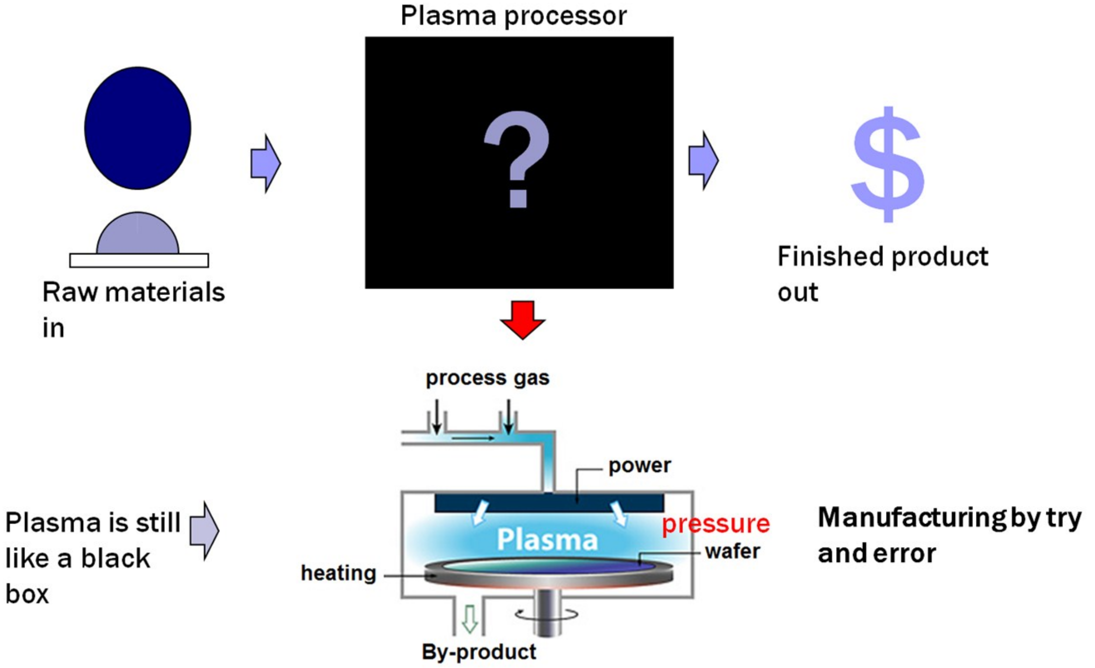
## Supplementary information

## Importance of RF/UHF dual frequency PECVD

Our earlier experience shows that RF/UHF dual frequency sources can produce significantly high plasma density even at low power. If we apply equal power by RF and UHF sources the plasma density is much smaller than that of their combined effect. Plasma density is also radially uniform, which favors the deposition of uniform film thickness up to larger area.

