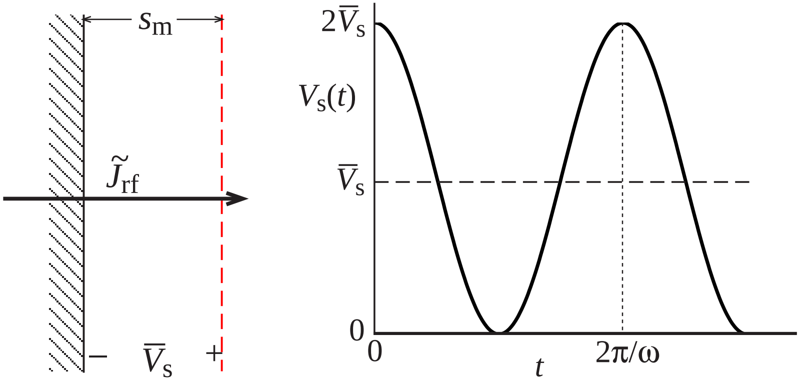
CAPACITIVE RF SHEATHS

ION TRANSIT TIME EFFECTS

COLLISIONLESS RF SHEATH REGIMES

- Recall capacitive sheath dynamics



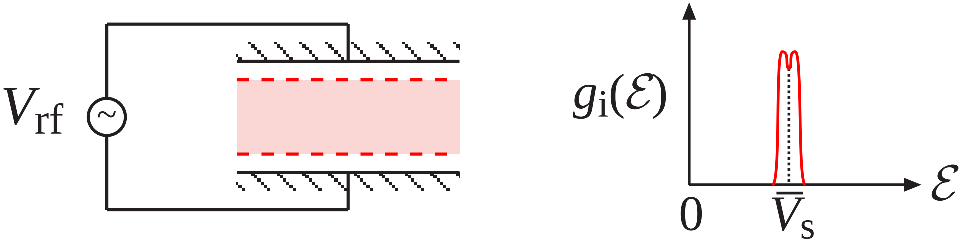
- Ion velocity in sheath $v_i = (2e\overline{V}_s/M)^{1/2}$
- Sheath thickness s_m from Child law [p. 76]

$$en_s u_B = 0.83\,\epsilon_0 \left(\frac{2e}{M}\right)^{1/2} \frac{\overline{V}_s^{3/2}}{s_m^2}$$

- Ion transit time $\tau_i = 3s_m/v_i \;\propto\; \overline{V}_s^{1/4}/n_s^{1/2}$
- RF period $\tau_{rf} = 2\pi/\omega$
- Two rf sheath regimes depending on the ordering of τ_i and τ_{rf}

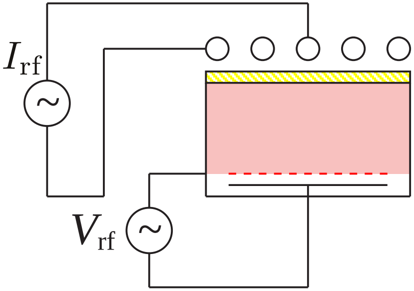
LONG ION TRANSIT TIME

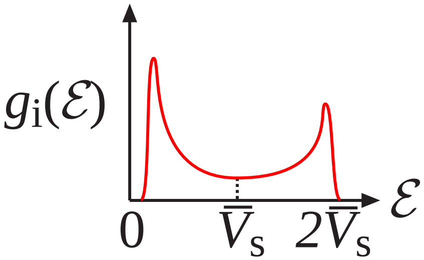
- Ion transit time $\tau_i = 3s_m/v_i \gg$ rf period $\tau_{\rm rf} = 2\pi/\omega$ (low plasma density, high frequency)
- Ions respond only to dc part $\overline{V}_s$ of the sheath voltage
- Sheath carries mostly displacement current
- Ion energy distribution is highly peaked about $\mathcal{E} = \overline{V}_s$
- Example: $\overline{V}_s \sim 100$ V, $n_s \sim 2 \times 10^9$ cm^{-3}, and $f = 13.56$ MHz $\Longrightarrow s_m \gtrsim 4.3$ mm and $\tau_i = 8\,\tau_{\rm rf}$
- Example of a "traditional" capacitive discharge



SHORT ION TRANSIT TIME

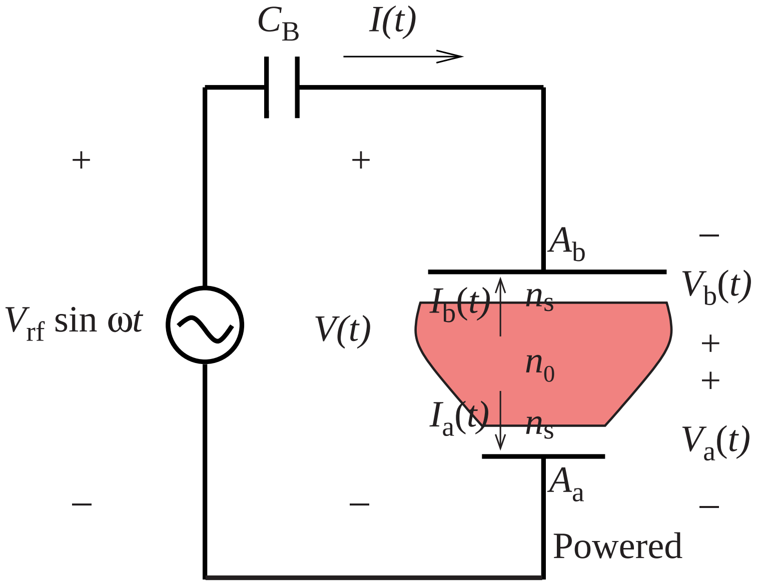
- Ion transit time $\tau_i = 3s_m/v_i \ll$ rf period $\tau_{\mathrm{rf}} = 2\pi/\omega$ (high plasma density, low frequency)
- Ions respond to instantaneous sheath voltage $V_s(t)$
- Sheath carries mostly electron and ion conduction current
- Ion energy distribution is broad, with $0 \lesssim \mathcal{E} \lesssim 2\,\overline{V}_s$
- Example: $\overline{V}_s \sim 100$ V, $n_s = 2 \times 10^{11}$ cm^{-3}, $f = 2$ MHz $\Longrightarrow s_m = 0.43$ mm, $\tau_i = 0.12\,\tau_{\mathrm{rf}}$
- Example of rf-biased wafer chuck in inductive discharge





SHORT ION TRANSIT TIME RF SHEATHS

- Return to asymmetric capacitive discharge; neglect displacement currents

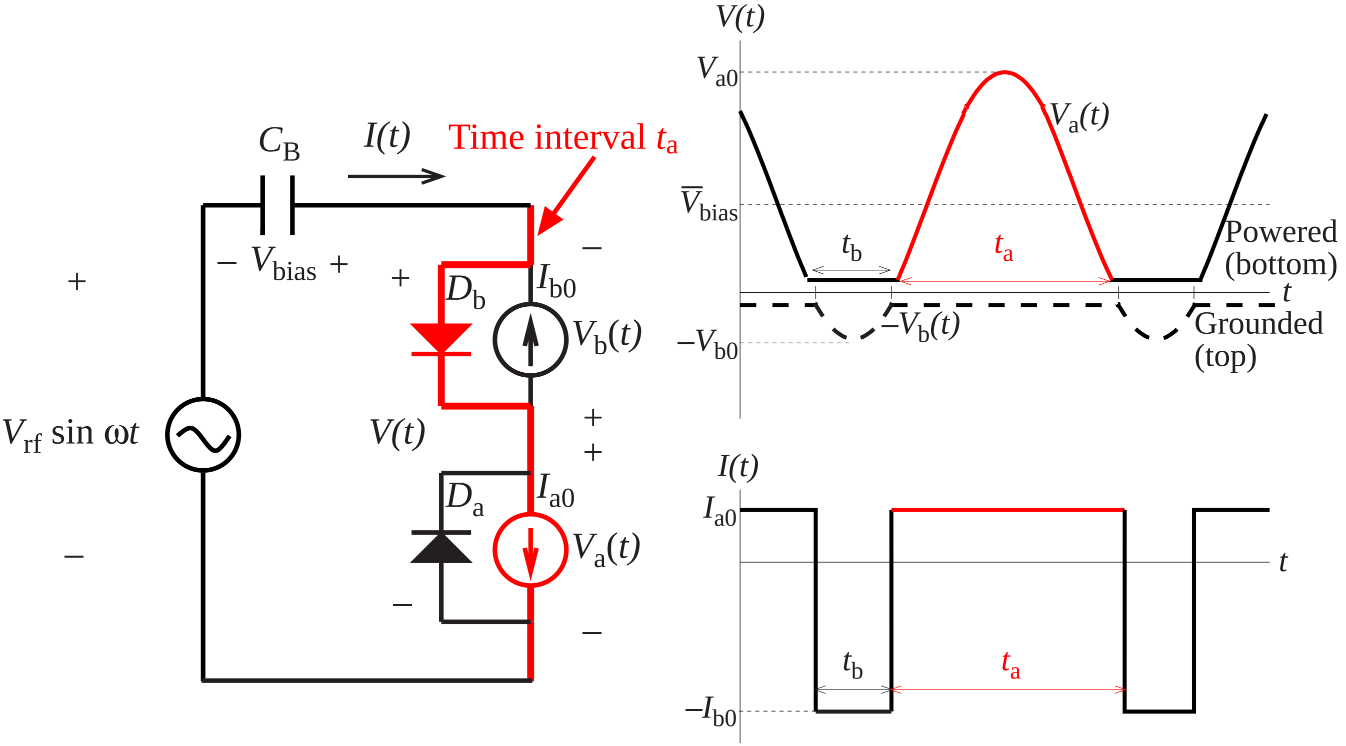


- Conduction currents to electrodes a and b are

$$I_a(t) = \overbrace{en_s u_B A_a}^{\text{Steady ion current}} - \overbrace{\tfrac{1}{4} en_s \bar{v}_e A_a \mathrm{e}^{-V_a(t)/\mathrm{T}_e}}^{\text{Like pn junction diode}} \qquad [p.\ 48]$$

$$I_b(t) = en_s u_B A_b - \tfrac{1}{4} en_s \bar{v}_e A_b \mathrm{e}^{-V_b(t)/\mathrm{T}_e} \qquad [p.\ 48]$$

SIMPLEST CIRCUIT MODEL



- $I(t)$ is a square wave because one or the other diode alternately conducts (is short circuited) and is open circuited
- During time t_a, diode D$_a$ is open and D$_b$ is shorted
$\Longrightarrow V_a = V(t)$, $V_b = 0$, and $I(t) = I_{a0}$, the ion current at sheath a

DC BIAS VOLTAGE FORMATION

- Note that $V_a(t)$ and $V_b(t)$ are alternately positive (corresponding diode is open-circuited) and near zero (diode is short-circuited)
- A dc bias voltage $\overline{V}_{\rm bias}$ builds up across the blocking capacitor C_B if $A_b \neq A_a$
- The voltage across the discharge is then [p. 120]

$$\boxed{V(t) = V_{\rm rf}\sin\omega t + \overline{V}_{\rm bias}}$$

- Charge conservation at the electrodes and in the bulk plasma yield

$$\boxed{\overline{V}_{\rm bias} = V_{\rm rf}\ \sin\left(\frac{\pi}{2}\,\frac{A_b - A_a}{A_b + A_a}\right)}$$

- $\overline{V}_{\rm bias} = 0$ for symmetric case $A_b = A_a$
- $\overline{V}_{\rm bias} \to V_{\rm rf}$ for highly asymmetric case $A_b \gg A_a$

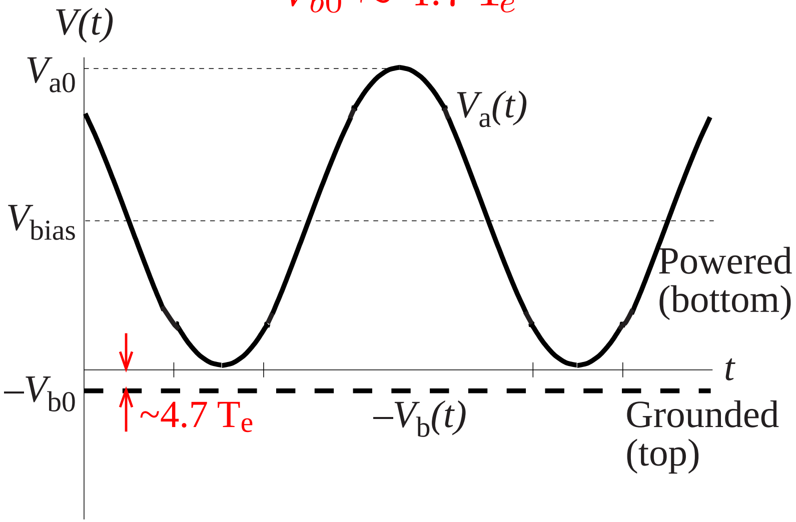
FINITE FLOATING POTENTIAL

- In the limit $A_b \gg A_a$, we see that

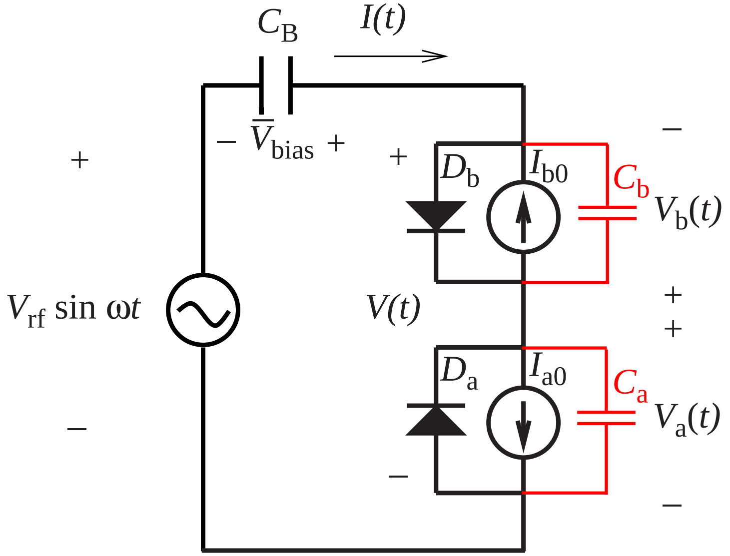
$$\overline{V}_{\rm bias} \rightarrow V_{\rm rf}\,, \qquad V_{a\rm max} \rightarrow 2\,V_{\rm rf}\,, \qquad V_{b0} \rightarrow 0$$

- Actually, the rf voltage across sheath b is zero, so we would expect to have of order the dc floating potential for a low voltage sheath [p. 48] appear across sheath b

$$V_{b0} \approx 4.7\,{\rm T}_e$$



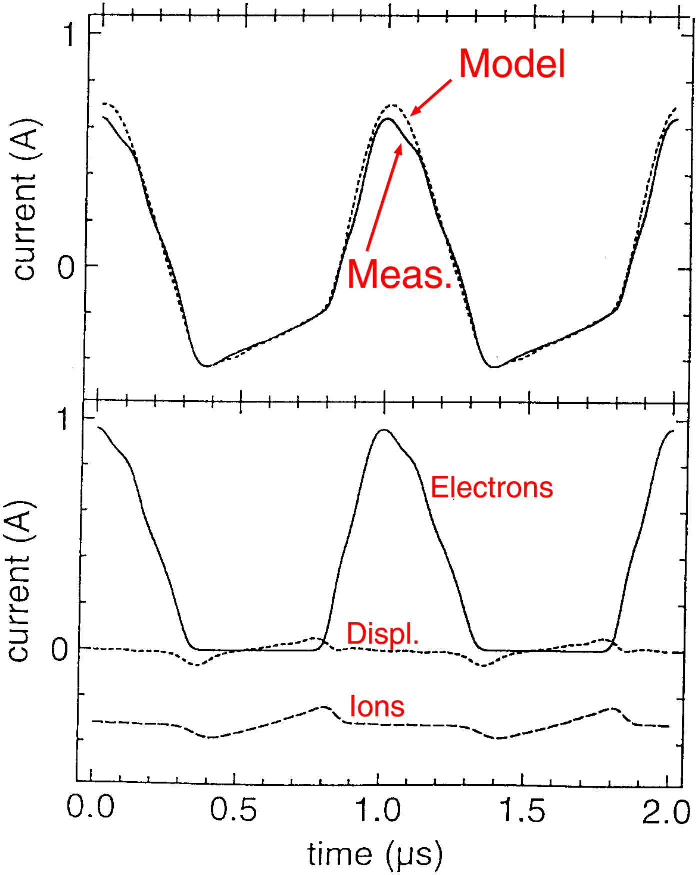
EFFECT OF DISPLACEMENT CURRENTS



- The sheath capacitors carry a small displacement current
- For an analytic treatment, see
  Kawamura et al, *Plasma Sources Sci. Technol.* **8,** R45 (1999)
- First numerical simulations appear in
  Metze et al, *J. Appl. Phys.* **60**, 3081 (1986)

SMALL BUT FINITE ION TRANSIT TIME

- An analytic model has been given by Sobolewski, *Phys. Rev. E*, **62,** 8540 (2000)
- It accounts for the finite ion transit time across a dc sheath whose thickness varies slowly with time
- Results agree with experiment better than the Metze et al model
- Example: 10 mTorr argon, 120 W ICP, 1 MHz rf bias, 68 V peak voltage



CAPACITIVE RF SHEATHS

ION ENERGY DISTRIBUTION (IED)

DEFINITION OF ION ENERGY DISTRIBUTION

- $g_i(\mathcal{E})$ = energy distribution of ions bombarding the substrate, averaged over one rf cycle (units are ion flux/energy)
- Fraction of ions entering the sheath during the phase interval $\frac{\omega}{2\pi}(t,\ t+dt)$ = fraction of ions bombarding the substrate within the energy interval $(\mathcal{E},\ \mathcal{E}+d\mathcal{E})$

$$\frac{\omega}{2\pi}\Gamma_i(\omega t)\,dt \equiv g_i(\mathcal{E})\,d\mathcal{E}$$

- Dividing by $d\mathcal{E}$ yields

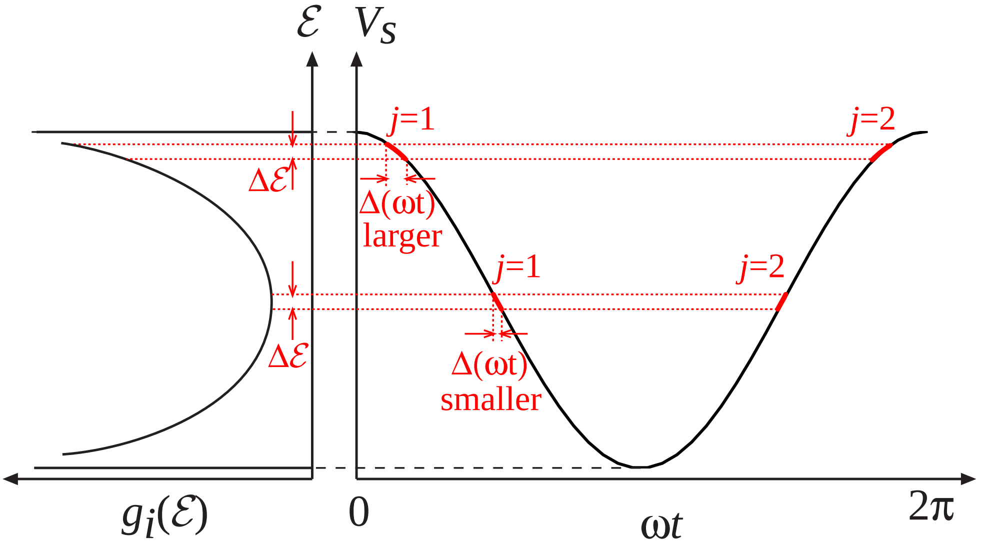
$$\boxed{g_i(\mathcal{E}) = \frac{1}{2\pi}\sum_{j=1}^{N_j}\Gamma_i(\omega t_j)\left|\frac{d\mathcal{E}}{d(\omega t_j)}\right|^{-1}}$$

- The sum is over all phases ωt_j during one rf cycle that map to the energy $\mathcal{E}$
- $N_j = 2$ for a sheath excited at a single rf frequency

ION ENERGY DISTRIBUTION (CONT'D)

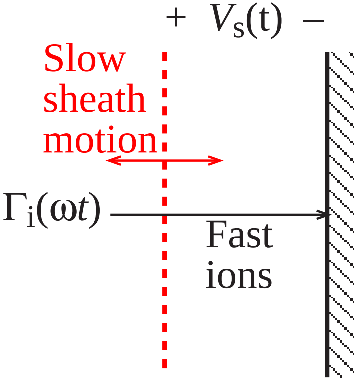
$$g_i(\mathcal{E}) = \frac{1}{2\pi}\sum_{j=1}^{N_j}\Gamma_i(\omega t_j)\left|\frac{d\mathcal{E}}{d(\omega t_j)}\right|^{-1}$$

- Why does $N_j = 2$ for a sheath excited at a single frequency?
  Two phase intervals $\Delta(\omega t)$ map into a single energy interval $\Delta\mathcal{E}$
- Why is $g_i(\mathcal{E})$ proportional to the derivative $|d(\omega t)/d\mathcal{E}|$?
  For a given $\Delta\mathcal{E}$, more ions strike the substrate if $\Delta(\omega t)$ is larger



EXAMPLE CALCULATION OF IED

- Ion transit time $\tau_i \ll$ rf period $\tau_{\rm rf}$
  $\Longrightarrow \mathcal{E}(\omega t) \approx V_s(\omega t)$ and $\Gamma_i(\omega t_0) \approx n_s u_B =$ const



- Consider highly asymmetric case with $A_a \ll A_b \Longrightarrow \overline{V}_{\rm bias} = V_{\rm rf}$

$$\boxed{\mathcal{E}(\omega t) = V_s(\omega t) = V_{\rm rf}(\sin\omega t + 1)} \qquad \text{[p. 121]}$$

$$d\mathcal{E}/d(\omega t) = V_{\rm rf}\cos(\omega t) = V_{\rm rf}(1 - \sin^2\omega t)^{1/2}$$

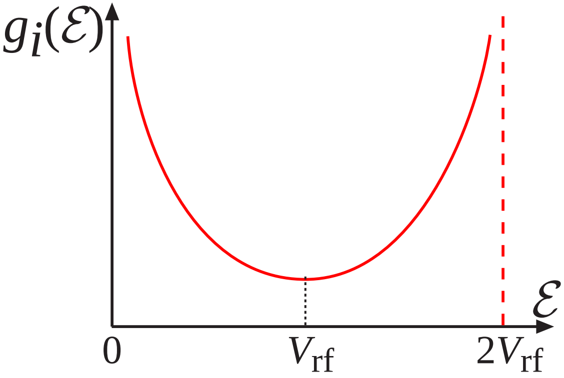
- From boxed equation, $\sin\omega t = \mathcal{E}/V_{\rm rf} - 1$, so

$$d\mathcal{E}/d(\omega t) = V_{\rm rf}[1 - (\mathcal{E}/V_{\rm rf} - 1)^2]^{1/2}$$

EXAMPLE CALCULATION OF IED (CONT'D)

- There are two times for each value of $\mathcal{E}$ ($N_j = 2$), so [p. 127]

$$\boxed{g_i(\mathcal{E}) = 2 \times \frac{n_s u_B}{2\pi}\left[V_{\rm rf}^2 - (V_{\rm rf} - \mathcal{E})^2\right]^{-1/2}}$$

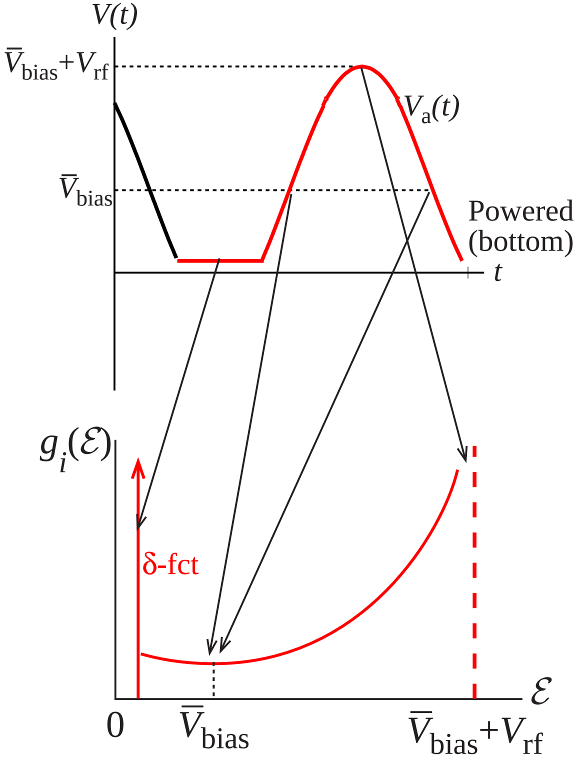


- The ion energy distribution is broad ($0 < \mathcal{E} < 2V_{\rm rf}$) and independent of ion mass

GENERAL CASE OF SHORT ION TRANSIT TIME

- Ion transit time $\tau_i \ll$ rf period τ_{rf}
  $\Longrightarrow \mathcal{E}(\omega t) \approx V_s(\omega t)$ and $\Gamma_i(\omega t_0) \approx n_s u_B = \text{const}$
- Consider general asymmetric case with $A_a < A_b \Longrightarrow \overline{V}_{\text{bias}}$ [p. 121]

