MODELING AND SIMULATION OF PLASMA PROCESSING: STATUS AND DATABASE REQUIREMENTS

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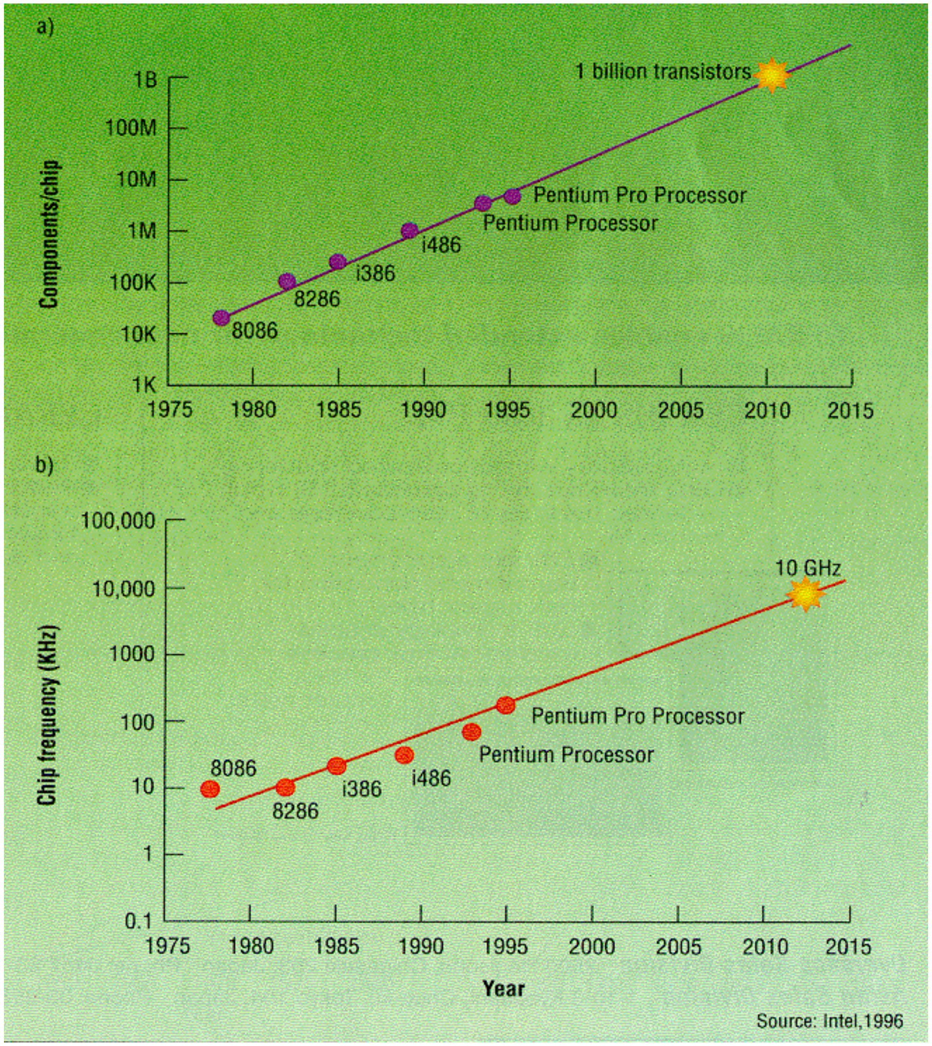
AGENDA

- Introduction to plasma processing and plasma equipment modeling.
- Background to initiatives in plasma modeling and database assessment
- Examples of plasma equipment and process modeling
- Assessment and needs in electron impact database
- How good does the data need to be?
- Concluding Remarks

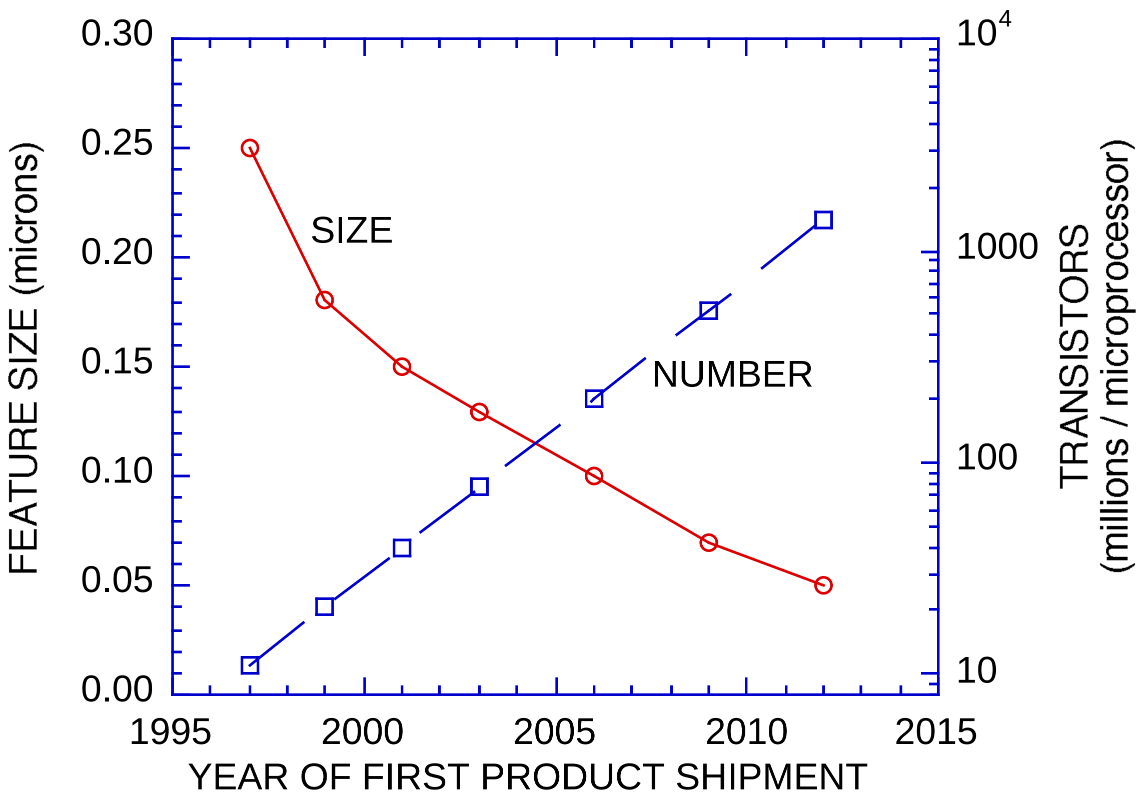
MOORE'S LAW IN MICROELECTRONICS FABRICATION



- In early 1980s Gordon Moore (Intel) observed that the complexity and performance of micrelectronics chips doubles every 18 months.
- The semiconductor industry has obeyed "Moore's Law" through 7 generations of devices.

NATIONAL TECHNOLOGY ROADMAP FOR SEMICONDUCTORS

- The NTRS sets goals for the microelectronics fabrication industry for future generation of devices.

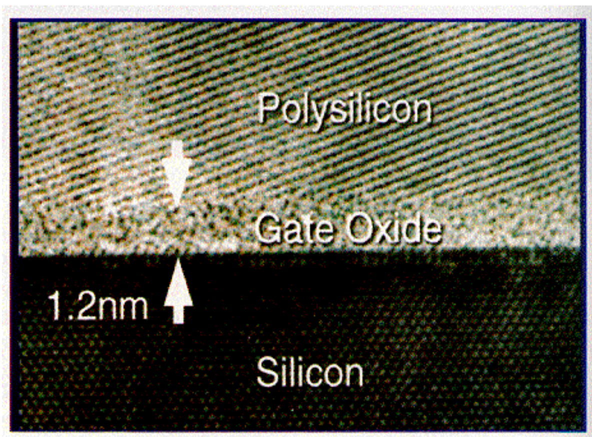


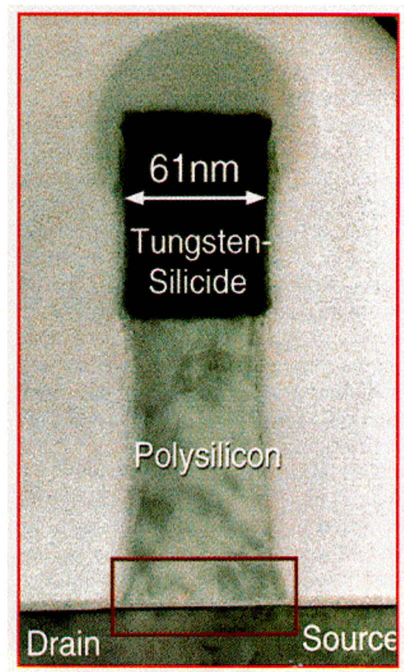
- Feature sizes will continue to shrink with more transistors per chip while....

- Ref: “National Technology Roadmap for Semiconductors”, SIA, 1997.

EVEN SMALLER DEVICES CAN BE BUILT...
BUT THEY ALSO MUST BE MANUFACTURABLE

- The technology to fabricate 0.06 micron devices currently exists. The additional challenge is to devise MANUFACTURABLE processes whereby 10^{12} devices per month can be successfully fabricated.

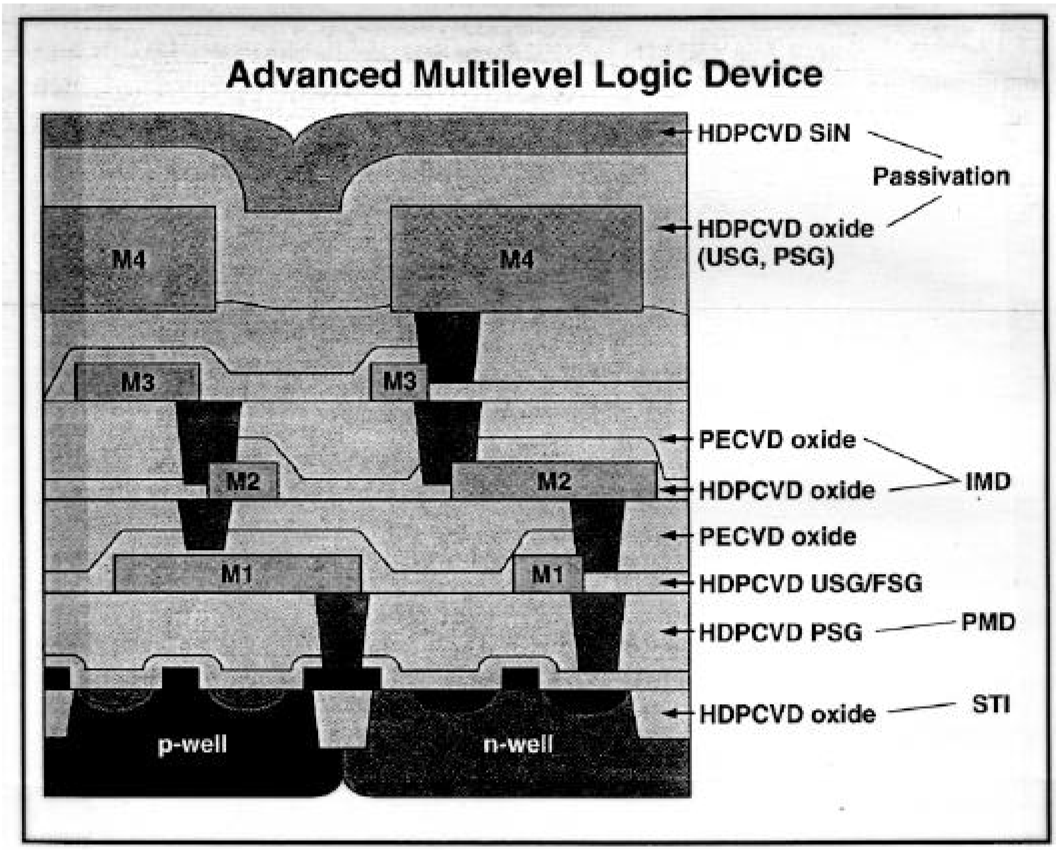




- IBM demonstration of a 0.06 micron CMOS transistor using e-beam mask exposure.

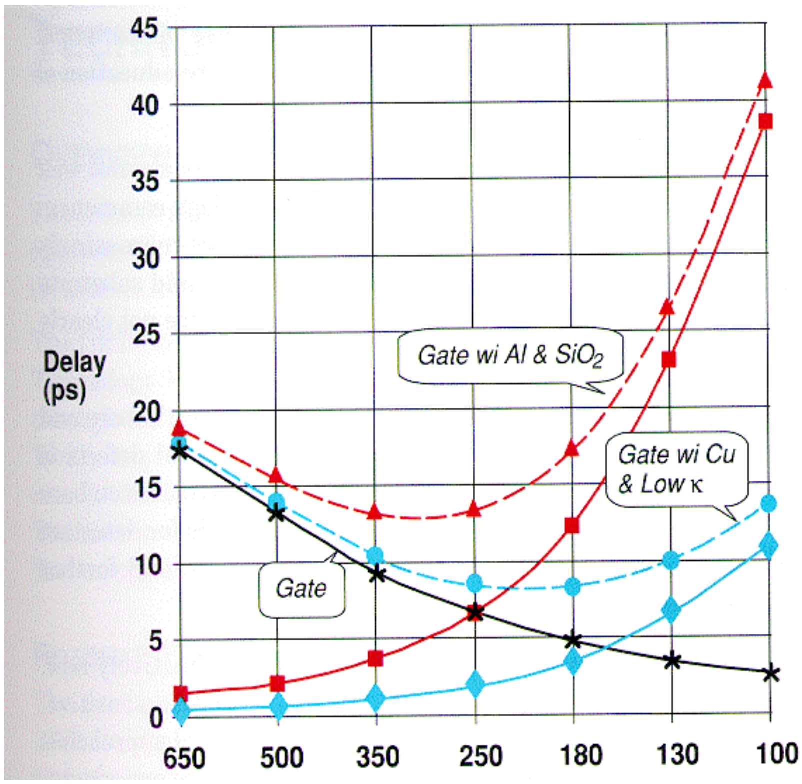
INCREASED COMPLEXITY REQUIRES NEW SOLUTIONS: INTERCONNECT WIRING

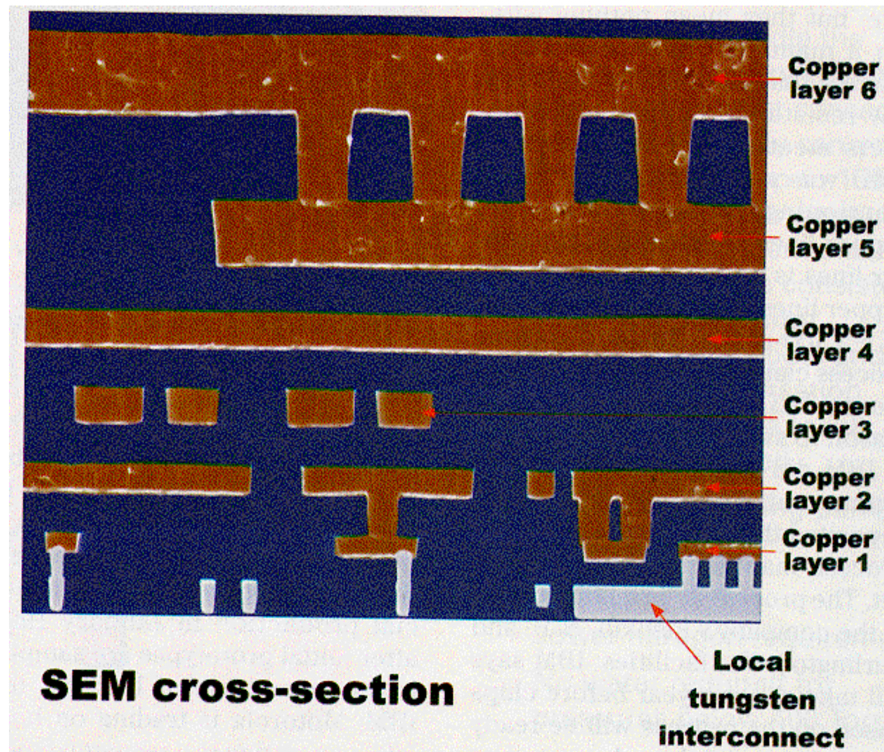
- **The levels of interconnect wiring will increase to 8-9 over the next decade resulting in unacceptable signal propogation delays.**



COPPER INTERCONNECT WIRING WITH LOW CAPACITANCE DIELECTRICS

- Copper interconnect wiring with low capacitance dielectrics, the current "best bet" solution will not satisfy requirements beyond 0.18 micron



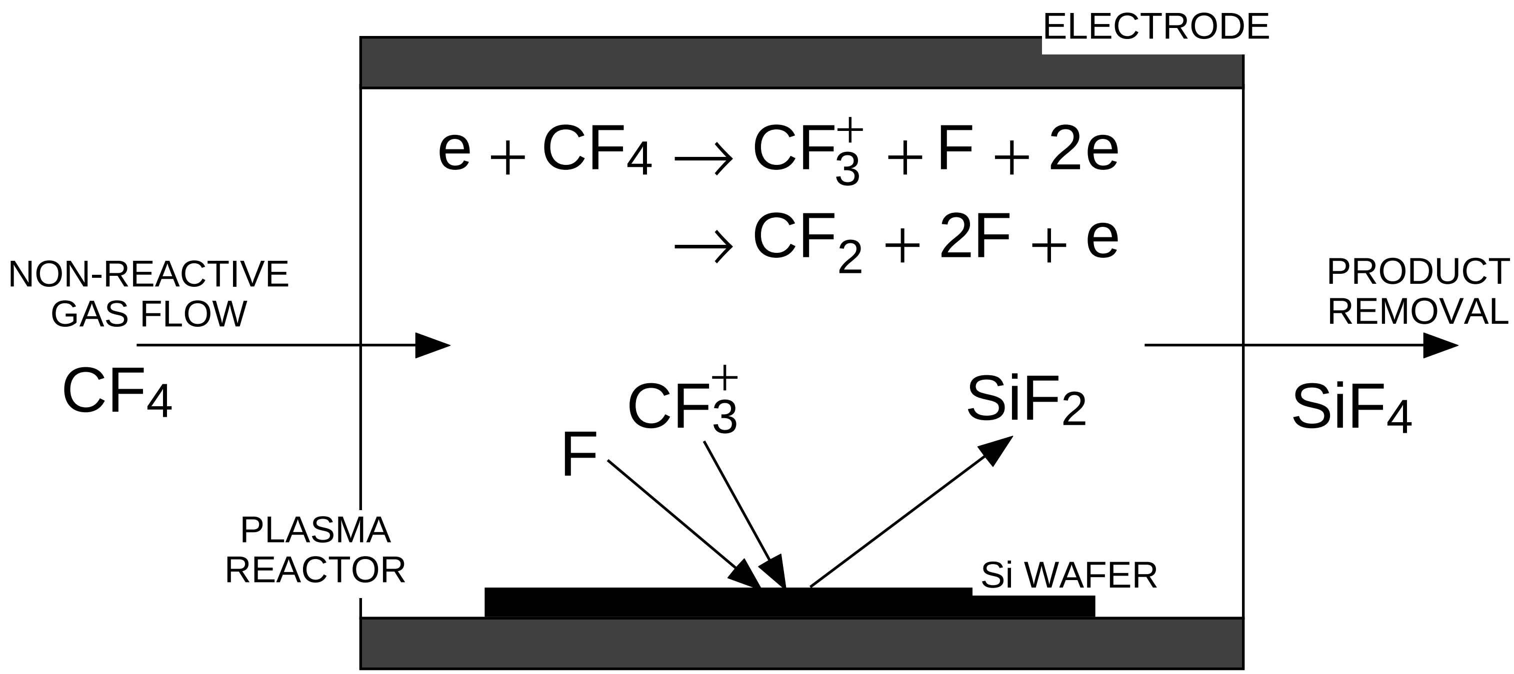


- Natl. Tech. Roadmap for Semiconductors

- IBM demonstration of Cu interconnect with SiO_2 dielectric.

PLASMA PROCESSING FOR MICROELECTRONICS

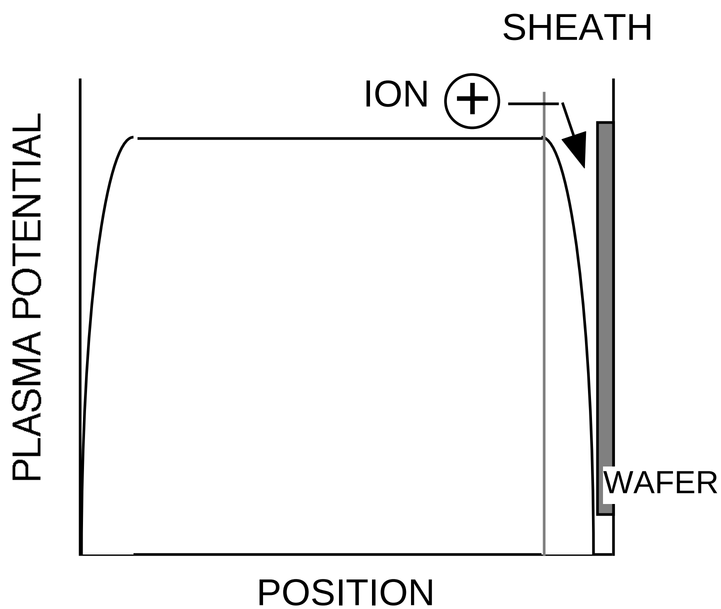
- In plasma processing of semiconductors, electron impact on feedstock gases produces neutral radicals and ions which drift or diffuse to the wafer where they remove or deposit materials.

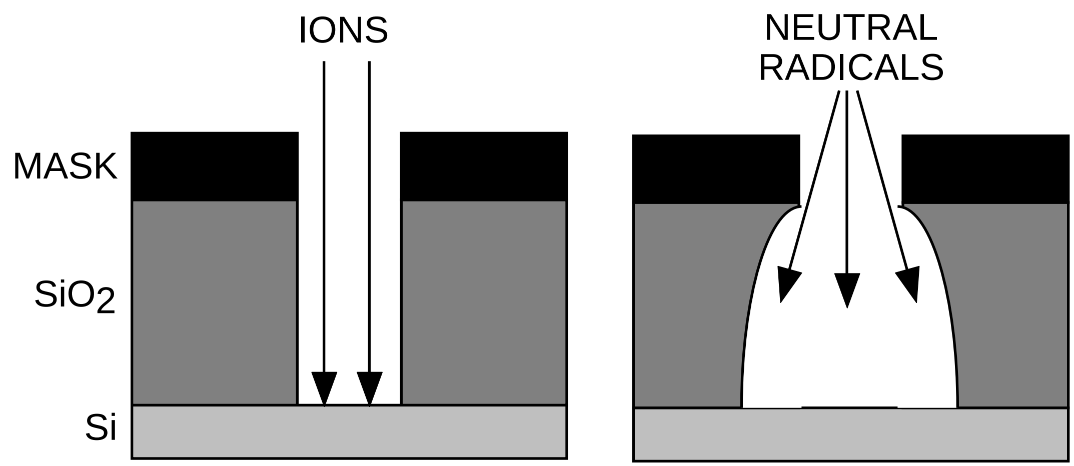


- This process is often called “cold combustion” since the feedstock gases are cool compared to the electrons.

PLASMAS ARE ESSENTIAL FOR ECONOMICALLY FABRICATING FINE FEATURES IN MICROELECTRONICS

- In plasma processing, ions are accelerated nearly vertically into the wafer, thereby activating etch processes which produce straight walled, anisotropic features





- Ion Assisted Etching
- Neutral Dominated Etching

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PHOTOGRAPHS OF PLASMA ETCHING TOOLS

Photographs of:

Tegal Corp. Plasma Etching Tool

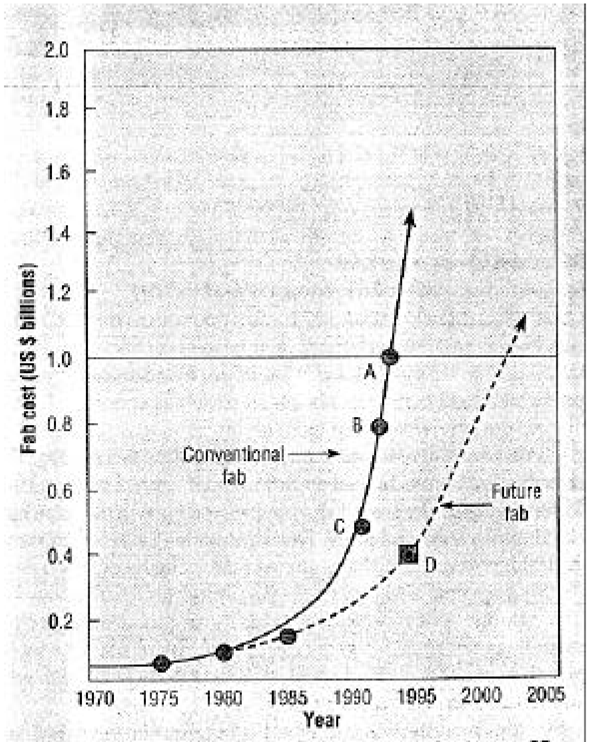
and

Applied Materials Decoupled Plasma Source

appear here.

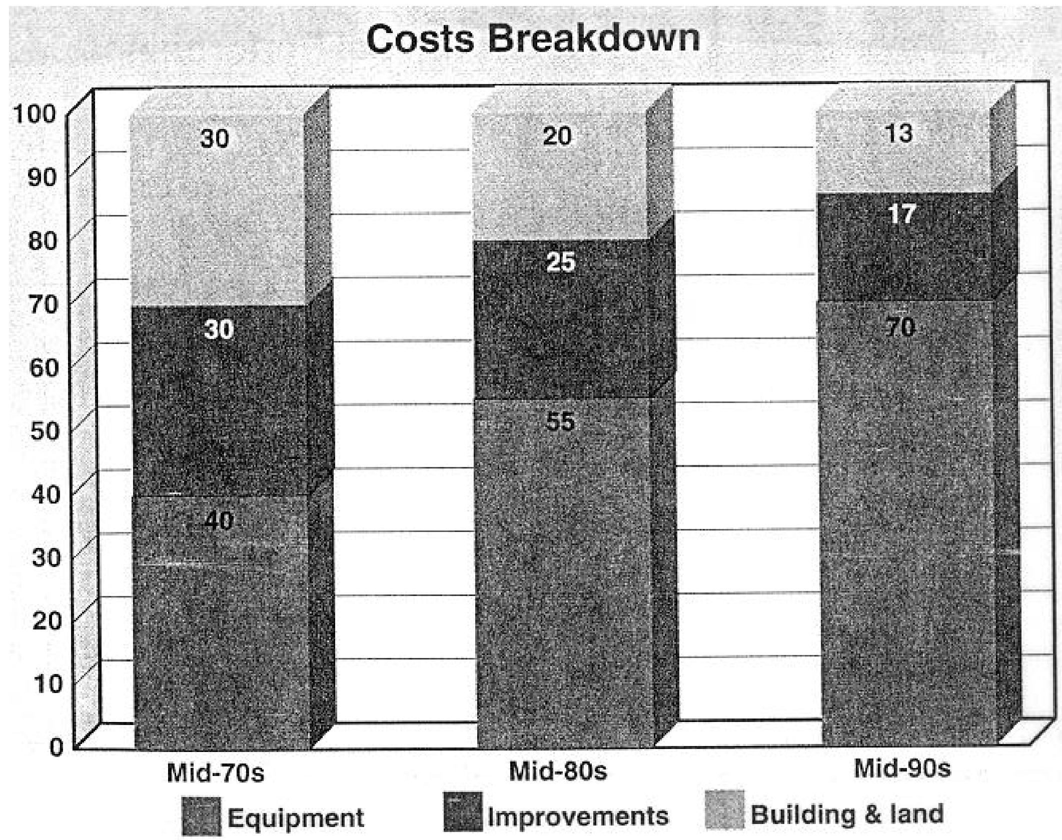
COST OF FABRICATION FACILITIES

- **The cost of a major (> 20,000 wafers/month) fabrication facility exceeds $1 Billion with an increasing fraction of the cost being the processing equipment.**



Point	DRAM (Mbit)	Wafer diam. (mm)	Throughput (wafers/mo.)	CD (μm)
A	64	200	25,000	0.35
B	16	200	20,000	0.50
C	1	150	20,000	0.80
D*	Logic (four-level metal)	200	15,000	0.35

* Paradigm shift: single wafer, cluster tooling, minienvironment.