### How some view plasma processing ?


Plasma processor

Raw materials in

Finished product out

Plasma is still like a black box

Manufacturing by try and error

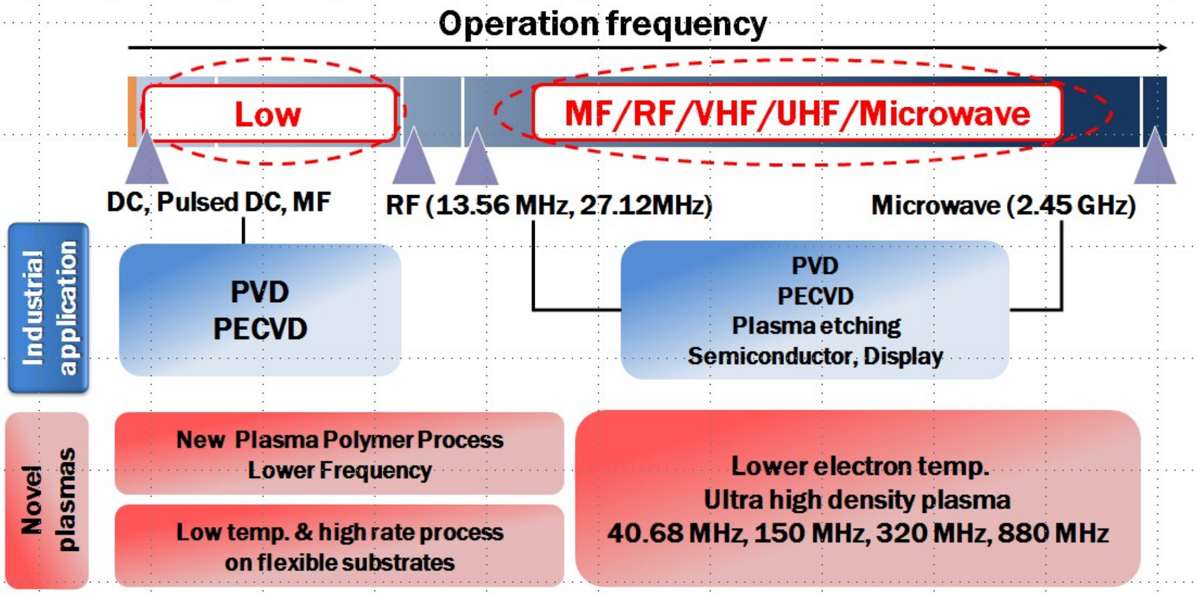
### How to control and make plasma based thin films?

**Design of Advanced Plasma Source and plasma process**

- **Control of electron temperature and plasma density**
  - -. **Advanced type of plasma sources (RF/UHF hybrid source)**
- **Control of plasma chemistry**
  - -. **Monitoring and controlling of plasma parameters and radicals**
- **Correlation of film formation mechanism in terms of plasma chemistry**
  - -. **Modeling and integrated plasma diagnostics**
  - -. **Film properties (depo. rate, microstructure, optical, electrical, etc.)**

**Nanostructured thin film growth and control**

# Exploring new plasmas and processes



**Operation frequency**

**Low**

**MF/RF/VHF/UHF/Microwave**

**DC, Pulsed DC, MF**

**RF (13.56 MHz, 27.12MHz)**

**Microwave (2.45 GHz)**

**Industrial application**

**PVD**
**PECVD**

**PVD**
**PECVD**
**Plasma etching**
**Semiconductor, Display**

**Novel plasmas**

**New Plasma Polymer Process**
**Lower Frequency**

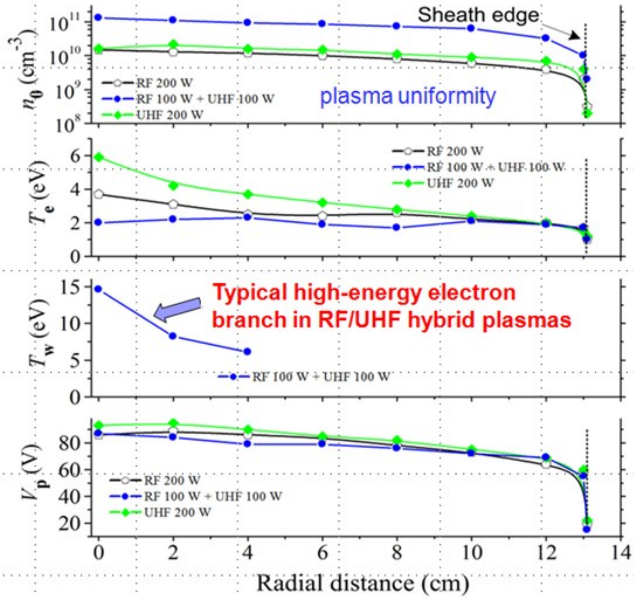
**Low temp. & high rate process**
**on flexible substrates**

**Lower electron temp.**
**Ultra high density plasma**
**40.68 MHz, 150 MHz, 320 MHz, 880 MHz**

One can lower reaction activation energy by increasing the plasma excitation frequency from radio frequency (RF) to very high frequency (VHF) and in the range of ultra high frequency (UHF) to microwave. J. Appl. Phys. 116, 134903 (2014).