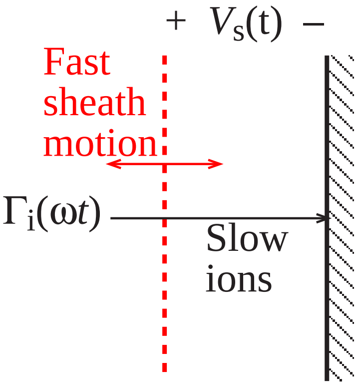
$$\mathcal{E}(\omega t) = V_s(\omega t) = V_{\text{rf}} \sin \omega t + \overline{V}_{\text{bias}}$$



- Ion energy distribution is broad
  $(0 < \mathcal{E} < \overline{V}_{\text{bias}} + V_{\text{rf}})$
  and independent of ion mass

LONG ION TRANSIT TIME

- Ion transit time $\tau_i \gg$ rf period τ_{rf}
  $\Longrightarrow \Gamma_i(\omega t_0) \approx n_s u_B = \text{const}$



- Sheath voltage approximately sinusoidal with $\overline{V}_s \approx 0.83\,\widetilde{V}_s$ [p. 76]

$$V_s(\omega t) = \widetilde{V}_s \sin \omega t + \overline{V}_s$$

- Ions "see" mostly the average sheath voltage $\overline{V}_s$ with a small time-varying perturbation $\Delta\mathcal{E}$

$$\mathcal{E}(\omega t) = \overline{V}_s + \Delta\mathcal{E}(\omega t)$$

- Ion energy distribution is narrow and centered about $\overline{V}_s$

LONG ION TRANSIT TIME (CONT'D)

- Calculation of $d\mathcal{E}/d(\omega t)$ is rather complicated and yields (Benoit-Cattin and Bernard, 1968)

$$\boxed{g_i(\mathcal{E}) = \frac{2n_s u_B}{2\pi}\left[1 - 4\left(\frac{\mathcal{E} - \overline{V}_s}{\Delta\mathcal{E}}\right)^2\right]^{-1/2}}$$

where

$$\boxed{\Delta\mathcal{E} = \frac{4}{\pi}\frac{\tau_{\text{rf}}}{\tau_i}\widetilde{V}_s}$$

- This is a bi-modal distribution with two peaks

$$\mathcal{E} = \overline{V}_s \pm \Delta\mathcal{E}/2$$

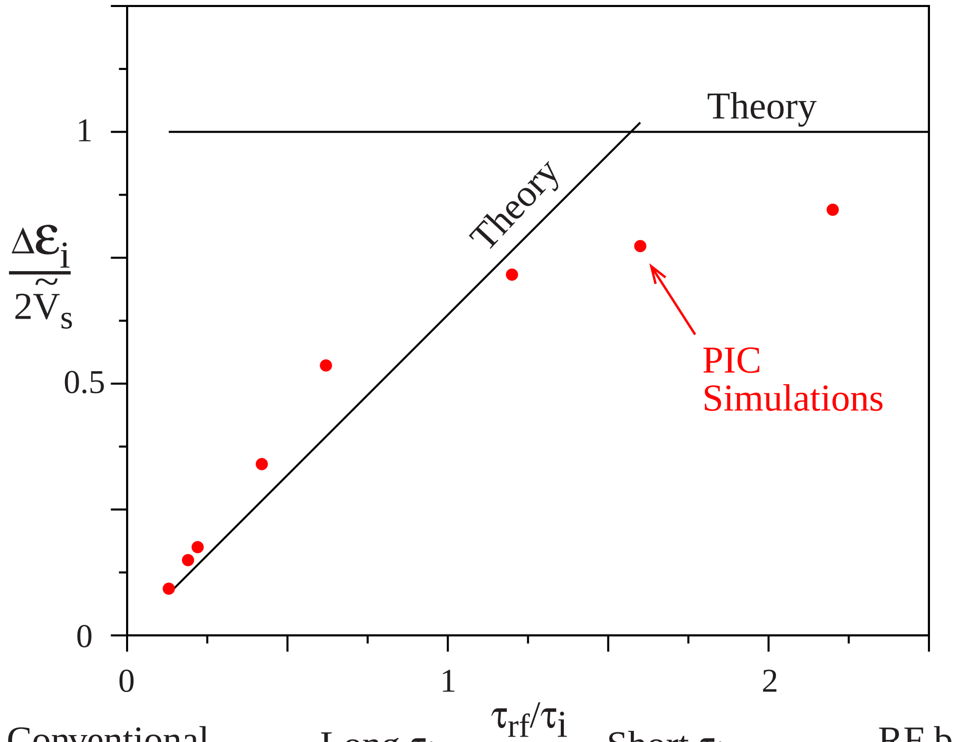
- Because [p. 116]

$$\tau_i = \frac{3s_m}{v_i} = 3s_m\sqrt{\frac{M}{2e\overline{V}_s}}$$

there is an ion mass dependence

$$\Delta\mathcal{E} \propto \frac{1}{\sqrt{M}}$$

ENERGY SPREAD $\Delta\mathcal{E}_i$ VERSUS $\tau_{\rm rf}/\tau_i$



Conventional capacitive discharge

Long τ_i ←

Low density
High frequency

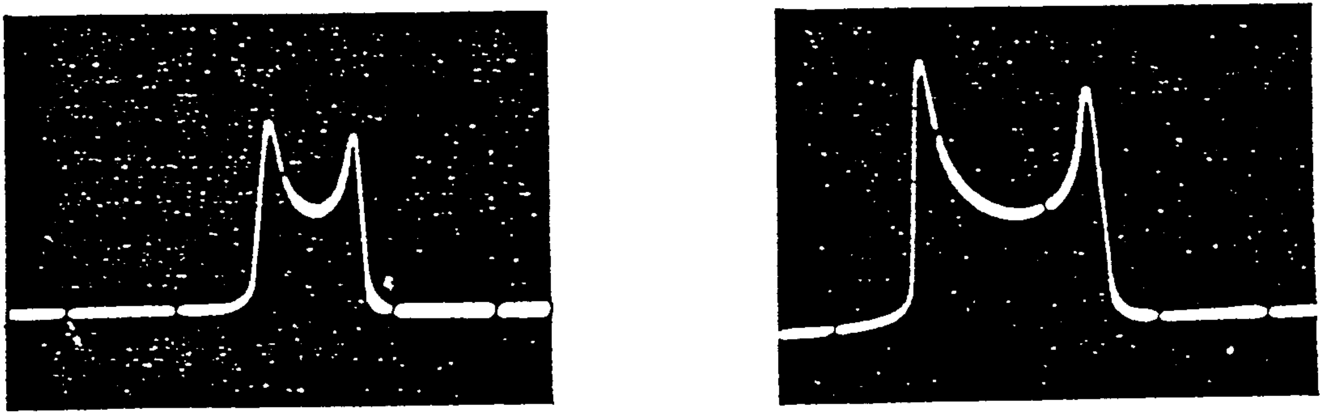
Short τ_i →

High density
Low frequency

RF bias on high density plasma tool

EARLIEST MEASUREMENT OF IED

- Erö (1958) showed the effect of rf modulation on IED's
  Energy spectrum has characteristic bi-modal shape

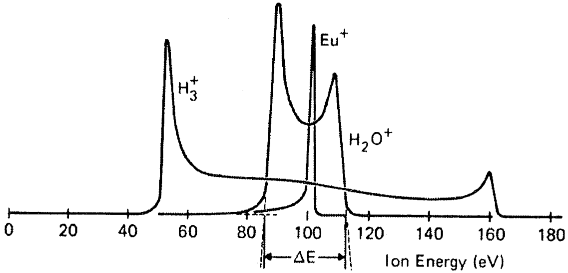


Low rf field High rf field

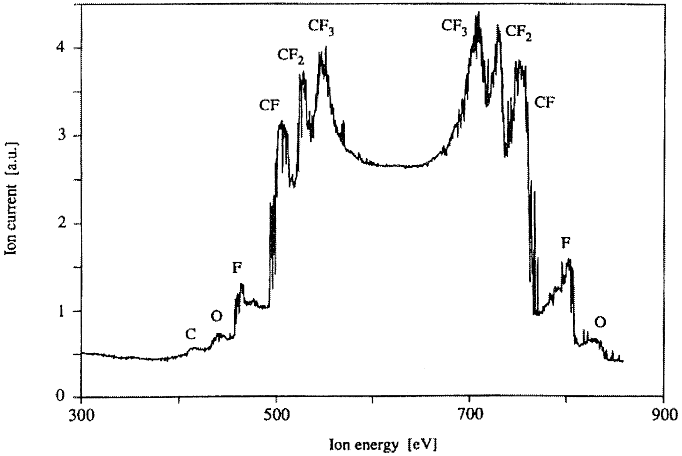
Energy spectra in case of a low intensity discharge
(distance between two marks is 55 V)

SOME EXPERIMENTAL RESULTS

- Capacitive discharge, 13.56 MHz, 75 mTorr
  Note Eu^+ (mass 152), $\mathrm{H_2O}^+$ (mass 18) and H_3^+ (mass 3)
  (Coburn and Kay, 1972)

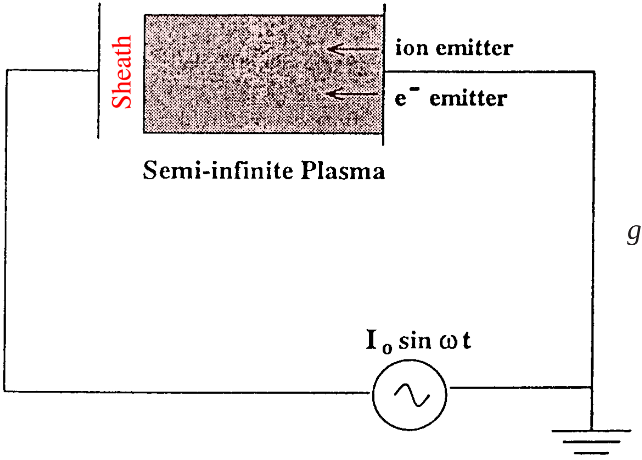


- Capacitive discharge, CF_4 at 3 mTorr (Note $\Delta\mathcal{E} \propto 1/\sqrt{M}$)
  (Kuypers and Hopman, 1980)

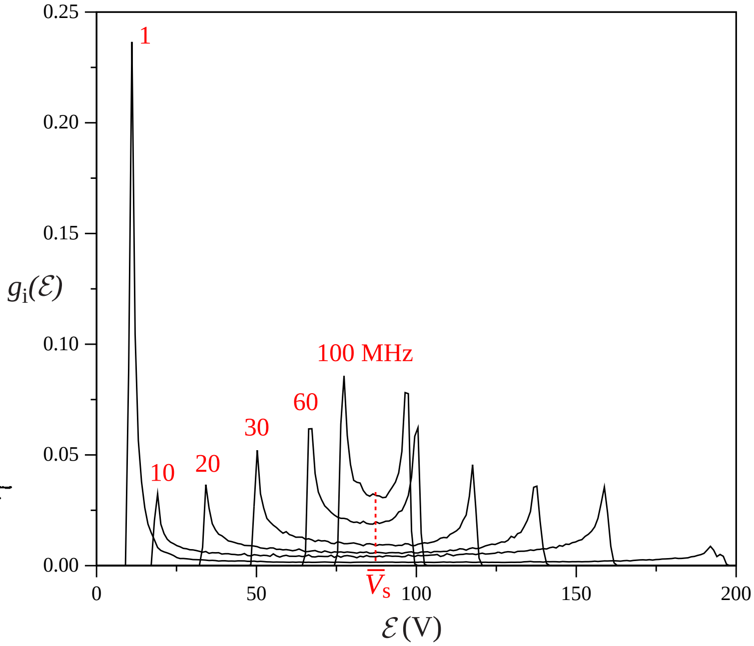


PIC SIMULATION RESULT

- Helium ion energy distributions for various discharge frequencies at the electrode; the maximum of $V_s(t)$ is 200 V in every case

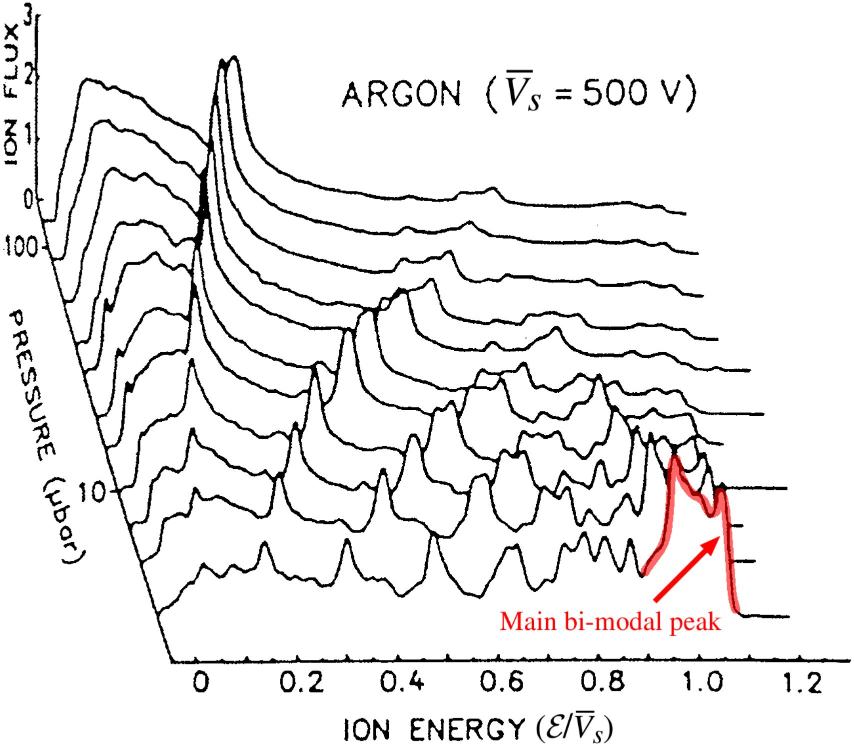


Current-driven sheath



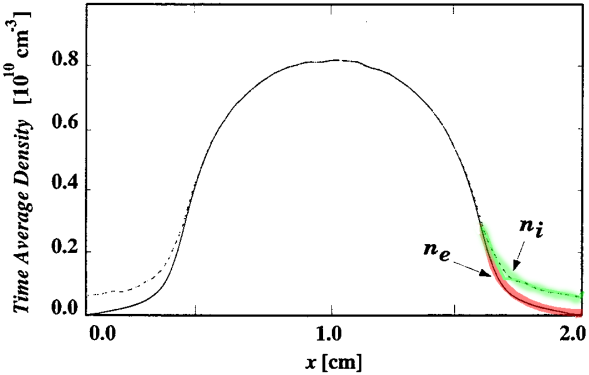
ION-NEUTRAL COLLISIONS IN THE SHEATH

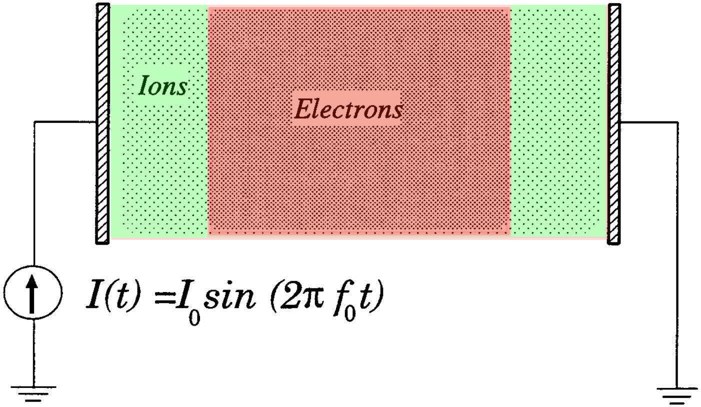
- Ion-neutral charge transfer collisions lead to additional peaks within the energy distribution
- The explanation is complicated and was given by Wild and Koidl (1991)



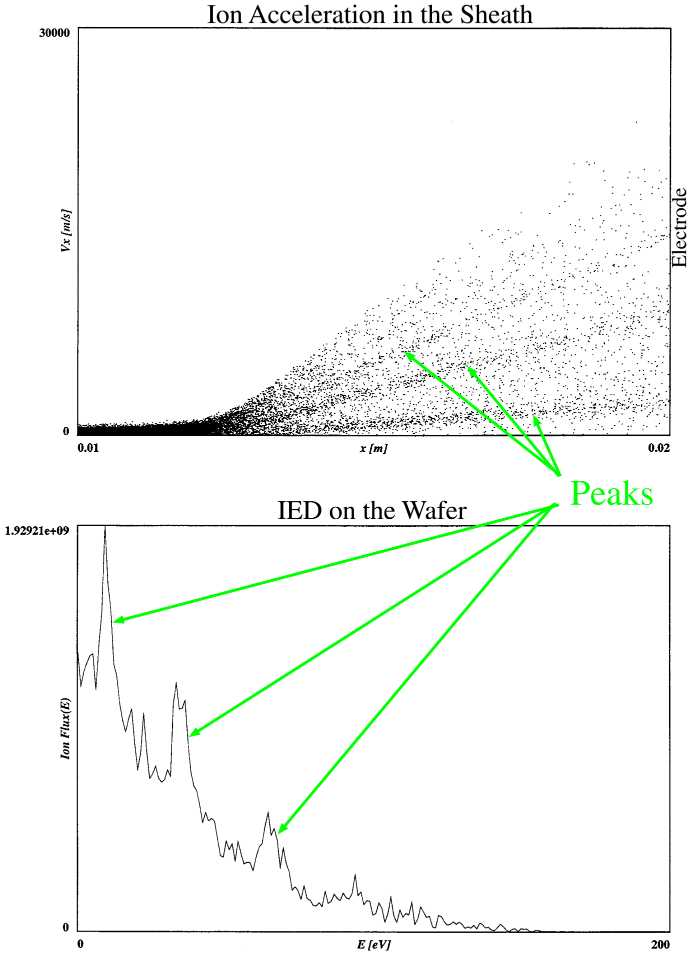
- IED's measured in a collisional rf discharge for various pressures; the secondary peaks arise from a combination of charge exchange collisions and rf modulation

SIMULATIONS OF COLLISIONAL IED





SIMULATIONS OF COLLISIONAL IED (CONT'D)



SUMMARY OF ION ENERGY DISTRIBUTIONS (IED'S)

- IED's are bi-modal (two peaks) in collisionless sheaths
- $\tau_i \gg \tau_{\rm rf} \Longrightarrow$
  Displacement current mainly flows in sheath
  Narrow IED centered around dc sheath potential $\overline{V}_s$

$$\boxed{\Delta\mathcal{E} \propto \tau_{\rm rf}/\tau_i \propto 1/\sqrt{M}}$$

- $\tau_i \ll \tau_{\rm rf} \Longrightarrow$
  Conduction currents mainly flow in sheath
  Broad IED

$$\boxed{4.7\,T_e < \mathcal{E} < \widetilde{V}_{\rm rf} + \overline{V}_{\rm bias}}$$

- Collisional sheaths have multiple peaks in the IED

CHEMICAL FUNDAMENTALS

ATOMS AND MOLECULES

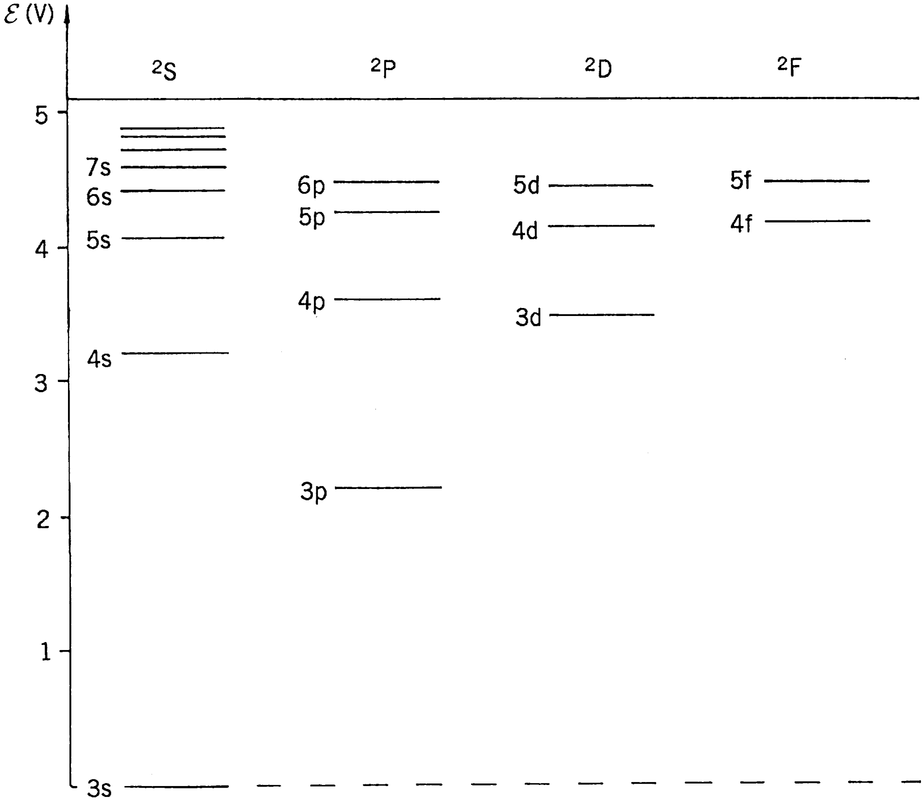
ATOMS

- Central field model (4 quantum numbers + Pauli exclusion)
  $n = 1, 2, 3, \ldots$
  $0 \leq l \leq n - 1 \quad (0, 1, 2, 3 \equiv s, p, d, f)$
  $|m_l| \leq l, \quad m_s = \pm 1/2$

- Spectroscopic notation: ${}^{2S+1}L_J \ (Z \leq 40)$
  L is total orbital angular momentum $(0, 1, 2, 3 \equiv S, P, D, F)$
  S is total spin angular momentum
  $\mathbf{J} = \mathbf{L} + \mathbf{S}; \quad (|L - S|, \ldots, L + S)$
  $\mathcal{E} = \mathcal{E}(L, S, J); \quad 2J + 1$ states
  Weak dependence of $\mathcal{E}$ on J ("fine structure")

- Electronic configurations
  Hydrogen: $1s \quad ({}^2S_{1/2})$
  Oxygen: $1s^2 2s^2 2p^4 \quad ({}^3P_2)$
  Argon: $1s^2 2s^2 2p^6 3s^2 3p^6 \quad ({}^1S_0)$
  Metastable argon: $1s^2 2s^2 2p^6 3s^2 3p^5 4s \ ({}^3P_0, {}^3P_2)$

ENERGY LEVELS FOR ATOMS



Atomic energy levels for the central field model of an atom, showing the dependence of the energy levels on the quantum numbers n and l; the energy levels are shown for sodium, without the fine structure

METASTABLE STATES

- Most excited states can radiate a photon and make a transition to a lower energy state

  $\Longrightarrow$ electric dipole radiation

- Selection rules for electric dipole radiation
  - For all elements: $\Delta l = \pm 1$; $\Delta J = 0, \pm 1$ (but $J = 0 \rightarrow J = 0$ is forbidden)
  - For light elements: $\Delta S = 0$; $\Delta L = 0, \pm 1$ (but $L = 0 \rightarrow L = 0$ is forbidden)

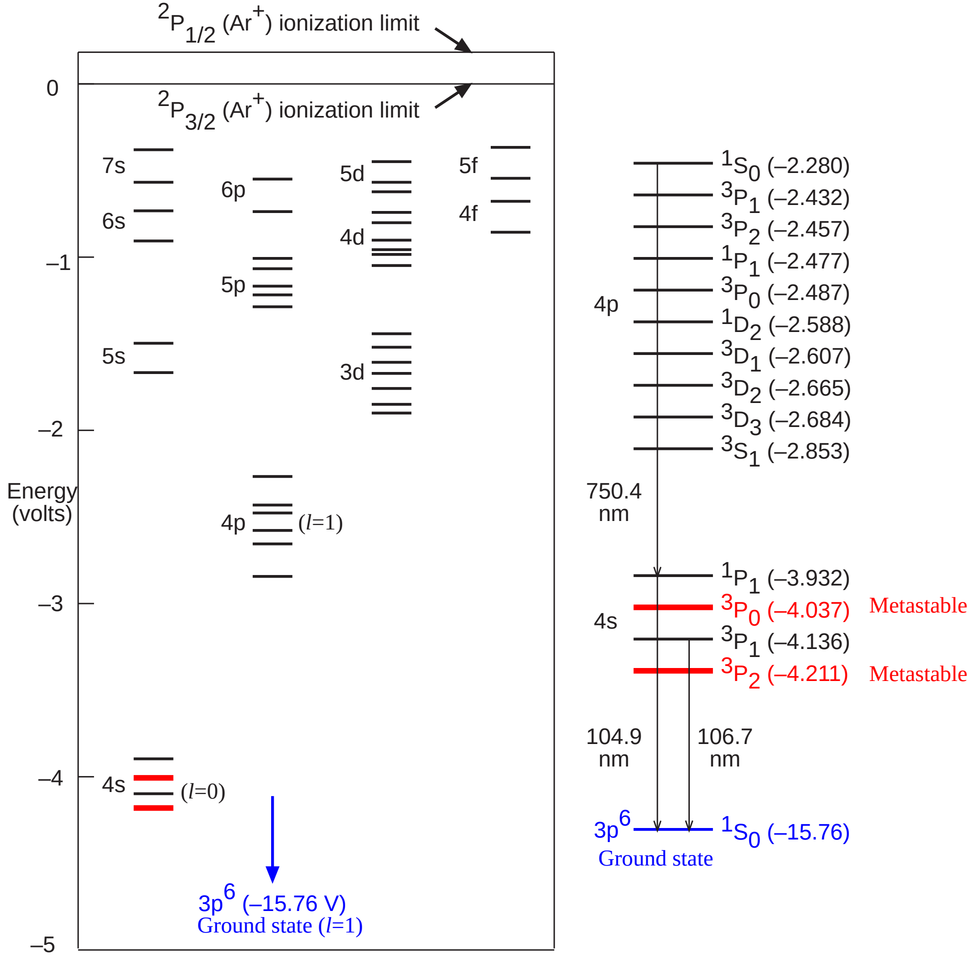
- Radiation lifetime $\tau_{\mathrm{rad}} \sim 10$–$100$ ns