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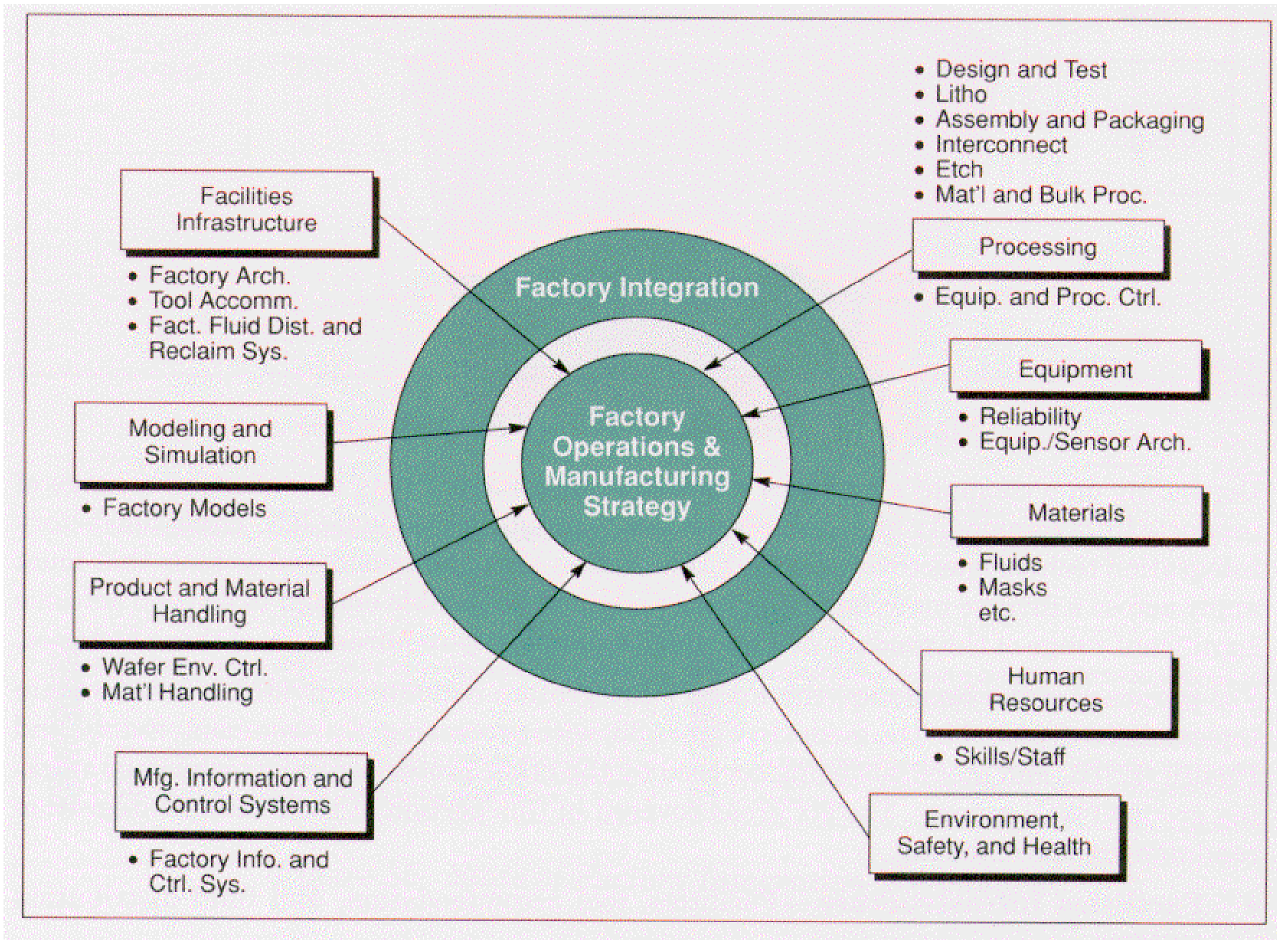
THE VIRTUAL FACTORY: A DESIGN PARADIGM

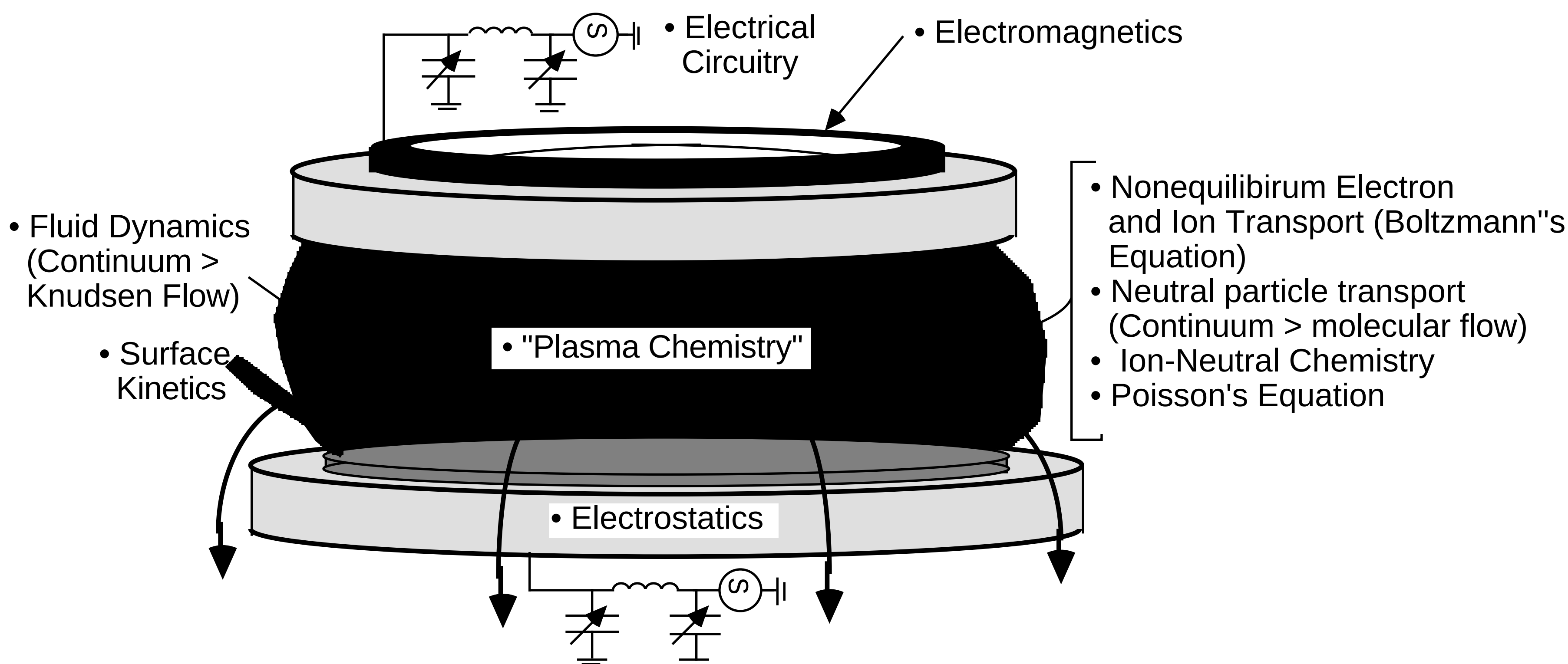
- **The "virtual factory" is a computer representation of a fabrication facility, modeled either heuristically or from basic principals.**



- **Ref: SIA Semiconductor Industry Association Roadmap, 1994.**

COMPONENTS OF A PLASMA EQUIPMENT MODEL

- In addition to "physics", a viable plasma equipment model must have the capability to easily define geometries, material properties, and reaction chemistries; while accessing a data base of transport coefficients.



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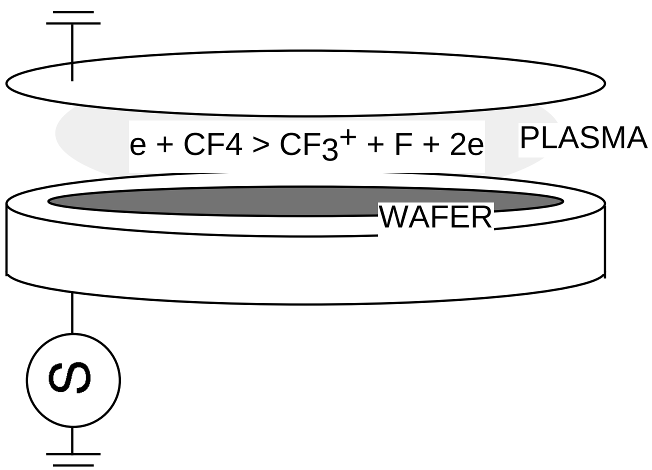
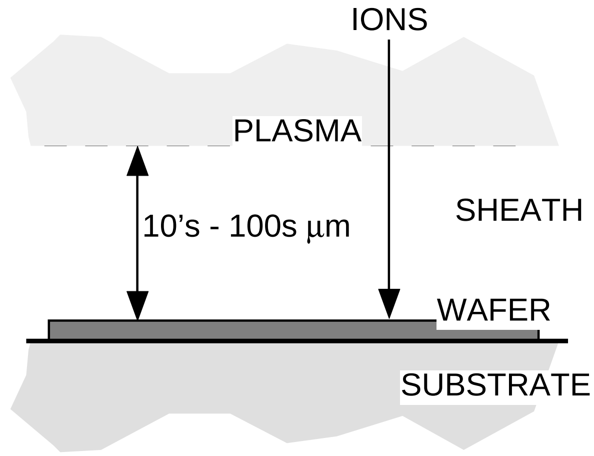
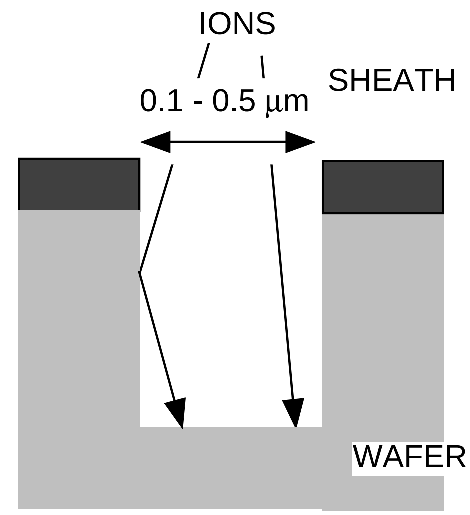
SPATIAL SCALES IN PLASMA PROCESSING SPAN MANY ORDERS OF MAGNITUDE



- EQUIPMENT SCALE (cm - 10s cm)
  - Gas Flow
  - Heat Transfer
  - Plasma Transport
  - Chemical Kinetics



- “TRANSITION SCALE” (10s -100s µm)
  - Electron and Ion Transport
  - Sparse Collsions
  - Electrodynamics

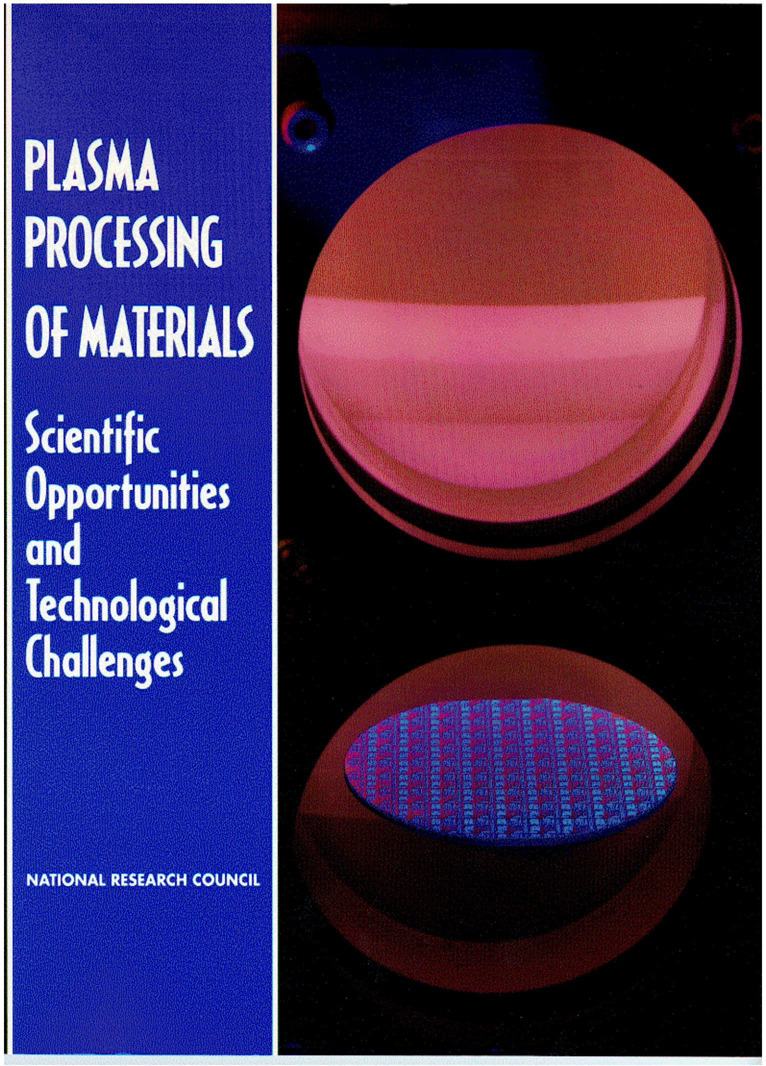


- FEATURE SCALE” (10s nm - µm)
  - Electron, Ion, Radical Transport
  - Plasma Surface Interaction
  - Surface chemistry

NRC PANEL ON PLASMA PROCESSING OF MATERIALS

- **1991 United States National Research Council (NRC) report "Plasma Processing: Scientific Opportunities and Technological Challenges"**

- **Evaluate impact of advances in low temperature plasma science on material processing (microelectronics).**
- **Identify key research problems in plasma physics, chemistry and surface interactions.**
- **Recommend means to bring strengths of plasma science community to address issues.**



NRC PANEL ON PLASMA PROCESSING OF MATERIALS: FINDINGS AND RECOMMENDATIONS

- **"Currently, computer-based modeling and plasma simulation are inadequate for developing plasma reactors. As a result, the detailed descriptions required to guide the transfer of processes form one reactor to another or to scale processes from a small reactor to a large reactor are not available"...The key missing ingredients are:**
  - **"Efficient numerical algorithms and supercomputers for simulating magnetized plasmas in 3-dimensions"**
  - **"A reliable and extensive input data base for calculating plasma generation, transport and surface interaction.**
- **The panel recommended a coordinated "Plasma Processing Program" which should:**
  - **"Include a thrust toward development of computer-aided design tools for developing and designing new reactors"**
  - **"Emphasize a coordinated approach toward generating the diagnostic and basic data needed for improved ...surface simulation capability.**

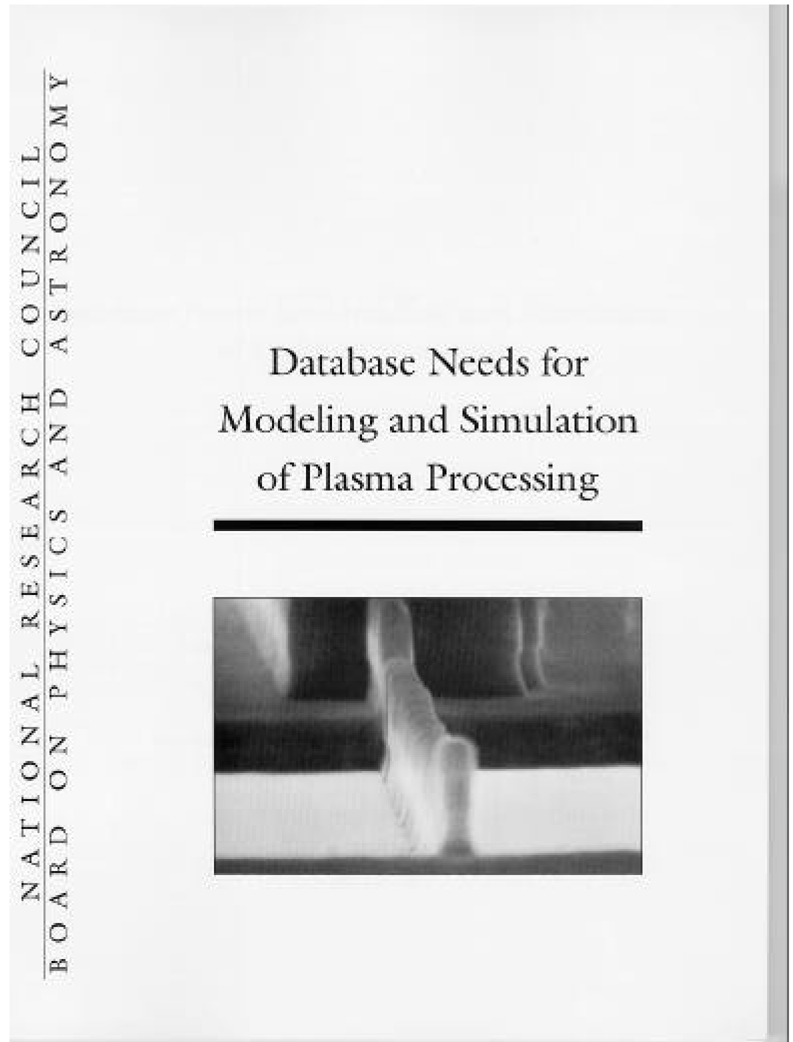
NRC PANEL ON PLASMA PROCESSING OF MATERIALS: IMPACT ON US RESEARCH

- **Recommendations of NRC PPPM created a great deal of excitment in the US plasma science community.**
  - **Microelectronics industry realized the need for improved simulation capability redirected emphasis in basic science expenditures.**
  - **Downturn in fusion and US defense funding redirected many large plasma research programs (Naval Research Lab, Lawrence Livermore National Lab, Sandia National Lab, NASA)**
  - **US Department of Energy and Sematch launched CRADAs (Cooperative Research and Developement Agreements) in plasma modeling and simulation.**
  - **High Performance Computing and Communications (HPCC) initiative sparked coordinated cross disciplinary activities.**
- **Great strides were made in development of plasma equipment models, however basic data needs were not emphasized.**

NRC PANEL ON DATABASE NEEDS FOR MODELING AND SIMULATION OF PLASMA PROCESSING

- **Spring 1994: US National Research Council commissioned the "Panel on Database Needs in Plasma Processing"**
- **Assess the status of current database for modeling, simulation and diagnostics of plasma materials processing.**
- **Make recommendations for strategies to meet cited needs**
- **Members:**

  David B. Graves, Co-Chair
  Mark J. Kushner, Co-Chair
  Jean W. Gallagher
  Alan Garscadden
  Gottlieb S. Oehrlein
  Arthur V. Phelps



PANEL ON DATABASE NEEDS: RECOMMENDATIONS

- Greater and more systematic efforts should be made by Federal and industrial agencies to address database needs with emphasis on plasma-surface interactions.
  - The current database was largely formulated for laser development and atmospheric chemistry. Similar emphasis should be applied here.
- A spectrum of plasma models which address subsets of problems, and particularly plasma surface interactions, should augment global plasma equipment models.
  - Low pressure plasma systems de-emphasize importance of gas phase chemistry in favor of surface chemistry.
- Target chemistries should have a high priority in database development because the applications are currently important and will continue to be important over the next 5-10 years.

TARGET GASES FOR PRIORITY DATABASE DEVELOPMENT

- **Polycrystalline silicon etching in chlorine- and bromine containing gases (gate electrode definition):**

  Cl_2, Br_2, HBr, O_2, N_2 (and since report.... BCl_3, HCl)

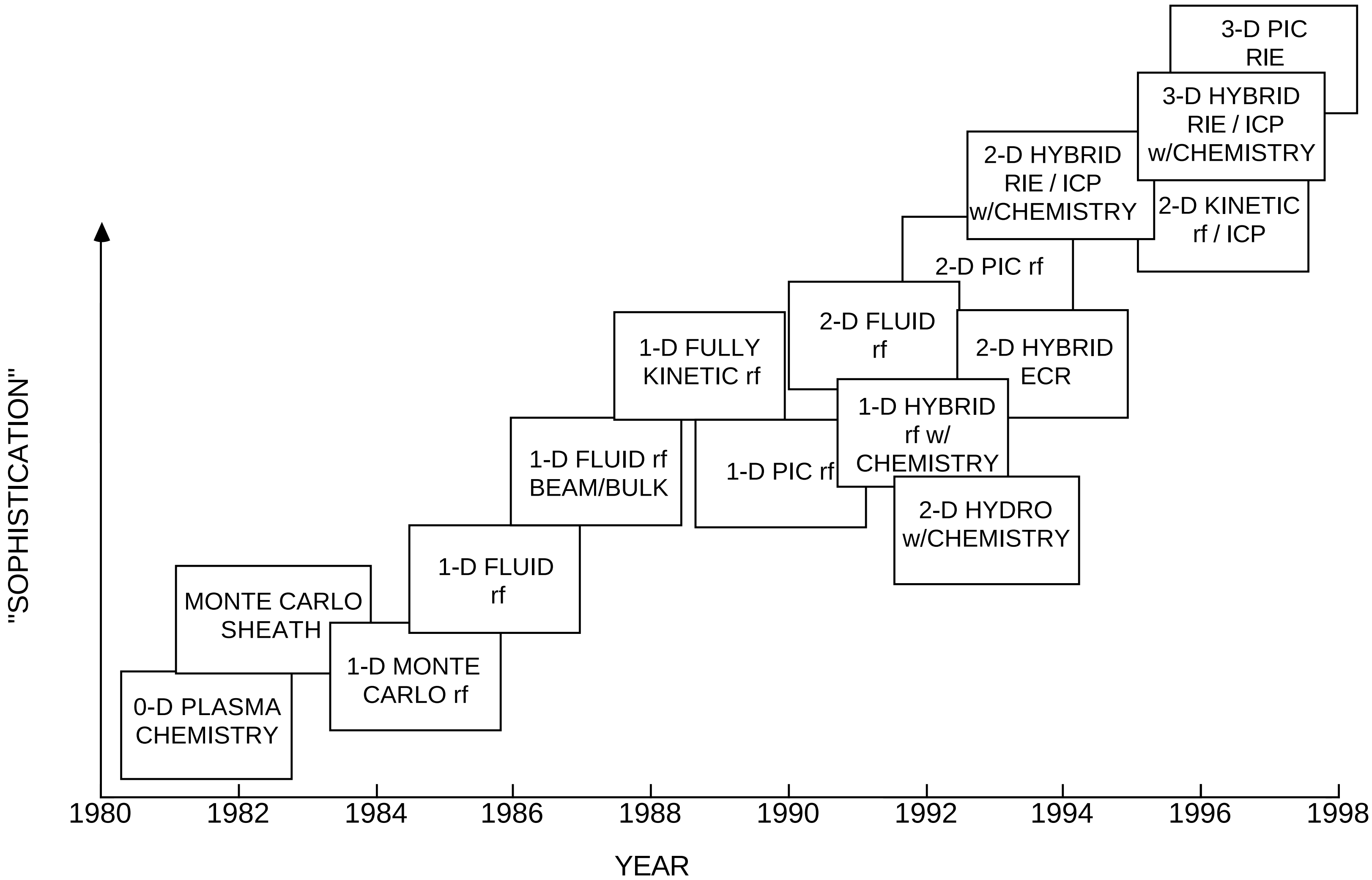
- **Silicon-dioxide etching in fluorocarbon-containing gases**

  CF_4, CHF_3, C_2F_6, O_2, N_2, CO, Ar (and since report.... C_3F_8, C_4F_8, NF_3)

- **Silicon dioxide deposition through plasma enchanced chemical vapor deposition (PECVD)**

  SiH_4, O_2, N_2O, Ar, TEOS [$Si(C_2H_4O)_4$] (and since report.... , $Si(CH_3)_4$, SiF_4)

HISTORICAL PERSPECTIVE OF DEVELOPMENT OF PLASMA ETCHING MODELS



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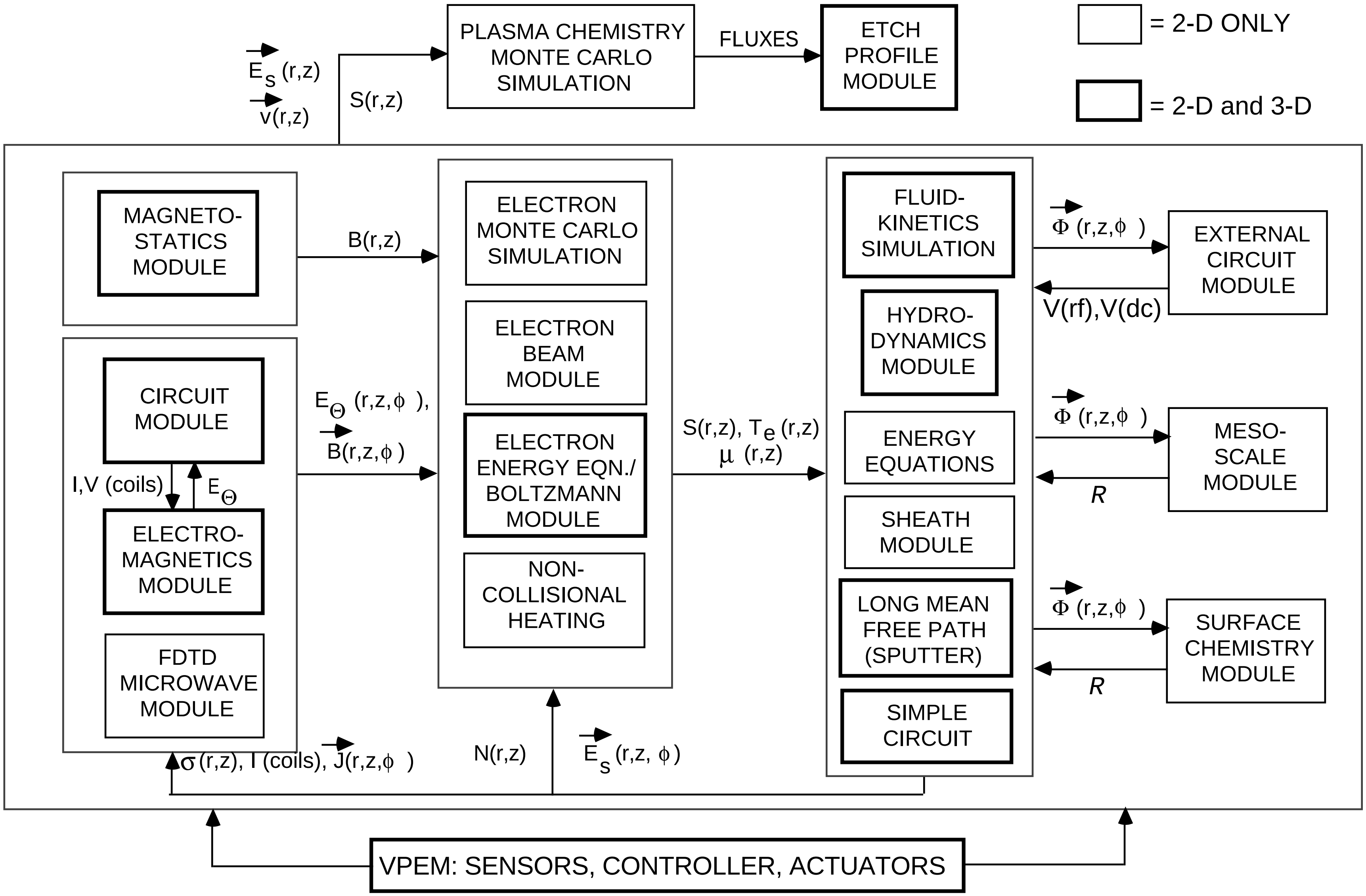
SCHEMATIC OF 2-D/3-D HYBRID PLASMA EQUIPMENT MODEL



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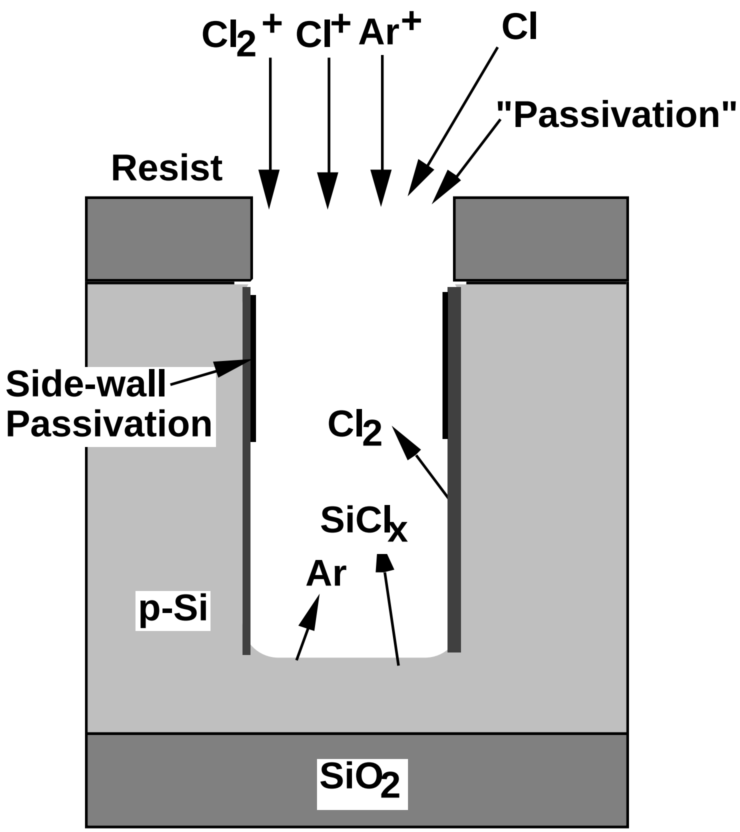
MONTE CARLO FEATURE PROFILE MODEL (MCFP)



- The MCFP model predicts time and spatially dependent etch profiles using neutral and ion fluxes from the PCMCS.

