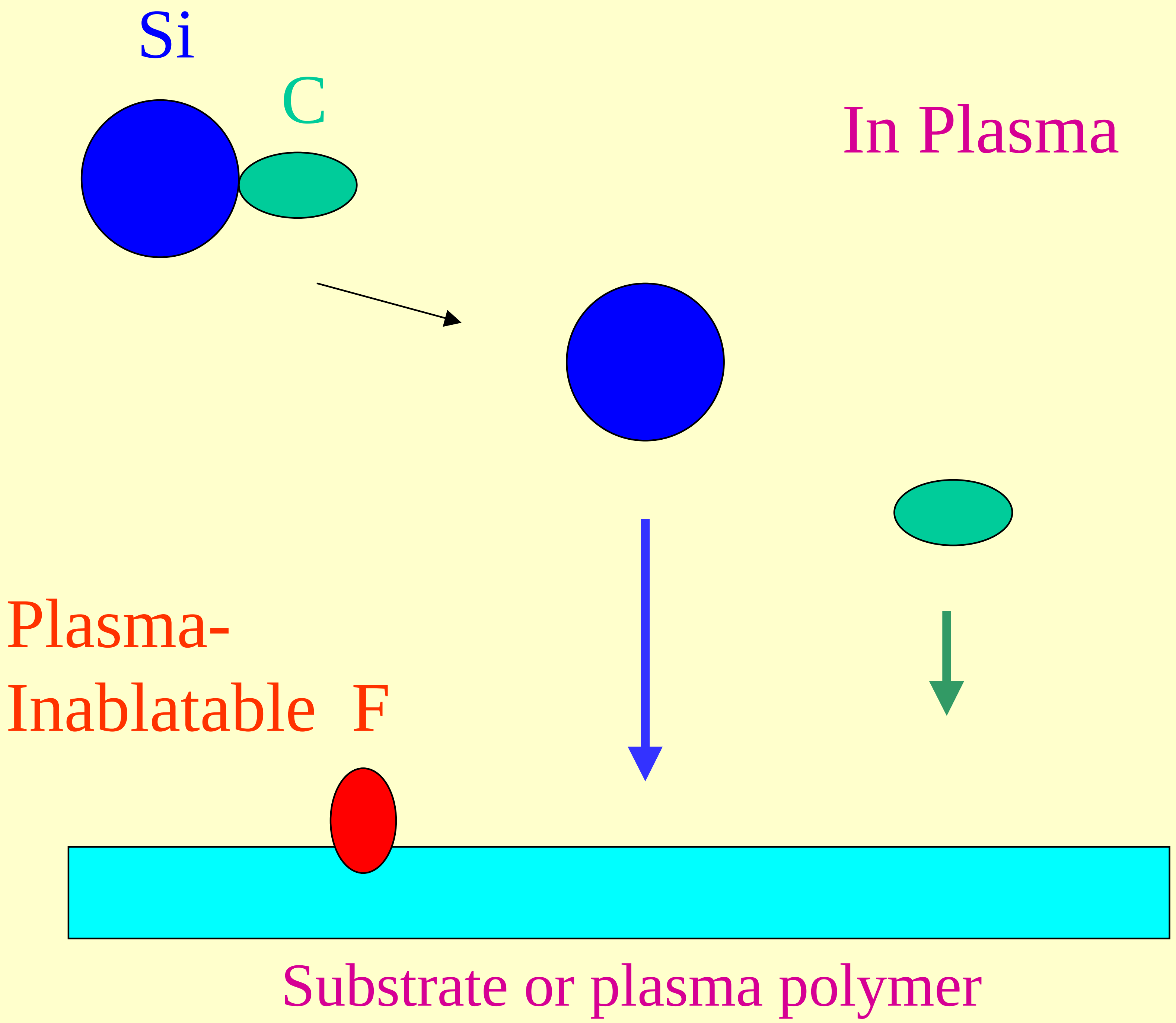
Evacuation of Reactor




Si
C
In Plasma
F
C

O_2 plasma treatment of contaminated substrate





Si
C
In Plasma
Plasma-
Inablatable F
Substrate or plasma polymer