- Electric dipole radiation forbidden

  $\Longrightarrow$ metastable state

- Examples: Ar(4s $^3\mathrm{P}_0$), Ar(4s $^3\mathrm{P}_2$)

ARGON ENERGY LEVELS

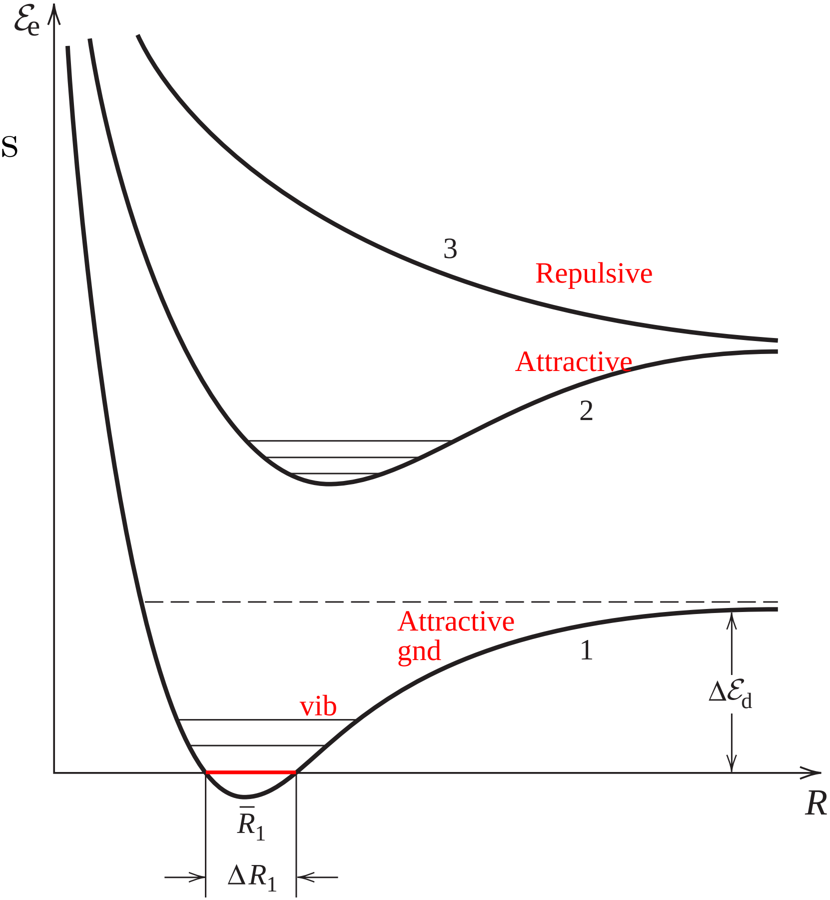


MOLECULES

- Electronic state is a function of nuclear separations
- Potential energy curves of electronic states of a diatomic molecule
- Attractive (1, 2) and repulsive (3) states
- Vibrations and rotations also quantized

$$e\mathcal{E}_v = \hbar\omega_{\rm vib}(v + \tfrac{1}{2}),$$

$$v = 0, 1, 2, \ldots$$



MOLECULAR STATES

- Notation for diatomic molecules: ${}^{2S+1}\Lambda$
  Λ = total orbital angular momentum about internuclear axis
  $(0, 1, 2, 3, \equiv \Sigma, \Pi, \Delta, \Phi)$
  S = total spin angular momentum

- For Σ states, Σ^+ and Σ^- denote symmetric or antisymmetric wave function with respect to reflection through internuclear axis

- For homonuclear molecules, Λ_g and Λ_u denote symmetric or antisymmetric wave function with respect to interchange of the nuclei

  (the two nuclei are the same; e.g., O_2, N_2, but not NO)

METASTABLE MOLECULAR STATES

- Most excited molecular states can radiate a photon and make a transition to a lower energy state

$$\Longrightarrow \text{electric dipole radiation}$$

- Selection rules for electric dipole radiation

$$\Delta\Lambda = 0,\ \pm 1$$
$$\Delta S = 0$$

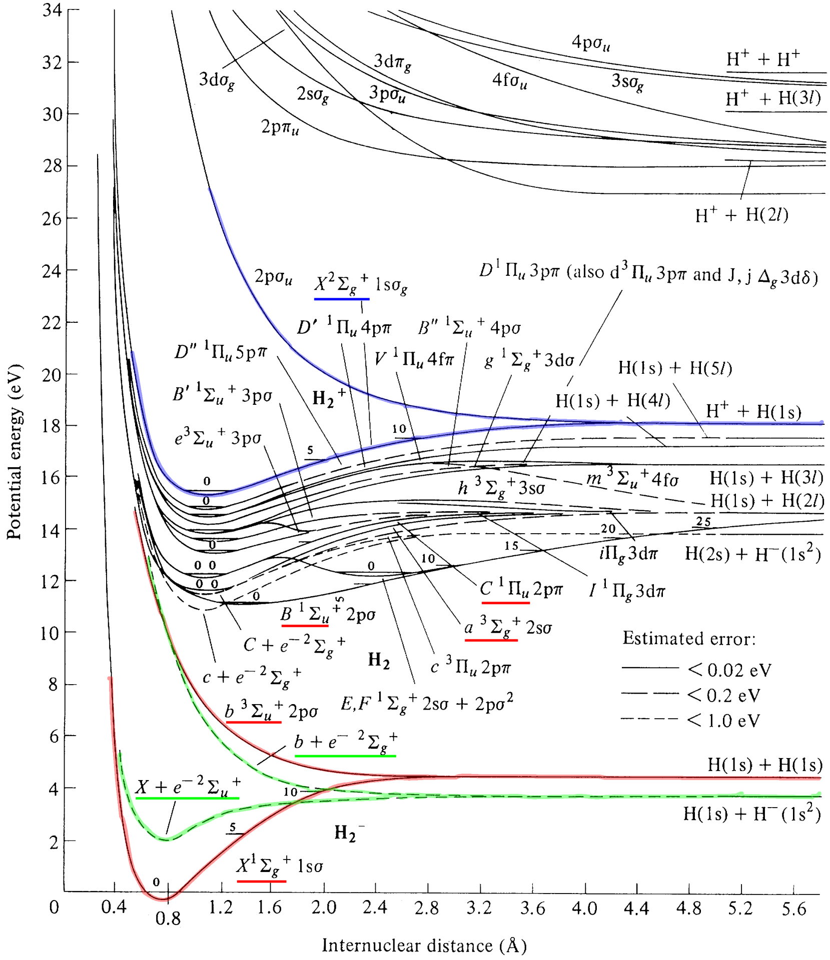
$$\Sigma^+ \to \Sigma^+ \text{ and } \Sigma^- \to \Sigma^-$$
$$g \to u \text{ and } u \to g$$

- Radiation lifetime $\tau_{\text{rad}} \sim$ 10–100 ns
- Electric dipole radiation forbidden ⇒ metastable state
- Examples are: $\text{O}_2(a\,^1\Delta_g)$, $\text{O}_2(b\,^1\Sigma_g^+)$

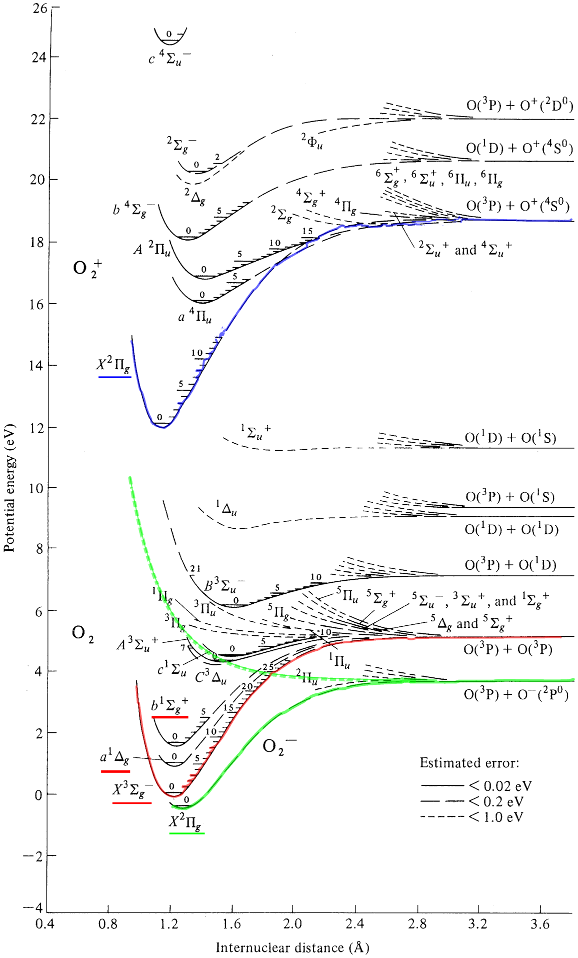
ATOMIC AND MOLECULAR NEGATIVE IONS

- The energy required to remove the electron from a negative ion (A^-) is called the affinity energy $\mathcal{E}_{\mathrm{aff}}$ of the neutral atom or molecule (A)
- Negative atomic and molecular ions (A^-) are stable if $\mathcal{E}_{\mathrm{aff}} > 0$
  Typically $\mathcal{E}_{\mathrm{aff}} \sim 0.5$–$3.5$ V for stable negative ions
- Examples of stable negative ions are: H^- (but not H_2^-), O_2^-, O^-, Cl_2^-, Cl^-, F_2^-, F^-
- Stable Ar^-, N^-, N_2^-, H_2^- negative ions do not exist
- Gas mixtures containing oxygen, hydrogen and/or the halogens are generally "attaching" or "electronegative" (stable negative ions can form)
- Nitrogen and the noble gases are "electropositive"

HYDROGEN


Potential energy (eV)
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
4.0
4.4
4.8
5.2
5.6
Internuclear distance (Å)
$H^+ + H^+$
$H^+ + H(3l)$
$H^+ + H(2l)$
$4p\sigma_u$
$3s\sigma_g$
$4f\sigma_u$
$3d\pi_g$
$3p\sigma_u$
$2s\sigma_g$
$3d\sigma_g$
$2p\pi_u$
$2p\sigma_u$
$X^2\Sigma_g^+ 1s\sigma_g$
$D^1\Pi_u 3p\pi$ (also $d^3\Pi_u 3p\pi$ and J, j $\Delta_g 3d\delta$)
$D'\ ^1\Pi_u 4p\pi$
$B''\ ^1\Sigma_u^+ 4p\sigma$
$D''\ ^1\Pi_u 5p\pi$
$V\ ^1\Pi_u 4f\pi$
$g\ ^1\Sigma_g^+ 3d\sigma$
H(1s) + H(5l)
H(1s) + H(4l)
H^+ + H(1s)
$B'\ ^1\Sigma_u^+ 3p\sigma$
H_2^+
$e^3\Sigma_u^+ 3p\sigma$
10
5
0
$m\ ^3\Sigma_u^+ 4f\sigma$
H(1s) + H(3l)
$h\ ^3\Sigma_g^+ 3s\sigma$
H(1s) + H(2l)
20
25
15
$i\Pi_g 3d\pi$
$H(2s) + H^-(1s^2)$
10
0
$C\ ^1\Pi_u 2p\pi$
$I\ ^1\Pi_g 3d\pi$
$B\ ^1\Sigma_u^+ 2p\sigma$
5
$a\ ^3\Sigma_g^+ 2s\sigma$
$C + e^-\ ^2\Sigma_g^+$
H_2
$c\ ^3\Pi_u 2p\pi$
$c + e^-\ ^2\Sigma_g^+$
$E,F\ ^1\Sigma_g^+ 2s\sigma + 2p\sigma^2$
$b\ ^3\Sigma_u^+ 2p\sigma$
$b + e^-\ ^2\Sigma_g^+$
Estimated error:
< 0.02 eV
< 0.2 eV
< 1.0 eV
H(1s) + H(1s)
$X + e^-\ ^2\Sigma_u^+$
10
H(1s) + $H^-(1s^2)$
5
H_2^-
0
$X^1\Sigma_g^+ 1s\sigma$

OXYGEN



PLASMA

COLLISION PRINCIPLES

- Two kinds of collisions
  - Electron collisions with atoms and molecules

$$e + A \rightarrow \text{products}$$

  - Heavy particle collisions with atoms and molecules

$$\begin{gathered} A + B \rightarrow \text{products} \\ A^+ + B \rightarrow \text{products} \\ A^- + B \rightarrow \text{products} \end{gathered}$$

- By Newton's laws, two bodies cannot elastically collide to form one body

$$\begin{gathered} e + A \not\rightarrow A^- \\ A + B \not\rightarrow AB \end{gathered}$$

- Two bodies can collide to form one body if the internal energy increases

$$\begin{gathered} e + A \longrightarrow A^{-\,*} \\ A + B \longrightarrow AB^* \end{gathered}$$

ELECTRON COLLISIONS WITH MOLECULES

- Frank-Condon principle
  Nuclear positions are fixed during an electronic transition
- Due to the ordering of timescales for an electron collision

$$\underbrace{\frac{2a_0}{v_e}}_{\text{interac. time}} \ll \tau_{\text{vib}} \sim \tau_{\text{diss}} \ll \tau_{\text{rad}}$$

  a_0 = radius of atom or molecule; v_e = speed of incoming electron

- Dissociation

$$\mathrm{e} + \mathrm{AB} \longrightarrow \mathrm{A} + \mathrm{B} + \mathrm{e}$$

- Excitation

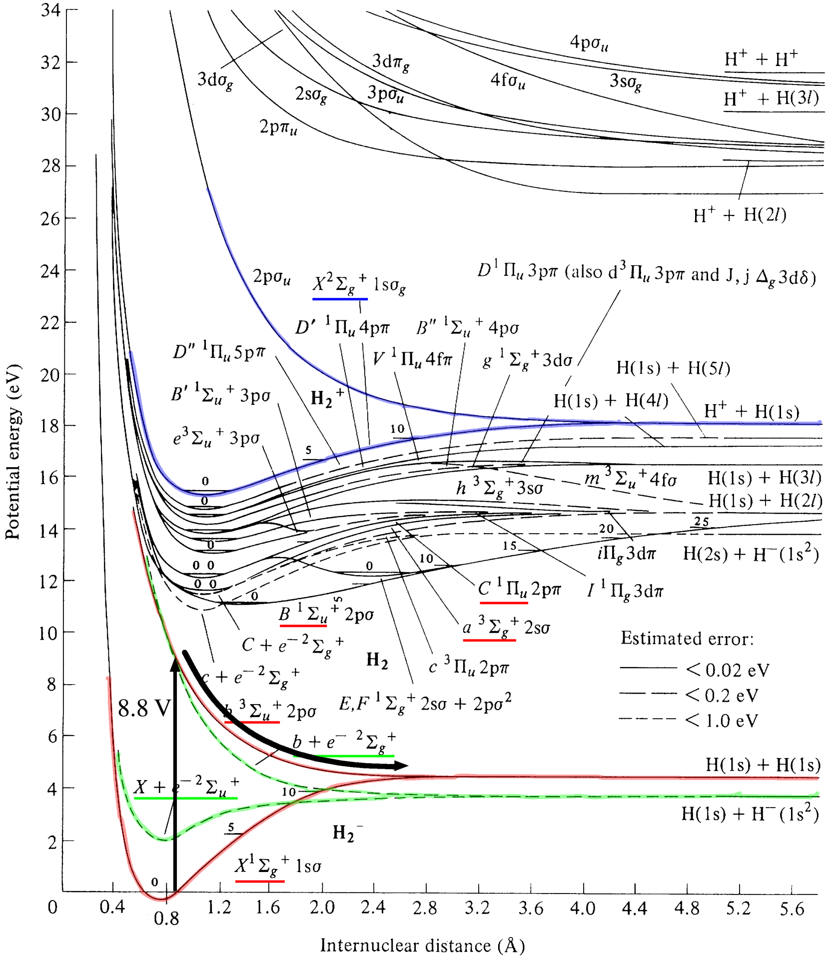
$$\mathrm{e} + \mathrm{AB} \longrightarrow \mathrm{AB}^* + \mathrm{e}$$

- Ionization

$$\mathrm{e} + \mathrm{AB} \longrightarrow \mathrm{AB}^+ + 2\mathrm{e}$$

EXAMPLE OF HYDROGEN

- Electronic transitions are vertical
- 8.8 V: $^3\Sigma_u^+ \rightarrow$ dissociation (2.2 V per atom)
- 11.5 V: $^1\Sigma_u^+ \rightarrow$ uv radiation
- 11.8 V: $^3\Sigma_g^+ \rightarrow$ radiation to $^3\Sigma_u^+ \rightarrow$ dissociation
- 12.6 V: $^1\Pi_u \rightarrow$ uv radiation
- 15.4 V: $^2\Sigma_g^+ \rightarrow H_2^+$ ions
- 28.0 V: $^2\Sigma_u^+ \rightarrow H + H^+$ (5 V per fragment)

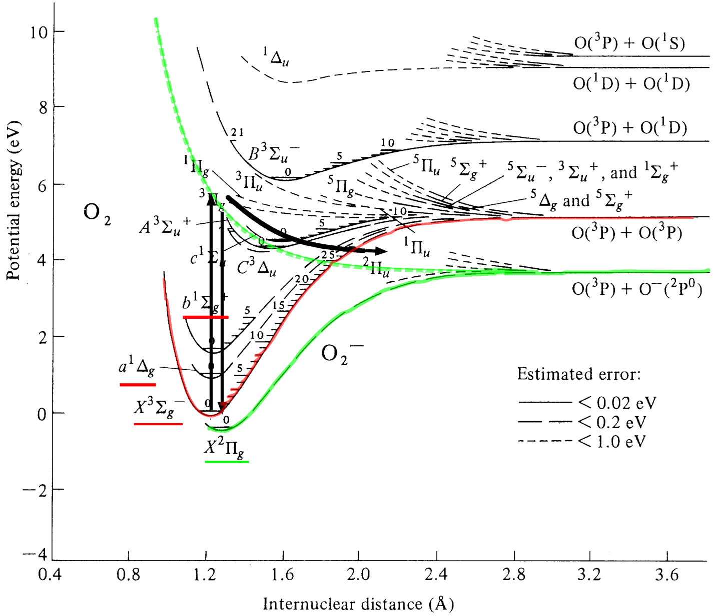


NEGATIVE ION PRODUCTION

- Dissociative attachment

$$
\begin{aligned}
e + O_2 \rightarrow O_2^- \,(\text{unstable}) &\rightarrow e + O_2 \qquad (99\%)\\
&\rightarrow O + O^- \qquad (1\%)
\end{aligned}
$$

Resonant process (no outgoing electron to carry away excess energy)
Small probability process (small cross section, but important)



NEGATIVE ION PRODUCTION (CONT'D)

- Dissociative attachment

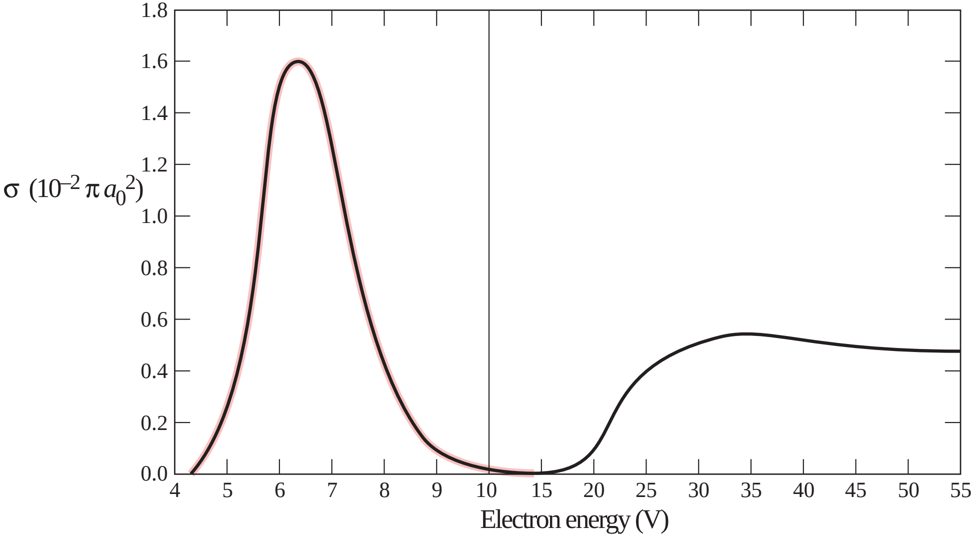
$$e + O_2 \rightarrow O_2^- \text{(unstable)} \rightarrow e + O_2 \qquad (99\%)$$

$$\rightarrow O + O^- \qquad (1\%)$$

- Polar dissociation

$$e + O_2 \rightarrow O^+ + O^- + e$$

Non-resonant, high threshold energy



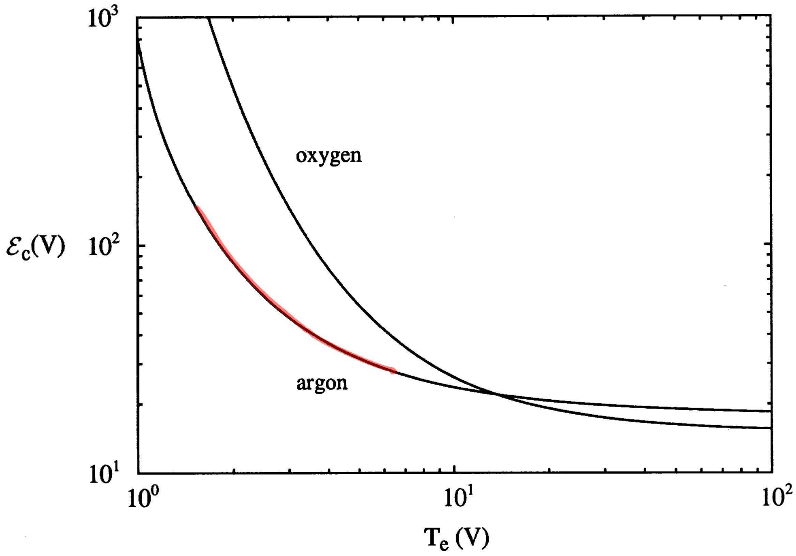
VIBRATIONAL AND ROTATIONAL EXCITATIONS

- Mechanism is often

$$\mathrm{e} + \mathrm{AB}(v=0) \to \mathrm{AB}^- \quad \text{(unstable)}$$
$$\mathrm{AB}^- \to \mathrm{AB}(v>0) + \mathrm{e}$$

ELECTRON COLLISIONAL ENERGY LOSSES

- Ionization
  Electronic excitation
  Elastic scattering
  Dissociation
  Vibrational excitation
  Rotational excitation
  etc.
- Electron collisional energy lost per electron-ion pair created, $\mathcal{E}_c$, is 2–10 times larger for molecules than for atoms [p. 40]



HEAVY PARTICLE COLLISIONS

- Ordering of timescales [p. 153]

$$\underbrace{\frac{2a_0}{v_e}}_{\text{electronic}} \ll \underbrace{\frac{2a_0}{v_i}}_{\text{ion collision}} \sim \tau_{\text{vib}} \ll \tau_{\text{rad}}$$

  v_i = speed of incoming ion or neutral

- Adiabatic Massey principle
  Potential energy curves must cross or nearly touch for a change of electronic state ($\Delta\mathcal{E} \lesssim 0.1$ V)

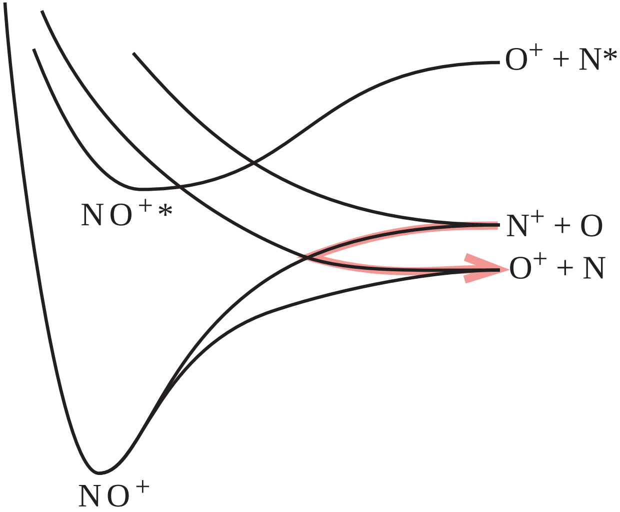
- Examples

  $\mathrm{A + B \rightarrow A^+ + B + e}$ heavy particle ionization (very small)
  (AB and $\mathrm{AB^+}$ curves do not cross or nearly touch)