- Any chemical mechanism may be implemented in the MCFP using a "plasma chemistry" input hierarchy.

  e.g., $Cl^+ + SiCl_2(s) > SiCl_2(g)$

- All pertinent processes can be included: thermal etch, ion assisted etch, sputter, redeposition, passivation.

- Energy dependent etch processes may be implemented using parametric forms.

- The MCFP may utilize ALL flux statistics from the PCMCS

  - Ion energy and angular distributions
  - Neutral energy and angular distributions
  - Position dependent fluxes

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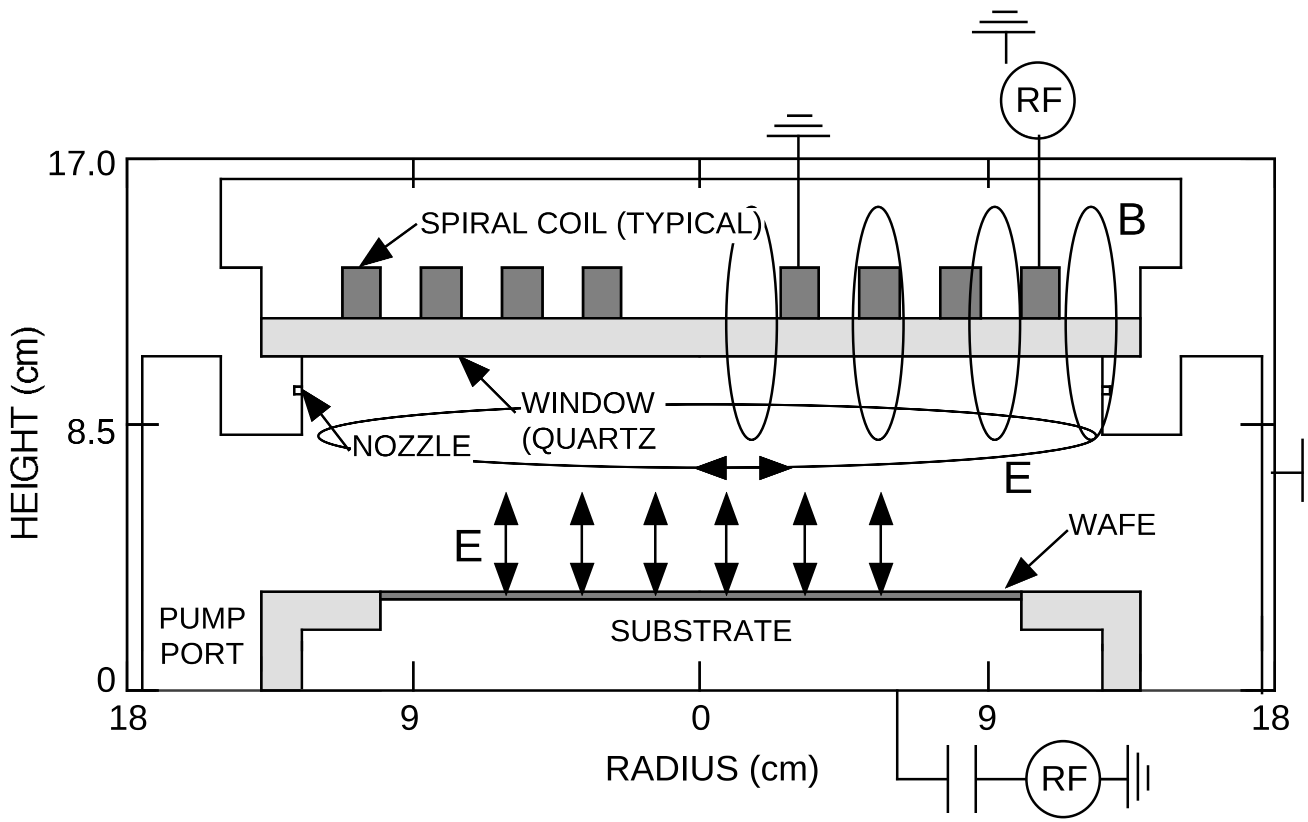
TRANSFORMER COUPLED PLASMA ETCHING TOOL

- Low gas pressure, high plasma density etching tools often use wave excitation to produce the plasma.

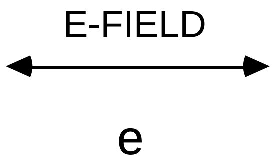
- Typical Operating Conditions:

- 5-20 mTorr
- 50-200 sccm
- 200-1500 W (ICP)
- 50-500 W bias
- [e] = 10^{11} - 10^{12} /cm^3
- T_e = 3-5 eV
- T_I = 0.05 - 0.1 eV



CECAM98M17

GENERATION OF ETCHING SPECIES, TRANSPORT, ETCHING

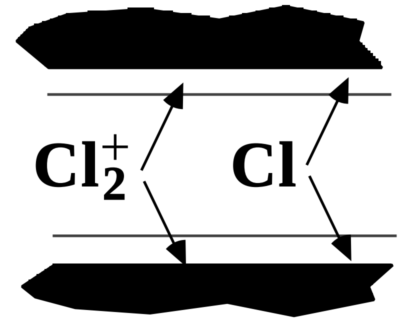


ELECTRON HEATING

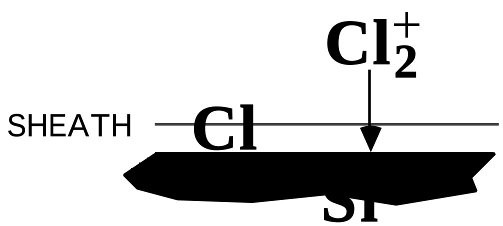
$$e + Cl_2 \rightarrow Cl_2^+ + e + e$$

$$e + Cl_2 \rightarrow Cl + Cl + e$$

RADICAL / ION GENERATION

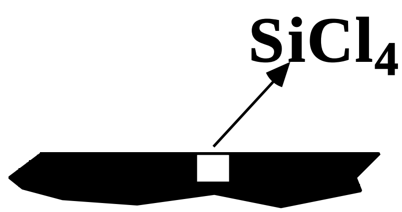


RADICAL / ION TRANSPORT TO WAFER



ION ACCELERATION INTO WAFER

RADICAL ADSORPTION



ETCHING

PRODUCT PUMPOUT

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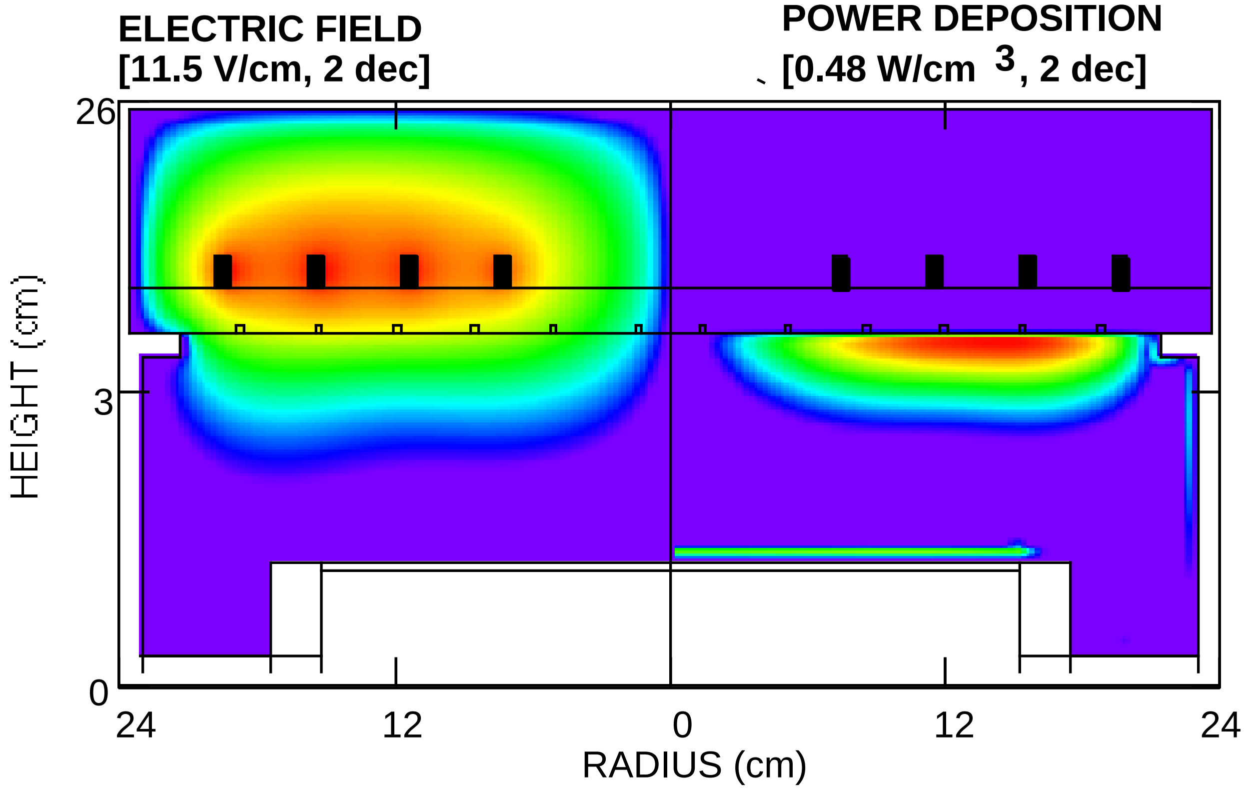
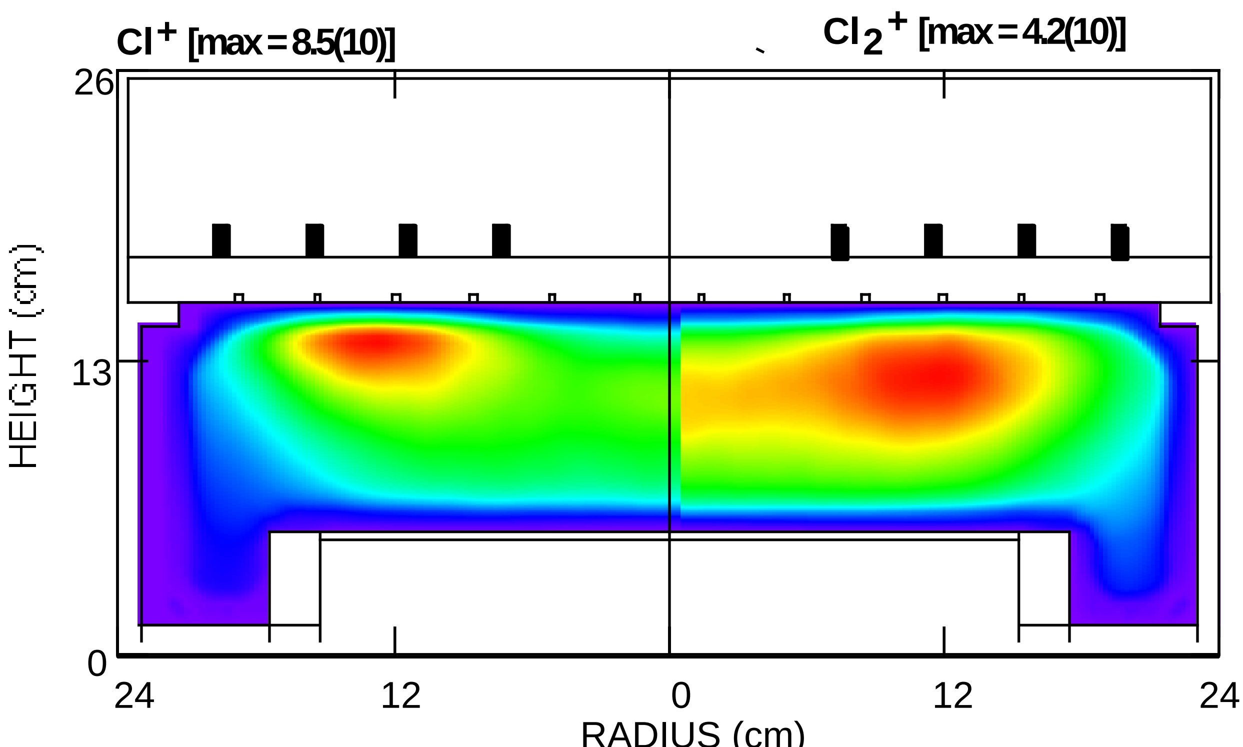
300 mm ETCH TOOL: ELECTRIC FIELD, POWER, ION DENSITIES





- $Ar/Cl_2/BCl_3$ = 1/1/1,
  10 mTorr, 600 W ICP,
  100 V bias, 150 sccm

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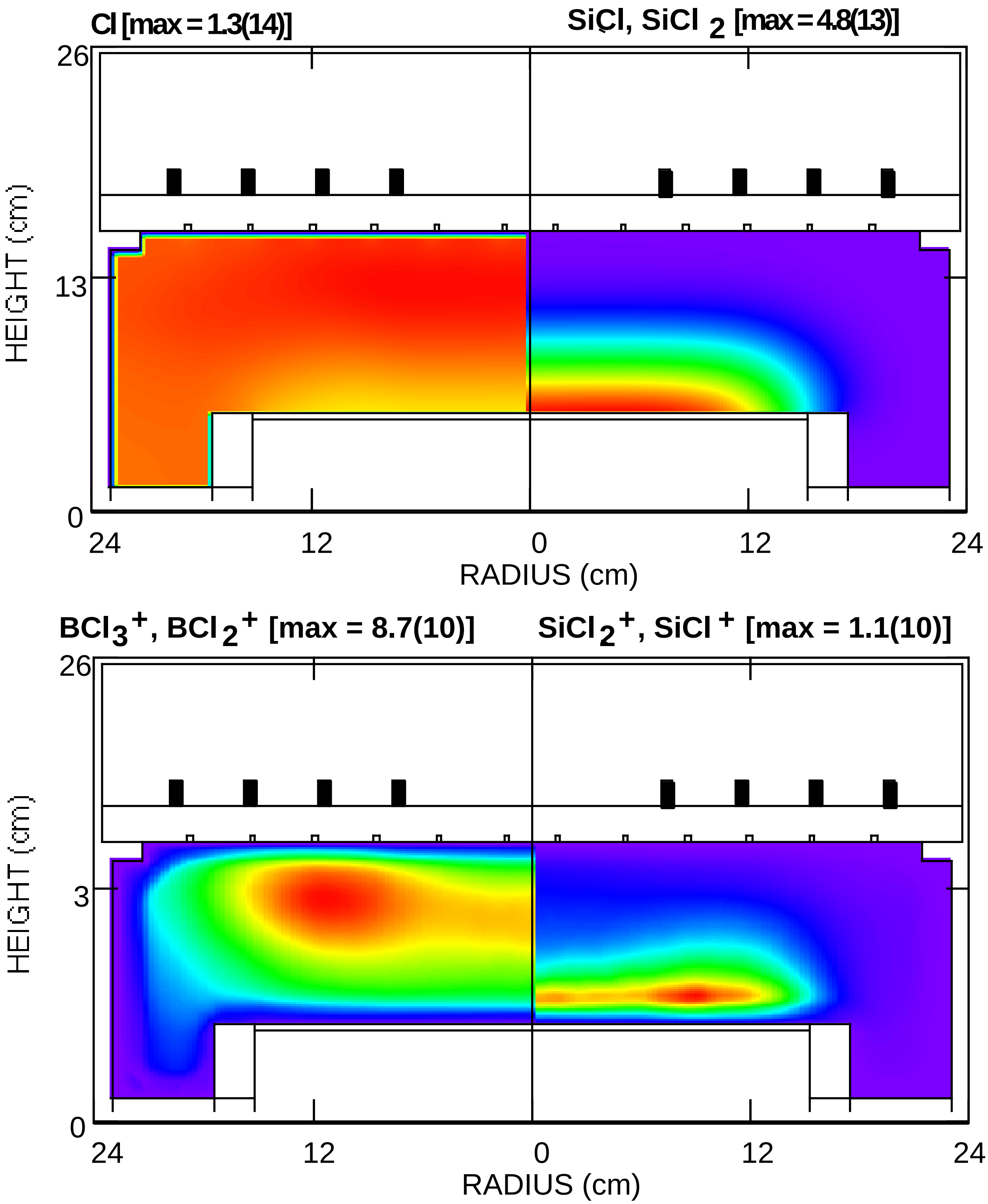
300 mm ETCH TOOL: PRECURSORS, ETCH PRODUCTS



- $Ar/Cl_2/BCl_3$ = 1/1/1,
  10 mTorr, 600 W ICP,
  100 V bias, 150 sccm

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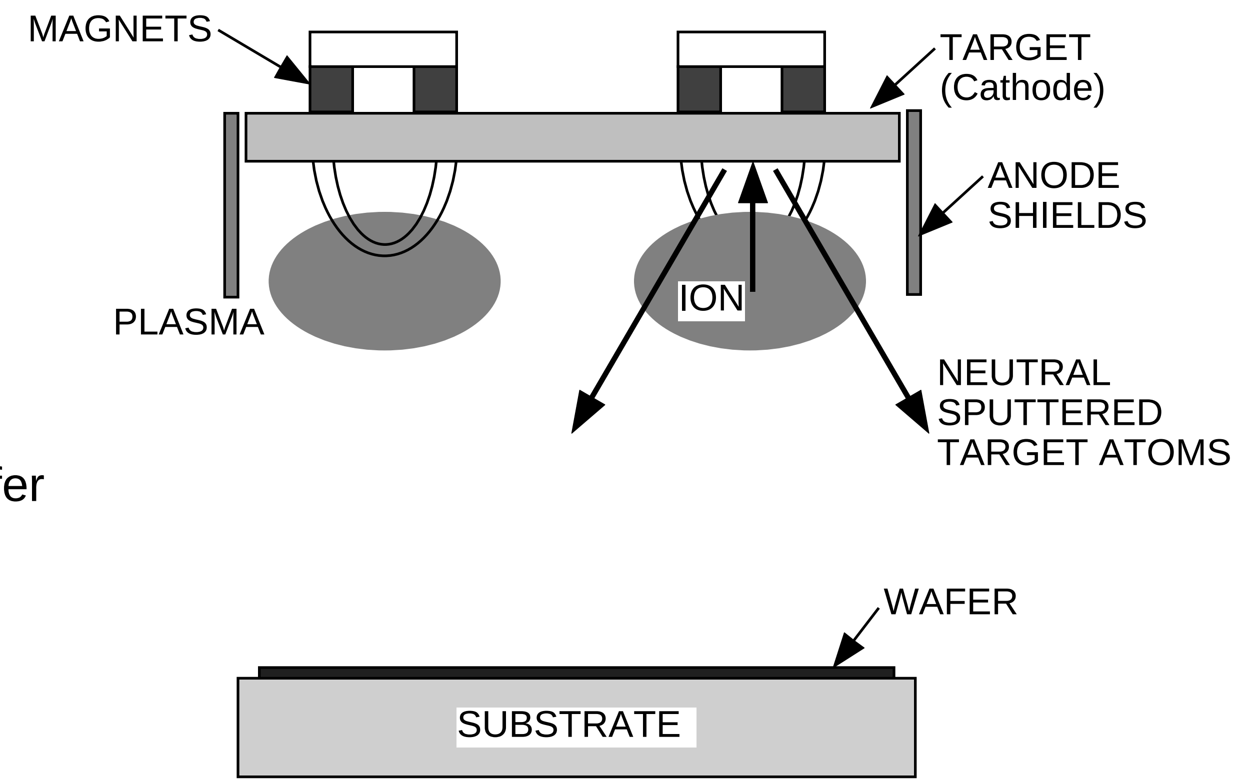
PHYSICAL VAPOR DEPOSITION OF METALS

• Physical-vapor-deposition (PVD) is a sputtering process in which metal (and other) layers are deposited for barrier coatings and interconnect wiring.



• Typical Conditions:

- < few mTorr Ar buffer
- 100s V bias
- 100s W - a few kW

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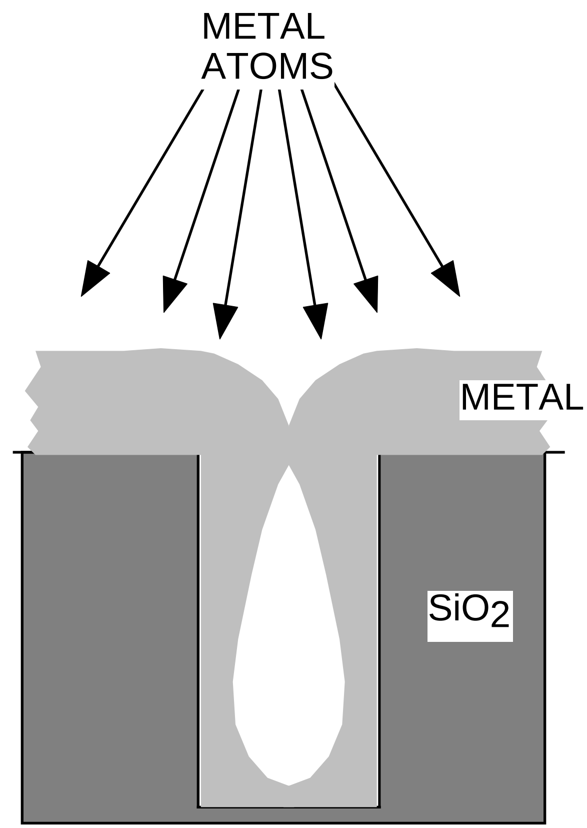
PVD DEPOSITION PROFILES

- In PVD, the atoms arriving at the substrate are mostly neutral with broad angular distributions.

- The corners of the trench see a larger solid angle of the metal atom flux, and so have a higher deposition rate.

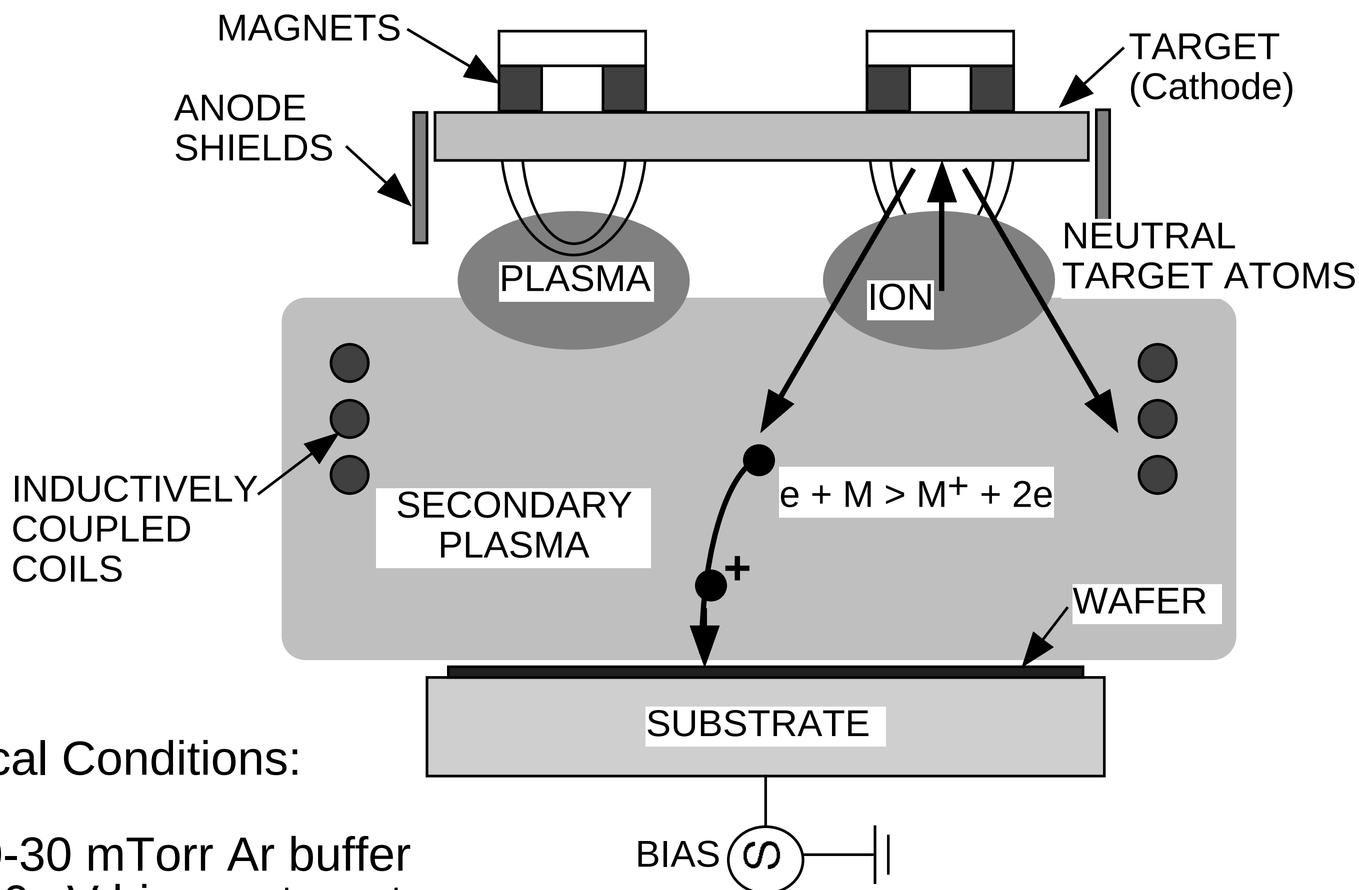
- The end result is a nonuniform deposition and void formation.

- Columnators are often used to filter out large angle flux; at the cost of deposition rate and particle formation.



IONIZED METAL PHYSICAL VAPOR DEPOSITION (IMPVD)

- In IMPVD, a second plasma source is used to ionize a large fraction of the the sputtered metal atoms prior to reaching the substrate.



- Typical Conditions:

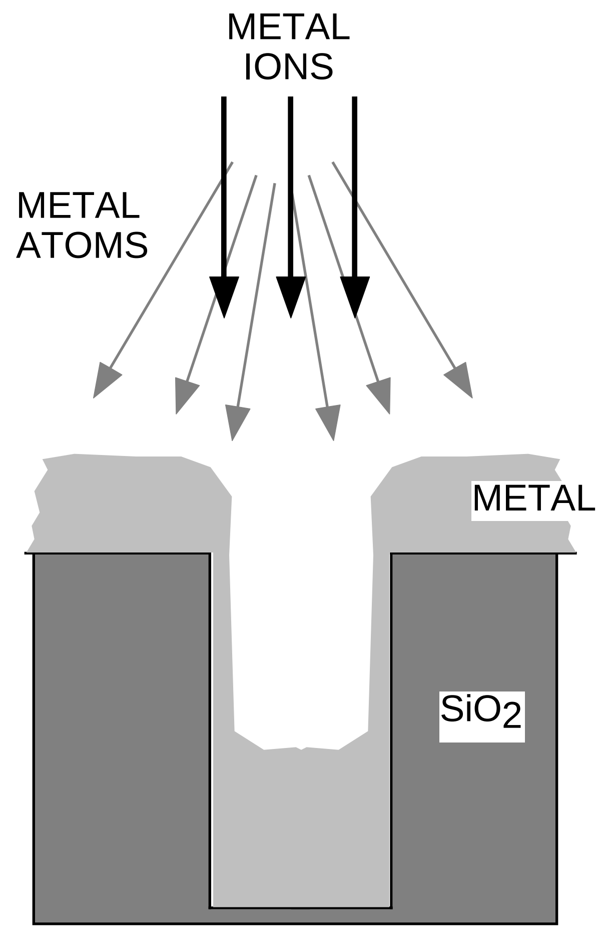
  - 10-30 mTorr Ar buffer
  - 100s V bias on target
  - 100s W - a few kW ICP
  - 10s V bias on substrate

IMPVD DEPOSITION PROFILES

- In IMPVD, a large fraction of the atoms arriving at the substrate are ionized.

- Applying a bias to the substrate narrows the angular distribution of the metal ions.

- The anisotropic deposition flux enables deep vias and trenches to be uniformly filled.