# Importance and suitability of RF/UHF hybrid plasma

Plasma ionization features (Equal power)



Sheath edge

plasma uniformity

Typical high-energy electron branch in RF/UHF hybrid plasmas

$n_o$: Plasma density
$T_e$: Electron temperature
$T_w$: High energy electron
$V_p$: Plasma potential

Significantly higher (at least one order) ionization efficiency using RF/UHF hybrid plasmas

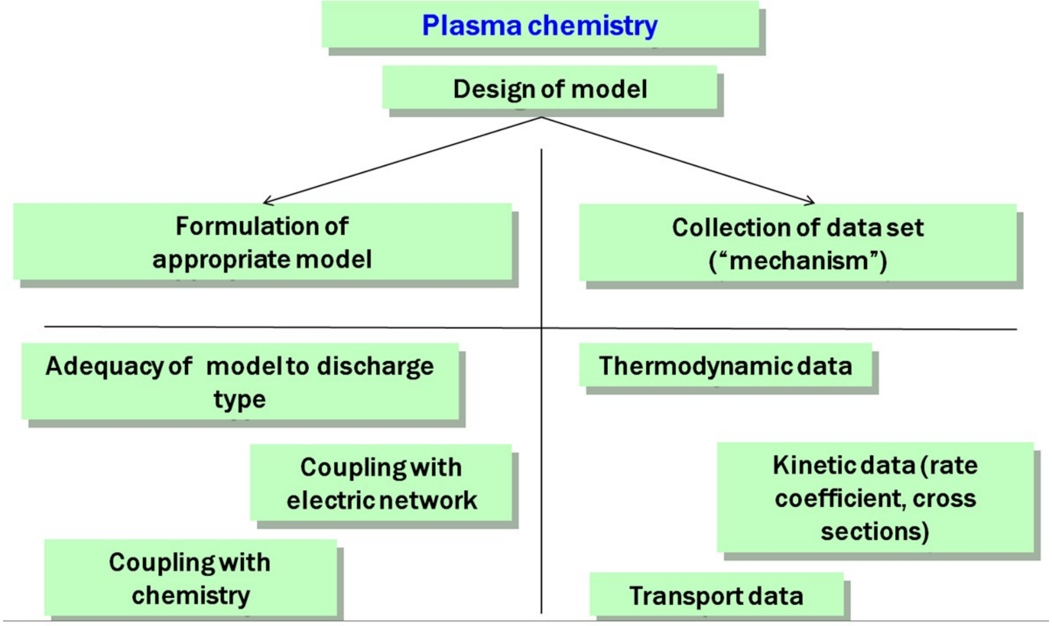
$n_o$ (RF) < $n_o$ (UHF) << $n_o$ (RF/UHF)

Plasma is quite uniform (up to ~ 6-8 cm) radially in hybrid plasma

Hybrid plasma have found to produce a very high $n_o$ at low $T_e$ and high energy tail in EEDF

Better plasma uniformity can provide better film uniformity

## Complexities in studying plasma chemistry



Plasma chemistry

Design of model

Formulation of appropriate model

Collection of data set (“mechanism”)

Adequacy of model to discharge type

Coupling with electric network

Coupling with chemistry

Thermodynamic data

Kinetic data (rate coefficient, cross sections)

Transport data

## Generation Rate of Plasma Species by Electron Collisions

$$y + e \rightarrow x + e$$

$$\frac{dn_x}{dt} = k_x \; n_e \; n_y$$

Example

$$Ar + e \rightarrow Ar^+ + e + e$$

$$\frac{dn_e}{dt} = k_{iz} \; n_e \; n_{gas}$$

*lhs =* *is the number of electrons (and ions) generated per cm$^3$ per second*

$k_{iz}$ = *rate coefficient*

## Simplified chemical model

### Theoretical Model

The number of interacting species at any time per unit volume during PECVD process is conserved. The governing rate equation is

$$\frac{\partial n_i}{\partial t} = \left( \sum_j \alpha_{jk} R_j \right)_i - \frac{A}{V} \Gamma_{tot} \qquad (1)$$

i → a particular species like neutral, ions, e, ...