  $\mathrm{A + B \rightarrow A^* + B}$ heavy particle excitation (very small)
  $\mathrm{A^+ + B \rightarrow A^+ + B}$ elastic scattering (large)
  $\mathrm{A^+ + A \rightarrow A + A^+}$ resonant charge transfer (large)

NONRESONANT CHARGE TRANSFER

- Example of nitrogen and oxygen atoms
  $N^+ + O \rightarrow N + O^+$ no threshold
  $O^+ + N \rightarrow O + N^+$ 0.92 V threshold

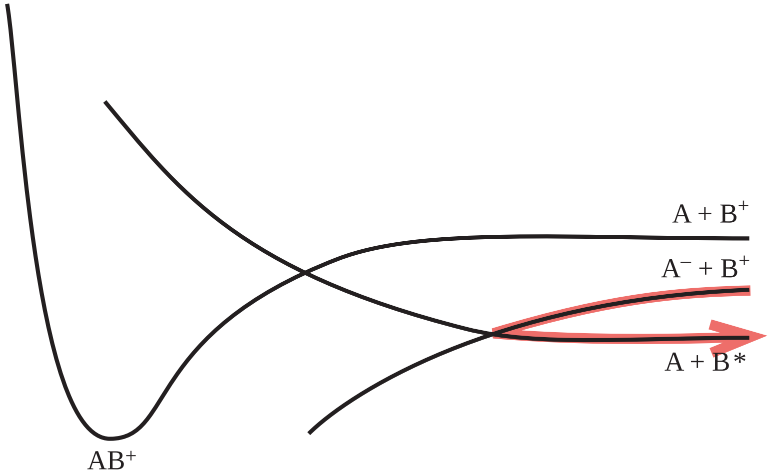


- Example of oxygen atoms and molecules
  $O^+ + O_2 \rightarrow O + O_2^+$ no threshold
  $O_2^+ + O \rightarrow O_2 + O^+$ 1.4 V threshold
- Charge transfer makes ions of easier-to-ionize neutrals

NEGATIVE ION LOSS

- Positive-negative ion recombination (mutual neutralization)

$$A^- + B^+ \rightarrow A + B^*$$



$\Longrightarrow$ large cross section; dominates negative ion destruction

- Electron detachment

$$e + A^- \rightarrow A + 2e$$

Like "ionization" of A^-; can be important

REACTION RATES

- Consider reaction

$$\mathrm{A} + \mathrm{B} \longrightarrow \text{products}$$

$$\frac{dn_A}{dt} = -K_{\mathrm{AB}} n_A n_B$$

- The rate coefficient is [p. 36]

$$K_{\mathrm{AB}}(\mathrm{T}) = \langle \sigma_{\mathrm{AB}} v_R \rangle_{\mathrm{Maxwellian}}$$

$$= \int_0^\infty f_m v_R \sigma_{\mathrm{AB}}(v_R)\, 4\pi v_R^2\, dv_R$$

- It often found to have an Arrhenius form

$$\boxed{K_{AB} = K_{\mathrm{AB0}}\, \mathrm{e}^{-\mathcal{E}_a/\mathrm{T}}}$$

$\mathcal{E}_a$ = threshold or “activation” energy for the process

K_{AB0} = “pre-exponential” factor (weakly depends on T)

DETAILED BALANCING

- Consider the reactions

$$\mathrm{A} + \mathrm{B} \underset{K'}{\overset{K}{\rightleftarrows}} \mathrm{C} + \mathrm{D}$$

  K has threshold or "activation" energy $\mathcal{E}_a$

- From quantum mechanics and time reversibility

$$\boxed{m_R^2 g_A g_B v_R^2 \sigma(v_R) = {m'_R}^2 g_C g_D {v'_R}^2 \sigma'(v'_R)}$$

  where

$$m_R = \frac{m_A m_B}{m_A + m_B}, \qquad m'_R = \frac{m_C m_D}{m_C + m_D}$$

$$\frac{1}{2} m_R v_R^2 = \frac{1}{2} m'_R {v'_R}^2 + e\mathcal{E}_a$$

  The g's are the degeneracies of the energy levels of the particles

- The boxed equation gives the relation between the cross sections for the forward and backward processes

DETAILED BALANCING (CONT'D)

- Integrate cross section relation [p. 162] over a Maxwellian distribution

$$\boxed{\frac{K(\mathrm{T})}{K'(\mathrm{T})} = \left(\frac{m'_R}{m_R}\right)^{3/2} \frac{\bar{g}_C\bar{g}_D}{\bar{g}_A\bar{g}_B}\,\mathrm{e}^{-\mathcal{E}_a/\mathrm{T}}}$$

- The $\bar{g}$'s are statistical weights (mean number of occupied states)
$\bar{g}_e = 2; \quad \bar{g}_{\mathrm{atom}} \sim 1$–$10; \quad \bar{g}_{\mathrm{mol}} \sim 100$–$1000$
$\Longrightarrow$ $\bar{g}$'s are given by thermodynamics

- The boxed equation gives the relation between the rate coefficients of the forward and backward processes

- Example

$$\mathrm{e} + \mathrm{A} \underset{K_{\mathrm{deexc}}}{\overset{K_{\mathrm{ex}}}{\rightleftarrows}} \mathrm{e} + \mathrm{A}^*$$

K_{ex} (threshold energy $\mathcal{E}_{\mathrm{ex}}$) is easy to measure or calculate
K_{deexc} is hard to measure or calculate, so use "detailed balancing"

CHEMICAL FUNDAMENTALS

GAS PHASE KINETICS

ELEMENTARY REACTIONS

- Elementary reactions
  A simultaneous collision or single decomposition
  - $A + B \to C + D$ can be elementary if A and B collide to immediately form C and D
  - $3A + 2B \to C + 2D$ is elementary if 3 molecules of A and 2 molecules of B simultaneously collide (not likely!)
- Types of elementary reactions

  $A \to$ products (unimolecular)

  $A + B \to$ products (bimolecular)

  $A + B + C \to$ products (usually not elementary at low pressure)
- But recall by Newton's laws [p. 152], the reaction

  $A + B \to C$ (bimolecular with one product)

  is prohibited unless internal energy is given to C

RATE COEFFICIENTS

- First order elementary reaction

$$\mathrm{A} \longrightarrow \text{products}$$

$$\frac{dn_A}{dt} = -K_1 n_A$$

Units of K_1 (or ν_1) are $[\mathrm{s}^{-1}]$

- Second order elementary reaction

$$\mathrm{A} + \mathrm{B} \longrightarrow \text{products}$$

$$\frac{dn_A}{dt} = \frac{dn_B}{dt} = -K_2 n_A n_B$$

Units of K_2 are $[\mathrm{m}^3/\mathrm{s}]$

RATE-LIMITING REACTION STEP

- Consider as an example the reaction chain

  $$\boxed{\mathrm{A} \xrightarrow{K_A} \mathrm{B} \xrightarrow{K_B} \mathrm{C}}$$

  with $n_A = n_{A0}$ at $t = 0$

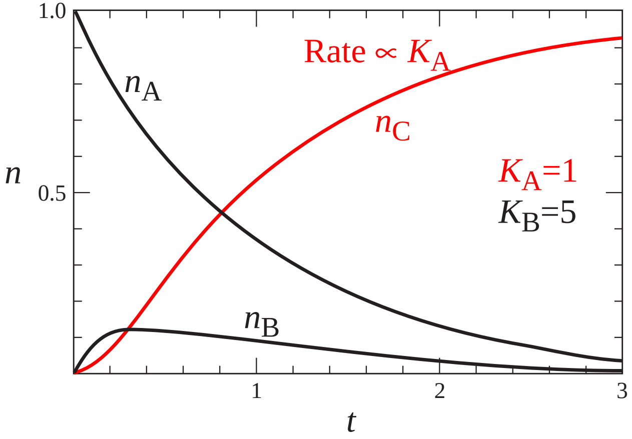
- The rate equations are

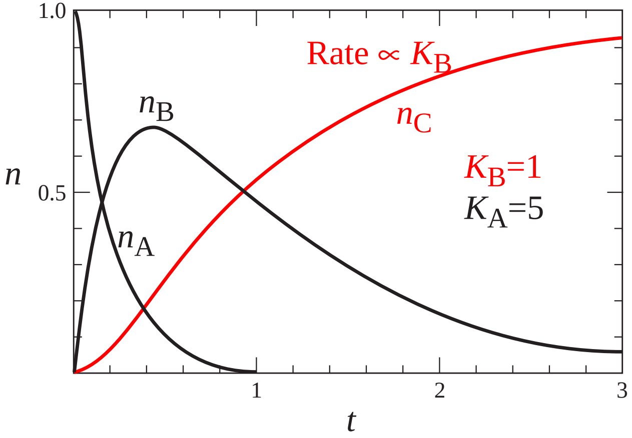
  $$\frac{dn_A}{dt} = -K_A n_A$$

  $$\frac{dn_B}{dt} = K_A n_A - K_B n_B$$

  $$\frac{dn_C}{dt} = K_B n_B$$

- The smallest K determines the rate





BIMOLECULAR REACTION WITH PHOTON EMISSION

- The reaction
$$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{AB}$$
can not conserve energy and momentum [p. 152, 165]
- This reaction can proceed by the chain
$$\boxed{\mathrm{A} + \mathrm{B} \underset{K_{-1}}{\overset{K_2}{\rightleftarrows}} \mathrm{AB}^* \xrightarrow{K_1} \mathrm{AB} + \hbar\omega}$$
- Solve for n_{AB^*}
$$\frac{dn_{AB^*}}{dt} = K_2 n_A n_B - K_{-1} n_{AB^*} - K_1 n_{AB^*} = 0$$
$$n_{AB^*} = \frac{K_2}{K_{-1} + K_1} n_A n_B$$
- The rate of formation of AB is then
$$\boxed{\frac{dn_{AB}}{dt} = K_1 n_{AB^*} = \frac{K_1 K_2}{K_{-1} + K_1} n_A n_B}$$
with an effective second order rate coefficient
$$K_2' = \frac{K_1 K_2}{K_{-1} + K_1}$$
- But this reaction is not elementary

CHEMICAL FUNDAMENTALS

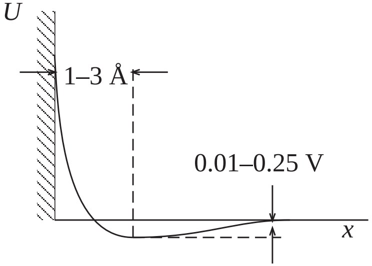
ADSORPTION AND DESORPTION

ADSORPTION

- Reaction of a molecule with the surface

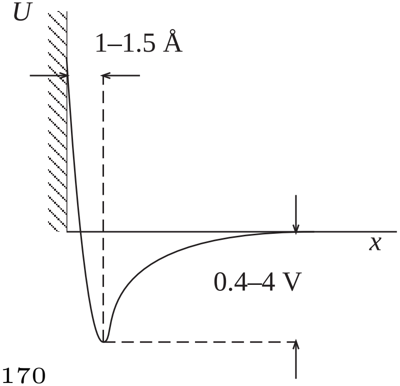
$$\boxed{\mathrm{A} + \mathrm{S} \underset{K_d}{\overset{K_a}{\rightleftharpoons}} \mathrm{A\!:\!S}}$$

- Physisorption (due to weak van der Waals forces)



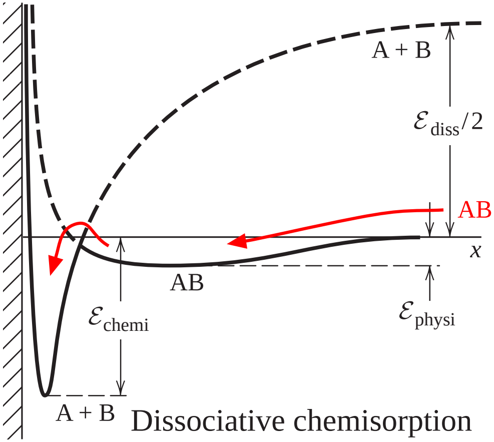
— $\mathcal{E}_{\text{physi}} \sim 0.01$–$0.25$ V
— Can move along surface
— $\omega_{\text{vib}} \sim 10^{12}$–$10^{13}$ s^{-1}
$\sim$ lifetime on surface

- Chemisorption (due to formation of chemical bonds)

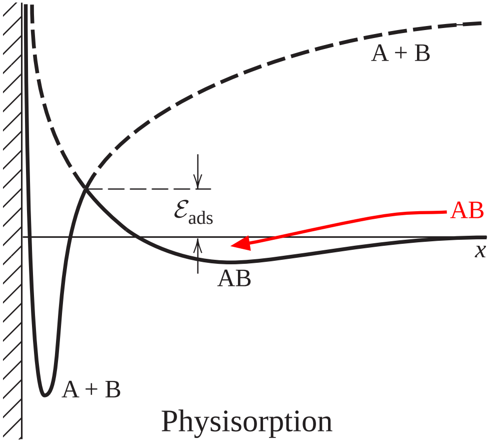


— $\mathcal{E}_{\text{chemi}} \sim 0.4$–$4$ V
— Tightly bound to site

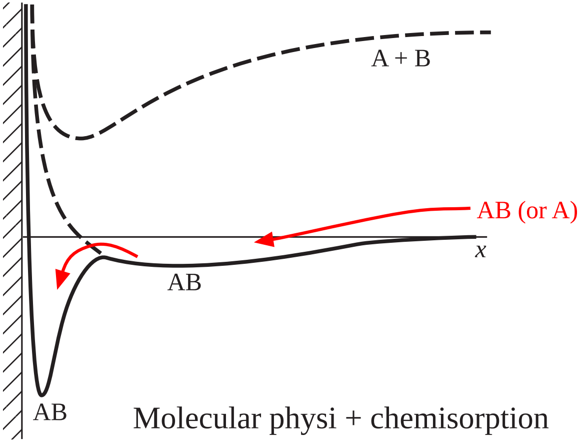
TYPES OF ADSORPTION



Dissociative chemisorption



Physisorption



Molecular physi + chemisorption

STICKING COEFFICIENT

- Adsorbed flux [p. 17]

$$\boxed{\Gamma_{\rm ads} = s\Gamma_A = s\cdot\frac{1}{4}n_{AS}\bar{v}_A}$$

$s(\theta, T)$ = sticking coefficient

θ = fraction of surface sites covered with absorbate

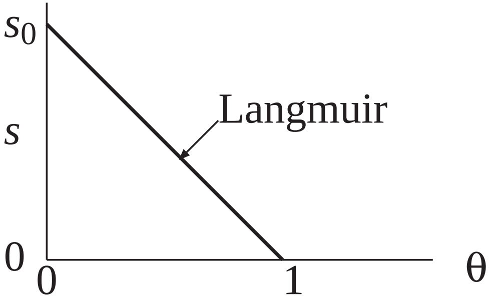
n_{AS} = gas phase density of A near the surface

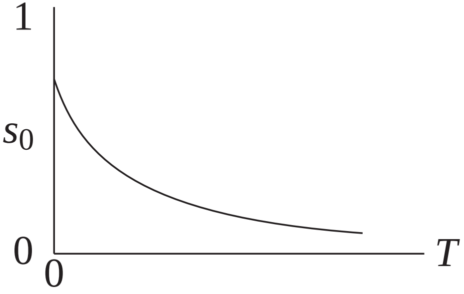
$\bar{v}_A = (8kT_A/\pi M_A)^{1/2}$ = mean thermal speed of A

- Langmuir kinetics

$$\boxed{s(\theta, T) = s_0(1-\theta)}$$

s_0 = zero-coverage sticking coefficient ($s_0 \sim 10^{-6}$–1)





DESORPTION

$$\boxed{\mathrm{A}\!:\!\mathrm{S} \xrightarrow{K_d} \mathrm{A} + \mathrm{S}}$$

- Rate coefficient has Arrhenius form [p. 161]

$$\boxed{K_d = K_{d0}\, \mathrm{e}^{-\mathcal{E}_{\mathrm{desor}}/\mathrm{T}}}$$

where $\mathcal{E}_{\mathrm{desor}} = \mathcal{E}_{\mathrm{chemi}}$ or $\mathcal{E}_{\mathrm{physi}}$

- Pre-exponential factors are typically

$$\begin{aligned} K_{d0} &\sim 10^{14}\text{–}10^{16}\ \mathrm{s}^{-1} \quad \text{physisorption} \\ &\sim 10^{13}\text{–}10^{15}\ \mathrm{s}^{-1} \quad \text{chemisorption} \end{aligned}$$

ADSORPTION-DESORPTION KINETICS

- Consider the reactions

$$\boxed{\mathrm{A} + \mathrm{S} \underset{K_d}{\overset{K_a}{\rightleftarrows}} \mathrm{A}\colon\mathrm{S}}$$

- Adsorbed flux is [p. 172]

$$\Gamma_{\mathrm{ads}} = K_a n_{AS} n_0'(1-\theta)$$

n_0' = area density (m^{-2}) of adsorption sites

n_{AS} = the gas phase density at the surface

$$K_a = s_0 \frac{1}{4} \bar{v}_A / n_0' \qquad [\mathrm{m}^3/\mathrm{s}] \qquad \text{(adsorption rate coef)}$$

- Desorbed flux is [p. 173]

$$\Gamma_{\mathrm{desor}} = K_d n_0' \theta$$

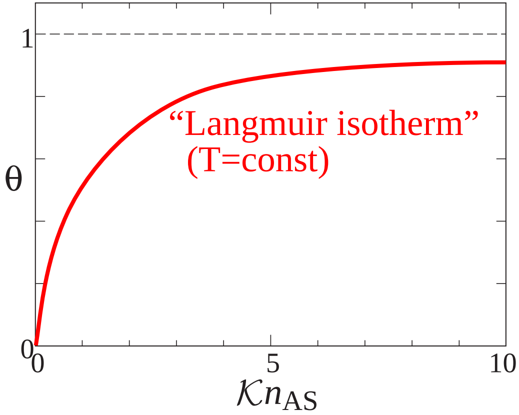
$$K_d = K_{d0}\, \mathrm{e}^{-\mathcal{E}_{\mathrm{desor}}/\mathrm{T}} \qquad [\mathrm{s}^{-1}] \qquad \text{(desorption rate coef)}$$

ADSORPTION-DESORPTION KINETICS (CONT'D)

- Equate adsorption and desorption fluxes ($\Gamma_{\text{ads}} = \Gamma_{\text{desor}}$)

$$\boxed{\Longrightarrow \theta = \frac{\mathcal{K} n_{AS}}{1 + \mathcal{K} n_{AS}}}$$

where $\mathcal{K} = K_a / K_d$



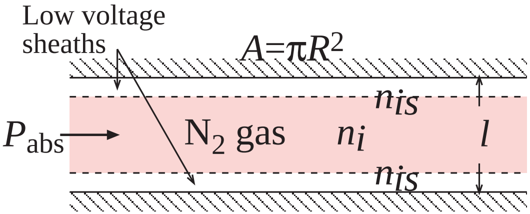
- Note that $T\uparrow$ $\Rightarrow$ $\mathcal{K}\downarrow$ $\Rightarrow$ $\theta\downarrow$

CHEMISTRY IN DISCHARGES

NEUTRAL FREE RADICALS

PLANE-PARALLEL DISCHARGE

- Example of N_2 discharge with low fractional ionization ($n_g \approx n_{N_2}$) and planar 1D geometry ($l \ll R$)



- Determine T_e

  Ion particle balance is [p. 46]

$$K_{iz} n_g n_i l A \approx 2 n_{is} u_B A$$

where $n_{is} = h_l n_i$ with $h_l = 0.86/(3 + l/2\lambda_i)^{1/2}$ [p. 43]

$$\boxed{\frac{K_{iz}(T_e)}{u_B(T_e)} \approx \frac{2h_l}{n_g l} \Longrightarrow T_e}$$

PLANE-PARALLEL DISCHARGE (CONT'D)

- Determine edge plasma density n_{is}
  Overall discharge power balance [p. 50] gives the plasma density at the sheath edge

$$\boxed{n_{is} \approx \frac{P_{\text{abs}}}{2e\mathcal{E}_T u_B A}}$$

- Determine central plasma density

$$\boxed{n_i = \frac{n_{is}}{h_l}}$$

- Determine ion flux to the surface

$$\boxed{\Gamma_{is} \approx n_{is} u_B}$$

- Determine ion bombarding energy

$$\boxed{\mathcal{E}_i = 5.2\,\mathrm{T}_e}$$

FREE RADICAL BALANCE

- For nitrogen

$$\boxed{\mathrm{e} + \mathrm{N}_2 \xrightarrow{K_\text{diss}} 2\mathrm{N} + \mathrm{e}}$$

- Assume low fractional dissociation and loss of N atoms only due to a vacuum pump S_p (m^3/s)

$$Al\frac{dn_\mathrm{N}}{dt} = Al\,2K_\text{diss}n_g n_i - S_p n_{\mathrm{N}S} = 0$$

- Solve for free radical density at the surface

$$\boxed{n_{\mathrm{N}S} = K_\text{diss}\frac{2Aln_g}{S_p}n_i}$$

- Use n_i [p. 178] to find

$$\boxed{n_{\mathrm{N}S} = K_\text{diss}\frac{2n_g l}{S_p}\frac{P_\text{abs}}{2e\mathcal{E}_T h_l u_B}}$$

FREE RADICAL BALANCE (CONT'D)

- Flux of N atoms to the surface

$$\boxed{\Gamma_{\mathrm{N}S} = \frac{1}{4} n_{\mathrm{N}S} \bar{v}_{\mathrm{N}}}$$

where $\bar{v}_{\mathrm{N}} = (8kT_{\mathrm{N}}/\pi M_{\mathrm{N}})^{1/2}$

- At low pressures, T_e, K_{diss}, $\mathcal{E}_T$ and h_l do not vary much with pressure

$$\Gamma_{NS} \propto \frac{n_g P_{\mathrm{abs}}}{S_p}$$

- The ion flux $\Gamma_{is} = n_{is} u_B$ scales as

$$\Gamma_{is} \propto P_{\mathrm{abs}}$$

$$\boxed{\text{Neutral/ion flux ratio} \propto n_g/S_p\text{, independent of power}}$$

LOADING EFFECT

- Consider recombination and/or reaction of N atoms on surfaces

$$\mathrm{N} + \mathrm{wall} \xrightarrow{\gamma_{\mathrm{rec}}} \tfrac{1}{2}\mathrm{N}_2$$

$$\mathrm{N} + \mathrm{substrate} \xrightarrow{\gamma_{\mathrm{reac}}} \mathrm{product}$$

- Pumping speed S_p in the expression for n_{NS} [p. 179] is replaced by

$$S_p \longrightarrow S_p + \gamma_{\mathrm{rec}}\frac{1}{4}\bar{v}_{\mathrm{N}}(2A - A_{\mathrm{subs}}) + \gamma_{\mathrm{reac}}\frac{1}{4}\bar{v}_{\mathrm{N}}A_{\mathrm{subs}}$$

  A_{subs} is the part of the substrate area reacting with N atoms

- $n_{\mathrm{N}S}$ (and $\Gamma_{\mathrm{N}S}$) are reduced due to recombination and reaction losses

- Therefore etch and deposition rates now depend on the part of the substrate area A_{subs} exposed to the free radicals, a *loading effect*

CHEMISTRY IN DISCHARGES

NEGATIVE IONS

INTRODUCTION

- Most materials processes use gases containing O, Cl, F, or Br-atoms

  $\Longrightarrow$ copious production of negative ions

- Negative ions tend to trap in the center of the discharge

  $\Longrightarrow$ volume production rate = volume loss rate (no wall losses)

- Negative ions complicate discharge analysis
  - Additional particle conservation equation is required
  - Ambipolar diffusion coefficient D_a is modified
  -

AMBIPOLAR DIFFUSION WITH NEGATIVE IONS

- Positive ion force equation [p. 18]

$$0 = en_+E - e\mathrm{T}_i\nabla n_+ - M\nu_i \underbrace{n_+u_+}_{\Gamma_+}$$

with ν_i the ion-neutral collision frequency [p. 38]

- Solve to find drift-diffusion equation for flux

$$\boxed{\Gamma_+ = -D_+\nabla n_+ + n_+\mu_+E}$$

with diffusion coefficient $D_+ = e\mathrm{T}_i/M\nu_i$, mobility $\mu_+ = e/M\nu_i$

- Electrons and negative ions are Boltzmann [p. 19]

$$n_e = n_{e0}\,\mathrm{e}^{\Phi/\mathrm{T}_e}, \qquad n_- = n_{-0}\,\mathrm{e}^{\Phi/\mathrm{T}_i}$$

- Plasma must be quasineutral [p. 21]

$$n_+ = n_- + n_e$$

- Solve to obtain Fick's law with ambipolar diffusion coefficient D_{a+}

$$\boxed{\Gamma_+ = -D_{a+}\nabla n_+}$$

AMBIPOLAR DIFFUSION COEFFICIENT

- Diffusion coefficient D_{a+} depends on electronegativity α and ratio γ of electron/ion temperature