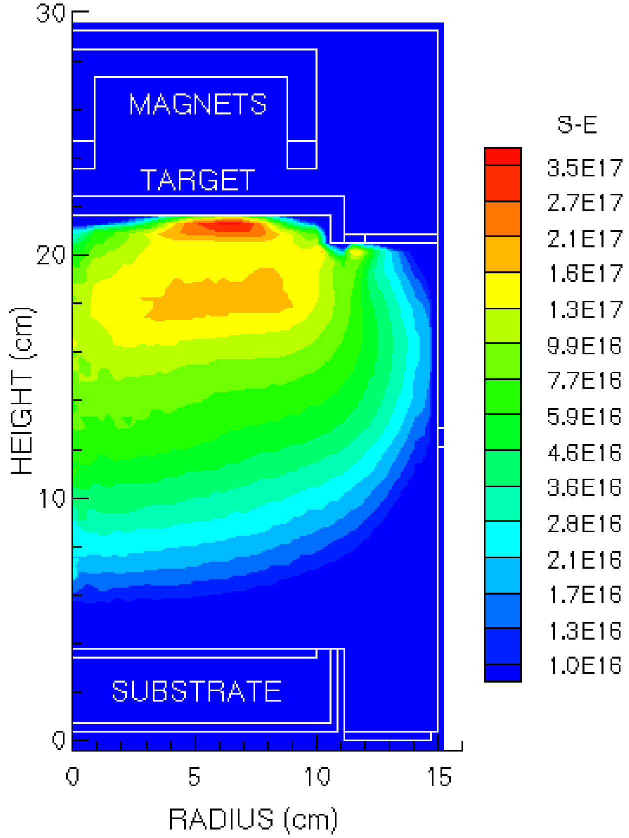


MAGNETRON SPUTTER TOOL: Ar/Cu

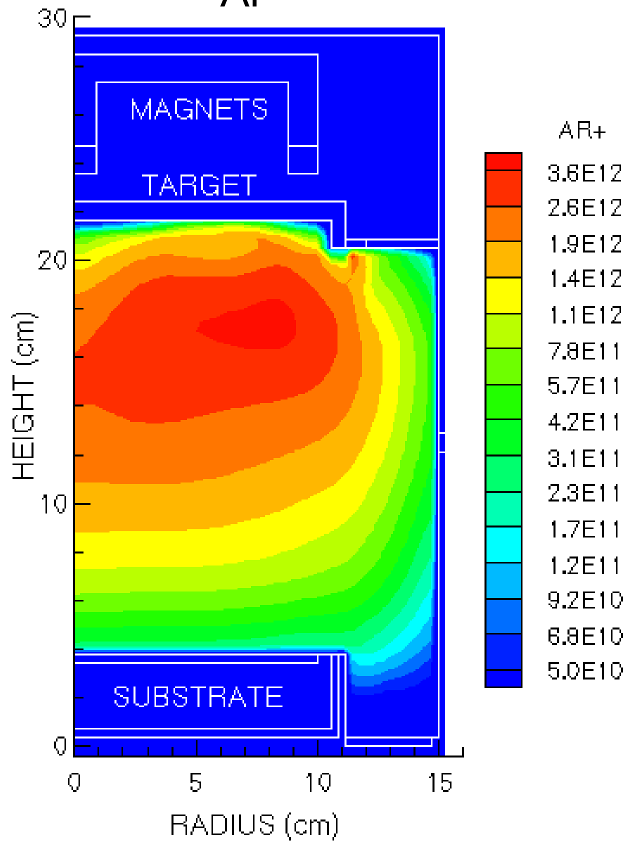
- Secondary electron emission from the target, and electron heating in the sheath, produces a torroidal electron source.

- Peak ion densities are mid-10^{12} cm^{-3}.

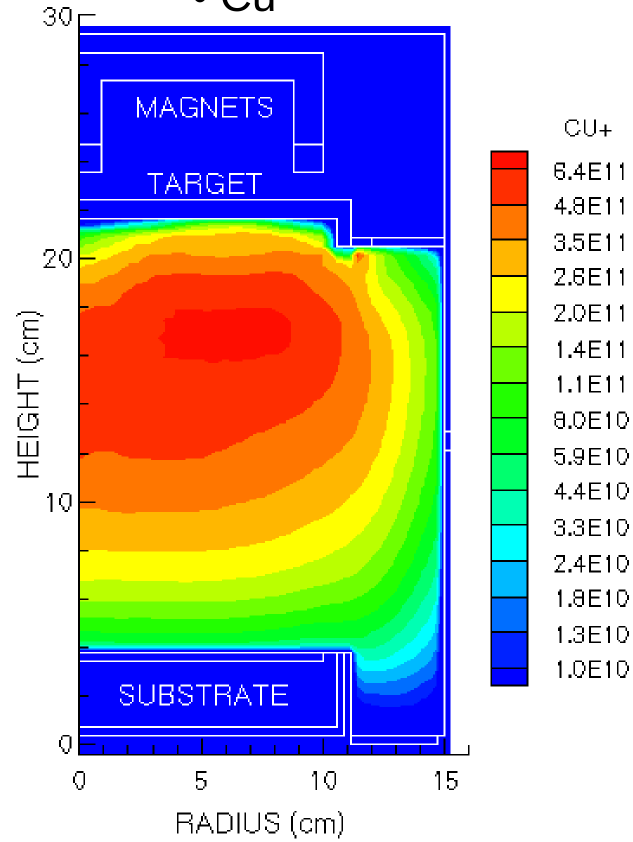
- e-Source



- Ar^+



- Cu^+



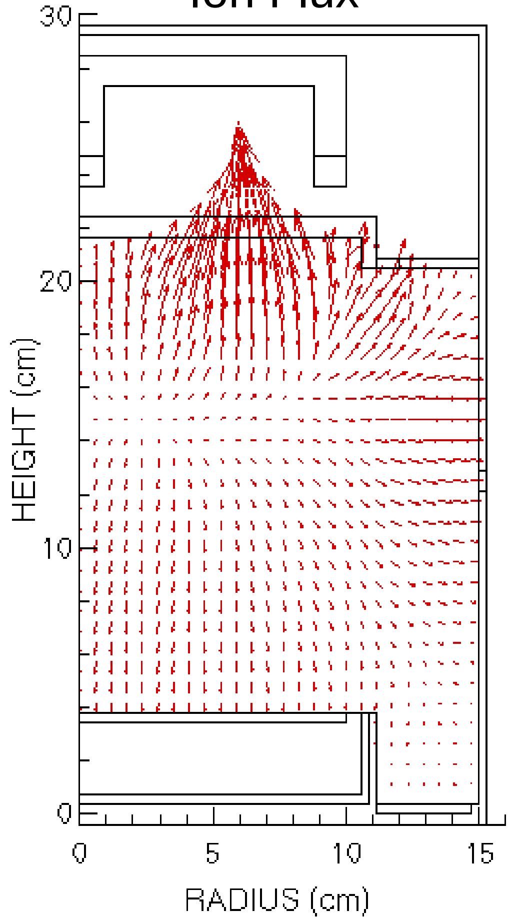
- Ar, 3.5 mTorr
- -200 V Target, 200 G

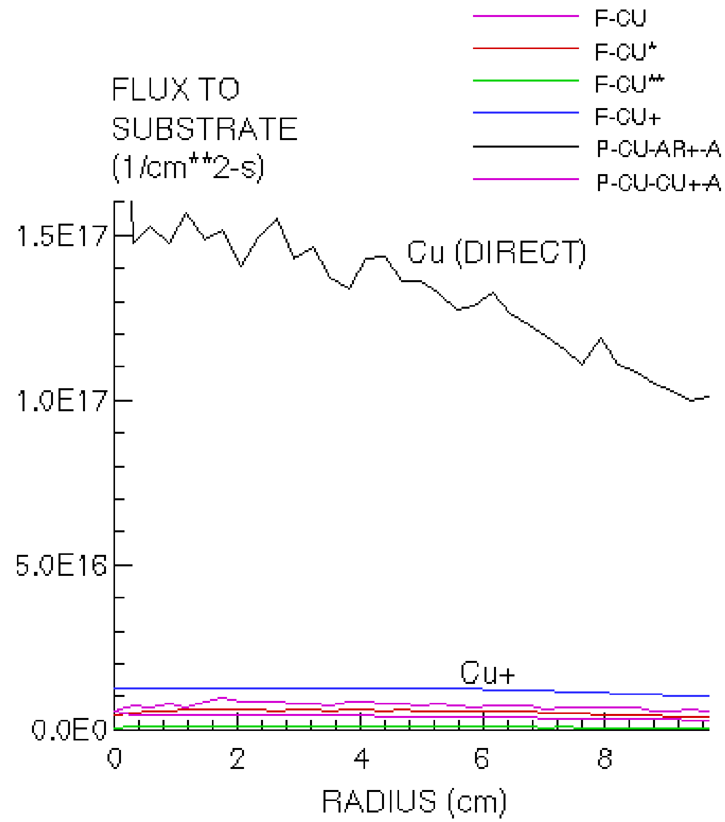
FLUXES IN THE Ar/Cu PVD TOOL

- Ion sputtering of the target produces a neutral Cu flux into the plasma.

- The low gas pressure and long mean free math of Cu atoms results in the flux to the substrate being “direct” neutrals.

- Ion Flux



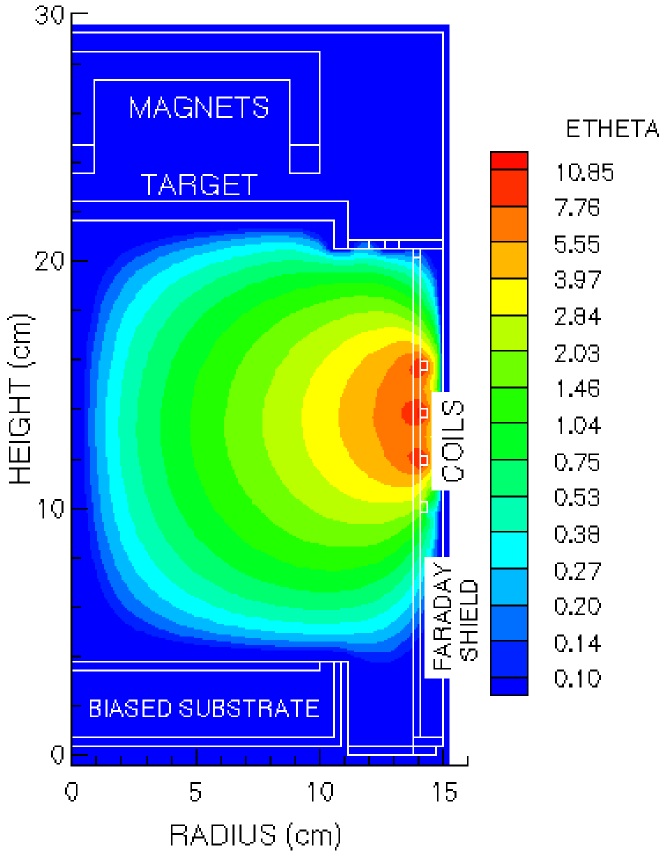


- Ar, 3.5 mTorr
- -200 V Target, 200 G

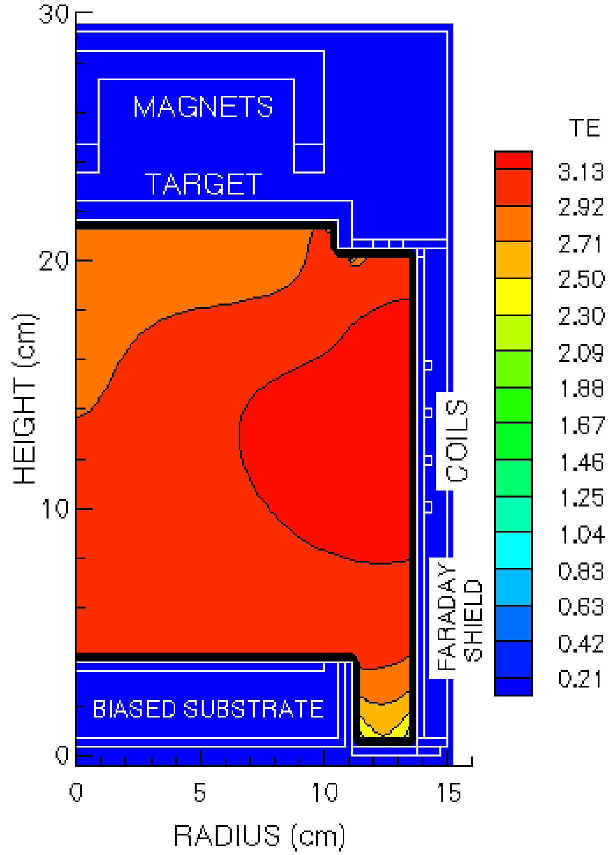
IMPVD TOOL: FIELDS AND TEMPERATURES

- The added inductively coupled electric field from the rf coils heats electrons in the bulk plasma producing a peak in temperature away from the target.

- Electric field



- Electron Temperature

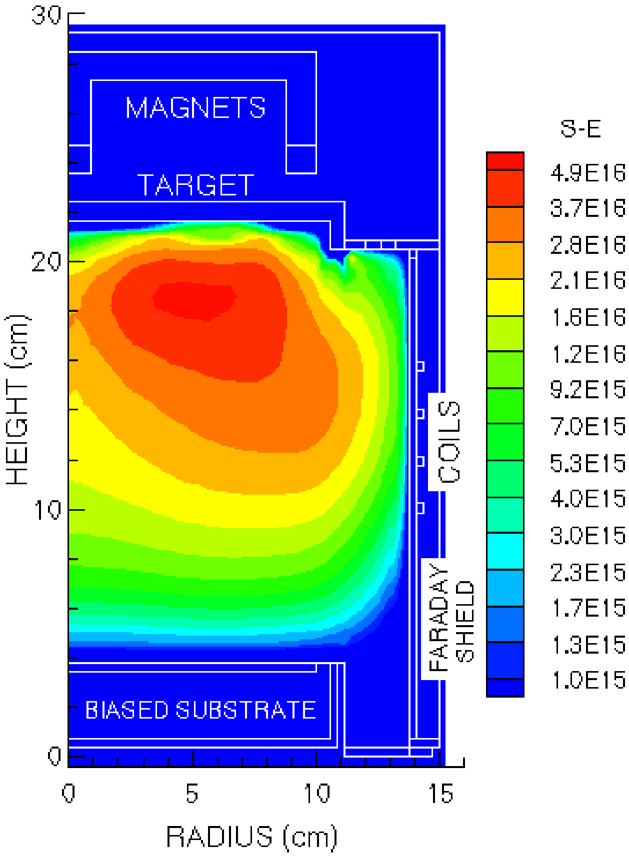


- Ar, 20 mTorr
- -200 V Target, 200 G
- 1.25 kW ICP, 2 MHz

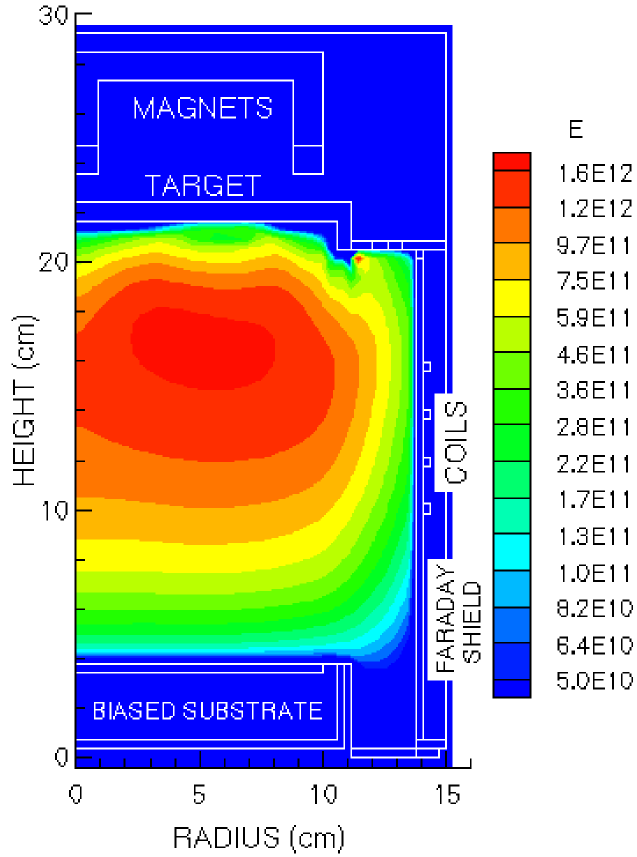
IMPVD TOOL: ELECTRON SOURCE AND DENSITY

- The combination of the magnetron fields and heating from the rf coils produces a more extended electron source and electron density. The ion density is 75% argon.

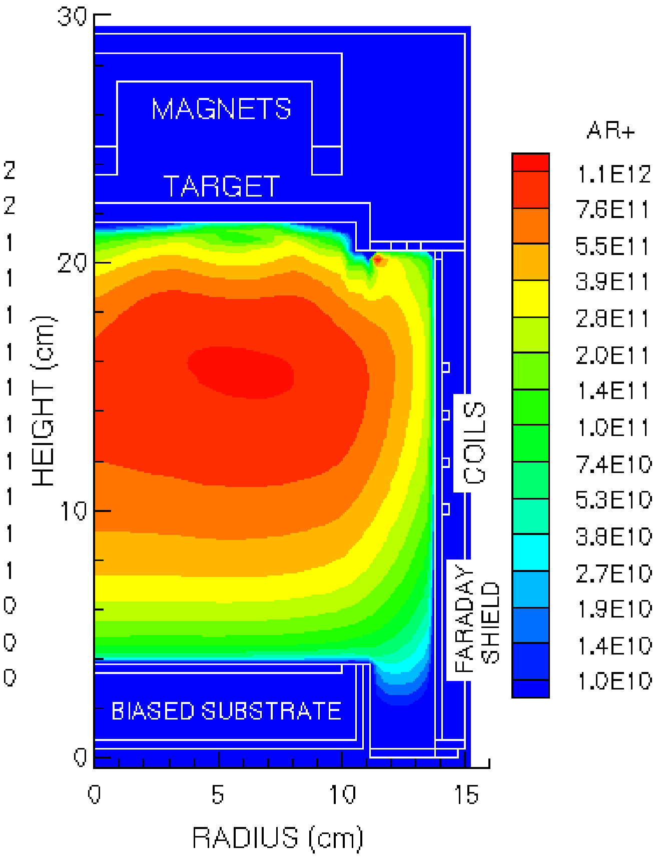
- Electron Source



- Electron Density



- Ar^+



- Ar, 20 mTorr
- -200 V Target, 200 G
- 1.25 kW ICP, 2 MHz

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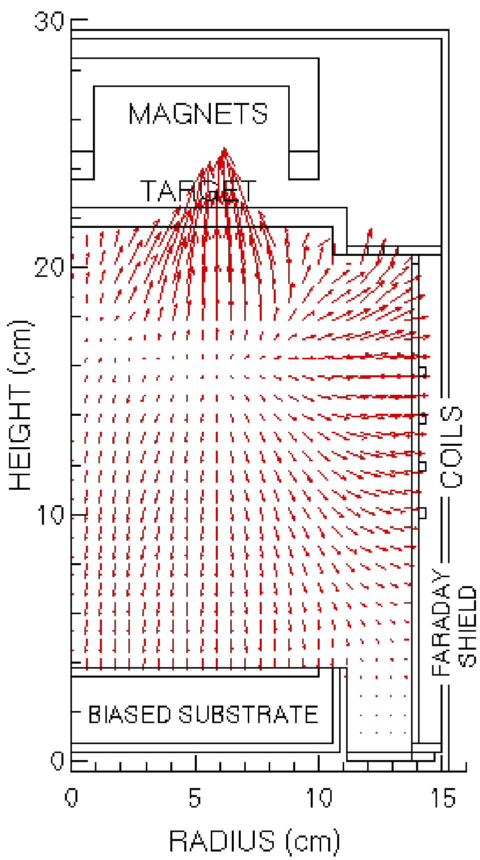
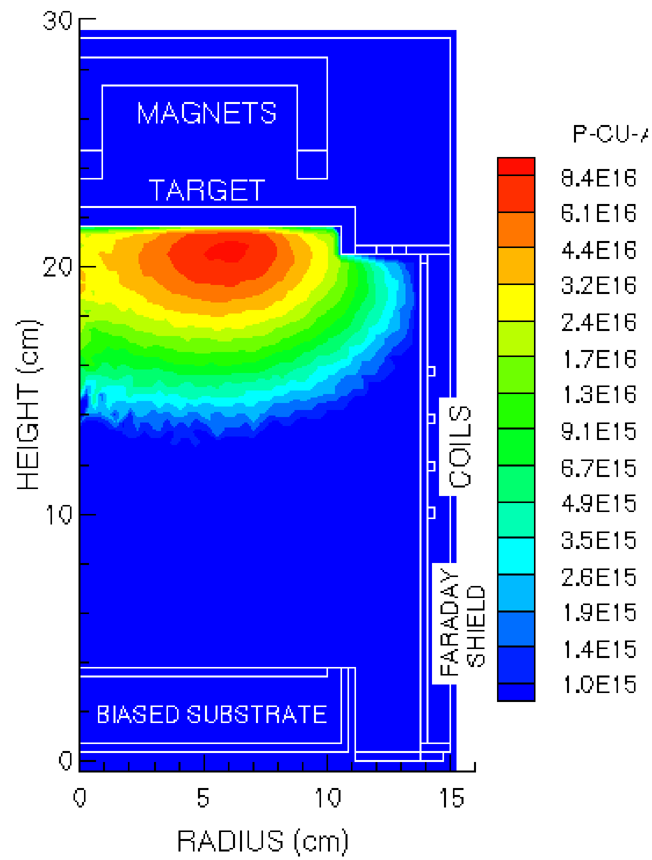
IMPVD TOOL: ION FLUX AND SPUTTER SOURCE

- The magnetron focus the ion flux to the target, producing a sputter source of Cu atoms.
- Due to the high gas pressure, the Cu atoms are thermalized in the vicinity of the target.

- Ion Flux





- Cu Source

- Ar, 20 mTorr
- -200 V Target, 200 G
- 1.25 kW ICP, 2 MHz

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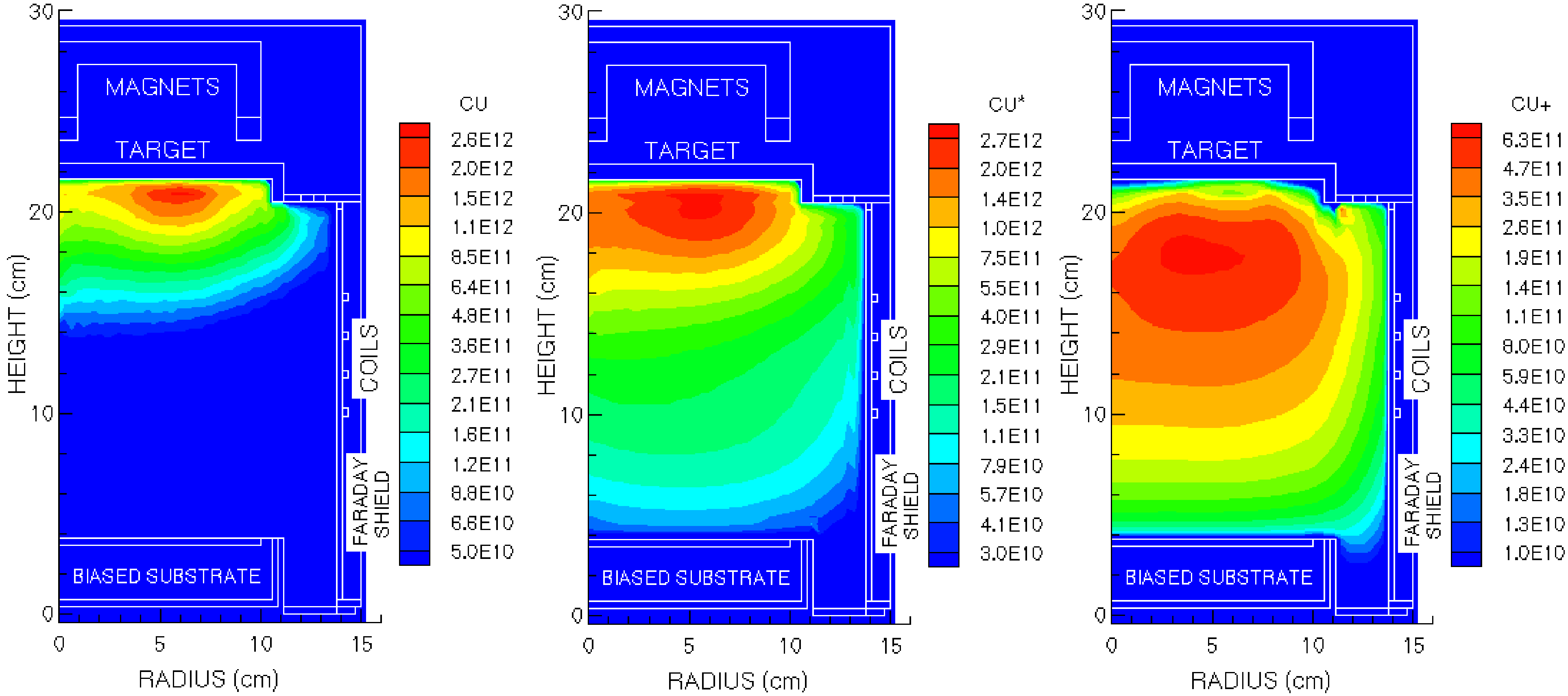
IMPVD TOOL: Cu DENSITIES

- Due to the longer residence time of Cu in the chamber and the higher electron temperature produced by the rf heating, the Cu inventory is largely converted to ions and metastables [Cu(^{2}D)].

• Cu(^{2}S) • Cu(^{2}D) • Cu^+



- Ar, 20 mTorr
- -200 V Target, 200 G
- 1.25 kW ICP, 2 MHz

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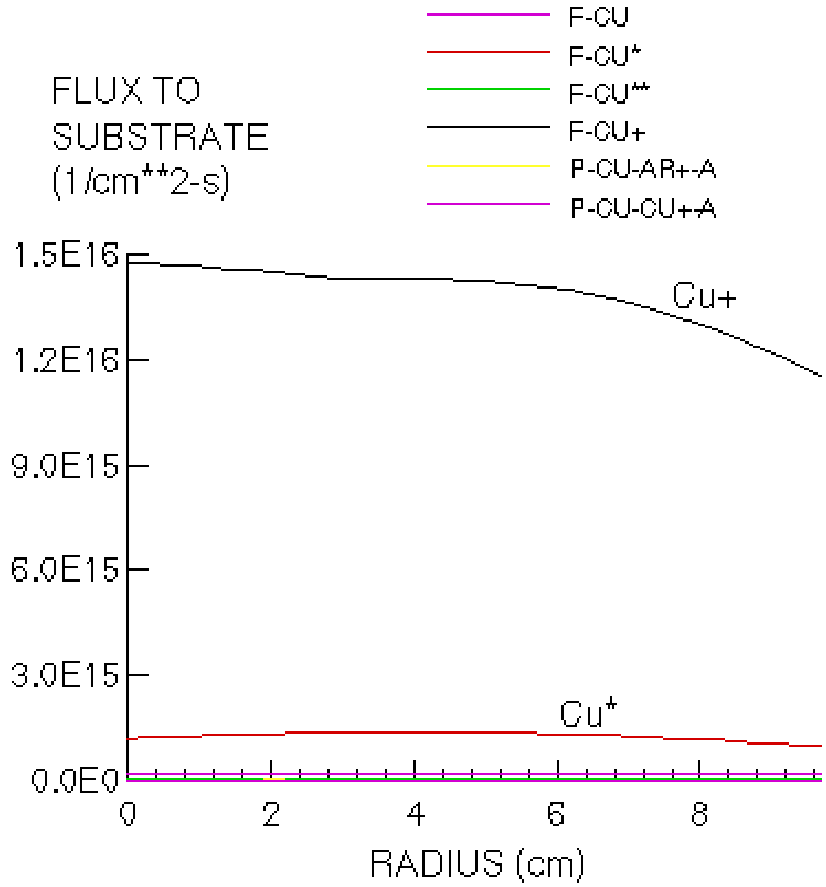
IMPVD TOOL: Cu FLUXES TO SUBSTRATE

- The flux of Cu to the substrate is 85-90% ionized.
- The neutral flux is largely metastable $Cu(^2D)$.