$\Sigma_i$ → sum over every reaction

Dimension of the Equation: $1/(m^3 . Sec)$

**Creation**
Ionization, dissociation, and chemical reaction

**Loss**
+ve & -ve ion recombination, excitation, ion-neutral charge exchange, energy transfer to neutrals by collision, etc.

lhs ≡ density of species at a given time

$\alpha \equiv$ Chemical species (reactant or product)

R ≡ Reactivity of chemical reaction

$\Gamma_{tot} \equiv$ Total flux; A = Area; V = Volume

### Assumption

Assumption: We consider the collisions and chemical reaction to be a two-body process

R is the reactivity of a particular reaction (a product of interacting species)

$$R_j = k_j n_{j1} n_{j2} \qquad (2)$$

$n_{j1}$ and $n_{j2}$ are number densities ($cm^{-3}$) of the two interacting species

$k_j$ is the integrated rate coefficient at a given temperature

$\alpha_{jk}$ → chemical species that can be a product or reactant

$\alpha_{jk}$ = + ve if the species k is a product
= - ve if the species k is a reactant
= 0 if not participate in the collision or chemical reaction
= 0 if equally balanced on both sides of the reaction

The magnitude of $\alpha_{jk}$ refers to new species produced or recombination reaction

Example: $H_2^+ + e \rightarrow 2\,H$ ($\alpha_{j,e}$ = -1, $\alpha_{j,H2}{}^+$ = -1, and $\alpha_{i,H}$ = 2)

### Computation scheme and procedure

Taking density rates for all species

$$\frac{\partial n_i}{\partial t} = \left( \sum_j C_{jk} R_j \right)_i - \frac{A}{V} \Gamma_{tot}$$

The rate coefficient: f ($T_e$)

$$k_j = \kappa \int_0^\infty E\, \sigma_i(E) \;\; f(E) \;\; dE \;\; ; \qquad \kappa = \sqrt{\frac{2e}{m_e}}$$

Energy/power balance

$$\frac{3}{2}\frac{d}{dt}(n_0 T_e) = \frac{P_{in}}{V} - P_1 - P_2 - P_3 - P_4$$

$P_{in}$: *Power input*

$P_1$: power density of excitation

$P_2$: power density loss due to electron-neutral collision

$P_3$: power density of ionization

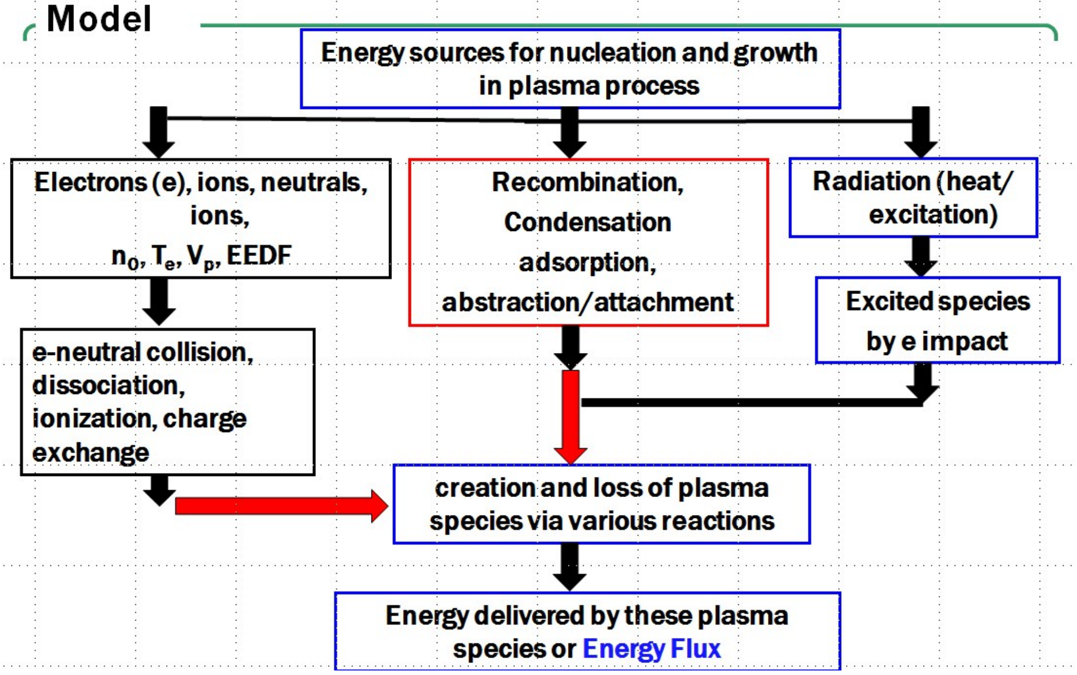
$P_4$: power loss to the wall due to the charged species