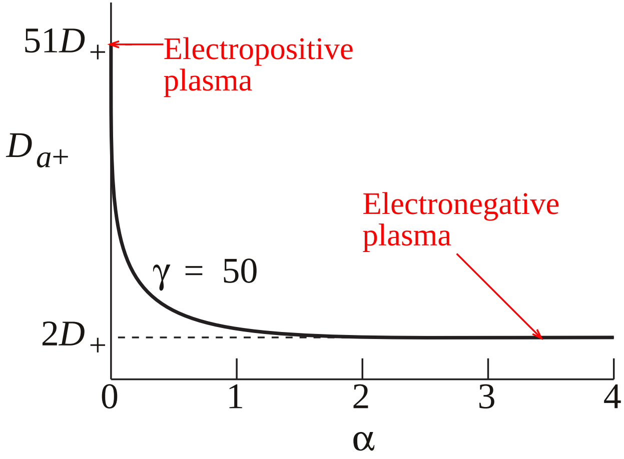
$$\boxed{\alpha \equiv \frac{n_-}{n_e}, \qquad \gamma \equiv \frac{\mathrm{T}_e}{\mathrm{T}_i} \sim 50}$$

- Electropositive plasma has $\alpha \ll 1$ and $D_{a+} = D_+(1+\gamma)$

  Electronegative plasma has $\alpha \gtrsim 1$ and $D_{a+} = 2D_+$

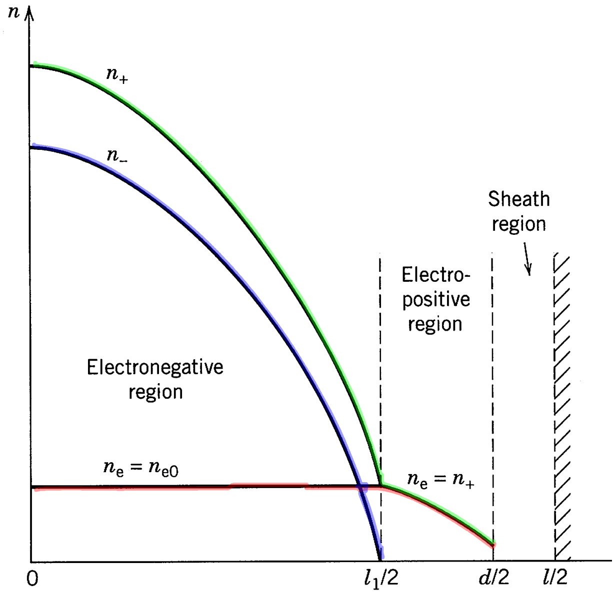
- Approximate form of diffusion coefficient

$$\boxed{D_{a+} \approx D_+ \frac{1+\gamma+2\gamma\alpha}{1+\gamma\alpha}}$$

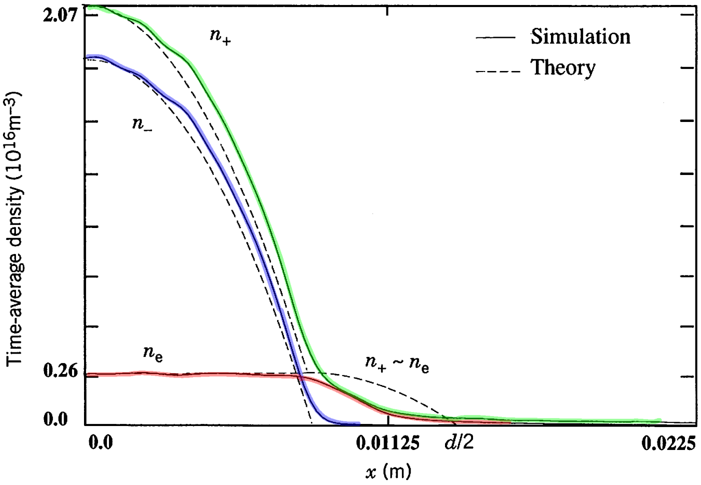


SPATIAL STRUCTURE OF EN DISCHARGE

- Discharge stratifies into EN core, EP edge, and sheath
- Electron density $n_e = \text{const}$ and negative ion density n_- is parabolic in the EN core



Theory



PIC simulation for $p = 50$ mTorr oxygen with $l = 4.5$ cm

CHEMISTRY IN DISCHARGES

EXAMPLE OF OXYGEN

BASIC CONSTANTS FOR OXYGEN

	State	$\mathcal{E}_{\text{diss}}$ (V)	$\mathcal{E}_{\text{iz}}$ (V)	Lifetime (s)	α_p (a_0^3)
→	$O(^3P)$	—	13.61	—	5.4
→	$O^-(^2P)$	—	1.463	—	—
	$O^*(^1D)$	—	11.64	147.1	—
→	$O_2(^3\Sigma_g^-)$	5.12	12.14	—	10.6
→	$O_2^+(^2\Pi_g)$	6.59	—	—	
	$O_2^-(^2\Pi_g)$	4.06	0.44	—	—
	$O_2^*(^1\Delta_g)$	4.14	11.16	2700	—
	O_3	1.05	12.67	—	
	O_3^-	1.69	2.10	—	

SECOND ORDER RATE COEFFICIENTS FOR OXYGEN

#	Reaction	Rate Coefficient ($\mathrm{cm^3/s}$)	Source
Reactions among e, O_2, O_2^+, and O^-			
1	$e + O_2$ momentum transfer	$4.7\mathrm{E{-}8}T_e^{0.5}$	a
2	$e + O_2 \rightarrow O^- + O$	$8.8\mathrm{E{-}11}\exp(-4.4/T_e)$	b
3	$e + O_2 \rightarrow 2O + e$	$4.2\mathrm{E{-}9}\exp(-5.6/T_e)$	d
4	$e + O_2 \rightarrow O_2^+ + 2e$	$9.0\mathrm{E{-}10}T_e^2\exp(-12.6/T_e)$	d
5	$e + O^- \rightarrow O + 2e$	$2.0\mathrm{E{-}7}\exp(-5.5/T_e)$	b
6	$e + O_2^+ \rightarrow 2O$	$5.2\mathrm{E{-}9}/T_e$	k
7	$O^- + O_2^+ \rightarrow O + O_2$	$(0.96,2)\mathrm{E{-}7}(300/T)^{0.5}$	e,k
8	$O^- + O \rightarrow O_2 + e$	$(1.4,5)\mathrm{E{-}10}$	e,k
9	$O^- + O_2^+ \rightarrow 3O$	$1\mathrm{E{-}7}$	k
Addition of O^+			
10	$e + O_2 \rightarrow O^- + O^+ + e$	$7.1\mathrm{E{-}11}T_e^{0.5}\exp(-17/T_e)$	r
11	$e + O_2 \rightarrow O + O^+ + 2e$	$5.3\mathrm{E{-}10}T_e^{0.9}\exp(-20/T_e)$	b
12	$e + O \rightarrow O^+ + 2e$	$9.0\mathrm{E{-}9}T_e^{0.7}\exp(-13.6/T_e)$	d
13	$O^- + O^+ \rightarrow 2O$	$(2.7,2)\mathrm{E{-}7}(300/T)^{0.5}$	e,k
14	$O^+ + O_2 \rightarrow O + O_2^+$	$2.0\mathrm{E{-}11}(300/T)^{0.5}$	e

SECOND ORDER RATE COEFFICIENTS FOR OXYGEN (CONT'D)

#	Reaction	Rate Coefficient (cm^3/s)	Source
Addition of metastable $O_2^*(^1\Delta_g)$*; see note f below*			
15	$e + O_2 \rightarrow O_2^* + e$	$1.7E\text{–}9\exp(-3.1/T_e)$	b
16	$e + O_2^* \rightarrow e + O_2$	$5.6E\text{–}9\exp(-2.2/T_e)$	b
17	$O_2^* + O_2 \rightarrow 2O_2$	$2.2E\text{–}18(T/300)^{0.8}$	ke
18	$O_2^* + O \rightarrow O_2 + O$	(1.0,7)E–16	e,k
Addition of metastable $O(^1D)$			
19	$e + O_2 \rightarrow O + O^* + e$	$5.0E\text{–}8\exp(-8.4/T_e)$	d
20	$e + O \rightarrow O^* + e$	$4.2E\text{–}9\exp(-2.25/T_e)$	d
21	$e + O^* \rightarrow e + O$	8E–9	d
22	$e + O^* \rightarrow O^+ + 2e$	$9.0E\text{–}9T_e^{0.7}\exp(-11.6/T_e)$	d
23	$O^* + O \rightarrow 2O$	8.0E–12	e
24	$O^* + O_2 \rightarrow O + O_2$	$(6.4,7.0)E\text{–}12\exp(67/T)$	k,e
25	$O^* + O_2 \rightarrow O + O_2^*$	1.0E–12	e

SECOND ORDER RATE CONSTANTS FOR OXYGEN (CONT'D)

#	Reaction	Rate Coefficient (cm^3/s)	Source
Addition of selected reactions for O_2^- *and* O_3			
26	$O^- + O_2 \rightarrow O_3 + e$	5E–15	k
27	$e + O_3 \rightarrow O_2^- + O$	1E–9	k
28	$O^- + O_2^* \rightarrow O_3 + e$	3E–10	k
29	$O^- + O_2^* \rightarrow O_2^- + O$	1E–10	k
30	$O_2^- + O_2^+ \rightarrow 2O_2$	$2E\text{–}7(300/T)^{0.5}$	k
31	$O_2^- + O^+ \rightarrow O_2 + O$	$2E\text{–}7(300/T)^{0.5}$	k
32	$O_3 + O_2 \rightarrow O_2 + O + O_2$	$7.3E\text{–}10\exp(-11400/T)$	e

Notes and references

[1] T_e in volts and heavy particle temperature T in kelvins

[2] Two values from different sources are sometimes given in parentheses

[a] Based on cross sections of Phelps (1985)

[b] Based on data of Eliasson and Kogelschatz (1986)

[d] Based on data of Lee et al (1993)

[e] Eliasson and Kogelschatz (1986)

[f] Reactions 1–4, 10–11 for O_2^* have activation energies reduced by ∼ 1 V

[k] Kossyi et al (1992)

[r] Based on Rapp and Briglia (1965)

THIRD ORDER RATE COEFFICIENTS FOR OXYGEN

#	Reaction	Rate Coefficient (cm^6/s)	Source
Reactions among e, O_2, O_2^+, and O^-			
1	$e + e + O_2^+ \rightarrow e + O_2$	$1E{-}19(0.026/T_e)^{4.5}$	ke
2	$e + O_2^+ + O_2 \rightarrow O_2 + O_2$	$6E{-}27(0.026/T_e)^{1.5}$, $1E{-}26$	k,e
3	$e + O + O_2 \rightarrow O^- + O_2$	$1E{-}31$	ke
4	$O^- + O_2^+ + O_2 \rightarrow O + O_2 + O_2$	$2E{-}25(300/T)^{2.5}$	k
5	$O + O + O_2 \rightarrow O_2 + O_2$	$2.45E{-}31T^{-0.63}$	k
		$1.3E{-}32(300/T)\exp(-170/T)$	e
6	$O + O + O \rightarrow O_2 + O$	$6.2E{-}32\exp(-750/T)$	e
Addition of O^+			
7	$e + e + O^+ \rightarrow e + O$	$1E{-}19(0.026/T_e)^{4.5}$	ke
8	$e + O^+ + O_2 \rightarrow O + O_2$	$6E{-}27(0.026/T_e)^{1.5}$, $1E{-}26$	k,e
9	$O^- + O^+ + O_2 \rightarrow O_2 + O_2$	$2E{-}25(300/T)^{2.5}$, $2E{-}25$	k,e
10	$O^- + O^+ + M \rightarrow O + O + M$	$2E{-}25(300/T)^{2.5}$	k
11	$O^+ + O + O_2 \rightarrow O_2^+ + O_2$	$1E{-}29$	ke
Addition of metastable $O(^1D)$			
12	$O + O^* + O_2 \rightarrow O_2 + O_2$	$9.9E{-}33$	e

Notes and references

[1] T_e in volts and T in kelvins; M denotes either O_2 or O.

[e] Eliasson and Kogelschatz (1986); [k] Kossyi et al (1992)

OXYGEN DISCHARGE

- Simplified set of volume reactions for O_2^+, O^- and electrons

$$\left.\begin{array}{ll}
e + O_2 \rightarrow O_2^+ + 2e & \text{(ionization)} \\
e + O_2 \rightarrow O^- + O & \text{(dissociative attachment)} \\
O_2^+ + O^- \rightarrow O_2 + O & \text{(recombination)}
\end{array}\right.$$

$$\left.\begin{array}{ll}
O_2^+ + O_2 \rightarrow O_2^+ + O_2 & \text{(elastic scattering)} \\
O_2^+ + O_2 \rightarrow O_2 + O_2^+ & \text{(charge transfer)} \\
O^- + O_2 \rightarrow O^- + O_2 & \text{(elastic scattering)}
\end{array}\right\}\text{momentum}$$

$$\text{(momentum transfer} \Longrightarrow \nu_i \Longrightarrow D_+ \text{ [p. 184])}$$

UNIFORM DENSITY MODEL

- Conservation of positive ions, negative ions and energy in plasma volume $\mathcal{V}$ having surface loss area A

$$K_{\mathrm{iz}} n_e n_g \mathcal{V} - K_{\mathrm{rec}} n_+ n_- \mathcal{V} - \Gamma_+ A = 0 \quad \text{(vol.+surf. loss)}$$

$$K_{\mathrm{att}} n_e n_g \mathcal{V} - K_{\mathrm{rec}} n_+ n_- \mathcal{V} = 0 \quad \text{(neg. ion bal)}$$

$$P_{\mathrm{abs}} = e\mathcal{E}_c K_{\mathrm{iz}} n_e n_g \mathcal{V} + \Gamma_+ A\, e(\mathcal{E}_e + \mathcal{E}_i) \quad \text{(vol.+surf. loss)}$$

- Quasi-neutrality [p. 21]

$$n_+ = n_- + n_e$$

- Electronegative discharge $\alpha \gtrsim 1$

$$\Gamma_+ = -D_{a+} \nabla n_+ \approx 2D_+ \cdot \frac{n_+}{d_{\mathrm{eff}}} \qquad [p.\ 184, 185]$$

where d_{eff} = effective length for diffusive ion loss to walls

- Solve to find n_+, n_-, n_e, and T$_e$, for specified pressure (n_g), absorbed power (P_{abs}) and geometry ($\mathcal{V}$, A, and d_{eff}).

(the solution is messy and not particularly illuminating)

NEGATIVE ION BALANCE

- Negative ion balance gives the electronegativity [p. 194]

$$\alpha \equiv \frac{n_-}{n_e} = \frac{K_{\text{att}} n_g}{K_{\text{rec}} n_+}$$

$$\boxed{\begin{array}{l} \text{High pressure/low plasma density} \Longrightarrow \text{high } \alpha \\ \text{Low pressure/high plasma density} \Longrightarrow \text{low } \alpha \end{array}}$$

- Capacitive discharges tend to have higher electronegativities (higher pressures, lower densities)
- Inductive discharges tend to have lower electronegativities (lower pressures, higher densities)

CHEMISTRY IN DISCHARGES

TIME-VARYING GLOBAL MODELS

EXAMPLE GLOBAL MODEL ASSUMPTIONS

- Cylindrical geometry with radius R and length l
- Uniform species densities for O_2^+, O^-, O-atoms, and electrons in the volume $\mathcal{V} = \pi R^2 l$
- Low fractional dissociation and ionization $\Longrightarrow n_g = n_{O_2} = \text{const}$
- Neglect O^+ ions, metastable O-atoms and O_2, O_3, etc (Low pressure and low power)
- Positive ion loss flux to the walls [p. 184, 194]

$$\Gamma_{O_2^+} = D_{a+} \cdot \frac{n_{O_2^+}}{d_{\text{eff}}}$$

- O-atoms lost to walls by recombination [p. 181]

$$O \xrightarrow{\gamma_{\text{rec}}} \tfrac{1}{2} O_2 \ \text{(on wall)}$$

with loss flux

$$\Gamma_O = \gamma_{\text{rec}} \cdot \tfrac{1}{4} n_O \bar{v}_O$$

with $\bar{v}_O = (8kT_O/\pi M_O)^{1/2}$

DIFFERENTIAL EQUATIONS FOR OXYGEN

- Particle balance using volume reactions 1–9 [p. 189]

$$\frac{dn_{\mathrm{O}_2^+}}{dt} = \text{volume generation} - \text{volume losses} \underbrace{-\nu_{\mathrm{O}_2^+} n_{\mathrm{O}_2^+}}_{\text{surface loss}}$$

$$\frac{dn_{\mathrm{O}^-}}{dt} = \text{volume generation} - \text{volume losses}$$

$$\frac{dn_{\mathrm{O}}}{dt} = \text{volume generation} - \text{volume losses} \underbrace{-\nu_{\mathrm{O}} n_{\mathrm{O}}}_{\text{surface loss}}$$

- Power balance [p. 50]

$$\frac{d}{dt}\left(\frac{3}{2} e n_e \mathrm{T}_e\right) = \frac{P_{\mathrm{abs}}}{\mathcal{V}} - e\mathcal{E}_c K_{\mathrm{iz}} n_e n_{\mathrm{O}_2} - e(\mathcal{E}_e + \mathcal{E}_i)\nu_{\mathrm{O}_2^+} n_{\mathrm{O}_2^+}$$

- Quasi-neutrality [p. 21] gives

$$n_e = n_{\mathrm{O}_2^+} - n_{\mathrm{O}^-}$$

DIFFERENTIAL EQUATIONS FOR OXYGEN (CONT'D)

- Second order rate coefficients $K(\mathrm{T}_e)$ given on [p. 189]
- First order rate coefficient $\nu_{\mathrm{O}_2^+}$ for positive ion loss to walls [p. 197]

$$\nu_{\mathrm{O}_2^+} = \frac{D_{a+}}{d_{\mathrm{eff}}} \frac{A}{\mathcal{V}}$$

with $A = 2\pi R^2 + 2\pi R l$, $\mathcal{V} = \pi R^2 l$, and a diffusion length d_{eff}

$$\frac{1}{d_{\mathrm{eff}}^2} = \left(\frac{\pi}{l}\right)^2 + \left(\frac{2.405}{R}\right)^2$$

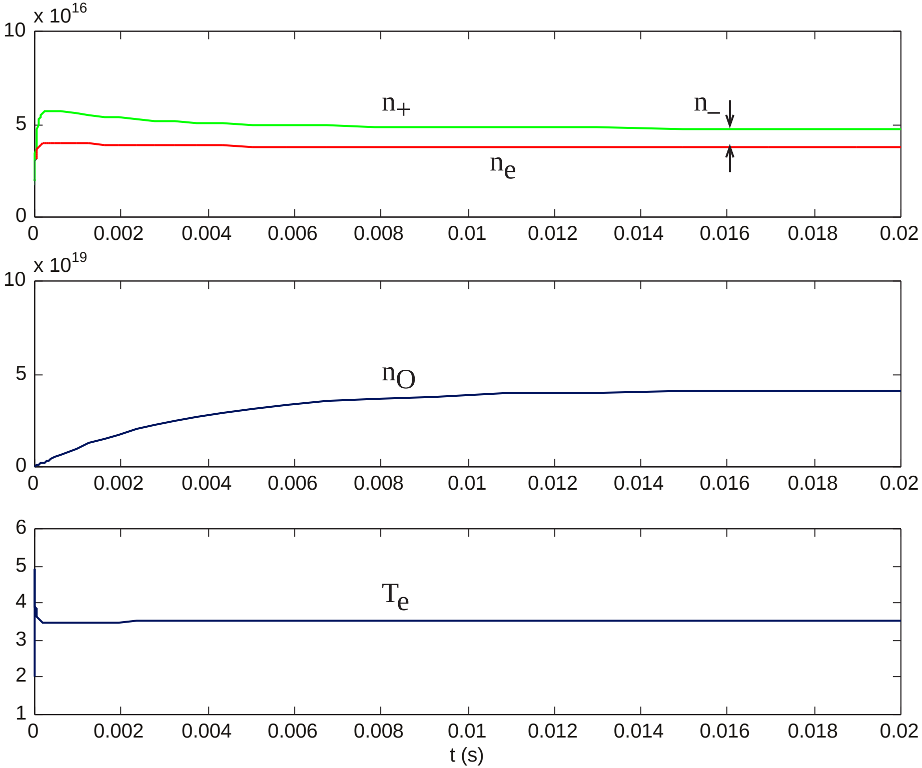
- First order rate coefficient ν_{O} for O-atom loss to walls [p. 197]

$$\nu_{\mathrm{O}} = \gamma_{\mathrm{rec}} \frac{\bar{v}_{\mathrm{O}} A}{4\mathcal{V}}$$

- Solve using Matlab/Mathematica/etc differential equation solver

LOW PRESSURE SOLUTION

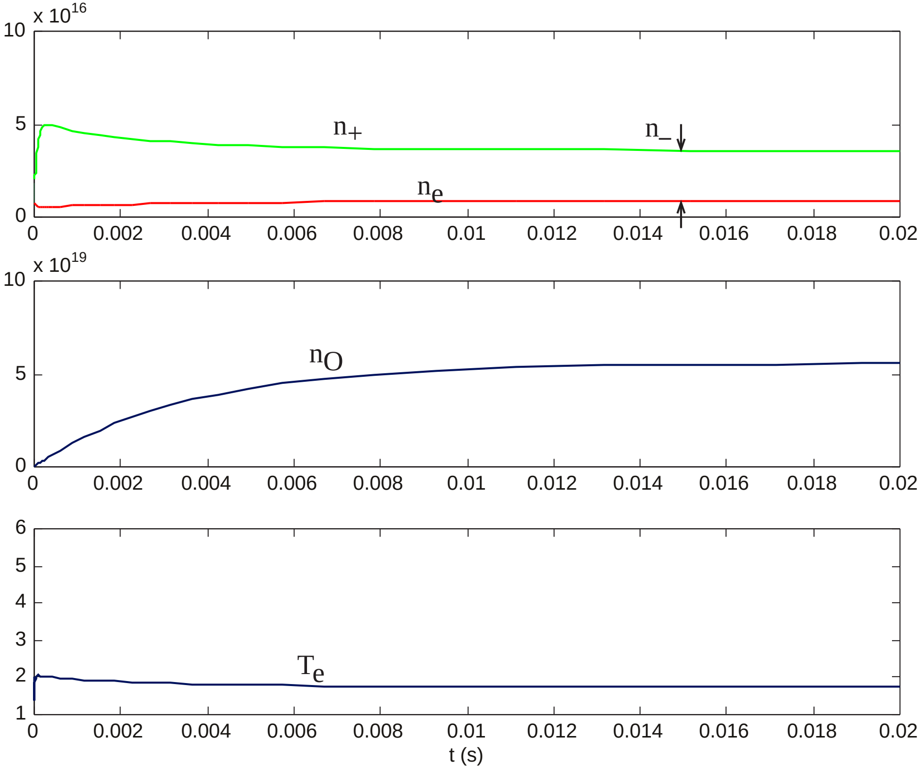
- $p = 10$ mTorr, $P_{\mathrm{abs}} = 30$ W, $R = 5$ cm, $l = 10$ cm, $\gamma_{\mathrm{rec}} = 0.02$



- Surface (diffusive) losses dominate
- Electronegativity is weak ($\alpha < 1$)

HIGH PRESSURE SOLUTION

- $p = 300$ mTorr, $P_{\mathrm{abs}} = 30$ W, $R = 5$ cm, $l = 10$ cm, $\gamma_{\mathrm{rec}} = 0.02$



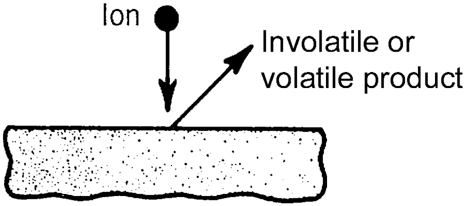
- Volume losses are most important
- Electronegativity is fairly high ($\alpha \approx 3.5$)

CHEMISTRY IN DISCHARGES

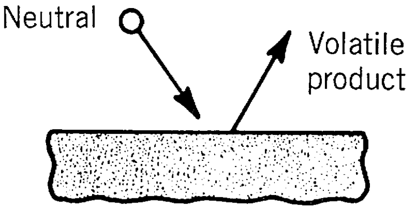
ETCHING PROCESSES

FOUR ETCHING PROCESSES

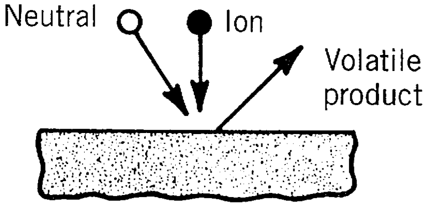
Sputtering



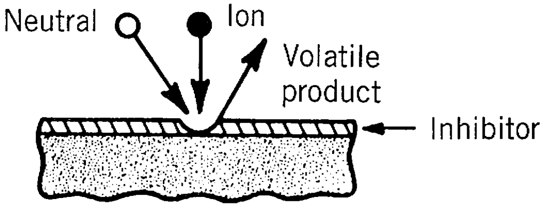
Chemical etching



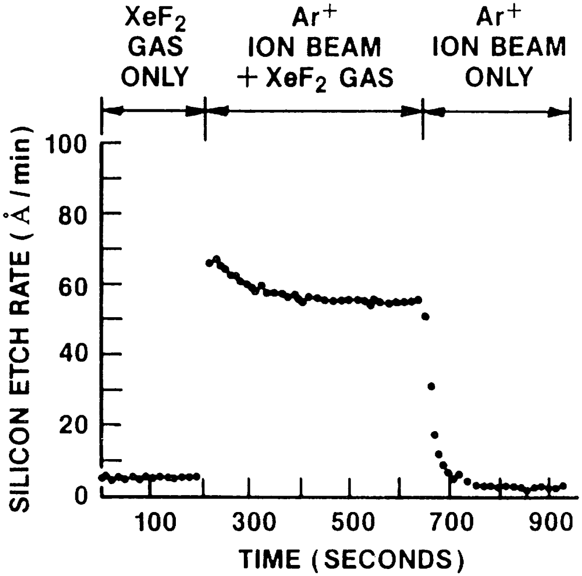
Ion-enhanced etching



Ion-enhanced inhibitor etching



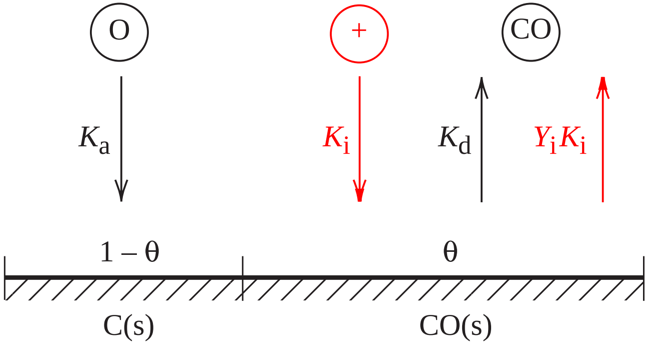
ION-ENHANCED PLASMA ETCHING



1. Low chemical etch rate of silicon substrate in XeF_2 etchant gas
2. Tenfold increase in etch rate with XeF_2 + 500 V argon ions, simulating ion-enhanced plasma etching
3. Very low “etch rate” due to the physical sputtering of silicon by ion bombardment alone