- Ar, 20 mTorr
- -200 V Target, 200 G
- 1.25 kW ICP, 2 MHz

TYPICAL PLASMA ETCHING CHEMISTRIES

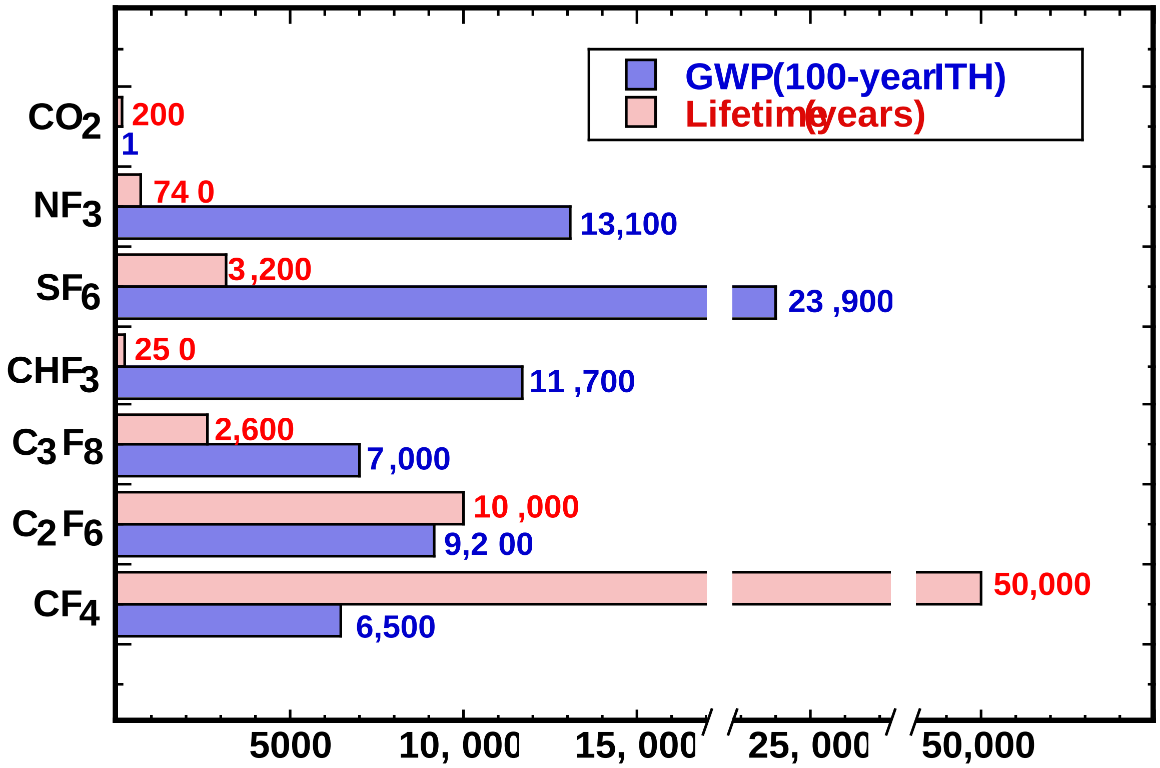
ETCHING SPECIES	SOURCE GAS	ADDITIVE	MATERIALS	MECHANISM	SELECTIVE OVER
F	CF_4 C_2F_6 SF_6 NF_3 ClF_3 F_2	O_2 O_2 O_2 None None None	Si	Chemical	SiO_2 Resist
CF_x-film	CF_4 C_2F_6 CHF_3	H_2 H_2 None or O_2	SiO_2/Si_3N_4	Ion-energetic	Si
Cl	Cl_2 Cl_2 CF_3Cl	None C_2F_6 None	undoped Si n-type Si	Ion-energetic Ion-Inhibitor	SiO_2
Cl	Cl_2	BCl_3 CCl_4 $CHCl_3$	Al	Ion-inhibitor	Resist SiO_2

Ref.: D. Flamm, "Plasma Etching: An Introduction"

PERFLUOROCOMPOUNDs (PFCs) LIFETIME

- Perfluorocompounds (PFCs) are important to the semiconductor industry since they are widely used as process gases in microelectronics fabrication for etching.

- However these PFCs are absorbers of infrared radiation having long atmospheric lifetimes and thus have high global warming potential.



EXAMPLE OF DATABASE NEEDS: Ar/CF_4 PLASMA ETCHING AND ABATEMENT

- Plasma etching of Si and SiO_2 typically use PFCs, greenhouse gases with large Global Warming Potential.

- Post-etch chamber abatement of PFCs is being investigated using downstream "burnboxes" with O_2 injection to oxidize PFCs to easily scrubable compounds.

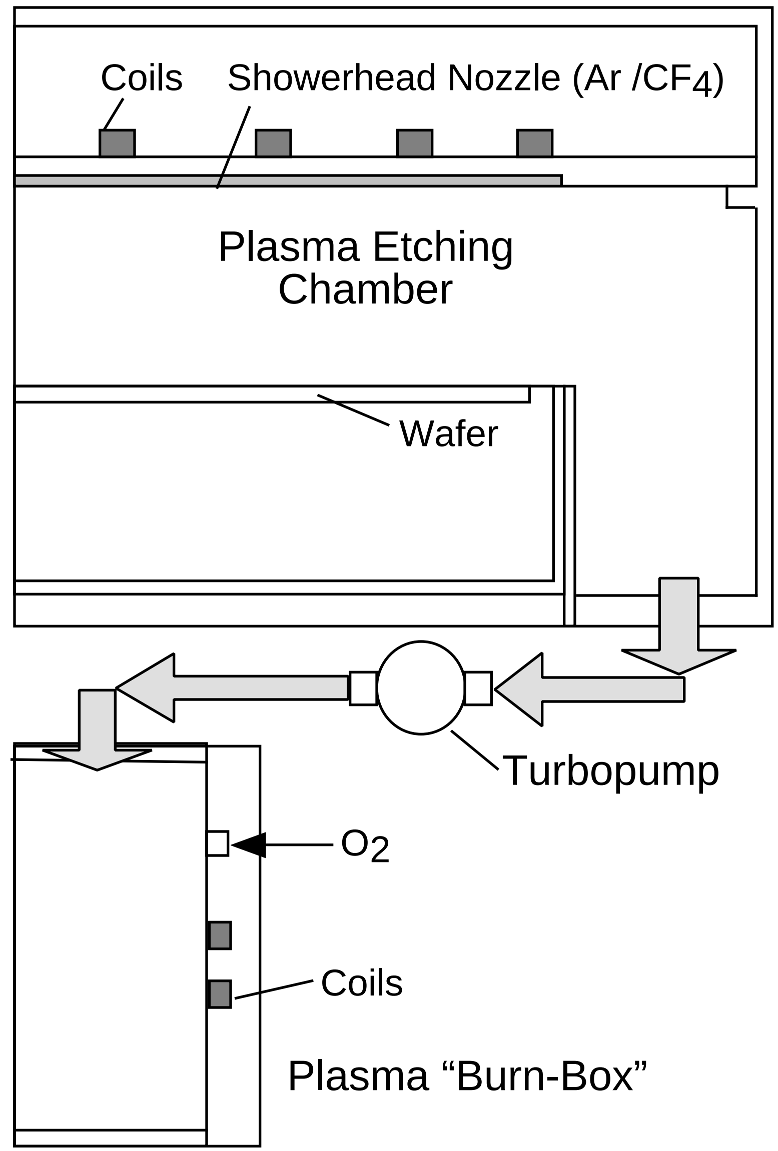
- Test conditions:

Etch Chamber:

13.56 MHz ICP reactor
Ar/CF_4 at 10 mTorr.

Burn-Box:

13.56 MHz ICP reactor
Effluent + O_2 injection
150 mTorr



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BURN-BOX PLASMA OXIDATION CHEMISTRY

- Downstream burn-box plasma oxidation chemistry involves a series of neutral and ion molecule reactions whose final products are CO, CO_2, COF_2.

$O + CF_3 \rightarrow COF_2 + F$

$O + CF_2 \rightarrow CO + F + F$

$O + COF \rightarrow CO_2 + F$

$O + CF_2 \rightarrow COF + F$

$O + CF \rightarrow CO + F$

$O(^1D) + CF_3 \rightarrow COF_2 + F$

$O(^1D) + CF_2 \rightarrow CO + F + F$

$O(^1D) + COF \rightarrow CO_2 + F$

$O(^1D) + CF_2 \rightarrow COF + F$

$O(^1D) + CF \rightarrow CO + F$

$O^+ + CF_4 \rightarrow CF_3^+ + FO$

$O^+ + C_2F_6 \rightarrow C_2F_5^+ + FO$

$O^+ + C_2F_6 \rightarrow CF_3^+ + CF_3 + O$

$COF + CF_2 \rightarrow CF_3 + CO$

$COF + CF_3 \rightarrow CF_4 + CO$

$COF + COF \rightarrow COF_2 + CO$

$COF + CF_2 \rightarrow COF_2 + CF$

$COF + CF_3 \rightarrow COF_2 + CF_2$

ION DENSITIES IN PLASMA ETCHING CHAMBER

- Positive ions are generated by electron impact ionization and dissociative charge exchange.

  $Ar + e \rightarrow Ar^{+} + e + e$

  $CF_4 + e \rightarrow CF_3^{+} + F + e + e$

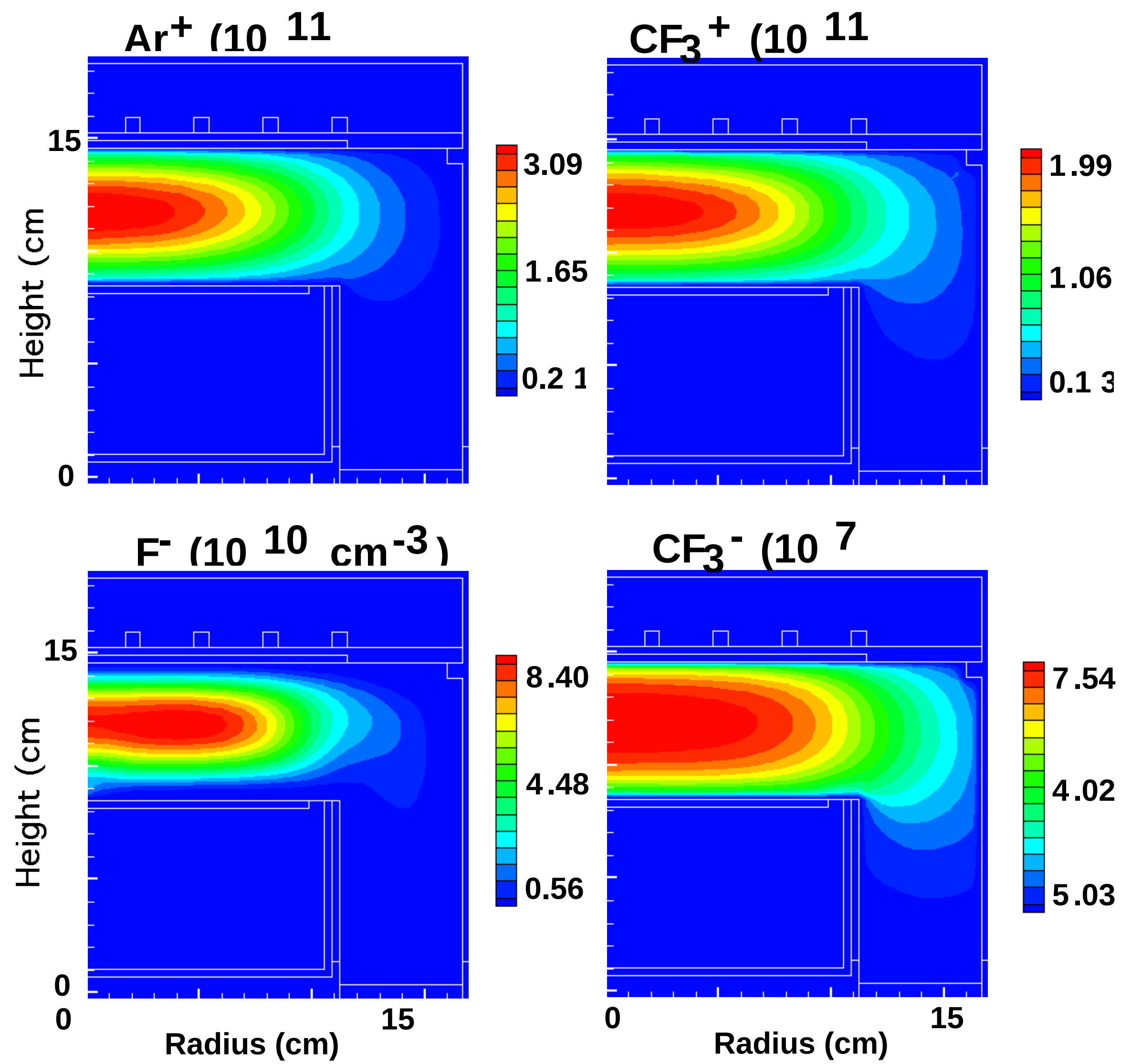
  $Ar^{+} + CF_4 \rightarrow CF_3^{+} + F + Ar$

- Negative ions are generated by electron impact dissociative attachment.

  $CF_4 + e \rightarrow CF_3^{-} + F$

  $CF_4 + e \rightarrow CF_3 + F^{-}$

- Ar/CF_4 = 60/40, 600 W, 200 sccm, 10 mTorr



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FEEDSTOCK DISSOCIATION

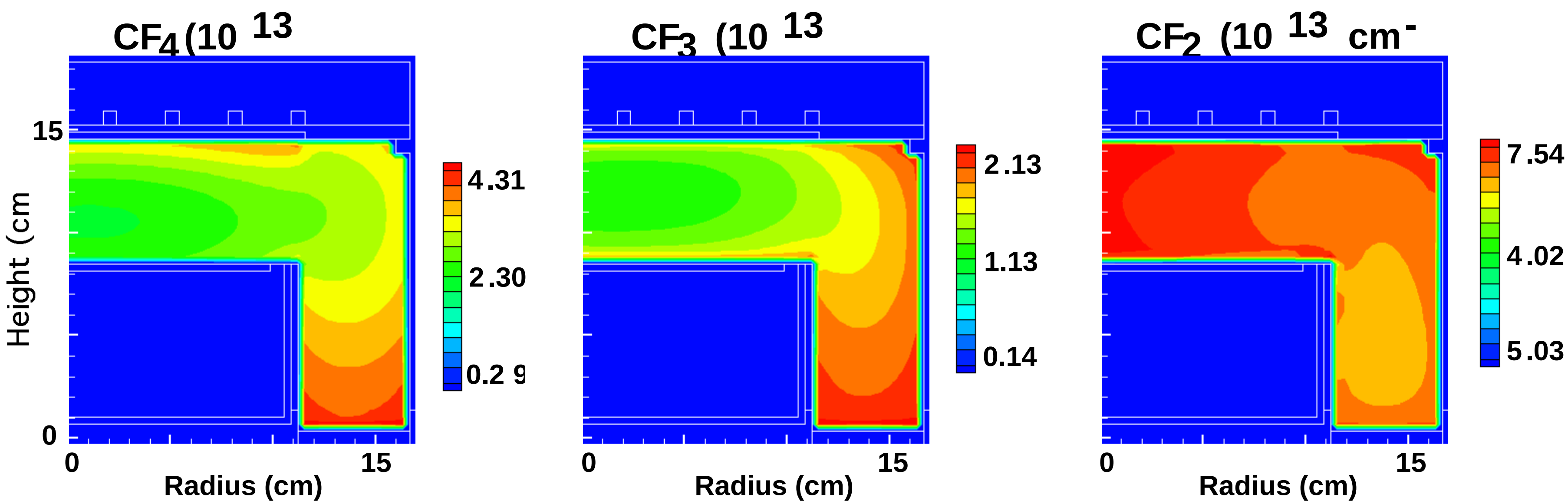
- CF_4 is dissociated by electron impact to CF_2 and CF_3. Due to subsequent reassociation, the densities of CF_4 and CF_3 increase near pump port.

$CF_4 + e \rightarrow CF_3 + F^-$ $\qquad$ $CF_4 + e \rightarrow CF_3 + F + e$

$CF_4 + e \rightarrow CF_2 + F + F + e$ $\qquad$ $CF_4 + Ar^* \rightarrow CF_2 + F_2 + Ar$

$CF_2 + F + M \rightarrow CF_3 + M$ $\qquad$ $CF_3 + F + M \rightarrow CF_4 + M$

$CF_2 + F_2 \rightarrow CF_3 + F$ $\qquad$ $CF_3 + F_2 \rightarrow CF_4 + F$



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PFC GENERATION IN ETCHING CHAMBER

- PFCs are generated as by products of the dissociation of feedstock gases. The majority of PFC generation is through wall reactions.

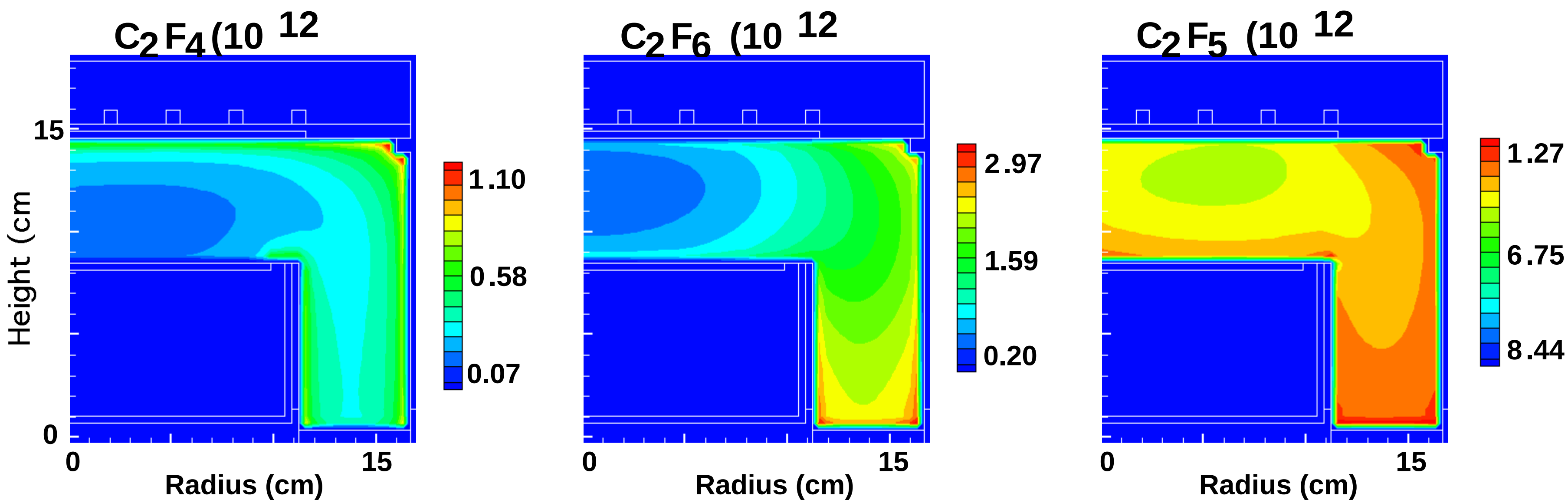
$CF_3 + CF_3 + M \rightarrow C_2F_6 + M$

$CF_2 + CF_3 + M \rightarrow C_2F_5 + M$

$CF_2 + F + M \rightarrow CF_3 + M$

$CF_3 + CF_3 \rightarrow C_2F_6$ (at surface)

$CF_2 + CF_2 \rightarrow C_2F_4$ (at surface)



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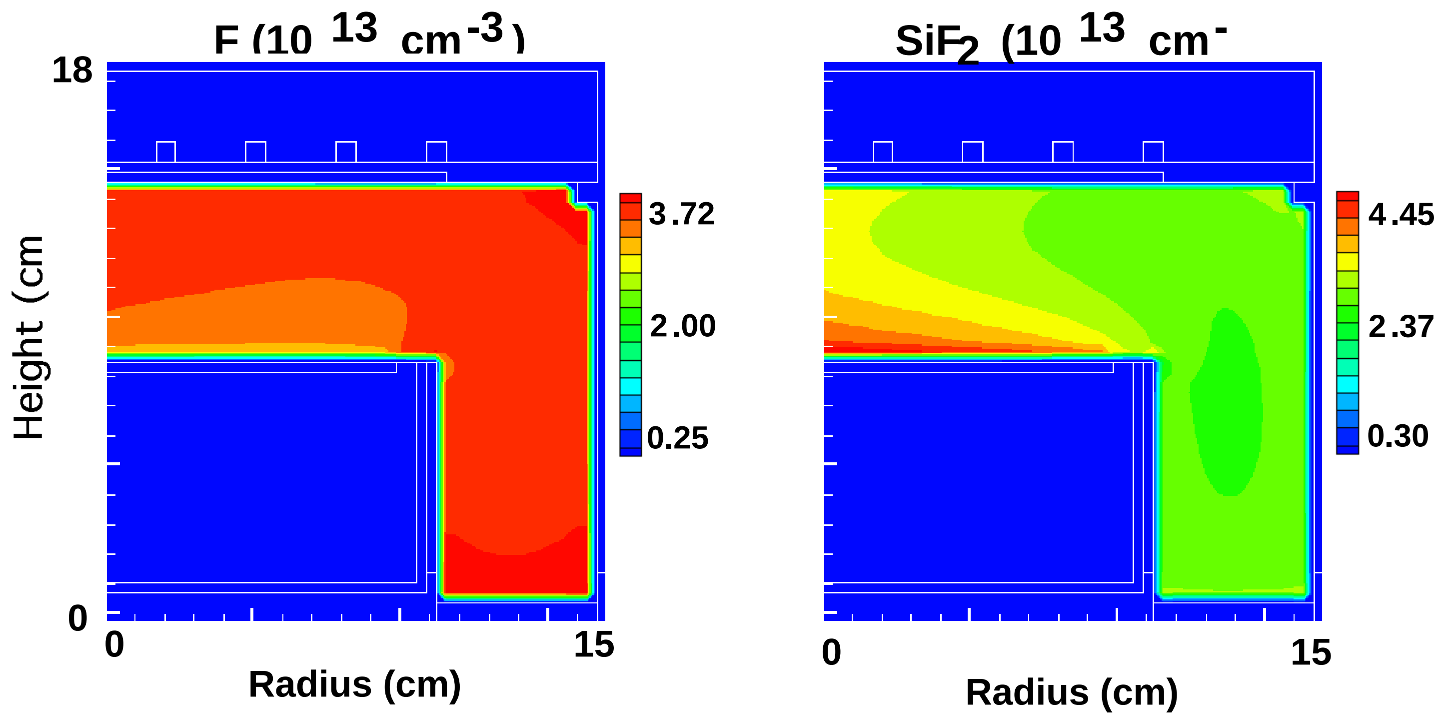
ETCHANT CONSUMPTION AND ETCH PRODUCT GENERATION

- F atoms, generated by electron impact dissociation of feedstocks, are consumed in the etching reactions.

- The SiF_2 etch product evolves from the wafer and is pumped away.



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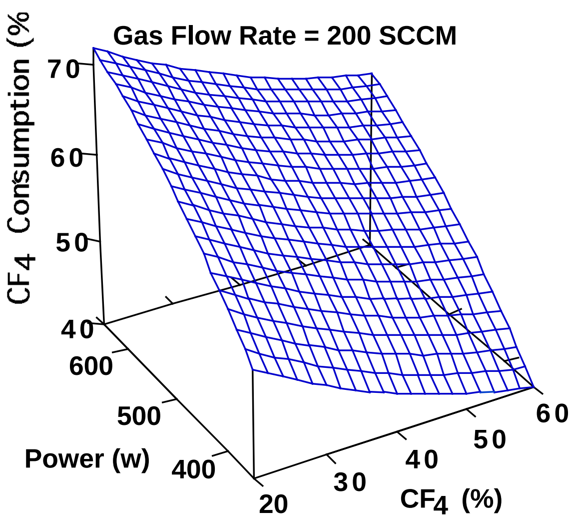
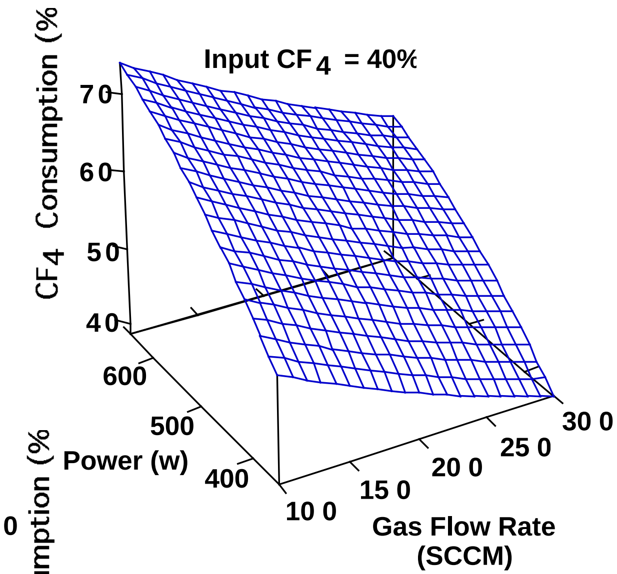
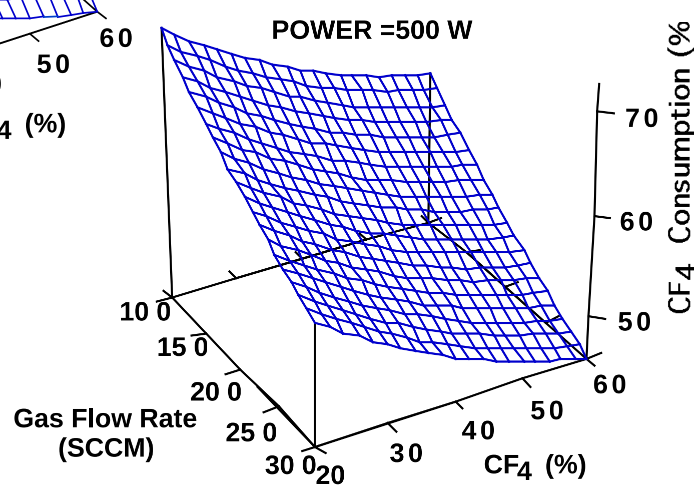
CF_4 CONSUMPTION IN ETCHING REACTOR

- A design of experiment has been performed to determine the functional relationships for CF_4 consumption.
- The consumption increases nearly linearly with a decrease in CF_4 percentage and gas flow rate, and with an increase of power deposition.