Taking density rates for all species and rate coefficients set of 45 equations involving 44 species (Table 1) in 62 bulk reactions (Table 2) are constructed in MathCAD and called by the "odesolve()" solver for the time-dependent $T_e$ and *density* of all plasma species.

*Computations in MathCAD ODE solver:* "odesolve()"

## Energy deposition

### Model



Energy sources for nucleation and growth in plasma process

Electrons (e), ions, neutrals, ions, $n_0$, $T_e$, $V_p$, EEDF

Recombination, Condensation adsorption, abstraction/attachment

Radiation (heat/ excitation)

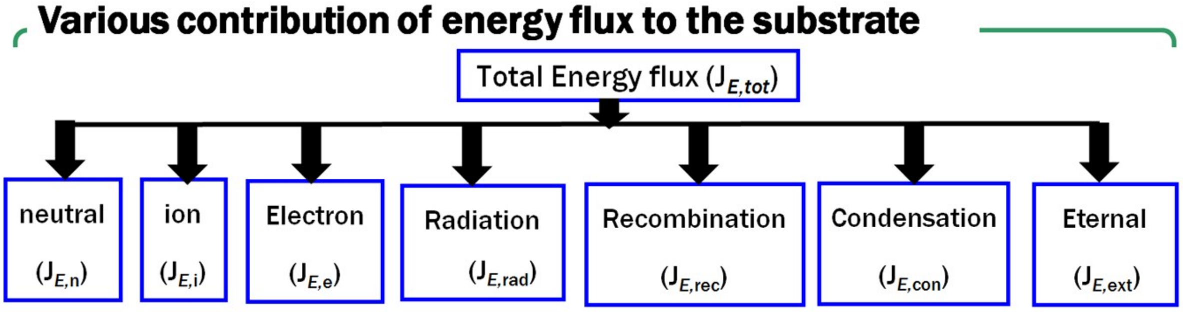
Excited species by e impact

e-neutral collision, dissociation, ionization, charge exchange

creation and loss of plasma species via various reactions

Energy delivered by these plasma species or Energy Flux

### Various contribution of energy flux to the substrate



Total Energy flux ($J_{E,tot}$)

neutral ($J_{E,n}$)

ion ($J_{E,i}$)

Electron ($J_{E,e}$)

Radiation ($J_{E,rad}$)

Recombination ($J_{E,rec}$)

Condensation ($J_{E,con}$)

Eternal ($J_{E,ext}$)

$J_{E,n} \equiv$ Contribution of neutral species of the background gas and the neutral particles contributing to the film growth

$J_{E,i} \equiv$ Contribution of ions (Bohm Flux, in the sheath covering the substrate,

$J_{E,e} \equiv$ Contribution of electrons

$J_{E,rad} \equiv$ Contribution of heat/light radiation from the surface

$J_{E,rec} \equiv$ Contribution of energy released by recombination

$J_{E,con} \equiv$ Contribution of energy released by condensation

$J_{E,ext} \equiv$ Contribution of any external source or chamber heating

# Film microstructure by TEM near the transition region

25 sccm of $SiH_4$ flow rate