STANDARD MODEL OF ETCH KINETICS

- Site model for O atom etching of a carbon substrate [p. 174–175]



- Let $n_0' =$ active surface sites$/\mathrm{m}^2$
- Let $\theta =$ fraction of surface sites covered with C : O bonds

$$\mathrm{O(g) + C(s)} \xrightarrow{K_a} \mathrm{C:O} \qquad \text{(O atom adsorption)}$$

$$\mathrm{C:O} \xrightarrow{K_d} \mathrm{CO(g)} \qquad \text{(CO thermal desorption)}$$

$$\text{ion} + \mathrm{C:O} \xrightarrow{Y_iK_i} \mathrm{CO(g)} \qquad \text{(CO ion-assisted desorption)}$$

SURFACE COVERAGE

- The steady-state surface coverage is found from [p. 174–175]

$$\frac{d\theta}{dt} = K_a n_{\rm OS}(1-\theta) - K_d\theta - Y_i K_i n_{\rm is}\theta = 0$$

- $n_{\rm OS}$ is the O-atom density near the surface

  $n_{\rm is}$ is the ion density at the plasma-sheath edge

- K_a is the rate coefficient for O-atom adsorption [p. 174]

  K_d is the rate coefficient for thermal desorption of CO [p. 174]

  $K_i = u_B/n_0'$ is the rate coefficient for ions incident on the surface

- Y_i is the yield of CO molecules desorbed per ion incident on a fully covered surface

  Typically $Y_i \gg 1$ and $Y_i \approx Y_{i0}\sqrt{\mathcal{E}_i - \mathcal{E}_{\rm thr}}$ (as for sputtering)

$$\Longrightarrow \theta = \frac{K_a n_{\rm OS}}{K_a n_{\rm OS} + K_d + Y_i K_i n_{\rm is}}$$

ETCH RATES

- The flux of CO molecules leaving the surface is

$$\Gamma_{\mathrm{CO}} = (K_d + Y_i K_i n_{\mathrm{is}})\, \theta\, n_0' \qquad [\mathrm{m}^{-2}\text{-}\mathrm{s}^{-1}]$$

  with n_0' = number of surface sites/m^2

- The vertical etch rate is

$$E_v = \frac{\Gamma_{\mathrm{CO}}}{n_{\mathrm{C}}} \qquad [\mathrm{m/s}]$$

  where n_{C} is the carbon atom density of the substrate

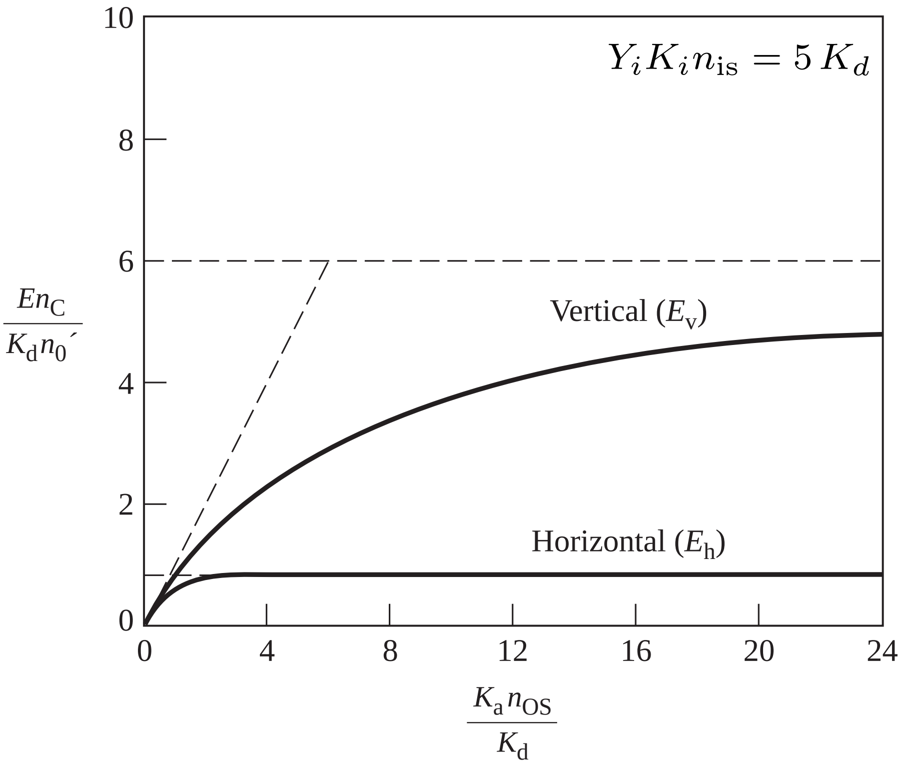
- The vertical (ion-enhanced) etch rate is

$$\boxed{E_v = \frac{n_0'}{n_{\mathrm{C}}} \frac{1}{\dfrac{1}{K_d + Y_i K_i n_{\mathrm{is}}} + \dfrac{1}{K_a n_{\mathrm{OS}}}}}$$

- The horizontal (non ion-enhanced) etch rate is

$$\boxed{E_h = \frac{n_0'}{n_{\mathrm{C}}} \frac{1}{\dfrac{1}{K_d} + \dfrac{1}{K_a n_{\mathrm{OS}}}}}$$

NORMALIZED ETCH RATES



- High O-atom flux ⇒ highest anisotropy $E_v/E_h = 1 + Y_i K_i n_{\text{is}}/K_d$
- Low O-atom flux ⇒ low etch rates with $E_v/E_h \to 1$

SIMPLEST MODEL OF ION-ENHANCED ETCHING

- In the usual ion-enhanced regime $Y_i K_i n_{\mathrm{is}} \gg K_d$

$$\boxed{\frac{1}{E_v} = n_C \left(\frac{1}{Y_i \underbrace{K_i n_{\mathrm{is}} n_0'}_{\Gamma_{\mathrm{is}}}} + \frac{1}{\underbrace{K_a n_{\mathrm{OS}} n_0'}_{\Gamma_{\mathrm{OS}}}} \right)}$$

- The ion and neutral fluxes and the yield (a function of ion energy) determine the ion-assisted etch rate
- The smallest flux (ions or neutrals) sets the etch rate (rate-limiting step) [p. 167]
- The discharge parameters set the ion and neutral fluxes and the ion bombarding energy

ADDITIONAL CHEMISTRY AND PHYSICS

- Sputtering of carbon

$$\Gamma_{\mathrm{C}} = \gamma_{\mathrm{sput}} K_i n_{\mathrm{is}} n_0'$$

- Associative and normal desorption of O atoms,

$$\mathrm{C : O} \longrightarrow \mathrm{C + O(g)}$$

$$\mathrm{2C : O} \longrightarrow \mathrm{2C + O_2(g)}$$

- Ion energy driven desorption of O atoms

$$\mathrm{ions + C : O} \longrightarrow \mathrm{C + O(g)}$$

- Formation and desorption of CO_2 as an etch product

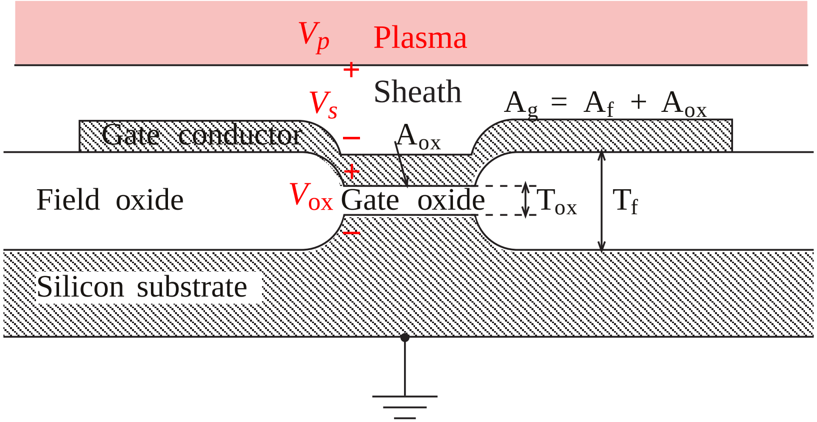
- Non-zero ion angular bombardment of sidewall surfaces

- Deposition kinetics (C-atoms, etc)

PLASMA-INDUCED CHARGING DAMAGE

DAMAGE DUE TO GATE OXIDE BREAKDOWN

- Consider grounded substrate with MOSFET exposed to plasma



- Typical gate oxide thickness $T_{\text{ox}} = 2\text{–}20$ nm
- Gate oxide voltage drop $V_{\text{ox}} = V_p - V_s$
  V_p = dc plasma potential (with respect to ground)
  V_s = dc voltage drop across sheath
- Breakdown when electric field in oxide satisfies

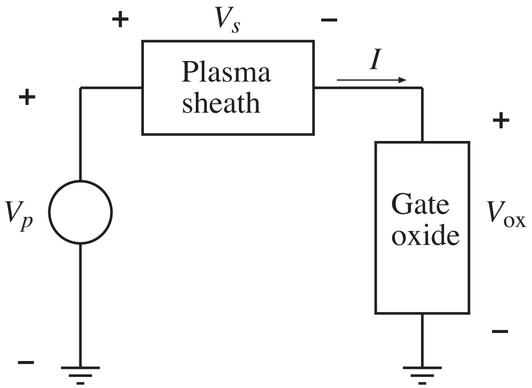
$$\boxed{E_{\text{ox}} = V_{\text{ox}}/T_{\text{ox}} \gtrsim E_{BD} \approx 10\ \text{MV/cm}}$$

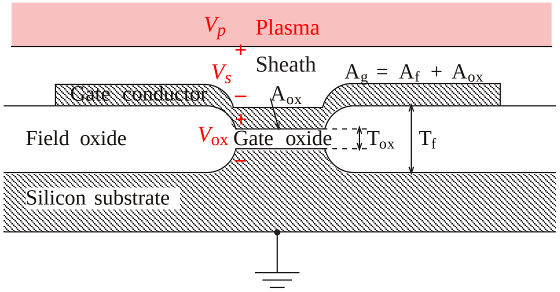
DAMAGE DUE TO GATE OXIDE CURRENT

- Even if $E_{\mathrm{ox}} < E_{BD}$, E_{ox} can induce a dc current flow through a thin gate oxide $\Rightarrow$ defects
- Fowler-Nordheim tunneling current density
$$J_{FN} = KE_{\mathrm{ox}}^2 \exp(-B/E_{\mathrm{ox}})$$
where $K = 20\ \mu\mathrm{A/cm}^2$ and $B \approx 250$ MV/cm
- Mean time for 50% of devices to fail
$$t_{BD} = t_0 \exp(G/E_{\mathrm{ox}})$$
where $t_0 = 10^{-11}$ s and $G \approx 350$ MV/cm
- Mean flow of charge for 50% device failures
$$\boxed{Q_{BD} = J_{FN} A_{\mathrm{ox}} t_{BD}}$$
- Even 1% of Q_{BD} can be deleterious (threshold voltage shifts)

OXIDE CURRENT FOR GROUNDED SUBSTRATE

- Both discharge and oxide have nonlinear I versus V relations





- Discharge conduction current I versus V_{ox} [p. 48, 119]

$$I = J_i A_g - J_{e0} A_g \exp\left(-\frac{V_p - V_{\text{ox}}}{\mathrm{T}_e}\right)$$

where $J_i = e n_s u_B$, $J_{e0} = \frac{1}{4} e n_s \bar{v}_e$, A_g = gate collecting area

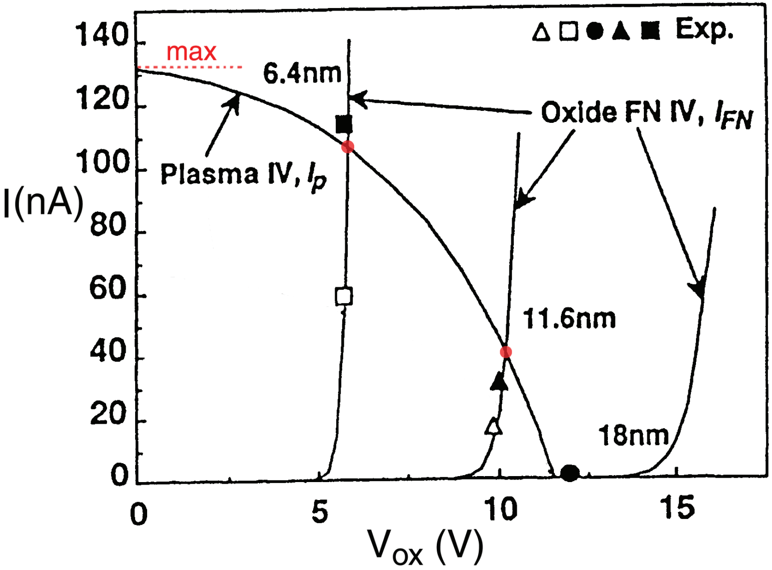
- Oxide Fowler-Nordheim tunneling current versus V_{ox} [p. 213]

$$I = \frac{K A_{\text{ox}} V_{\text{ox}}^2}{T_{\text{ox}}^2} \exp\left(-\frac{B T_{\text{ox}}}{V_{\text{ox}}}\right)$$

- Antenna ratio (AR) $= A_g/A_{\text{ox}}$

OXIDE CURRENT (CONT'D)

- Plot I versus V_{ox} for discharge and oxide
  The intersection is the operating point (I, V_{ox})



- For thin oxides, maximum current density

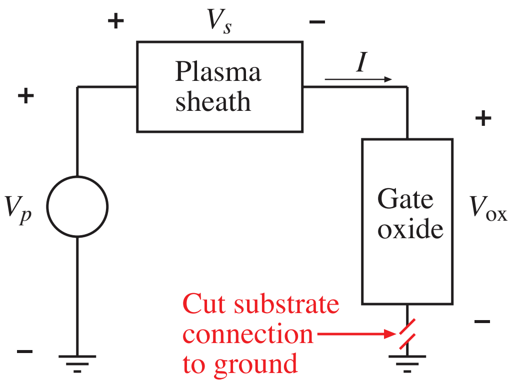
$$J_{\text{ox}} = \text{AR} \cdot J_i$$

$$\Longrightarrow \text{minimize antenna ratio}$$

- Thicker oxides $\Longrightarrow$ less gate oxide current

DAMAGE FROM NONUNIFORM PLASMAS

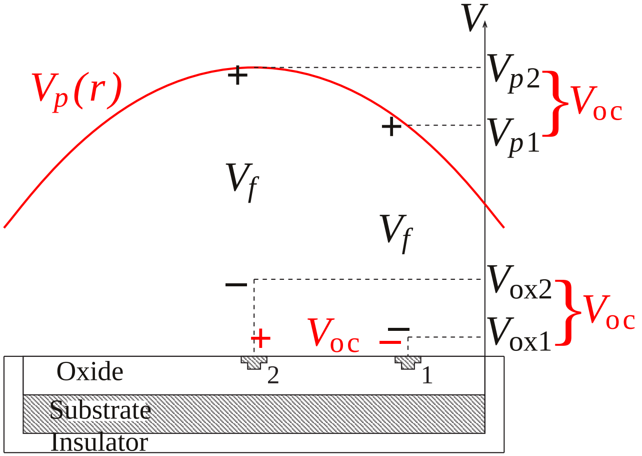
- To eliminate damage, float the substrate during plasma processing $\Longrightarrow$ no oxide current or voltage



- However, consider an entire floating wafer in a nonuniform plasma
- The Boltzmann relation [p. 19] requires that a radially decreasing density $n_e(r)$ have a radially decreasing potential

$$\boxed{V_p(r) = \mathrm{T}_e \ln \frac{n_e(r)}{n_e(0)}}$$

OPEN CIRCUIT VOLTAGE ACROSS THICK OXIDE



- $V_{\rm ox2}$ and $V_{\rm ox1}$ at the wafer center and off-center are

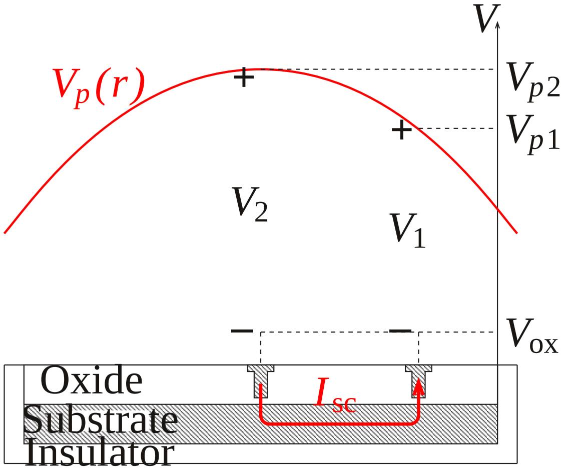
$$V_{\rm ox2} = V_{p2} - V_f\,, \qquad V_{\rm ox1} = V_{p1} - V_f$$

where the floating potential across the sheath is [p. 48]

$$V_f = \frac{{\rm T}_e}{2} \ln \frac{M}{2\pi m} \sim 4.7\,{\rm T}_e$$

- A voltage $V_{\rm oc} = V_{p2} - V_{p1}$ appears across the two gate oxides
- The voltage capacitively divides across the oxides depending on their thicknesses and areas

SHORT CIRCUIT CURRENT THROUGH THIN OXIDE



- Oxides nearly conducting $\Longrightarrow$ gate potentials nearly equal

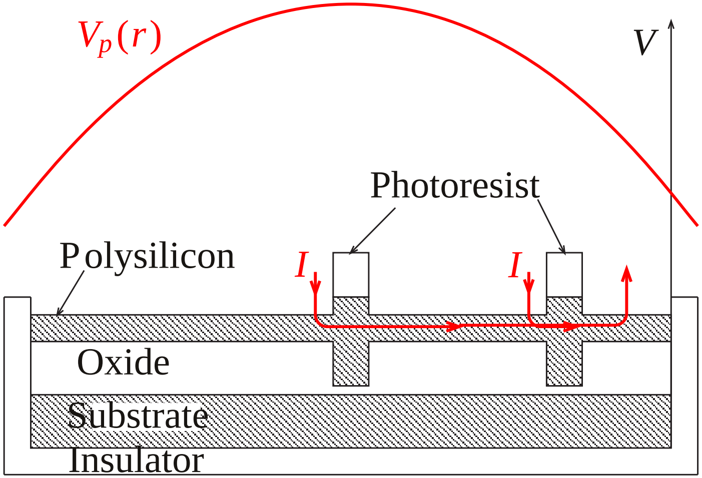
$$\boxed{V_{ox} = V_{p2} - V_2 = V_{p1} - V_1}$$

V_2 and V_1 are the center and off-center sheath potentials

- $V_2 > V_f \Longrightarrow$ net ion current is collected in center
- $V_1 < V_f \Longrightarrow$ net electron current is collected at edge
- A short circuit current I_{sc} flows from center to off-center

TRANSIENT DAMAGE DURING ETCHING

- Consider the etching of a deposited polysilicon film to form the gate electrodes

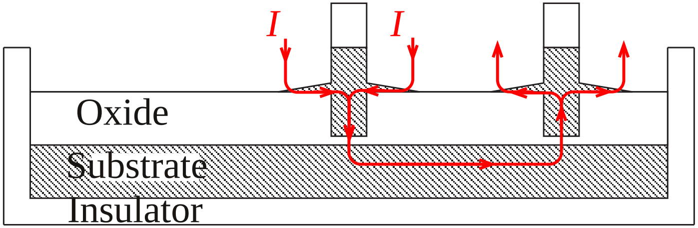


- During most of the etch, the poly film is continuous

  Currents do not flow through the gate oxides $\Longrightarrow$ no damage

TRANSIENT DAMAGE DURING ETCH (CONT'D)

- Near the end of the etch, the film clears first in the middle of the unpatterned areas

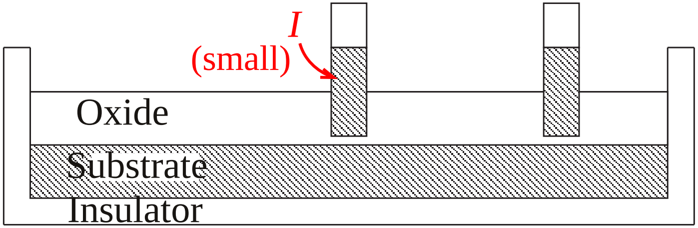


- There are isolated gates with large antenna ratios

  Currents flow through the gate oxides ⇒ damage

TRANSIENT DAMAGE DURING ETCH (CONT'D)

- After a sufficient overetch, the polysilicon has been entirely cleared



Little or no current is collected at the gates $\Longrightarrow$ little damage

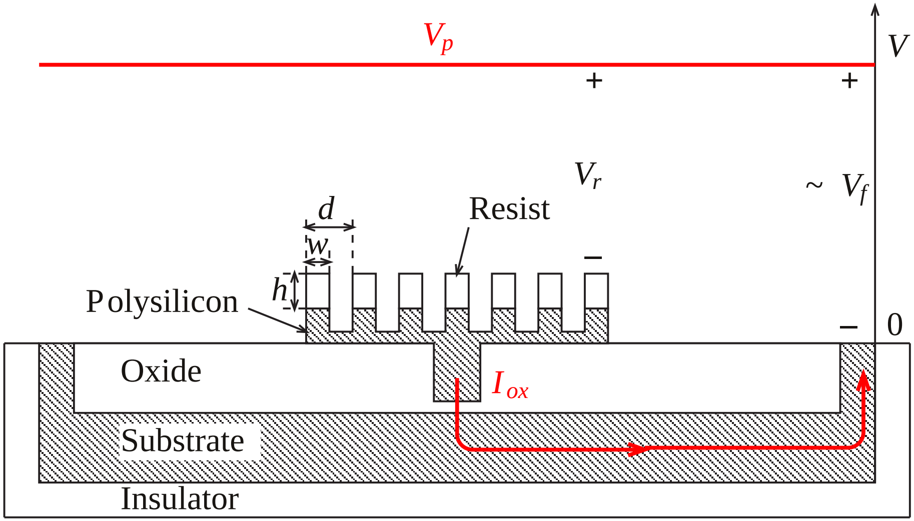
- Solutions to all these damage mechanisms

$$\boxed{\Longrightarrow \text{ Make the plasma uniform}}$$

ELECTRON SHADING EFFECT

(Vahedi, Benjamin, Perry, 1997)

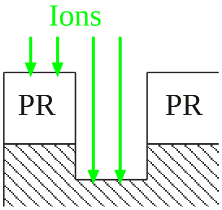
- Damage can be due to topography even for a uniform plasma
- An example is near the endpoint for etching a pattern of conducting lines covered with (insulating) resist



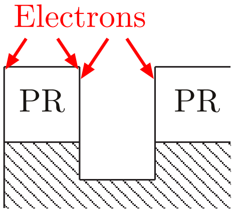
- The plasma is uniform and the substrate is exposed to the plasma
- For a thin (low resistance) gate oxide, a dc current can flow through the oxide

EXPLANATION OF ELECTRON SHADING EFFECT

- The photoresist collecting area is different for ions and electrons



(Anisotropic)



(Isotropic)

- Fraction α_i of ions collected < fraction α_e of electrons collected
- Current flowing to the resist surface must vanish

$$I_r = \alpha_i I_i - \alpha_e I_{e0}\, \mathrm{e}^{-V_r/\mathrm{T}_e} = 0$$

- Solve for resist potential

$$V_r = V_f + \mathrm{T}_e \ln \frac{\alpha_e}{\alpha_i}$$

Since $\alpha_e > \alpha_i$, $V_r > V_f$

- Current collected by gate is that not collected by resist

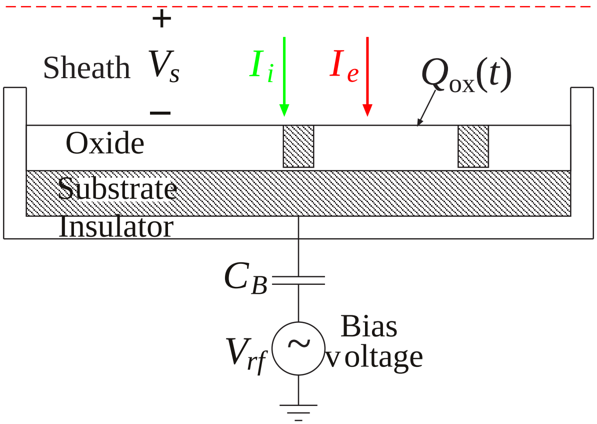
$$I_{\mathrm{ox}} = (1 - \alpha_i) I_i - (1 - \alpha_e) I_{e0}\, \mathrm{e}^{-V_r/\mathrm{T}_e}$$