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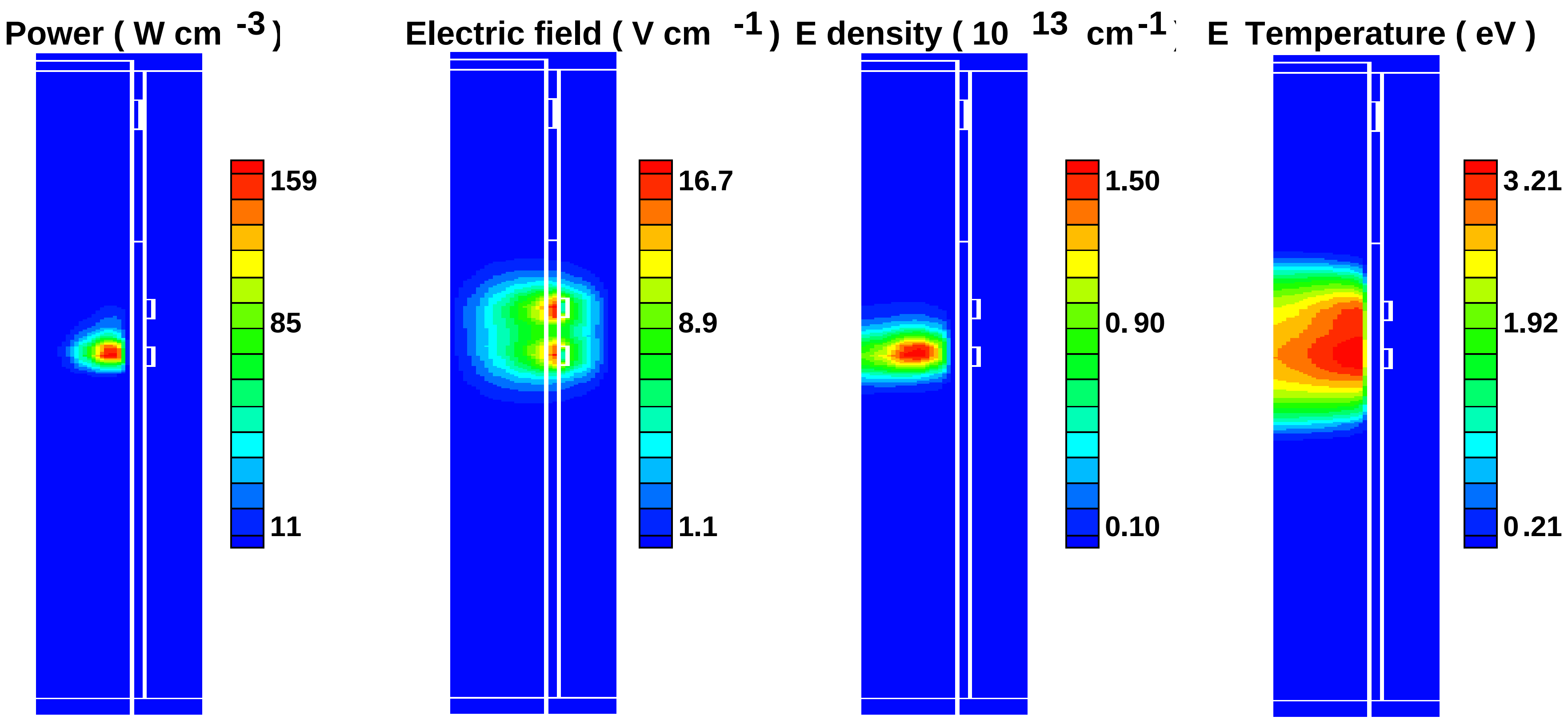
PLASMA PARAMETERS IN BURN BOX

- ICP burn box:
  - 2-turn coil
  - Radius = 2.5 cm
  - Height = 24 cm

- Power: 600 W
- Effluent: 207.5 sccm
- O_2 injection: 100 sccm
- Pressure: 150 mTorr



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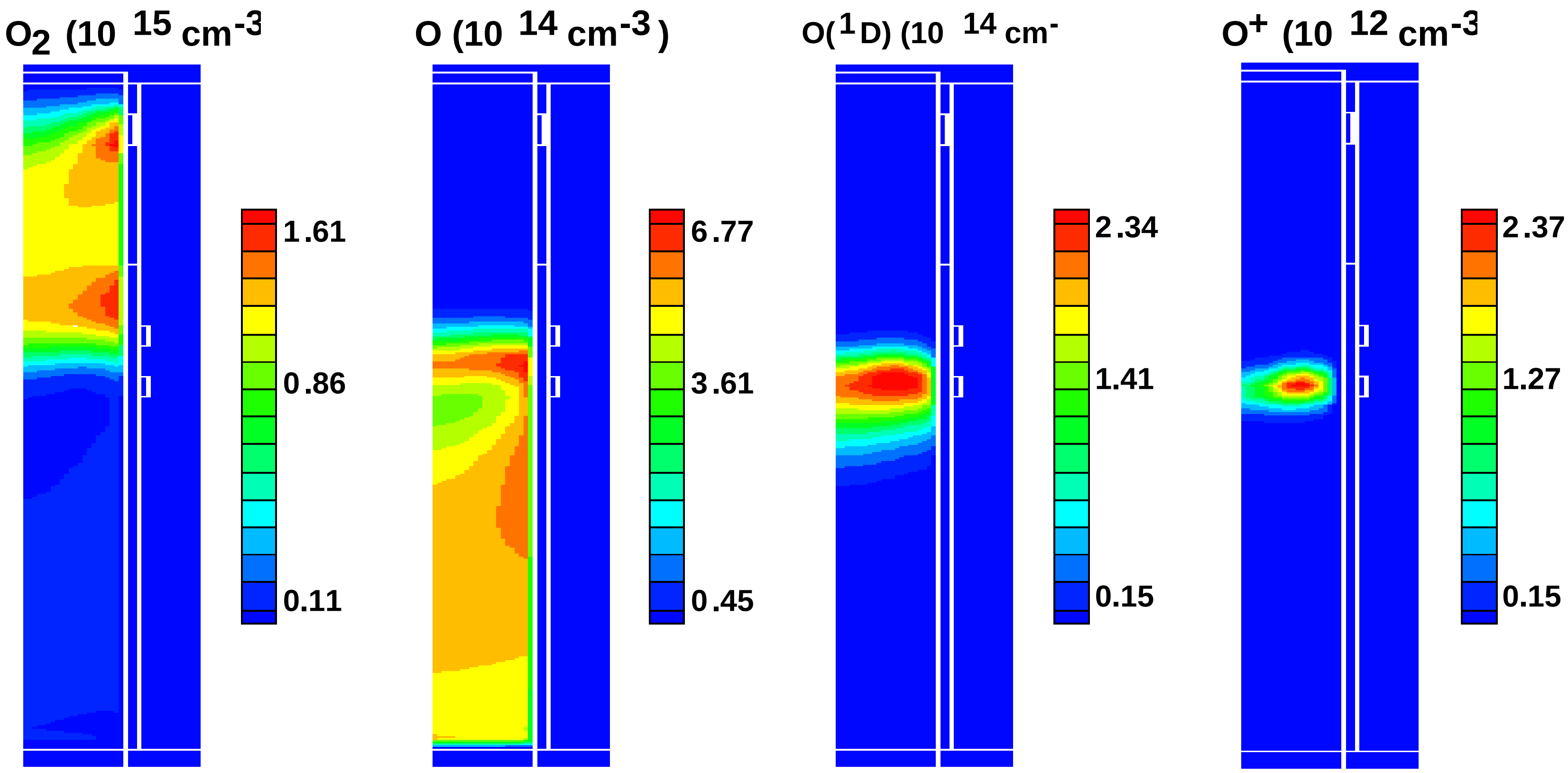
OXYGEN RADICAL PRODUCTION IN BURN BOX

- Electron impact dissociation of O_2 and excitation of O generates O, O(^{1}D) and O^+ which oxidize the PFCs and CF_x radicals in the plasma chamber effluent.



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EFFLUENT C_nF_m ABATEMENT IN PLASMA BURN BOX

- C_nF_m abatement in the burn-box has varying degrees of success, though conditions can usually be found where abatement is near 100% with less efficiency.

CF_4 (0-1.3(15) cm^{-3}
70% Abatement

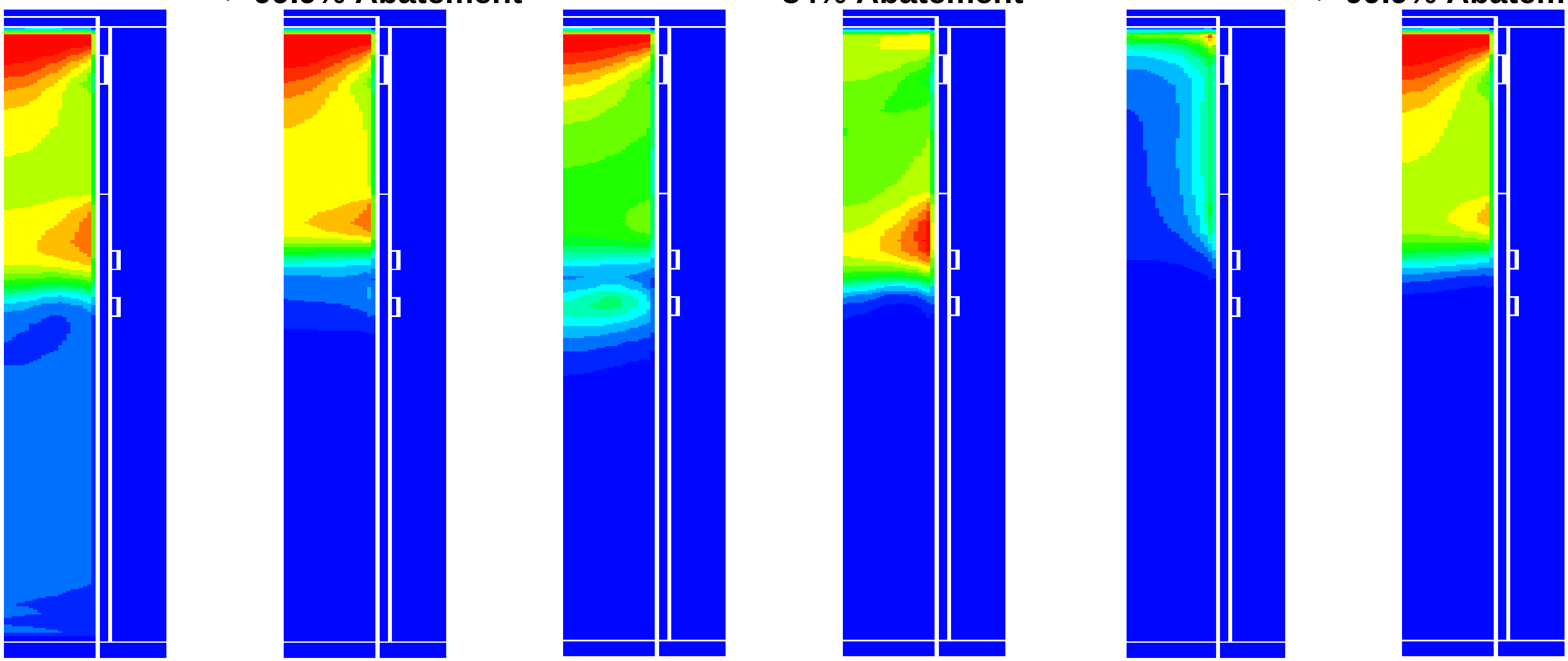
CF_3 (0-2.3(15) cm^{-3}
> 99.9% Abatement

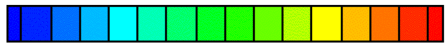
CF_2 (0-1.8(14)cm
> 99.9% Abatement

C_2F_6 (0-6 (13)cm^{-3})
84% Abatement

C_2F_4 (0 - 5(12)cm^{-3}
> 99.9% Abatement

C_2F_5 (0 - 1.1(14)cm
> 99.9% Abatement





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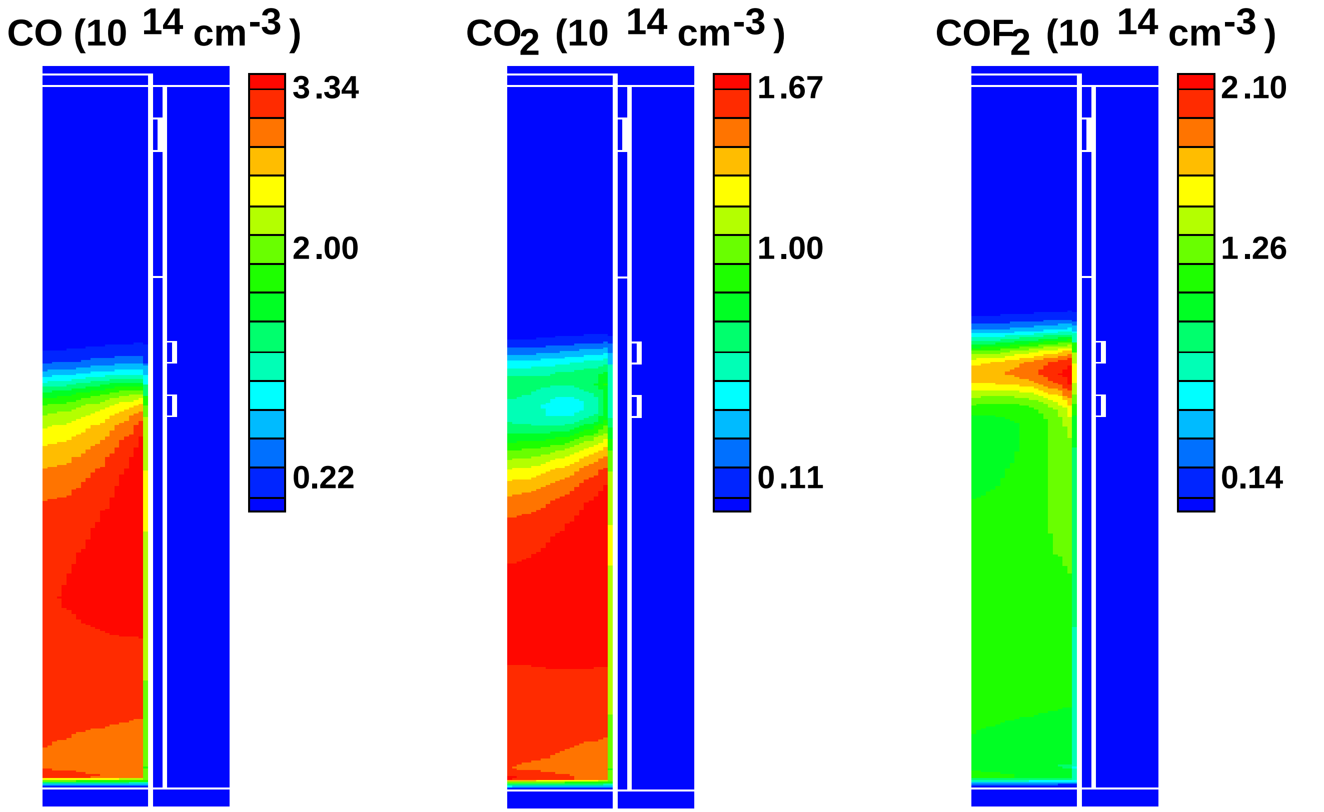
C_nF_m ABATEMENT PRODUCTS

- The major oxidation products are CO, CO_2, and COF_2 which can be removed by conventional scrubbing, spraying or catalytic methods.

- The large proportion of CO results from the low processing temperature.



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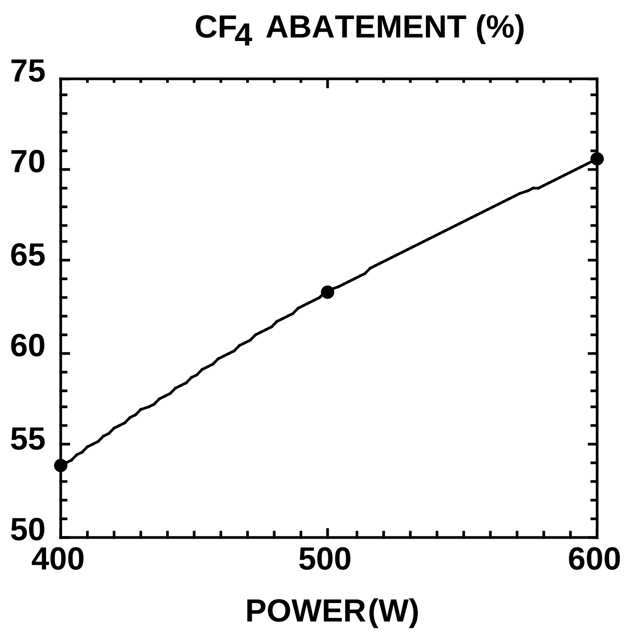
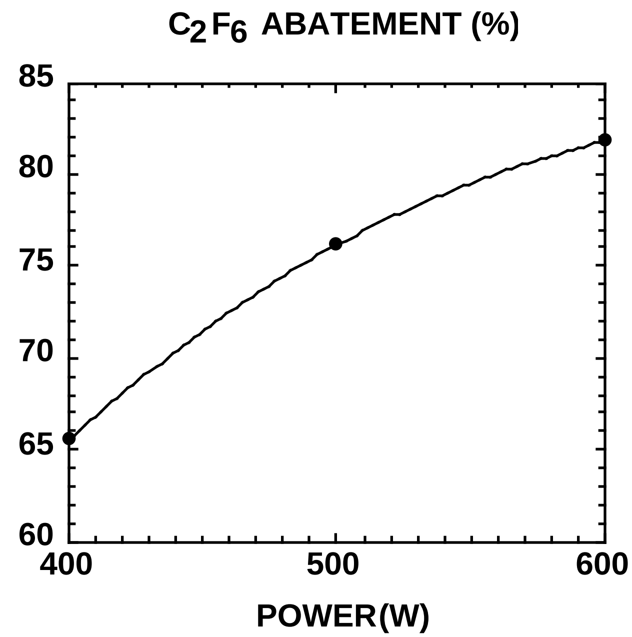
PFC ABATEMENT vs BURN BOX POWER

- With increasing burn box power, PFC abatement increases, however the energy cost (eV/molecule) for destroying PFCs increases (the process becomes less efficient).





- In evaluating the plasma abatement, the full enviromental impact must be considered.

- How much CO_2 is produced in generating the power to run the burn-box? What is THAT impact on global warming?

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CURRENT STATUS OF PLASMA MODELING AND SIMULATION FOR MATERIALS PROCESSING

- **Plasma equipment modeling is beginning to mature.**
  - **Basic physics is moderately well understood**
  - **Equations are moderately well solved**
  - **"Natural" advances in computing (algorithms and speed) will enable "better" 2-d and 3-d simulations**
- **Large gaps in the knowledge base, however, inhibit our ability to address industrially relevant problems. *THIS IS CURRENTLY THE RATE LIMITING STEP!!***
  - **Lack of cross sections and rate coefficients for chemistries of interest (e.g., C_4F_8/N_2O)**
  - **Lack of reactive sticking coefficients on surfaces (e.g., Cl(g) + Si(s) $\rightarrow$ $SiCl_n$(g))**

WHAT DATA ARE REQUIRED?

- ***Electron impact processes:***

  - **Energy resolved cross sections required for kinetic codes ($\leq$ 200 eV).**
  - **Average energy (or temperature) dependent rate coefficients for fluid codes ($\leq$ 15 eV).**

    Momentum Transfer | **Electronic excitation**
    Vibrational excitation | **Dissociative excitation**
    Attachment | **Ionization**

  - **Important: Branching ratios for dissociative processes**

$$\text{e.g.,} \quad e + CF_4 \rightarrow \begin{cases} CF_3 + F + e \\ CF_2 + F + F + e \end{cases}$$

  - **Important: Collisions with fragments (e.g., CF_3).** ***MOST PLASMA ETCHING TOOLS OPERATE WITH NEAR 100% DISSOCIATION OF FEEDSTOCK GASES.***

  - **Important for diagnostics and validation: Emission cross sections**

WHAT DATA ARE REQUIRED?

- ***Ion-Molecule;***

e.g., $Ar^+ + Si_2H_6 \rightarrow$ $Si_2H^+ + H_2 + H_2 + H + Ar$
$Si_2H_2^+ + H_2 + H_2 + Ar$
$Si_2H_3^+ + H_2 + H + Ar$

- **Important:** Energy range $\leq$ 1.0 eV WITH branching ratios
  Reactions with radical fragments.
- **Less important:** Multi-kV cross sections, ionization states > 2+

- ***Excitation Transfer and Penning Ionizaton:***

e.g., $Ar^* + Si_2H_6 \rightarrow Si_2H_4 + H + H + Ar$

- **Important:** Energy range $\leq$ 1.0 eV WITH branching ratios
  Reactions with radical fragments.

WHAT DATA ARE REQUIRED?

- ***Heavy Particle Momentum Transfer (neutral-neutral, ion-neutral, ion-ion)***

  e.g., Ar^{+}(hot) + Cl^{-}(cold) $\rightarrow$ Ar^{+}(cold) + Cl^{-}(hot)
  CF_3^{+}(hot) + C_2F_6(cold) $\rightarrow$ CF_3^{+}(cold) + C_2F_6(hot)

  - **Important:** **Energy range $\leq$ 1.0 eV WITH branching ratios**
    Reactions with radical fragments.

- ***Electron-ion Dissociative Recombination***

  e.g., $e + C_2F_4^{+} \rightarrow C_2F_2 + F + F$

  - **Important:** **Energy range $\leq$ 1.0 eV WITH branching ratios**
    Reactions with radical fragments.

- ***Neutral Chemical Reactions: (T £ 1500 K)***

TETRAFLUORMETHANE (CF_4)

- **The fluorine containing etching gas most studied is CF_4. Electron impact cross sections for CF_4 were recently reviewed:**

L. G. Christophorou et al, J. Phys. Chem. Ref. Data 25, 1341 (1996)

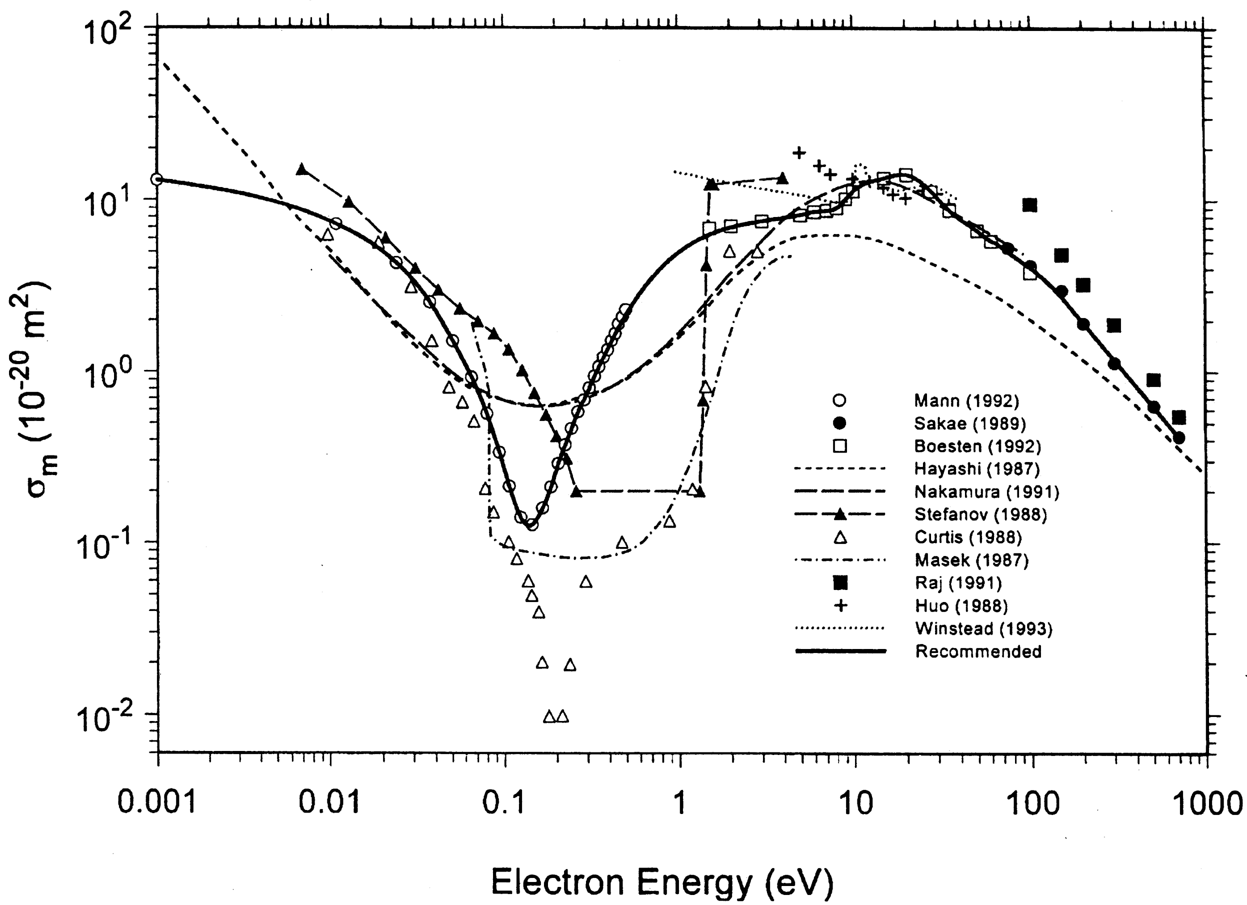
- **Momentum Transfer, vibrational excitation and dissociative attachment:**
  - **Well characterized by swarm data. General agreement between workers.**

- **Dissociative (neutral) excitation and ionization:**
  - **Very large differences in both branching ratios and magnitudes of cross sections.**

- **Greatest Need: Cross sections for CF_n fragments**

TETRAFLUORMETHANE (CF_4): MOMENTUM TRANSFER

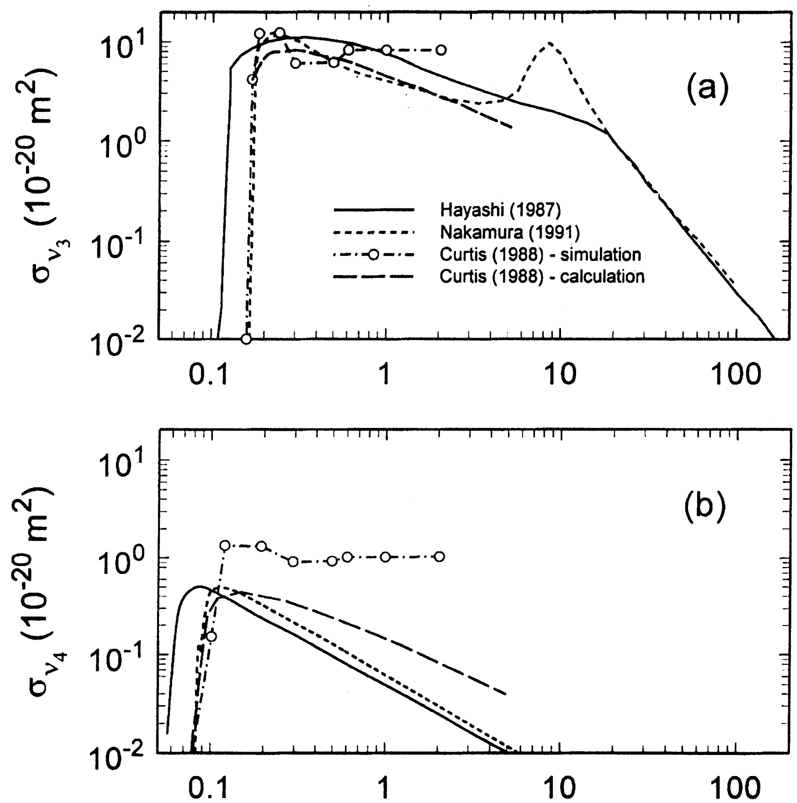
- **The majority of momentum transfer cross sections are derived from swarm data. Agreement between investigators is generally good.**

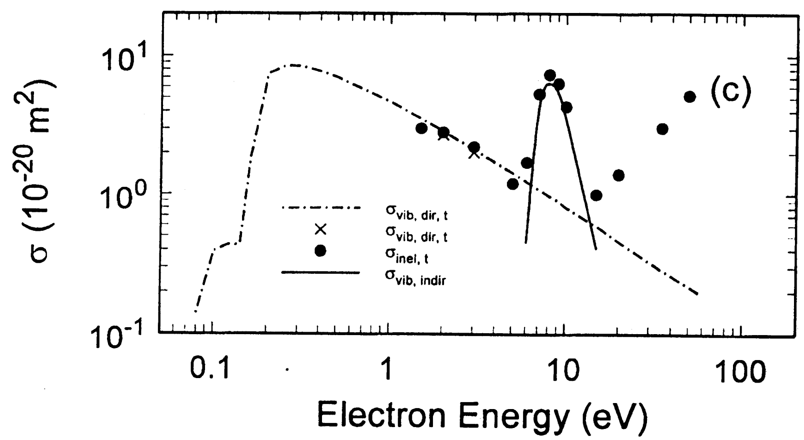


L. Christophorou, J. Phys. Chem. Ref. Data 25, 1341, 1996

TETRAFLUORMETHANE (CF_4): VIBRATIONAL EXCITATION

- **Vibrational excitation cross sections (ν_3, ν_4, ν_{ind}) from swarm data and Born calculations agree well. The 8 eV process (obtained from σ_{total}) also appears in swarm cross sections.**

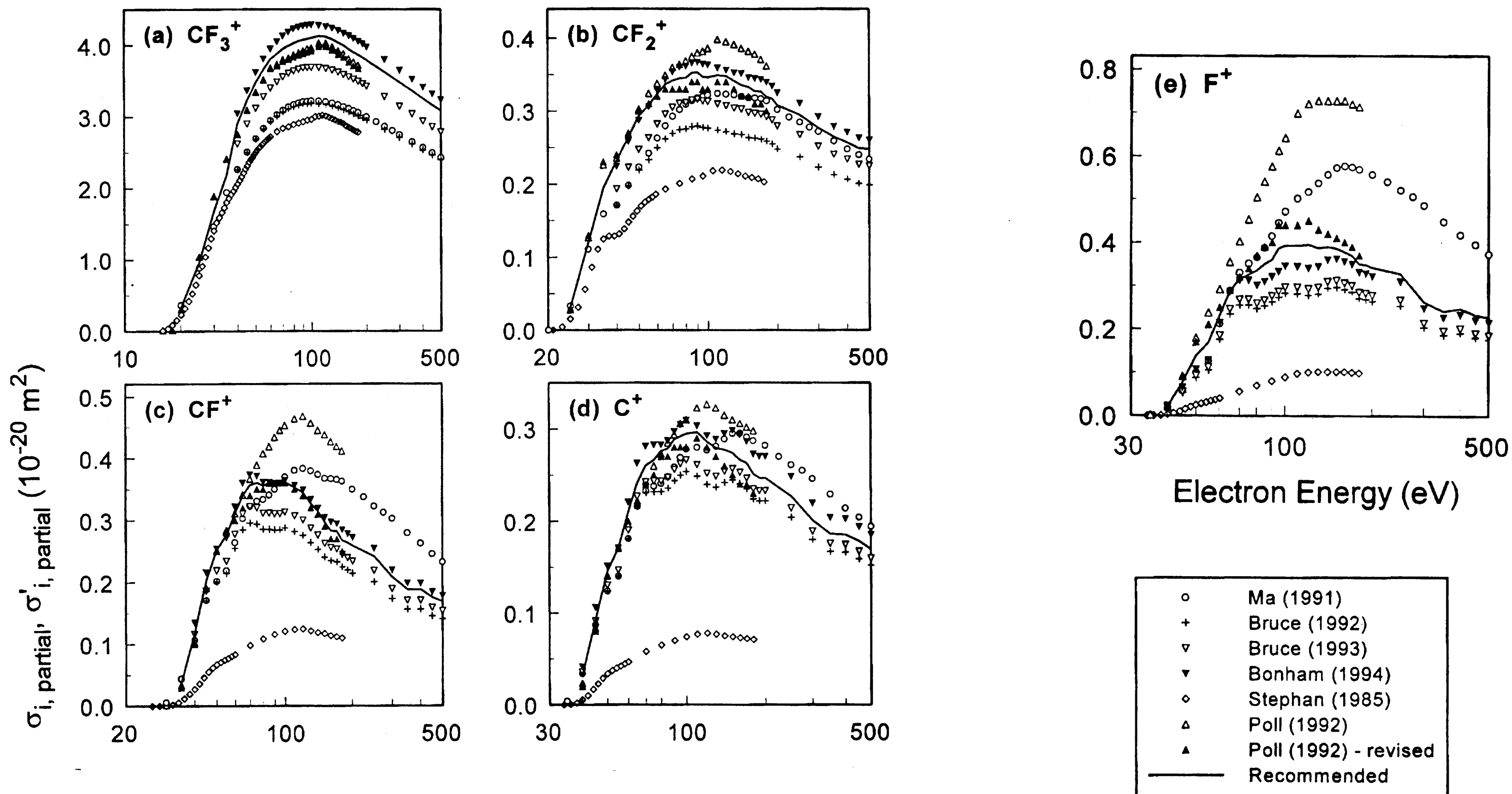




- **L. Christophorou, J. Phys. Chem. Ref. Data 25, 1341, 1996**

TETRAFLUORMETHANE (CF_4): DISSOCIATIVE IONIZATION

- **Dissociative ionization cross sections, though more easily measured, have been complicated by instrumental effects for large dynamic range of mass of fragments.**



L. Christophorou, J. Phys. Chem. Ref. Data 25, 1341, 1996

TETRAFLUORMETHANE (CF_4): DISSOCIATION

- **The most critical cross sections for process simulation are for dissociation (dissociative ionization) since these processes generate the radicals.**

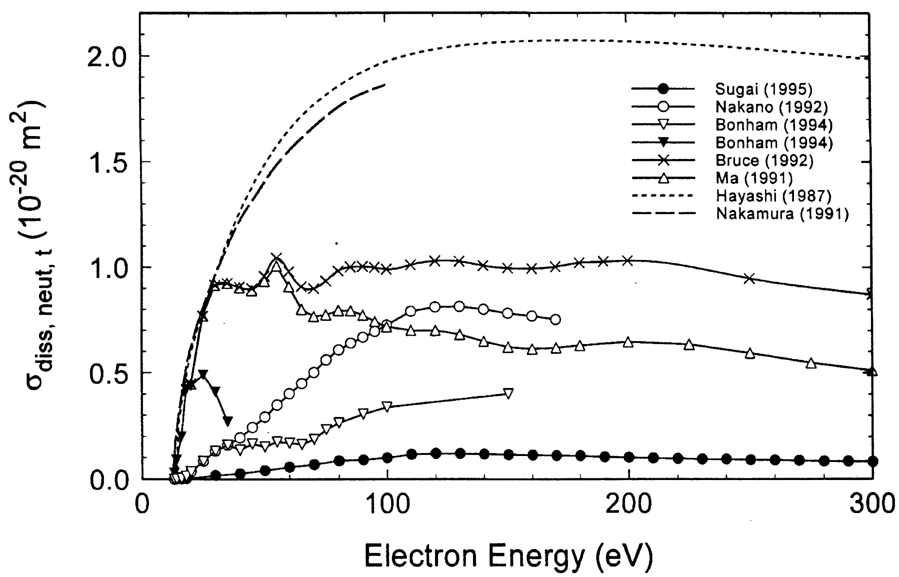
- **Both the magnitude and branching ratios are required.**

  $e + CF_4 \rightarrow CF_n + mF_{(2)} + e$

  $e + CF_4 \rightarrow CF_n^+ + F^{(-)} + 2e$

- **These are, unfortunately, the most uncertain and controversial.**

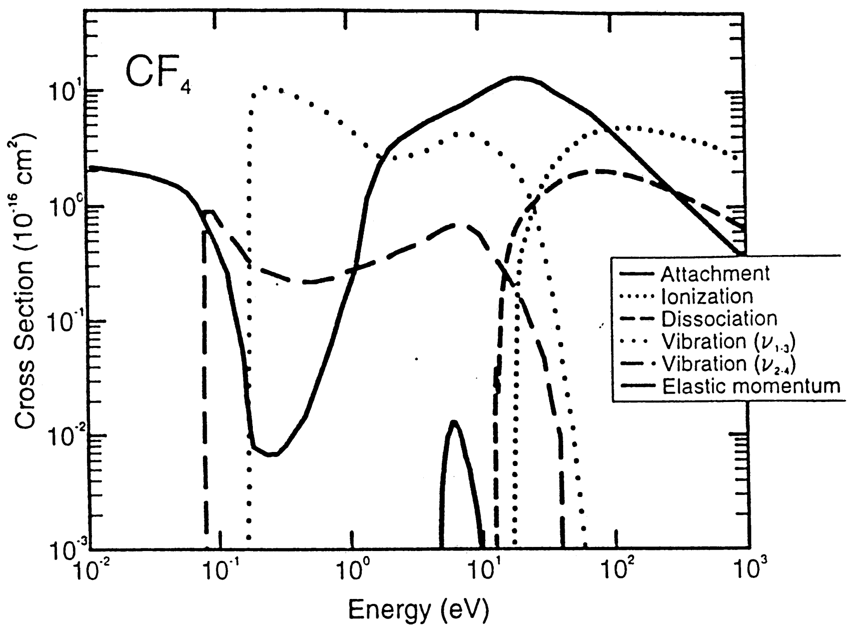
- **Measurements of neutral dissociation cross sections by double-cross-beam techniques differ by an order of magnitude.**

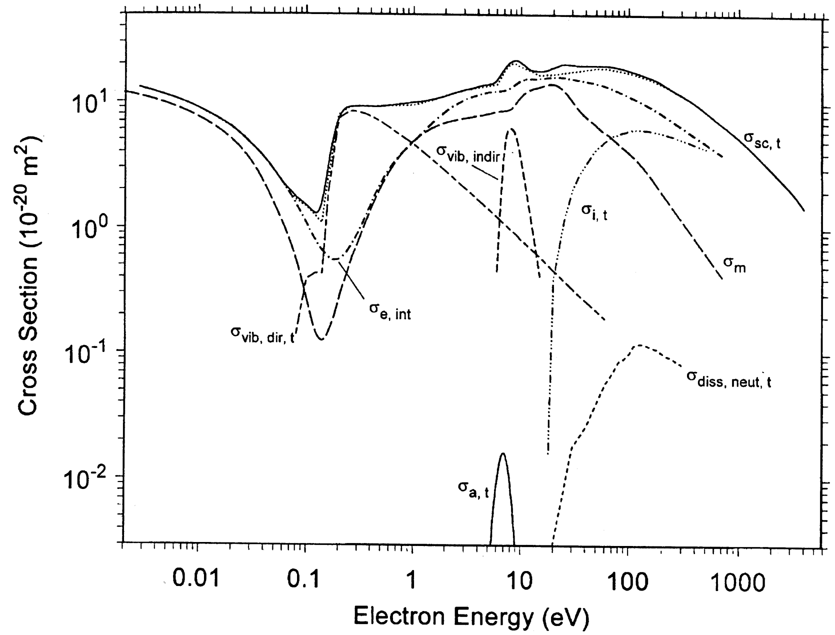


- **L. Christophorou, J. Phys. Chem. Ref. Data 25, 1341, 1996**

TETRAFLUORMETHANE (CF_4): "BEAM" vs SWARM

- **A cross section set composed of the "best" critically evaluated beam measurements may be significantly different from swarm derived cross sections which reproduce v(drift), ionization coefficient, etc.**



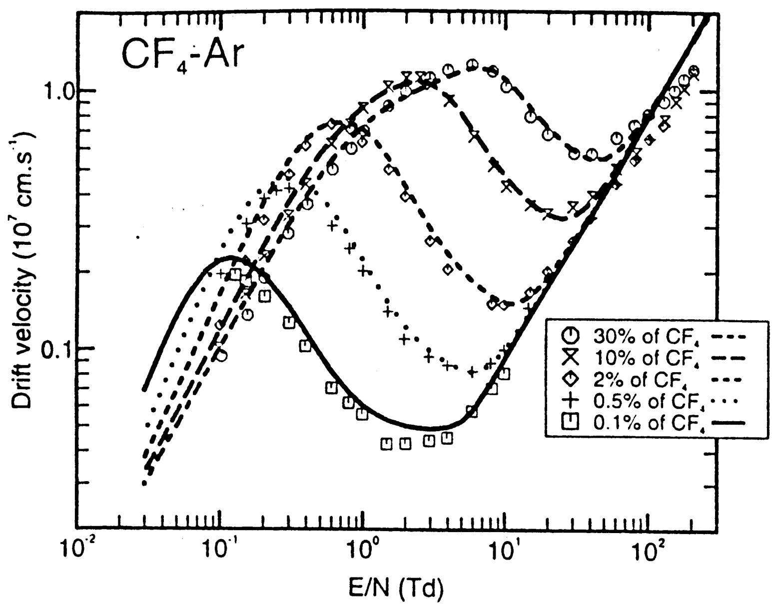


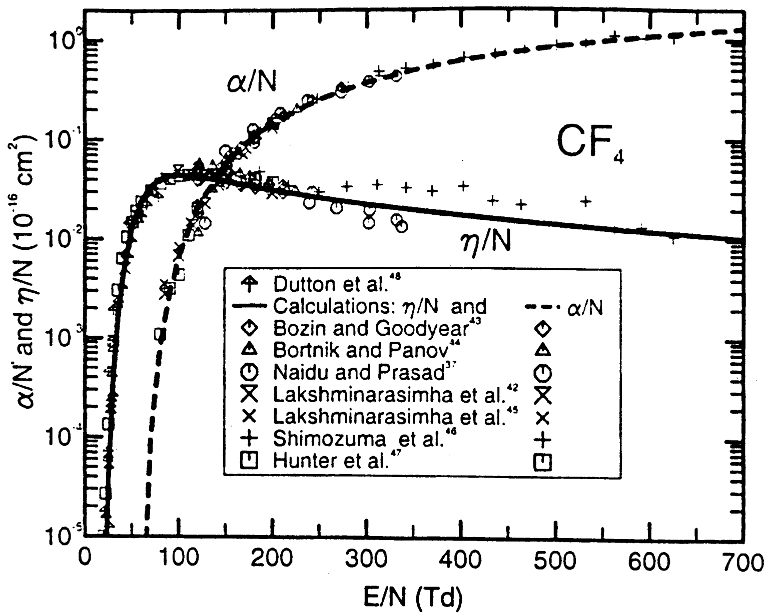
- **Swarm: M. Bordage et al, J. Appl. Phys. 80, 1325 (1996)**
- **Beam: L. Christophorou, et al, J. Phys. Ref. Data 25, 1341 (1996)**

- ***"Assembling" cross sections, though necessary, is not always sufficient........***

TETRAFLUORMETHANE (CF_4): MEASURE OF GOODNESS

- The "measure of goodness" of a cross section set is using cross sections in Boltzmann's equation to reproduce experimental transport coefficients.





- M. Bordage et al, J. Appl. Phys. 80, 1325 (1996)

TARGET CHEMISTRIES CITED IN NRC REPORT

Application	Cited in NRC Report (Including Fragments)	Gases Recently Coming to Prominence
p-Si Etching	Cl_2, Br_2, HBr, O_2, N_2	BCl_3, HCl
SiO_2 Etching	CF_4, CHF_3, C_2F_6, O_2, N_2, CO, Ar	C_4F_8
SiO_2 Deposition	SiH_4, O_2, N_2O, Ar, TEOS [$Si(C_2H_4O)_4$]	SiF_4
Ionized PVD (Physical Vapor Deposition)		Cu, Al, Ti, Ba, W, Sr
Chamber Cleaning		NF_3, COF, COF_2

ASSESSMENT OF ELECTRON IMPACT DATABASES

System	Status	Comments
Rare Gases: He, Ne, Ar, Xe, Kr	Very Good	• Lacking some excited state cross sections
Atmospheric Gases: O_2, N_2, H_2, CO, CO_2, H_2O	Fair to Good	• Beam and swarm measurements • Neutral dissociation branchings are required. • Atoms are well treated analytically.
Deposition Gases • SiH_4, Si_2H_6, NH_3, N_2O, SiF_4 • CH_4	Fair Good	• Momentum transfer and ionization are well known. • Neutral dissociation branchings poorly known • Radicals are poorly characterized with exception of ionization

ASSESSMENT OF ELECTRON IMPACT DATABASES

• TEOS, DMSO	Poor	• Only isolated data available • Momentum transfer fair • Dissociative ionization branchings are known.
• Etch Gases: • CF_4, C_2F_6 • CCl_4, Cl_2, HCl	Fair	• Momentum transfer, vib swarm derived. • Dissociative ionization characterized though with disagreements • Neutral dissociation branchings available but with large variance • Cl, F have theoretical data • Radical data is largely missing.

ASSESSMENT OF ELECTRON IMPACT DATABASES

• SF_6, CHF_3	Fair to Poor	• Swarm derived (SF_6 mostly high pressure limit) • Dissociative ionization with branchings available • Controversy with neutral dissociation • Radical dissociative ionization for SF_n.

ASSESSMENT OF ELECTRON IMPACT DATABASES

• BCl_3, HBr, NF_3, $SiCl_4$	Fair to Poor	• Reliable swarm data is missing to derive momentum transfer, attachment. • Calculations have provided good start for radicals • Dissociative ionization available.
• C_4F_8,C_3F_8,C_2H_3F	Poor	• Swarm derived data with some initial calculations • Total ionization available from theory.

NEUTRAL DISSOCIATIVE EXCITATION

- The majority of experimental cross sections for electron impact dissociative excitation for for excited products.
- Cross beam measurements of producing partial cross sections for neutral cross sections are available for a small subset of process gases.

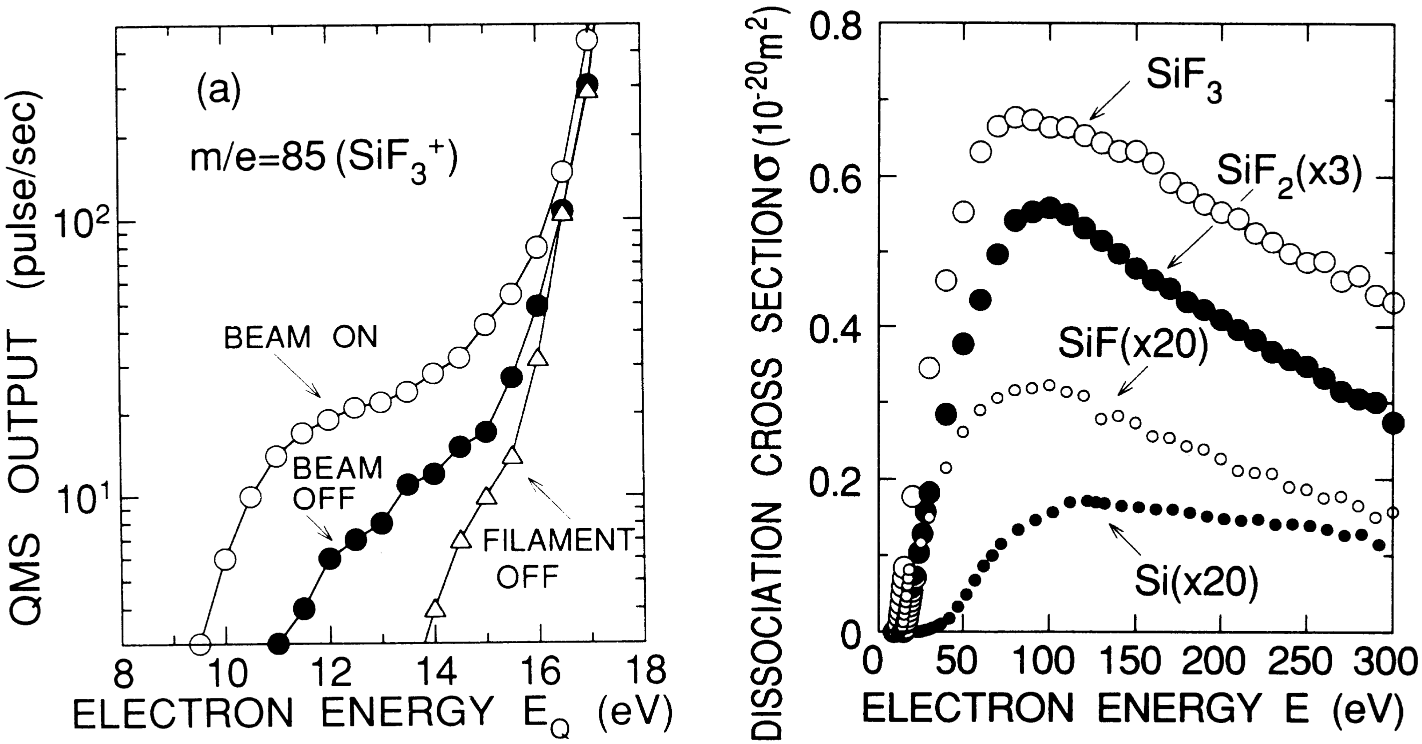
Molecule	Authors/Group	Year	Cross Sections
BCl_3	Gilbert,Siegel, Becker	1990	Emission [B,BCl(A)]
BCl_3	Toku, et al	1992	Emission [B,BCl(A)]
CF_4,CF_3H, C_2F_6,C_3F_8	Winters	1982	Total dissociation
C_4F_8	Toyoda, Iio, Sugai	1997	CF,CF_2,C_3F_5, and ions
CF_4,CHF_3	McConkey	1989	Metastable products
CF_4	Bonham	1992	CF_3,CF_2
CF_4	Nakano and Sugai	1992	CF,CF_2,CF_3
NF_3,CF_4, SF_6	Blanks,Tabor, Becker	1983	Emission [F(3p-3s)]

NEUTRAL DISSOCIATIVE EXCITATION

$CXCl_3$ X=H,F,Cl, Br	Kusakabe, Ito, Tokue	1993	Emission [CCl(A)]
C_2FCl_2	Martinez,Castano, Rayo	1992	Emission
CBr_4, $CHBr_3$ $CFBr_3$	Tokue and Ito	1988	Emission
SiF_4	Nakano and Sugai	1991	SiF,SiF_2,SiF_3
SiH_4, Si_2H_6	Perrin et al	1982	Total Dissociation
SiH_4	Sato, Kono, Goto	1988	Emission [H,Si]
GeH_4	Tint,Kono,Goto	1989	Emission [H,Ge,GeH]
N_2O	Mason and Newell	1991	Metastables

DISSOCIATION OF SiF_4 INTO NEUTRAL FRAGMENTS

- **Dissociation of SiF_4 into neutral fragments (0-300 eV) was measured using appearance potential mass spectroscopy in a dual beam device.**



- **T. Nakano and H. Sugai, "Cross section measurement for electron-impact dissociation of SiF_4 into neutral fragments", J. Phys. D 26, 1909 (1993)**

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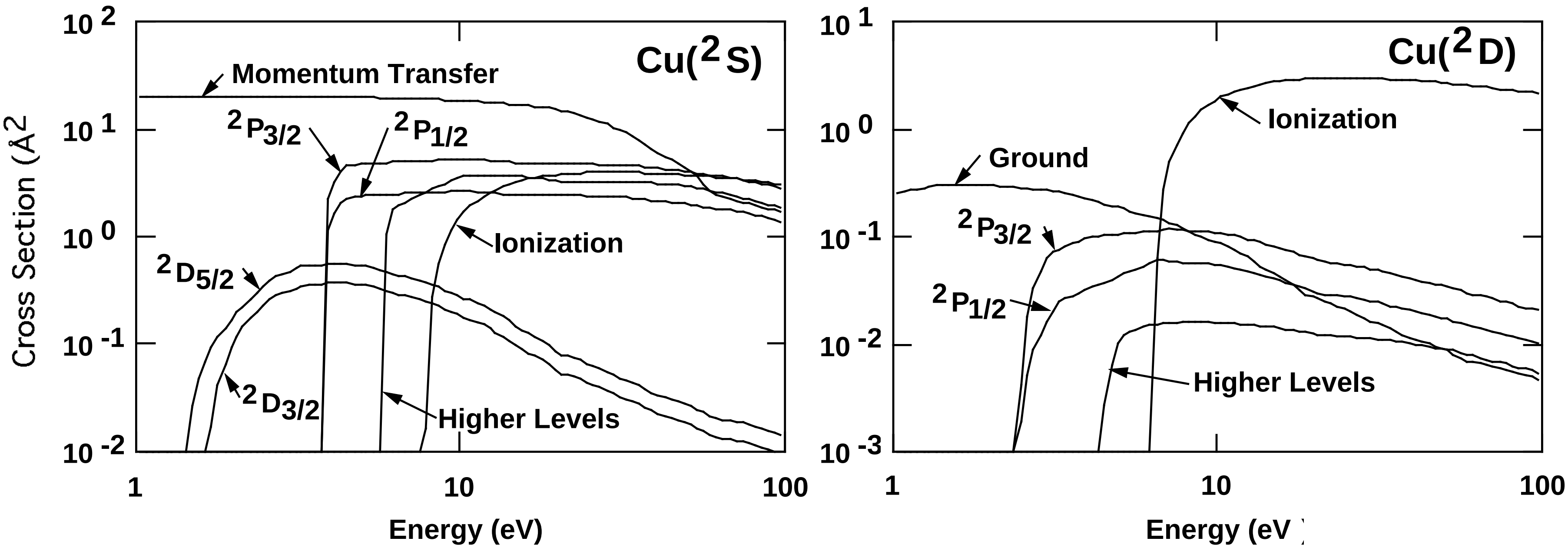
DATABASE NEEDS FOR RARE GAS-METAL CHEMISTRIES

- **Newly developed techniques for ionized metal physical vapor deposition (IMPVD) are being used for for interconnect wiring, barrier coatings and high permittivy dielectrics.**
- **These applications have increased needs for electron impact and rare gas excitation transfer data for metal atoms.**
- **Metals of interest: Cu, Al, W, Ti, Ba, Sr**
- **The prevalance of low lying metastable states of the metals emphasizes the need for electron impact cross sections for excited states. (Recall, in Cu IMPVD tools, the flux of Cu(^{2}D) to the substrate can exceed that of Cu(^{2}S).)**
- **Due to the low mole fractions of the metals in rare gas buffers, reliable inelastic cross sections are more important than elastic, though development of self-sputtering systems may change this assertion.**
- **Penning ionization and rare gas charge exchange are dominant sources of ionization, and so those rate coefficients are also required.**

DATABASE NEEDS FOR RARE GAS-METAL CHEMISTRIES

- Fortunately, due to interest in metal vapor lasers using rare gas buffers, data for a select number of systems is available (eg., Cu)



- Example: E-impact cross sections for Cu. (Ref: R. Carman, A. Hazi)

HOW GOOD DOES THE DATA NEED TO BE?
What is your application?

- The goodness of database varies by the application, and is often a case of science vs. technology.

- <u>Screening</u>:

    - There is a tremendous need for electron impact cross section datasets which can be generated quickly, though are not necessarily "99.99% accurate".

    - The application is performing zeroth order evaluations or screening of new processes or equipment.

    - The absolute accuracy of the screening is not as important as is consistent case-to-case systematic trends.

HOW GOOD DOES THE DATA NEED TO BE?
What is your application?

- **Equipment Design:**
  - **The details of how a chamber is designed (with respect to uniformity of fluxes, parasitic capacitance) do not critically depend on the details of the chemistry.**
  - **Since a given tool will be used with many chemistries during its lifetime, "tuning" a tool for the quirks of a specific chemistry is not advisable.**
  - **Well characterized datasets for "classes" of chemistries are required to cover the parameter space of anticipated applications.**
    - **Non- or moderately attaching (e.g., Ar/N_2/O_2)**
    - **Highly attaching (e.g., Cl_2)**
    - **Rapidly dissociated (e.g., SF_6)**

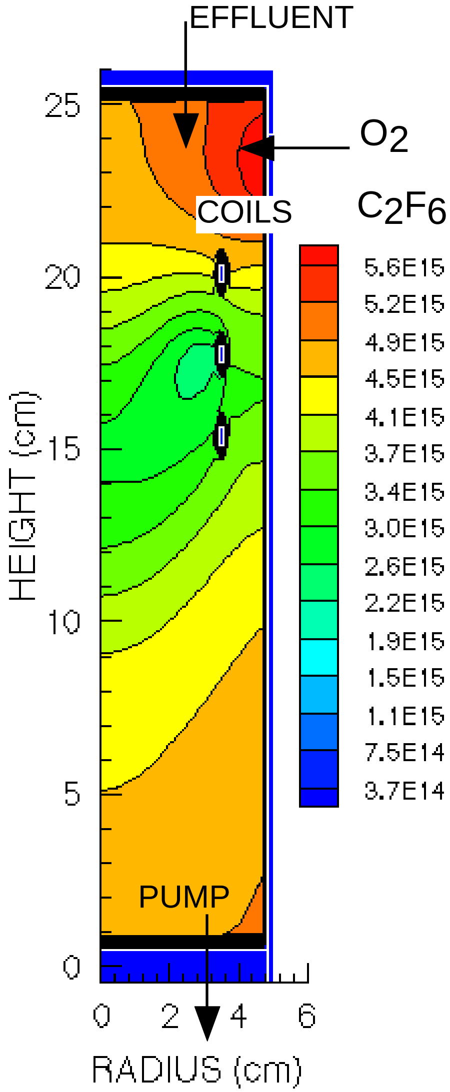
HOW GOOD DOES THE DATA NEED TO BE?
What is your application?

- **Model Validation:**
  - **Similar to equipment design, well characterized datasets for "classes" of chemistries are required to cover the parameter space of anticipated applications.**
  - **Since the "faith" in the models will be largely based on these validation exercises, it is important that ambiguities and caveats in these datasets be well advertised and understood by their users.**

- **Process Design:**
  - **The most critical requirements for accuracy of the data are in process design where specifics of the reactant fluxes (magnitudes and mole fractions) have large impacts on the final product.**

HOW ACCURATE DOES THE DATA NEED TO BE?

- In plasma abatement of C_2F_6, O_2 is injected into a downstream "burn-box" with the goal of oxidizing PFCs to CO2 and COF2.



- C_2F_6 is dissociated by

Attachment: e + C2F6 > CF_3 + CF_3^-
, C_2F_5 + F^-

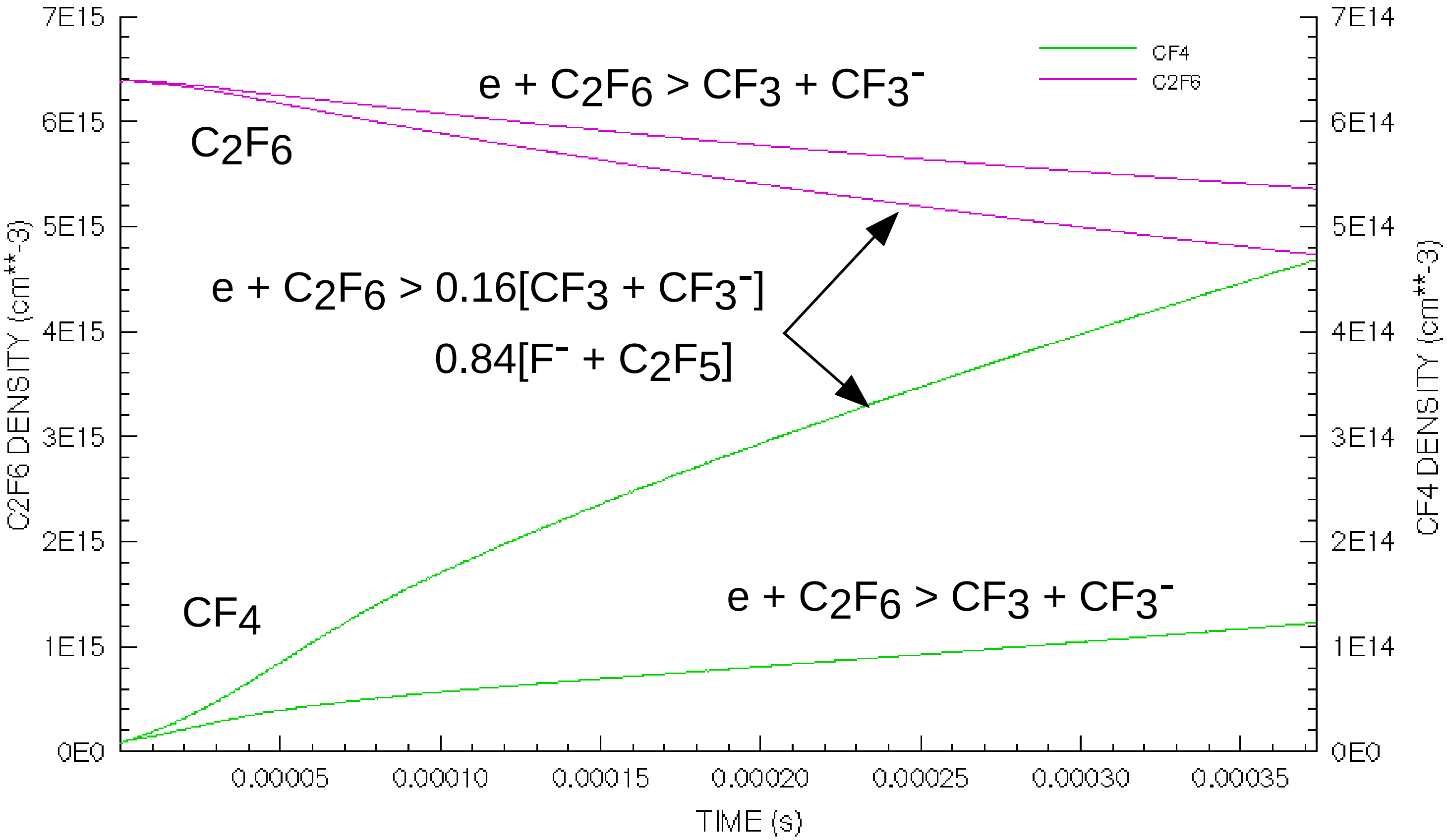
Electronic Excitation: e + C2F6 > CF_3 + CF_3 + e
C_2F_5 + F + e
....