- Eliminate V_r to obtain

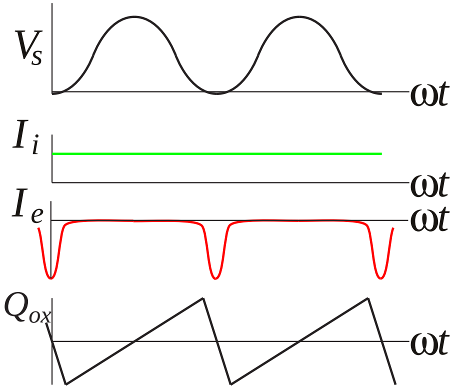
$$\boxed{I_{\mathrm{ox}} = I_i \left(1 - \frac{\alpha_i}{\alpha_e}\right)}$$

$\Longrightarrow$ damage

DAMAGE DUE TO RF BIASING

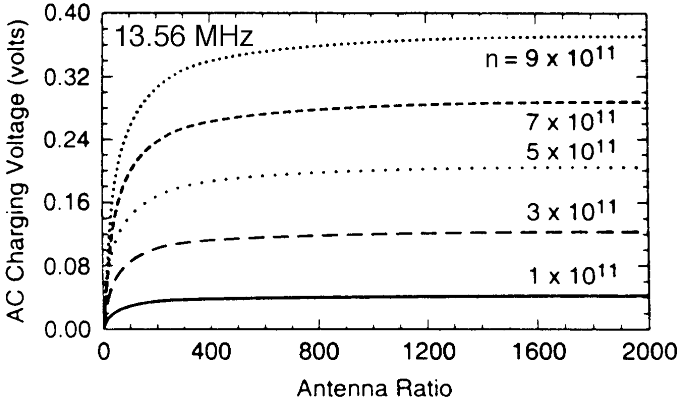


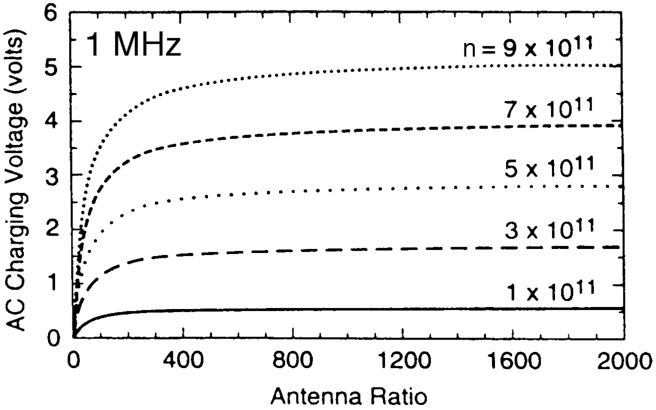
- Sheath voltage V_s, currents I_i and I_e, and charge collected Q_{ox} versus time t



DAMAGE DUE TO RF BIASING (CONT'D)

- The oscillating Q_{ox} produces an oscillating voltage V_{ox} across the gate oxide
- Cheung and Chang (1994) plot "charging voltage" V_{ox} versus antenna ratio $\text{AR} = A_g/A_{\text{ox}}$ [p. 214]



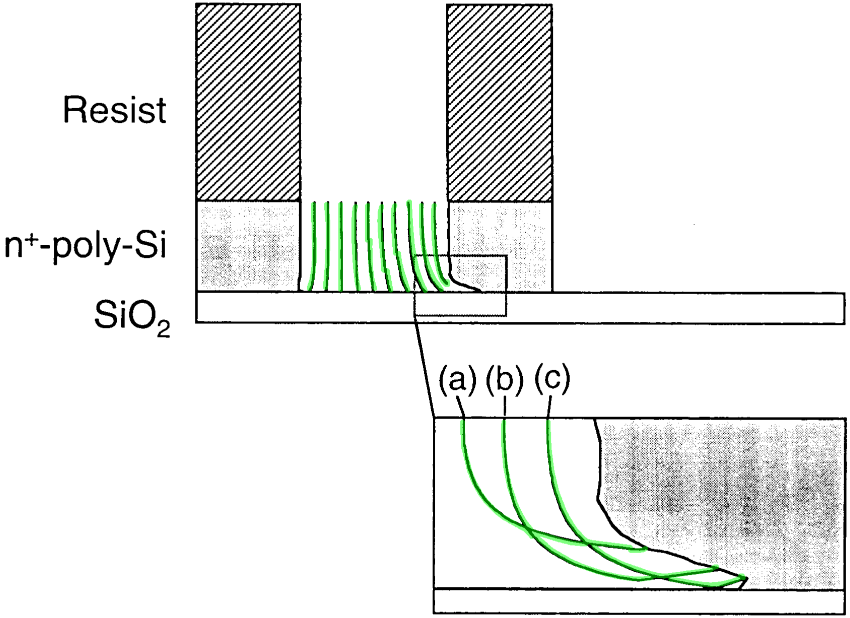


- For a thin oxide, $V_{\text{ox}}(t)$ produces an oscillating (conduction) current

$$\boxed{\Longrightarrow \text{damage}}$$

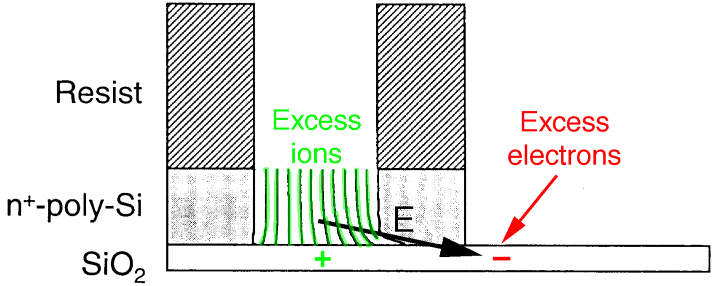
ETCH PROFILE DISTORTIONS

- Undercut, tapered, or bowed sidewalls
- Microtrenches (“notching”) at the bases of sidewalls after etching masked features
- Deflection and subsequent scattering of incoming ions within trenches due to localized buildup of charge on insulating surfaces



MECHANISM FOR NOTCHING

- Notching driven by potential difference between the last polysilicon line and insulating trench bottom
- Last polysilicon line attracts excess electrons at the side facing the open area
- Insulating trench bottom attracts excess ions because the trench topography inhibits collection of electrons on the trench bottoms, compared to the open area



- Potential leads to an electric field pointing from the trench bottom to the open area
- Electric field can deflect the low energy part of the incoming ion distribution into the trench corner nearest to the open area

PULSED DISCHARGES

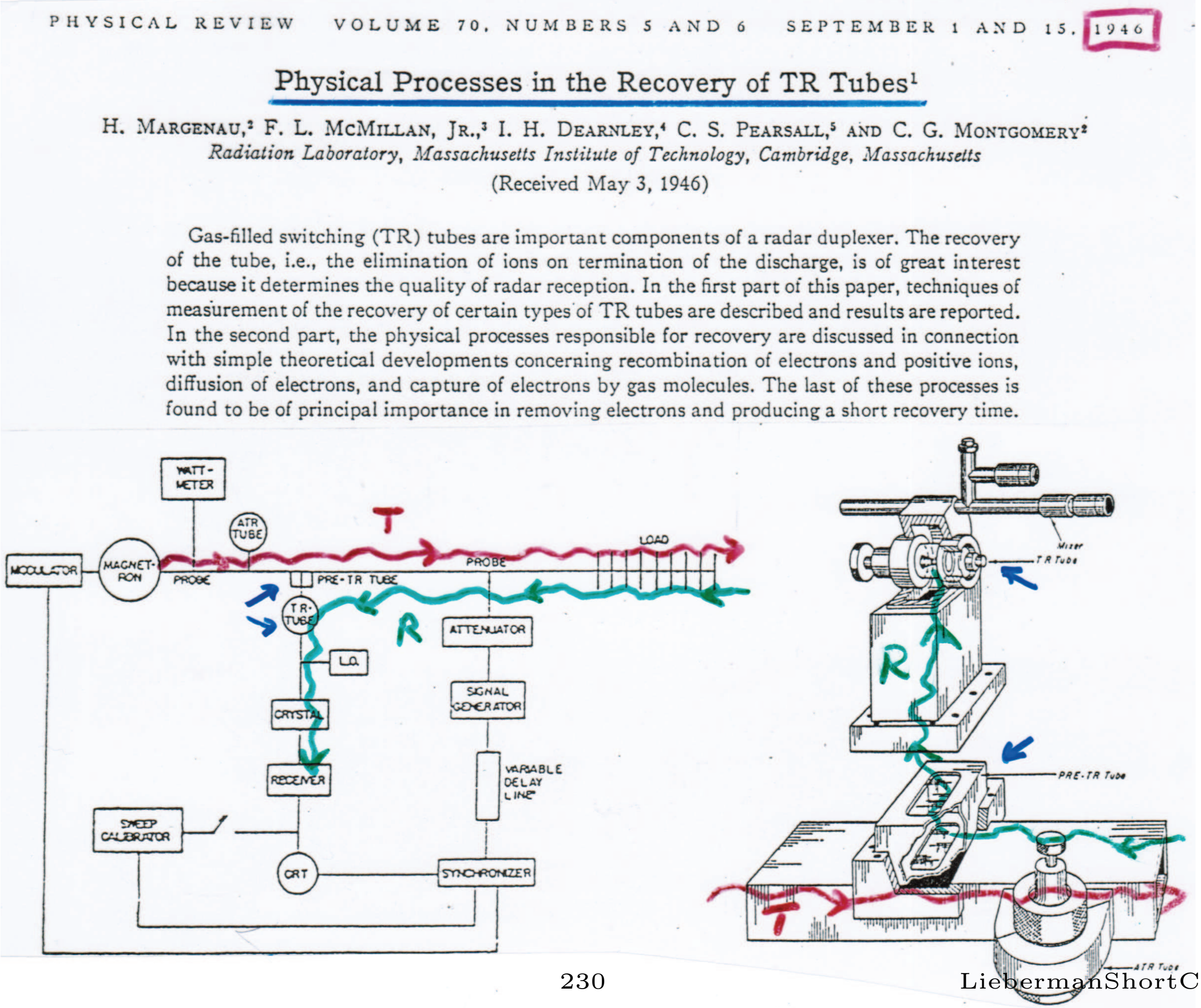
Review article: Lieberman and Ashida, *Plasma Sources Sci. Technol.* **5**, 145 (1996)

WHAT CAN BE PULSED, AND WHY?

1. Discharge power (100 Hz – 1 MHz)
2. Bias power (0.1 Hz – 1 MHz)
3. Gases, pressure (0.1 – 10 Hz)

- Additional “knobs” to optimize performance
  But $10^N_{\text{knobs}} \Rightarrow$ “combinatorial explosion”
- Access “forbidden” steady-state discharge regimes
- Pulse rf power ⇒ reduce aspect ratio dependent etch effects, reduce charging damage, increase etch/deposition rates, increase uniformity, reduce heat flux to substrate, etc
- Pulse bias and gases ⇒ atomic layer deposition and etching

PULSED MICROWAVE DISCHARGE — HISTORY



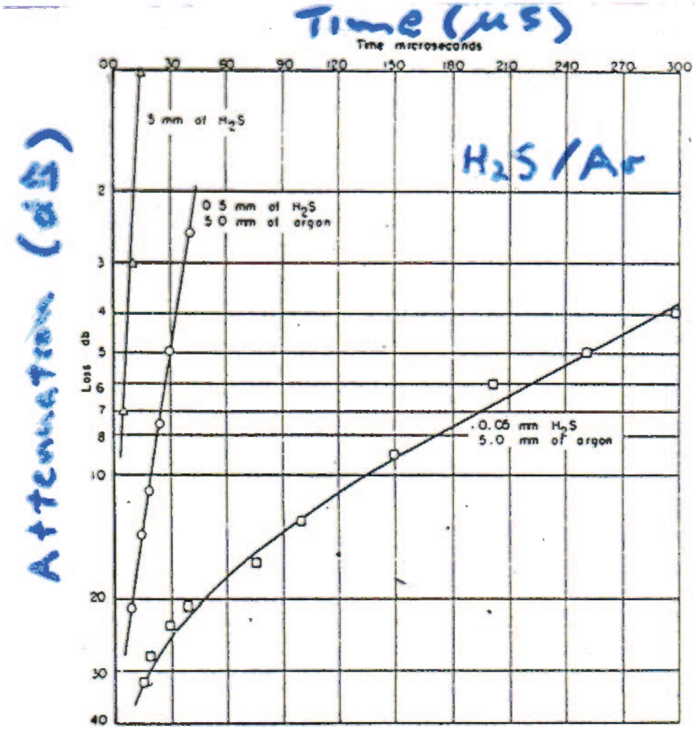
PHYSICAL REVIEW VOLUME 70, NUMBERS 5 AND 6 SEPTEMBER 1 AND 15, 1946

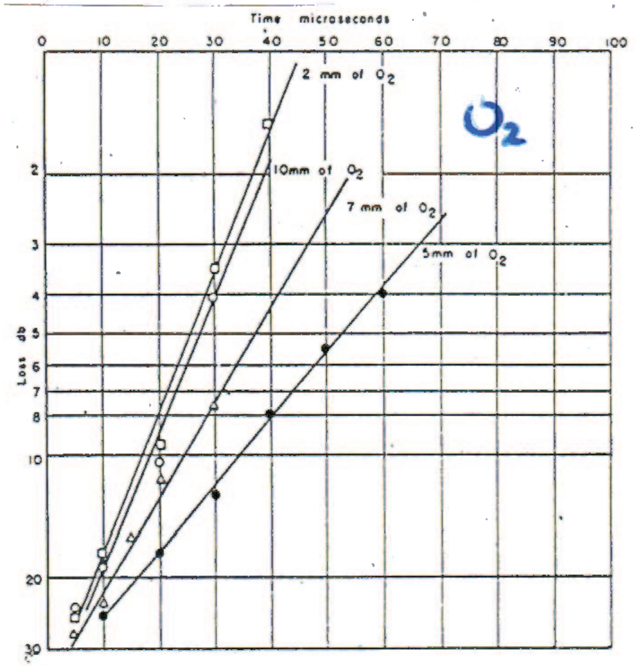
Physical Processes in the Recovery of TR Tubes[1]

H. MARGENAU,[2] F. L. MCMILLAN, JR.,[3] I. H. DEARNLEY,[4] C. S. PEARSALL,[5] AND C. G. MONTGOMERY[2]
Radiation Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts
(Received May 3, 1946)

Gas-filled switching (TR) tubes are important components of a radar duplexer. The recovery of the tube, i.e., the elimination of ions on termination of the discharge, is of great interest because it determines the quality of radar reception. In the first part of this paper, techniques of measurement of the recovery of certain types of TR tubes are described and results are reported. In the second part, the physical processes responsible for recovery are discussed in connection with simple theoretical developments concerning recombination of electrons and positive ions, diffusion of electrons, and capture of electrons by gas molecules. The last of these processes is found to be of principal importance in removing electrons and producing a short recovery time.

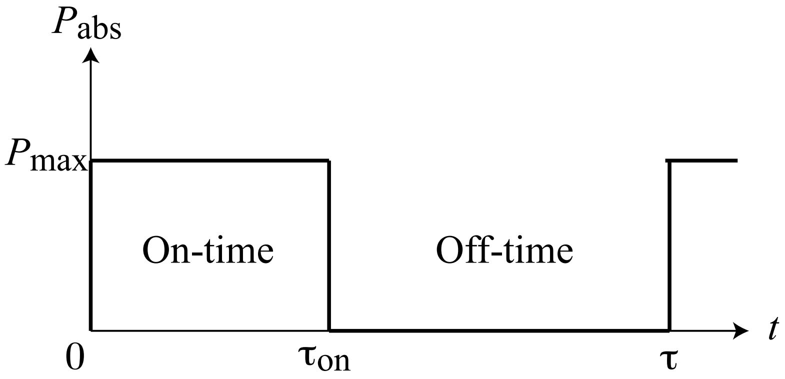
ELECTRONEGATIVE DISCHARGE — HISTORY





- Attaching gases soak up electrons fast

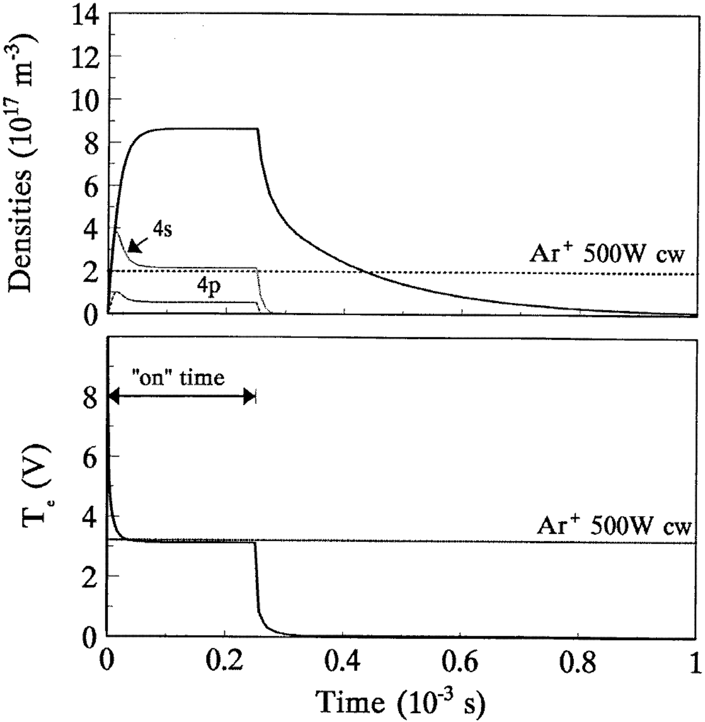
IDEAL RECTANGULAR POWER WAVEFORM



- Duty ratio $\eta = \tau_{\text{on}}/\tau$
- Pulsing frequency $f = 1/\tau$
- P_{abs} may vary from an ideal rectangular shape as the electron density builds up and decays, because the matching network is set for no reflected power at a single density
- It is usually most useful to compare a cw discharge with a pulsed discharge at the same average power

LOW PRESSURE ELECTROPOSITIVE DISCHARGES

- 5 mTorr cylindrical argon discharge with $P_{\max} = 2000$ W, $\eta = 0.25$ ($\bar{P}_{\text{abs}} = 500$ W), $R = 15.25$ cm, $l = 7.5$ cm



(Argon 4s and 4p excited states also shown)

THREE PHASES DURING PULSE PERIOD

- Phase 1
  Just after pulse turn-on, n_e remains low and T_e jumps to a large value
- Phase 2
  During the remaining on-time, T_e decays and n_e increases with time toward a steady state value
- Phase 3
  After pulse turn-off, T_e decays rapidly and n_e decays more slowly with time

GLOBAL MODEL OF CYLINDRICAL DISCHARGE

- Particle balance [p. 198]

$$\mathcal{V}\frac{dn_e}{dt} = \underbrace{K_{\text{iz}} n_e n_g \mathcal{V}}_{\substack{\text{ionization} \\ \text{in volume}}} - \underbrace{n_e u_B A_{\text{eff}}}_{\substack{\text{collisional} \\ \text{energy loss}}}$$

where $\mathcal{V} = \pi R^2 l$ and $A_{\text{eff}} = 2\pi R(Rh_l + lh_R)$ [p. 50]

- Energy balance [p. 198]

$$P_{\text{abs}}(t) = \overbrace{\mathcal{V}\frac{d}{dt}\left(\frac{3}{2}en_e \mathrm{T}_e\right)}^{\substack{\text{plasma energy} \\ \text{increase}}} + \overbrace{\mathcal{V}en_e n_g \sum_i K_i \mathcal{E}_i}^{\substack{\text{collisional} \\ \text{energy loss}}}$$

$$+ \underbrace{A_{\text{eff}}\left[e\left(\overline{V}_s + \frac{5}{2}\mathrm{T}_e\right)n_e u_B\right]}_{\text{energy loss to wall}}$$

- Solve to obtain $n_e(t)$ and $\mathrm{T}_e(t)$

DIFFERENTIAL EQUATIONS

- Particle balance reduces to

$$\boxed{\frac{1}{n_e}\frac{dn_e}{dt} = \nu_{\mathrm{iz}} - \nu_{\mathrm{loss}}}$$

with $\nu_{\mathrm{iz}}(t) = K_{\mathrm{iz}} n_g$, $\nu_{\mathrm{loss}}(t) = u_B A_{\mathrm{eff}}/\mathcal{V}$

- Eliminating dn_e/dt in the energy balance equation

$$\boxed{\frac{1}{\mathrm{T}_e}\frac{d\mathrm{T}_e}{dt} = \frac{P_{\mathrm{abs}}(t)}{W_e} - \left(\frac{2}{3}\frac{\mathcal{E}_c}{\mathrm{T}_e} + 1\right)\nu_{\mathrm{iz}} - \frac{2}{3}\left(\frac{\overline{V}_s}{\mathrm{T}_e} + 1\right)\nu_{\mathrm{loss}}}$$

with $W_e(t) = \frac{3}{2} e n_e \mathrm{T}_e \mathcal{V}$, $\mathcal{E}_c(t)$ = collisional energy loss per e-i pair [p. 39–40], and $\overline{V}_s(t)$ = dc sheath voltage

PULSED POWER ON

- Just after pulse turn-on, n_e and T_e are initially low

$$\frac{1}{n_e}\frac{dn_e}{dt} \approx \nu_{\mathrm{iz}}$$

$$\frac{1}{\mathrm{T}_e}\frac{d\mathrm{T}_e}{dt} \approx \frac{P_{\max}}{W_e} - \left(\frac{2}{3}\frac{\mathcal{E}_c}{\mathrm{T}_e} + 1\right)\nu_{\mathrm{iz}}$$

- 2nd term on the RHS of the $d\mathrm{T}_e/dt$ equation is initially low
  ⇒ Phase 1 (fast increase in T_e)

- Later during the on-time, ν_{iz} increases and the two terms on the RHS of the $d\mathrm{T}_e/dt$ equation nearly balance
  ⇒ Phase 2 (T_e decays, n_e increases)

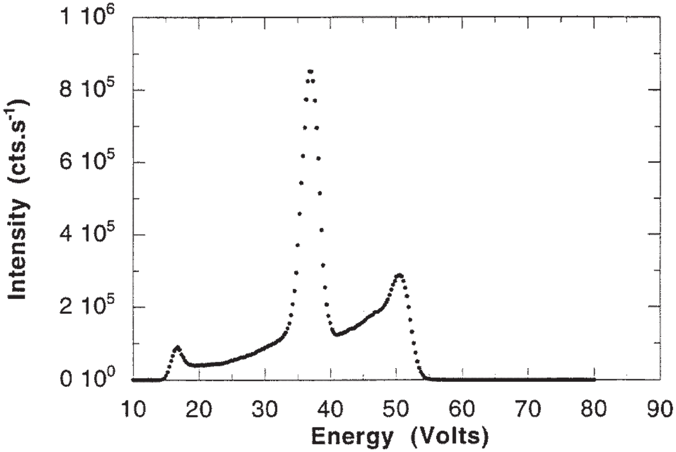
PULSED POWER OFF

- T_e falls such that $\nu_{\mathrm{iz}} \ll \nu_{\mathrm{loss}}$

$$\frac{1}{n_e}\frac{dn_e}{dt} \approx -\nu_{\mathrm{loss}}$$

$$\frac{1}{\mathrm{T}_e}\frac{d\mathrm{T}_e}{dt} \approx -\underbrace{\frac{2}{3}\left(\frac{V_s}{\mathrm{T}_e}+1\right)}_{\approx\, 4 \text{ for argon}}\nu_{\mathrm{loss}}$$

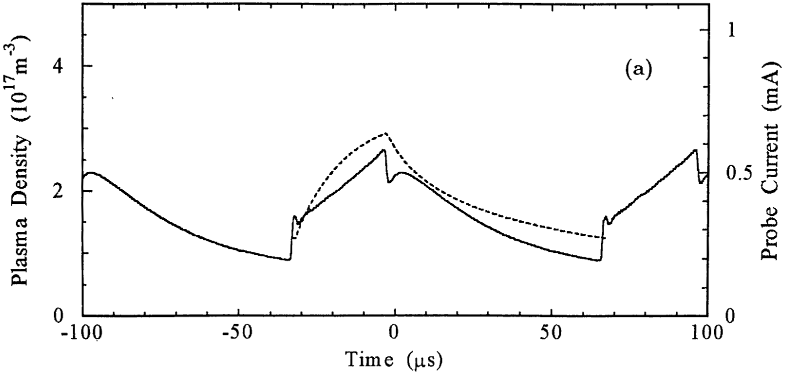
- Hence T_e decays 4× faster than n_e for argon ⇒ Phase 3
- Note IEDF for O_2^+ ions escaping radially to the walls, for a helicon pulsed discharge, 250 μs on, 125 μs off