Ionization: e + C2F6 > F + $C_2F_5^+$ + 2e
....

- What impact do branching ratios have on the abatement efficiency? How accurate should these quantities be?

BRANCHING RATIO FOR C_2F_6 DISSOCIATIVE ATTACHMENT

- In plasma abatement of C_2F_6 in C_2F_6/O_2 mixtures, the formation of CF_4 largely depends on the availability of F atoms to recombine with CF_3.



- The branching ratio for e + C_2F_6 > negative ions significantly impacts the formation of PFCs through production of CF_4.

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IMPORTANCE OF RAPIDLY GENERATING “APPROXIMATE” DATASETS

- There are obvious tradeoffs between the length of time required to generate a dataset, and its accuracy or reliability.

- There are many “screening” applications where “completeness” and consistency between rapidly generated datasets is more important than their accuracy.

- (Semi-)Analytic, rapid numerical or analogous experimental methods for generating electron impact cross sections must be relied on to provided to meet the majority of these needs.

EXAMPLE: ELECTRON IMPACT EXCITATION CROSS SECTIONS FOR PHOSPHORUS FROM GENERALIZED OSCILLATOR STRENGTHS

- **Electron impact cross sections for phosphorus were obtained from ground state $3p^3(^4S_{3/2})$ to s,p,d excited states using a Generalized Oscillator Strength and a Born Approximation.**

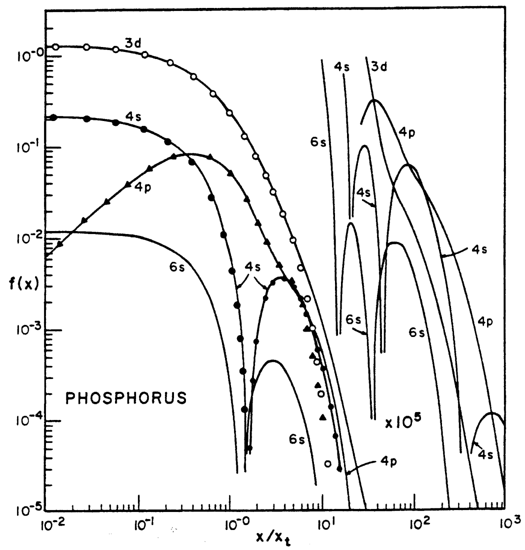

Fig. 1. GOS for 3p-ns, 3p-np and 3p-nd transitions in P as functions of reduced square of momentum transfer. The curves are the results of the present calculations. The solid dots (•), open circles (o), and triangles (▲) are representative fits using equations (5 and 6). Values of the GOS below 10^{-5} have been multiplied by 10^5.

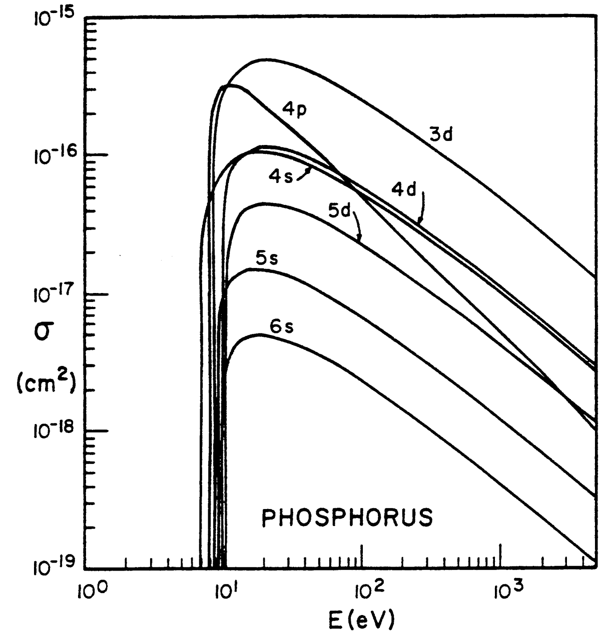

Fig. 2. Integrated cross sections for 3p-ns, 3p-np, 3p-nd excitations in P *vs.* electron impact energy.

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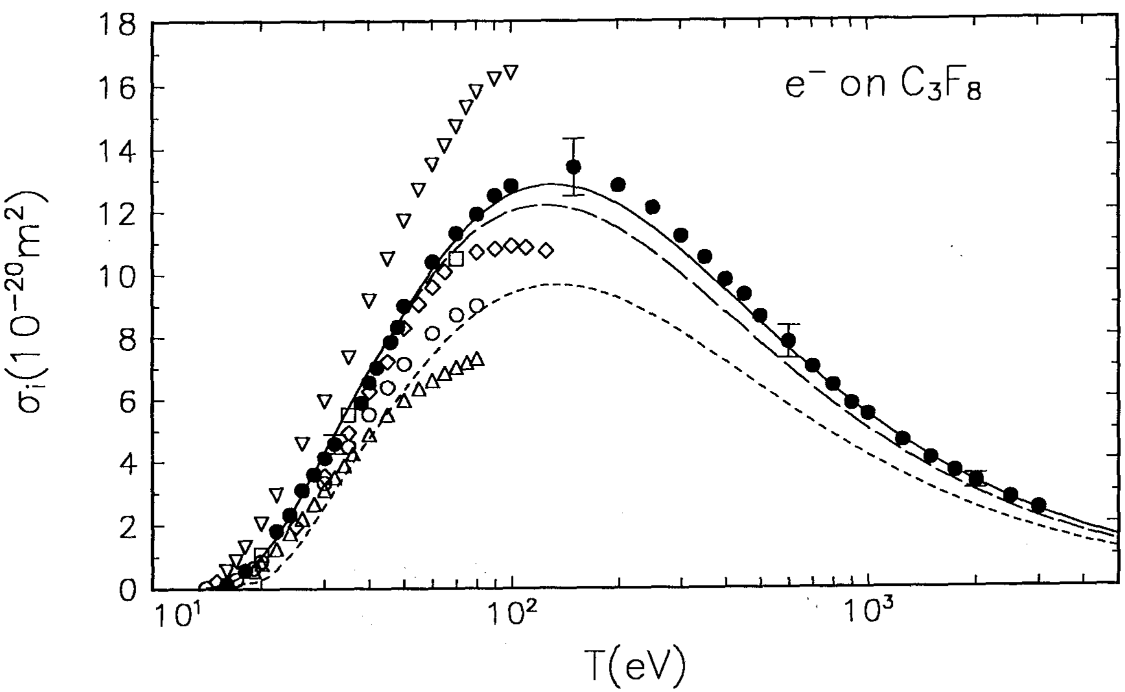
Ref: P. Ganas, Eur. Phys. J. D 1, 165 (1998)

SEMIANALYTIC IONIZATION CROSS SECTIONS FOR MOLECULES

- Semianlystic ionization cross sections for CnFm have been derived using the binary-encounter-Bethe (BEB) method, which has been determined to include dissociative ionization channels.

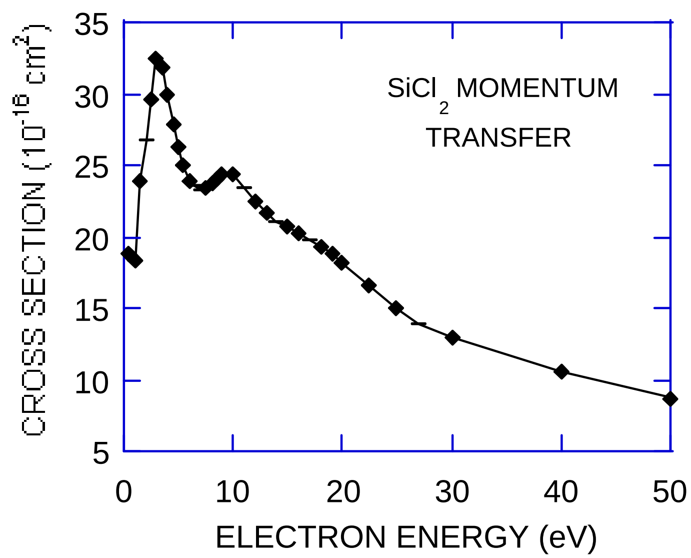


- H. Nishimura, W. Huo, M. Ali and Y-K. Kim, "Electron impact total ionization cross sections of CF_4, C_2F_6 and C_3F_8", tbp in J. Chem. Phys.

AB INITIO CALCULATIONS OF E-IMPACT X-SECTIONS: V. McKoy

- **Experimental momentum and vibrational excitation cross sections are typically obtained from swarm experiments and so are not easily availabie for radicals. Progress has been made in calculations of these quantities.**

- **V. McKoy (Caltech) has employed Schwinger multichannel variational methods to computing elastic and inelastic cross sections for a variety of molecules and radicals.**



BCl_x(x=1-3), $SiCl_x$(x=1-4)

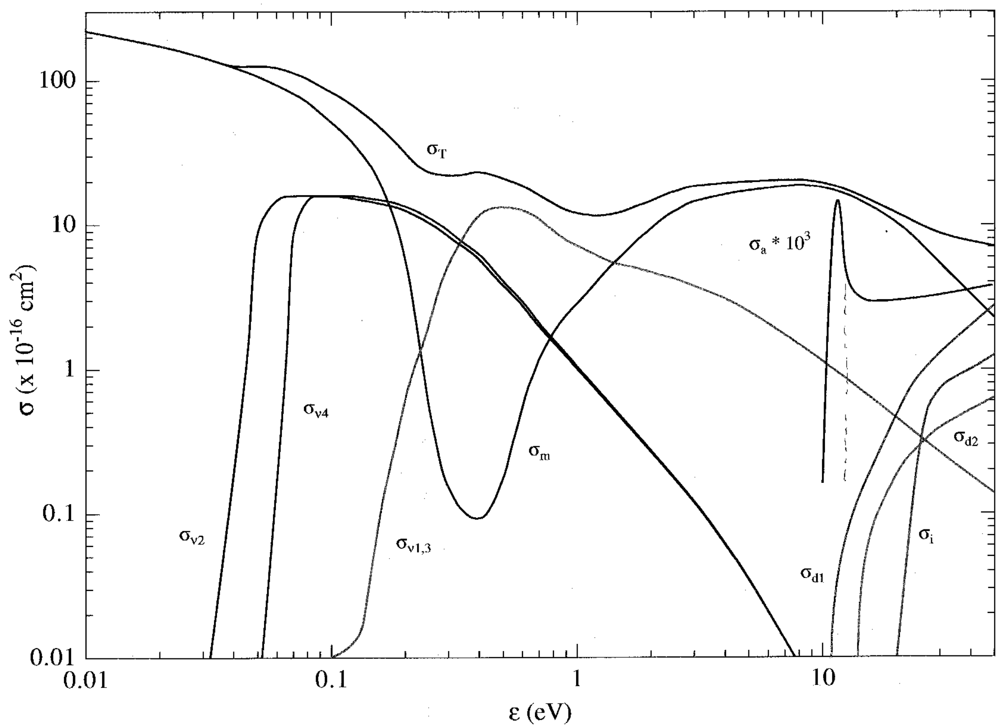
Various NF_x, CHF_x, C_xF_y species

N_2O, CO_2, HCl, $Al(CH_3)$

(V. McKoy, private communication)

SWARM DERIVED SiF_4 CROSS SECTION SET

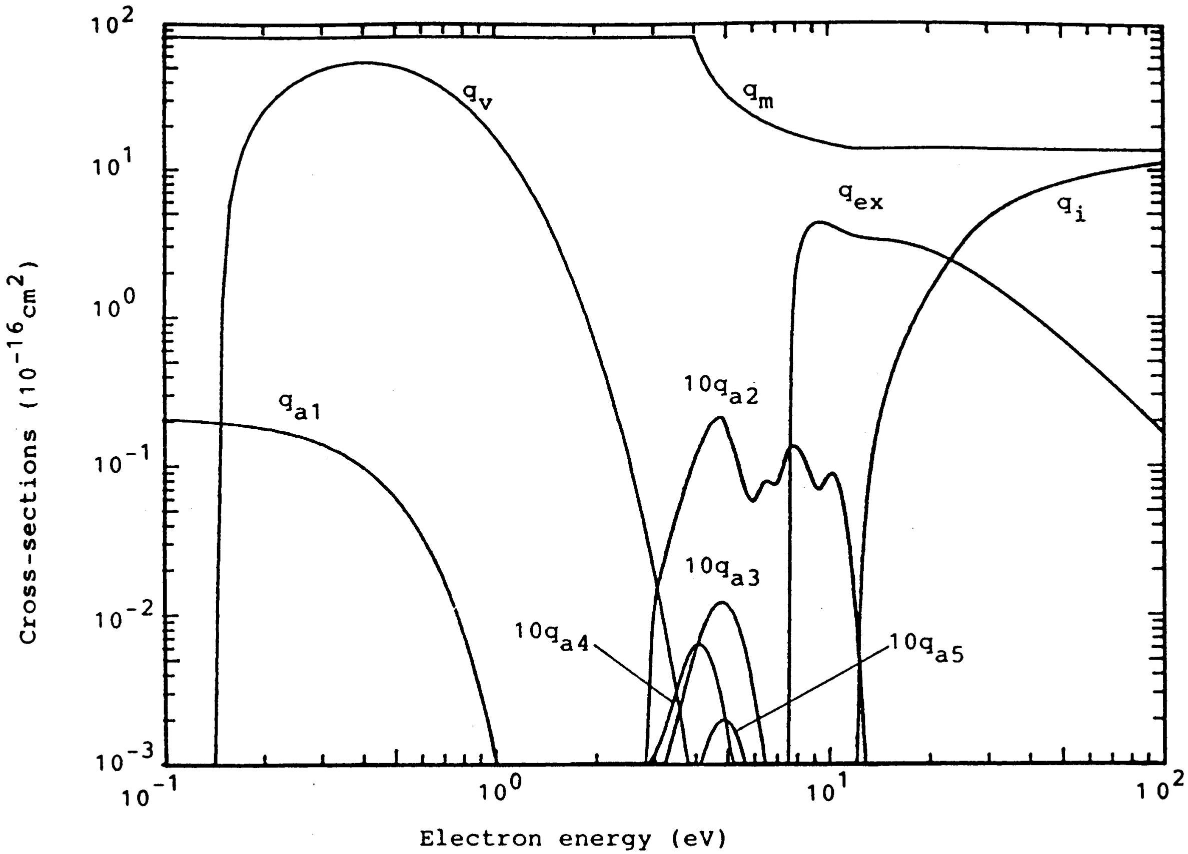
- **Most cross section sets currently used in plasma processing modeling are amalgams of beam and swarm derived data, validated against swarm derived electron transport coefficients.**



- **R. Nagpal, A. Garscadden and J. D. Clark, Appl. Phys. Lett. 68, 2189 (1996), and 49th Gaseous Electronics Conference.**

C_4F_8 SWARM DERIVED CROSS SECTIONS

- **Cross sections for more complex gases are generally only available from swarm data. The lack of data for fragments is even more critical due to their large dissociation cross sections (attachment, neutral, ionization)**



- **H. Itoh, et al. J. Phys. D 24, 277 (1991)**

PRESENT CAPABILITY AND FUTURE DEVELOPMENT

- ***Virtual prototyping of new equipment designs and optimization of current designs are, with realistic expectations, accessible today.***

- **General acceptance of this ability will require further improvements in presently available models.**

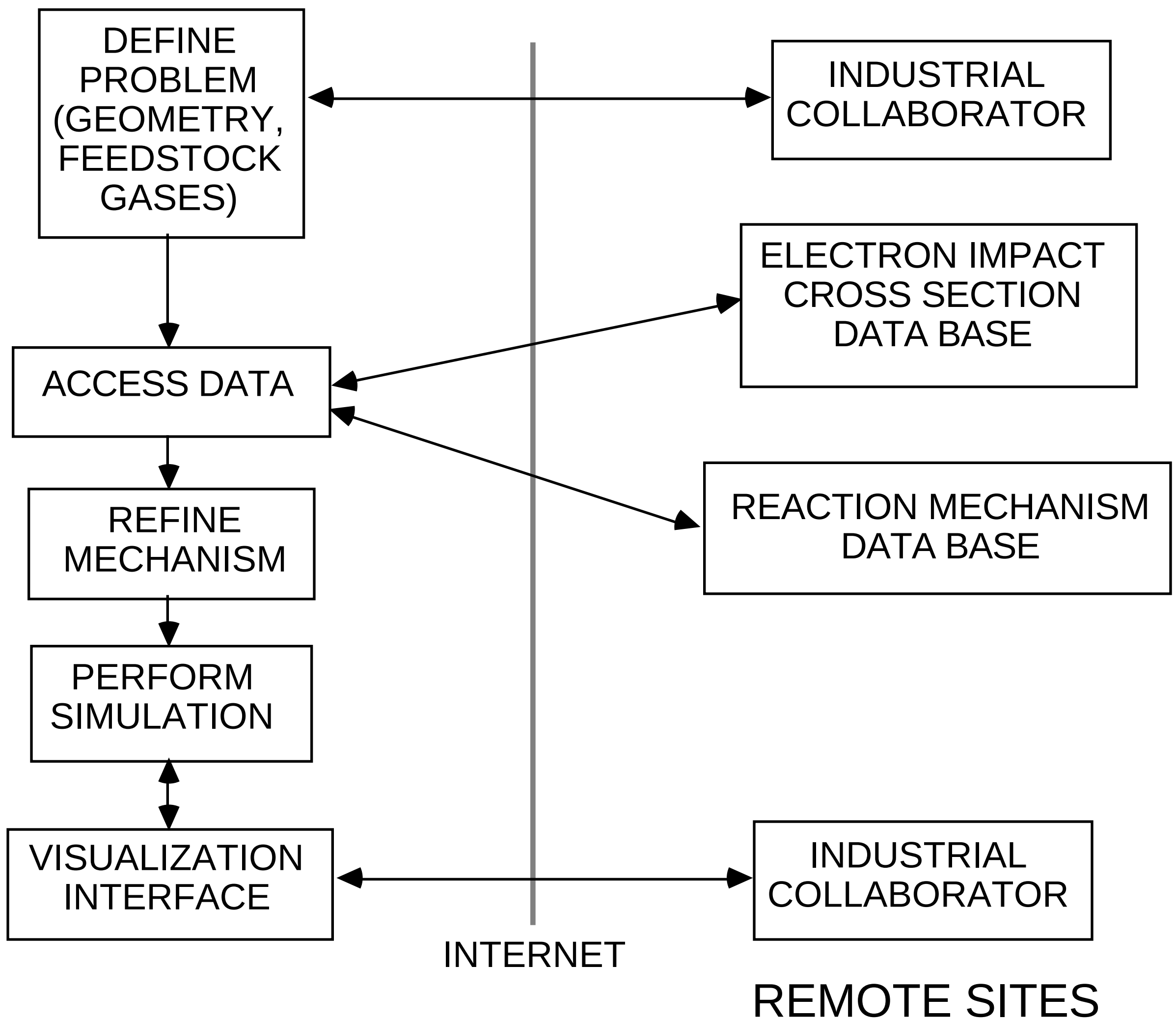
  - **Modular simulations able to address a variety of plasma equipment.**

  - **Databases and reaction mechanisms which are integrated into the model or are internet accessble**

  - **Expert systems which, given equpment parameters provide the user**
    - **"Good guess" initial conditions**
    - **Optimally chosen algorithms**

  - **Seamless coupling CAD mesh generators to PEMS; and PEMS to profile simulators**

HORIZONTALLY INTEGRATED MODELING



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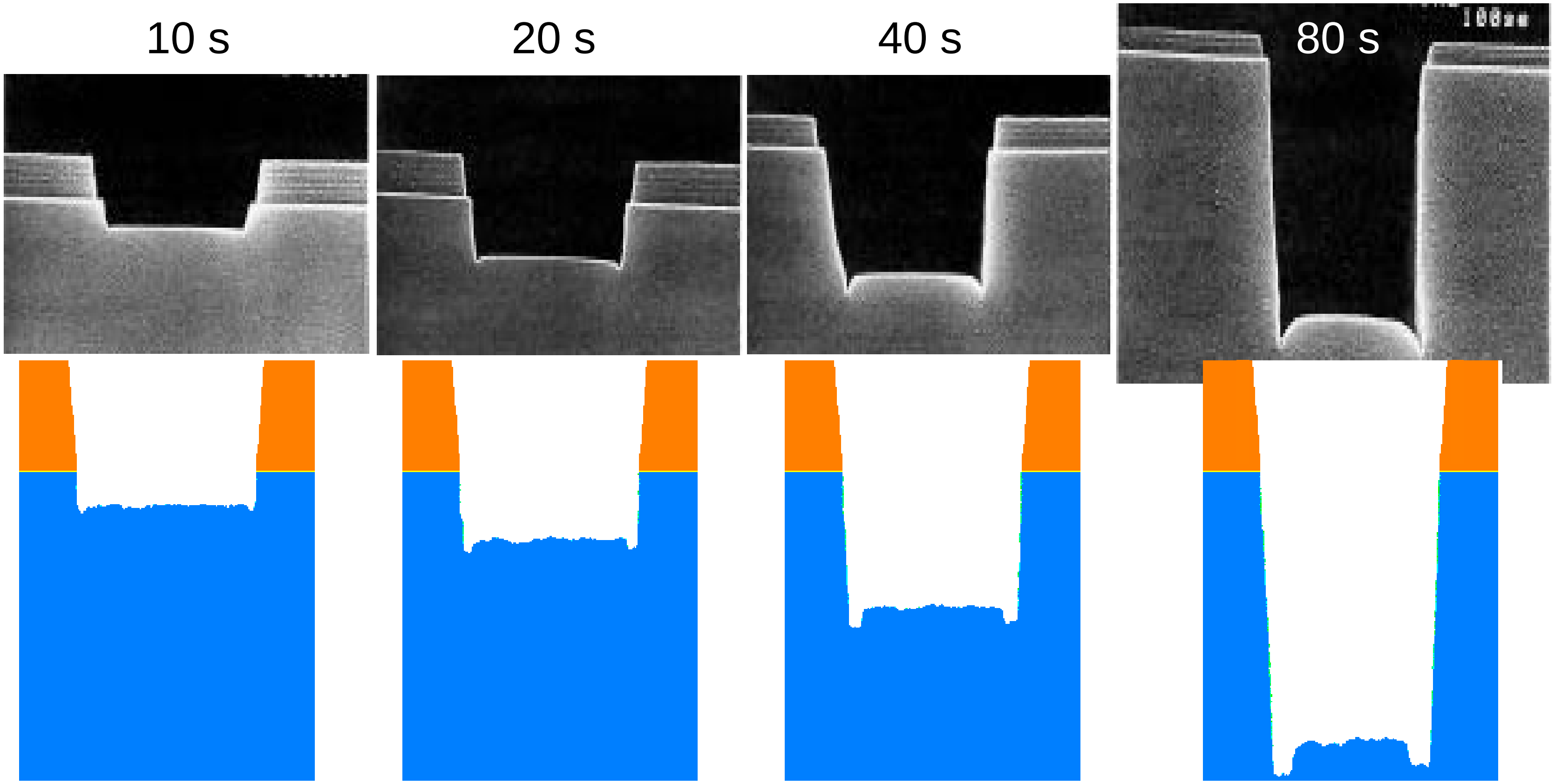
ETCH PROFILE EVOLUTION



• The time evolution of the trench etch is well matched by the simulation.

• The microtrenching develops more slowly for the experimental results possibly due to differences in slope of the resist sidewalls.

• 9400SE LAM TCP Reactor
10 mTorr Cl_2 (60 sccm) 600 W , 100 W bias
LSI Logic Corporation

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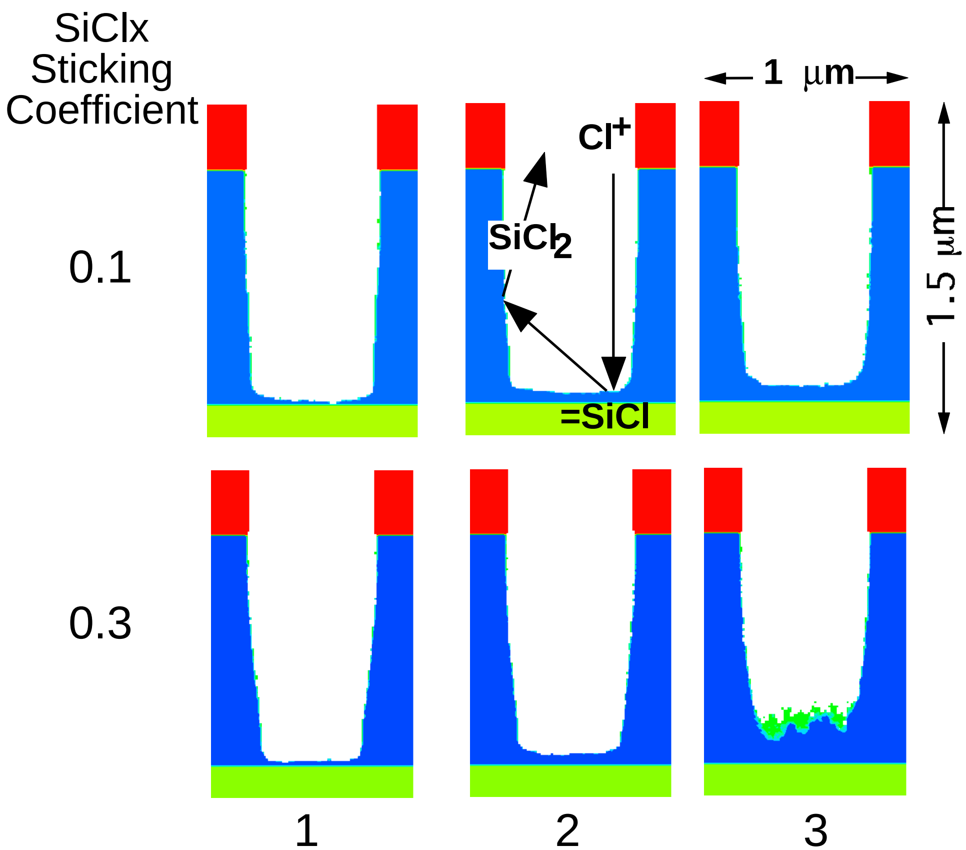
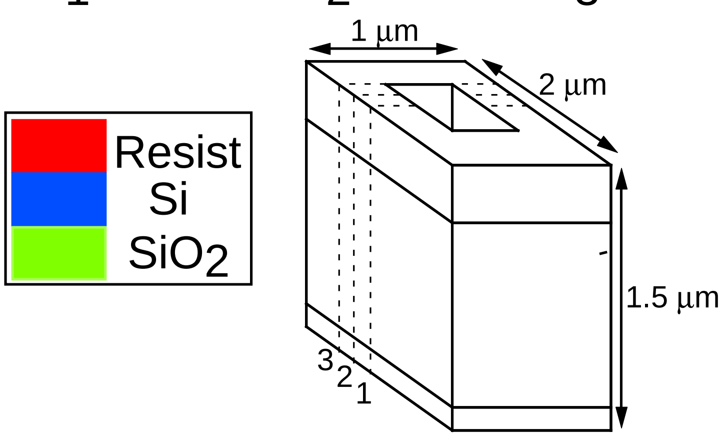
3-D FINITE TRENCH: $SiCl_x$ STICKING COEFFICIENT





- When the redeposition of $SiCl_x$ (etch product) is low, a narrow angular spread of the IEAD produces “crisp” 3-plane corners.
- As the sticking coefficient increases (due to temperature excursions), the narrow IEAD is not able to remove reposited etch products from side/end walls.
- The result is inward sloping of the side/end walls.

- **LAM TCP 9400SE Reactor, 10 mTorr Cl_2 (60 sccm) 100 W RF Bias**

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CONCLUDING REMARKS

- **Plasma equipment modeling has made great strides over the past 5 years in developing an infrastructure for process design.**

- **"Natural" advances in computing power, algorithms and validation will continued to improve those capabilities.**

- **The rate limiting step in application of plasma equipment models is incomplete databases.**

- **The database for plasma processing is a bit schizophrenic: For some systems, the database is very good, for other systems very poor.**

- **The "database" is very "distributed" in the literature. Simply compiling what is available into a reasonable "reaction mechanism" is a large undertaking.**

CONCLUDING REMARKS

- **Large unknowns in the electron impact database include**

  - **Branching ratios for (neutral) dissociative processes**
  - **All parameters for fragment/radical ions**

- **Methodologies are required to rapidly produce “adequate” cross section sets to meet short term “technological” needs. Meeting these needs will form the basis of longer term relationships which will support more accurate “science”**