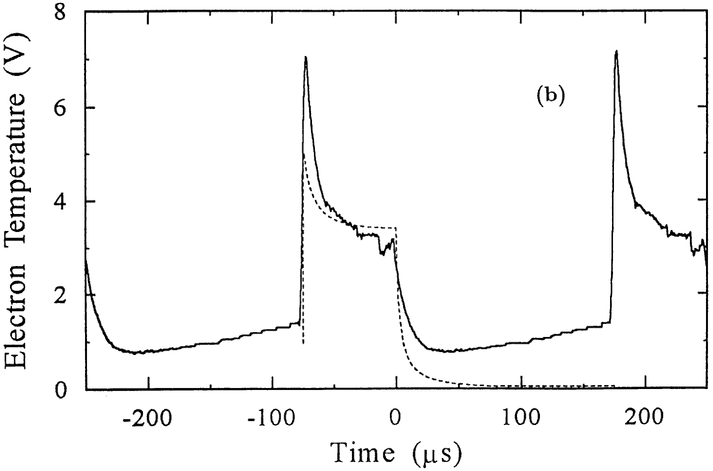
COMPARISON OF MEASUREMENTS AND MODEL

- Argon ICP, $\bar{P}_{\rm abs} = 51$ W, 5 mTorr, $R = 15.25$ cm, $l = 7.5$ cm

Electron density, pulse period $\tau = 100\ \mu$s

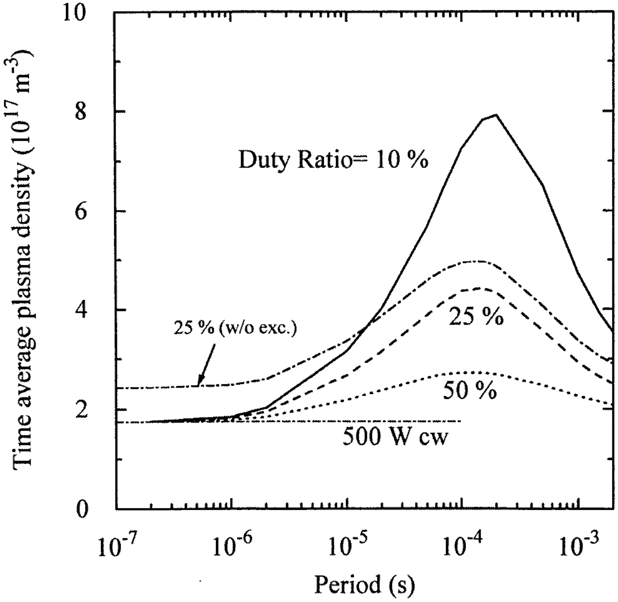


Electron temperature, $\tau = 250\ \mu$s



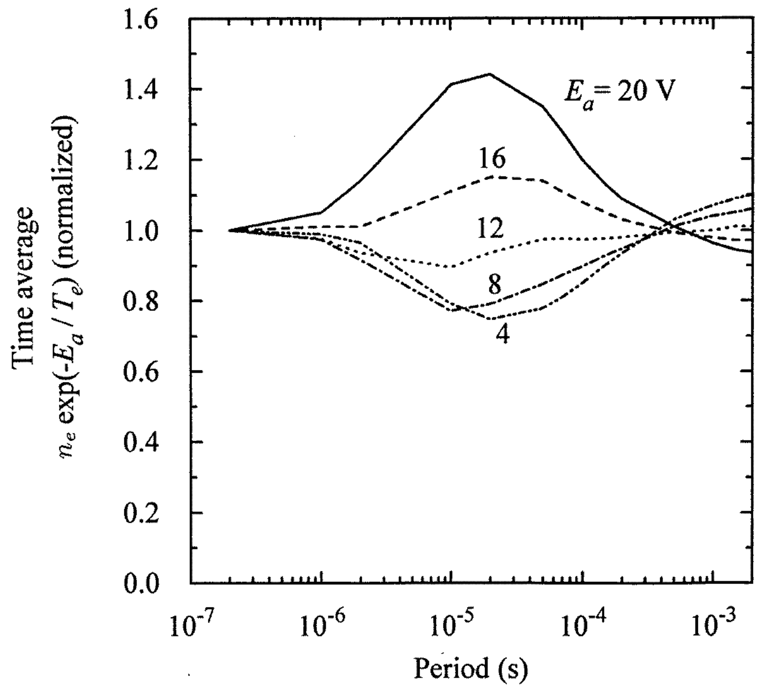
AVERAGE PLASMA DENSITY

- For the same time-average power $\bar{P}_{\text{abs}}$, the average plasma density for a pulsed discharge can be higher than for a cw discharge
  $\Rightarrow$ higher etch / dep rates



- The average T_e is low due to low T_e in the afterglow
  $\Rightarrow$ the loss frequency $\nu_{\text{loss}} \propto (e\mathrm{T}_e/M)^{1/2}$ decreases
  $\Rightarrow$ higher average densities

AVERAGE RADICAL / ION GENERATION RATES



- High T_e peak after pulse turn-on enhances high activation energies
- Increased average n_e enhances very low activation energies
- Low T_e during afterglow reduces medium activation

  ⇒ Radical/ion generation is different in pulsed discharges

PULSED POWER CHLORINE DISCHARGE

- Neutral radical dynamics

$$\frac{\mathrm{d}n_{\mathrm{Cl}}}{\mathrm{d}t} = 2K_{\mathrm{diss}}n_e n_{\mathrm{Cl}_2} - \nu_{\mathrm{rec,Cl}}\, n_{\mathrm{Cl}}$$

— n_{Cl} depends on wall recombination probability $\gamma_{\mathrm{rec,Cl}}$
— $n_{\mathrm{Cl}} \approx$ const in time because generation and loss rates are slow
— Can have same radical flux with less average power

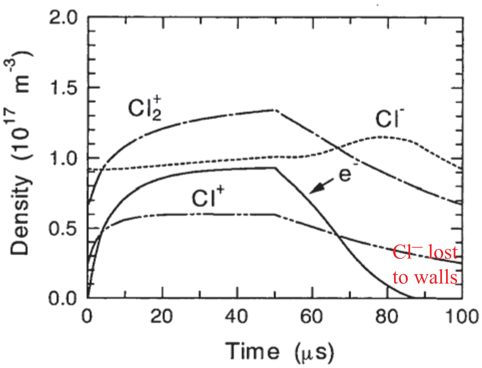
- Negative ion dynamics at power turn-off

$$\frac{\mathrm{d}n_{\mathrm{Cl}_-}}{\mathrm{d}t} = K_{\mathrm{att}}n_e n_{\mathrm{Cl}_2} - K_{\mathrm{rec}}n_{\mathrm{Cl}_{2+}}n_{\mathrm{Cl}_-}$$

— Attachment rate increases due to decay of T_e
— Fast loss of n_e by attachment and to walls
— After 30-50 μs, Cl_- ions can be lost to walls

PULSED POWER CHLORINE TCP

Model ($\gamma_{\mathrm{rec,Cl}} = 0.3$)



Experiment (Ahn et al, 1995)

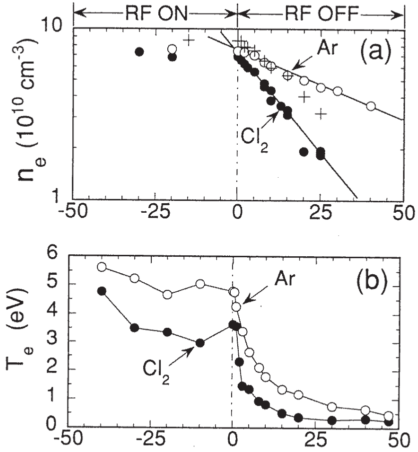


Figure 10. The time variation of (a) electron density n_e and (b) electron temperature T_e for 100 μs period and 50% duty cycle in chlorine (8 mTorr, 400 W) and in argon (6 mTorr, 200 W); the open and closed circles indicate the data for Ar and Cl_2, respectively; the crosses in (a) indicate the data obtained after photodetachment (from [10]).

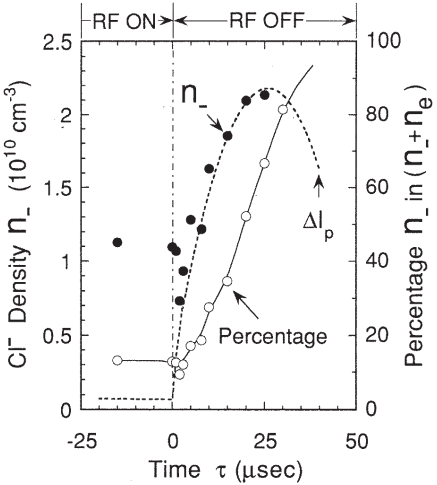


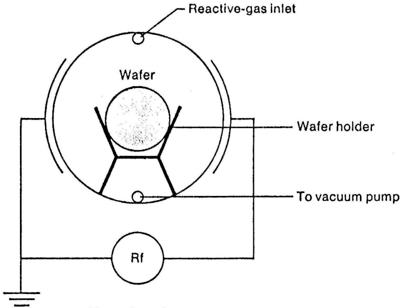
Figure 11. The time variation of negative ion density n_{Cl^-} and of n_{Cl^-}/n_{Cl^+} ratio (as a percentage); the broken line indicates the relative n_{Cl^-} obtained from Langmuir probe measurements, matched to n_{Cl^-} at 25 μs; the relative measurements are not valid for $t < 0$ (from [10]).

DUAL FREQUENCY CAPACITIVE DISCHARGES

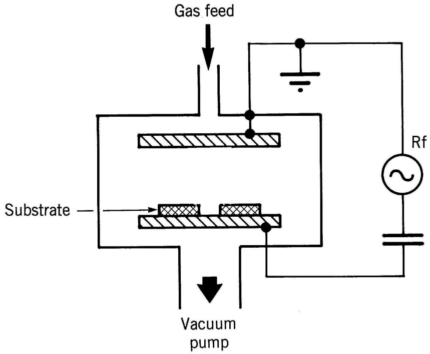
EVOLUTION OF ETCHING DISCHARGES — FIRST AND SECOND GENERATIONS

FIRST GENERATION

(1 rf source, multi-wafer, low density)



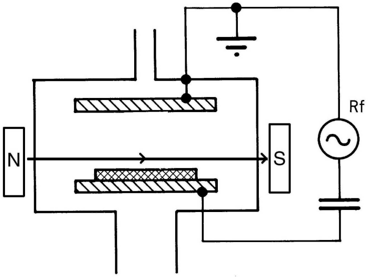
Barrel etcher
(Isotropic etch)



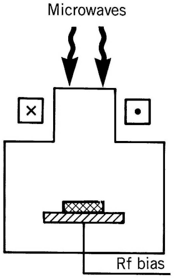
Capacitive
(Anisotropic etch)

SECOND GENERATION

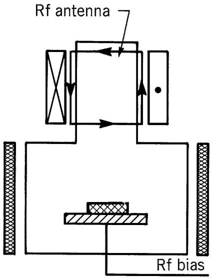
(2 sources, single wafer, high density)



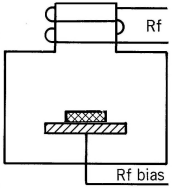
Magnetically enhanced
capacitive discharge



ECR



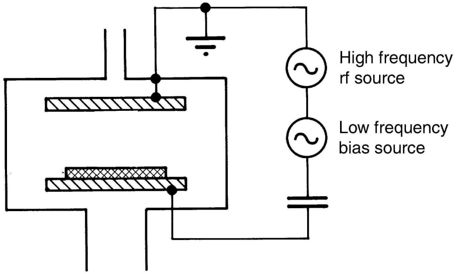
Helicon



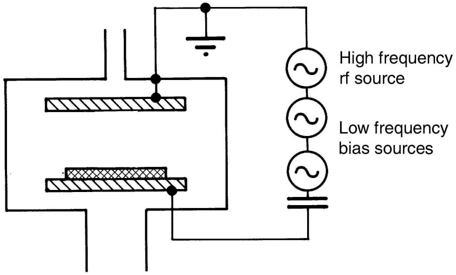
Inductive

THIRD GENERATION — DIELECTRIC ETCH

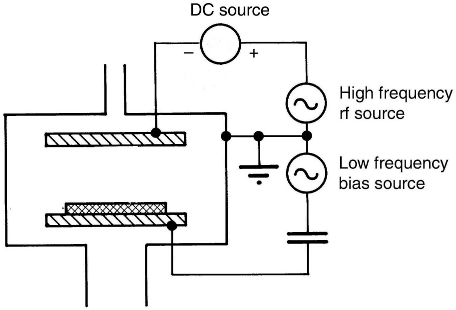
(Multi-frequency, single wafer, moderate density)



Dual frequency capacitive discharge



Triple frequency capacitive discharge



DC/dual frequency capacitive discharge

- In the year 2020
  — 6nm gate width, 6 billion transistors, 73 GHz on-chip clock
  — 14–18 wiring levels (dielectric layers)
- Why capacitive discharge?
  — low surface area seen by plasma (inexpensive)
  — good stability and control of chemistry (F/CF$_x$ ratio)
  — robust uniformity over wide pressure range

WHY DUAL FREQUENCY CAPACITIVE DISCHARGES?

- Independent control of ion flux and ion energy

High frequency source controls ion flux
Low frequency source controls ion energy

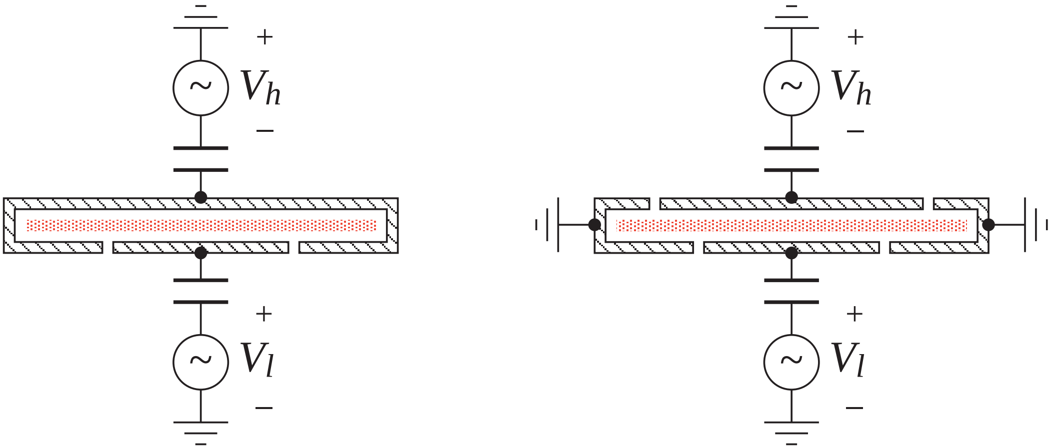
- $R \sim 15$–30 cm, $L \sim 1$–3 cm

  $p \sim 30$–300 mTorr, $C_4F_8/O_2/Ar$ feedstock

  $f_h \sim 27.1$–160 MHz, $V_h \sim 50$–200 V

  $f_l \sim 2$–13.56 MHz, $V_l \sim 500$–1500 V

  Absorbed powers $P_h,\ P_l \sim 500$–3000 W



CONTROL OF PLASMA DENSITY

- Consider capacitive discharge with equal area electrodes
- For a single frequency source

  Electron power balance $\Longrightarrow$ plasma density n [p. 84]

$$n \;\propto\; P_e$$

- For stochastic heating (with $V_{\text{rf}} = 2\,\widetilde{V}_s$)

  $P_e =$ power absorbed by electrons $\propto\; \omega^2 V_{\text{rf}}$ [p. 76, 84]

$$\boxed{\Longrightarrow n \;\propto\; \omega^2 V_{\text{rf}}}$$

(similar scaling for ohmic heating)

- For two frequencies with $\omega_h^2 V_h \gg \omega_l^2 V_l$

$$\boxed{\text{High frequency source controls plasma density (ion flux)}}$$

CONTROL OF ION ENERGY

- Ion bombarding energy tracks the sum of low and high frequency rf source voltages

$$\mathcal{E}_i \approx 0.41\,(V_l + V_h)$$

- Make $V_l \gg V_h$

$$\boxed{\text{Low frequency source controls ion energy}}$$

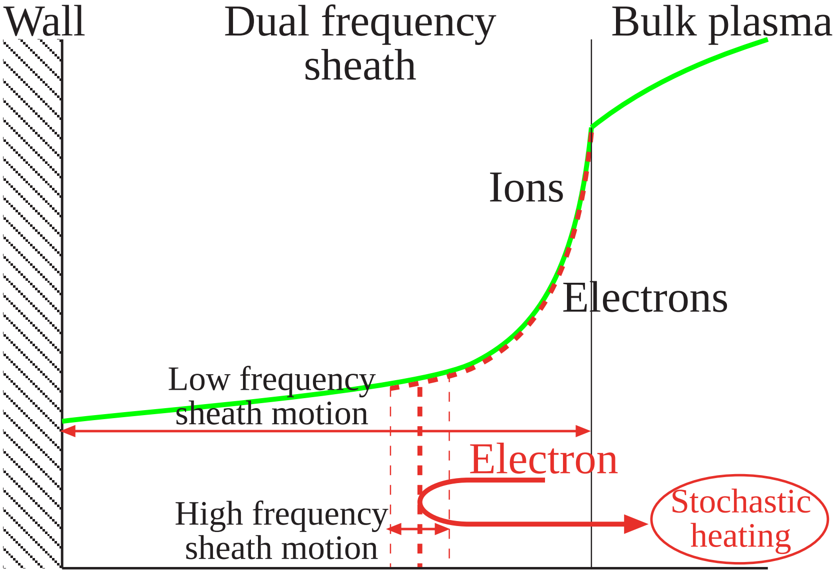
- Ideal dual frequency operating regime

$$\boxed{\frac{\omega_h^2}{\omega_l^2} \gg \frac{V_l}{V_h} \gg 1}$$

ENERGY AND POWER DEPOSITION ISSUES

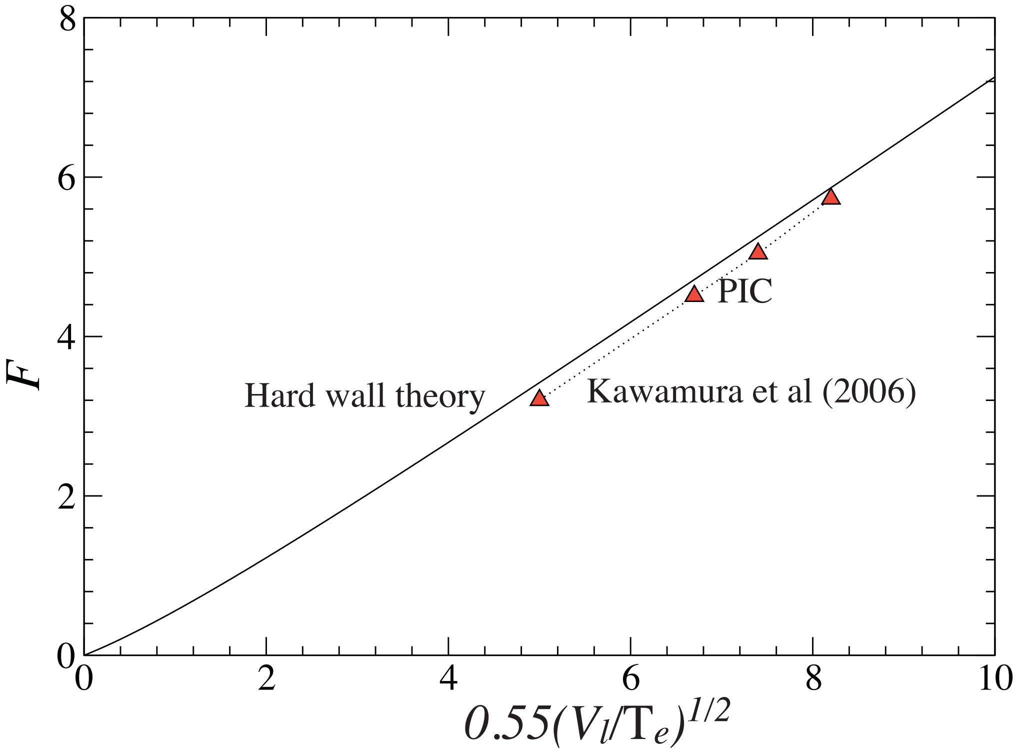
DUAL FREQUENCY STOCHASTIC HEATING

- The main electron heating mechanism below 100 mTorr



- How are electrons heated by the high frequency oscillations?

DUAL FREQUENCY ENHANCEMENT FACTOR F



- Stochastic heating increases with low frequency voltage V_l

COUPLING OF VOLTAGES

- The additive assumption for ion energy gives [p. 249]

$$\mathcal{E}_i \approx 0.41\,(V_l + V_h)$$

- Modeling results give a cross term

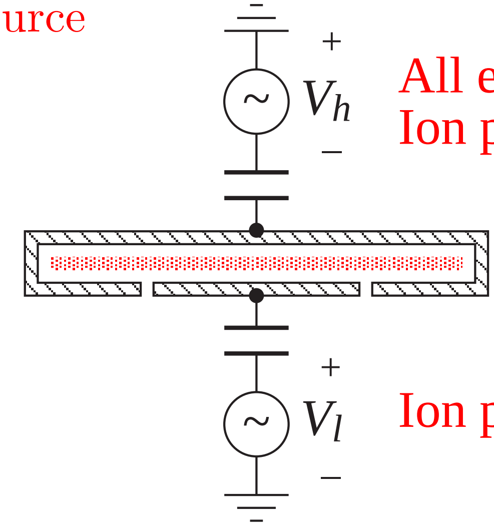
$$\boxed{\mathcal{E}_i \approx 0.41\left(V_l + V_h \underbrace{-\frac{2}{3}\frac{V_l V_h}{V_l + V_h}}_{\text{cross term}}\right)}$$

- A 17% worst-case effect for equal rf source voltages ($V_l = V_h$)

ION POWER SUPPLIED BY SOURCES

- High frequency source supplies electron power P_e

- Low and high frequency sources supply ion bombarding power P_i in proportion to their rf source voltages



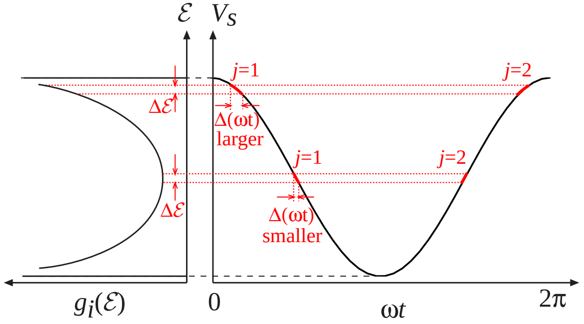
All electron power
Ion power $\propto V_h$

Ion power $\propto V_l$

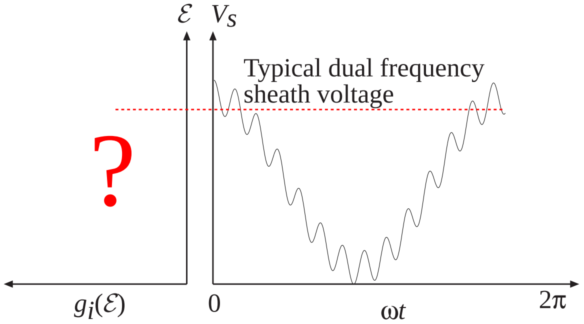
ION ENERGY DISTRIBUTION (IED)
ON THE SUBSTRATE SURFACE

FORMATION OF PERIOD-AVERAGED IED

- Single frequency [p. 127]
  Two times/cycle map to a given ion energy $\mathcal{E}$



- Dual frequency
  More than two times/cycle map to a given ion energy $\mathcal{E}$



- For $\omega\tau_i \ll 1$, ions respond to the full time-varying sheath voltage

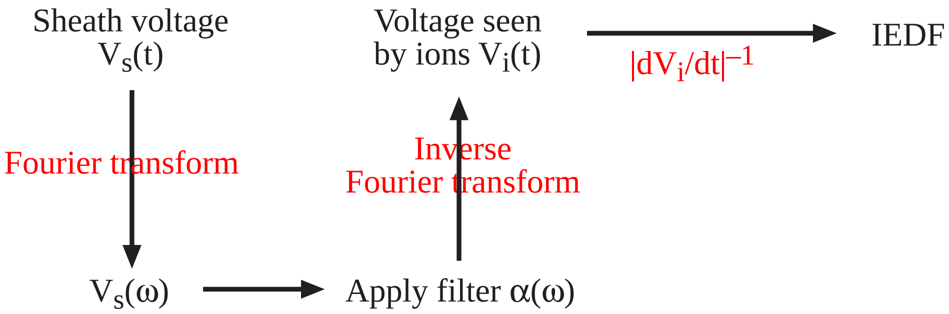
  For $\omega\tau_i \gg 1$, ions respond to the time-average sheath voltage

  (τ_i = ion transit time across the sheath)

$$\boxed{\Longrightarrow \text{ low-pass filter}}$$

ION ENERGY DISTRIBUTION (IED)

- What is energy distribution of ion flux incident on the substrate?
- Fast algorithm for collisionless ions with many frequencies



Sheath voltage $V_s(t)$

Fourier transform

$V_s(\omega)$

Apply filter $\alpha(\omega)$

Inverse Fourier transform

Voltage seen by ions $V_i(t)$

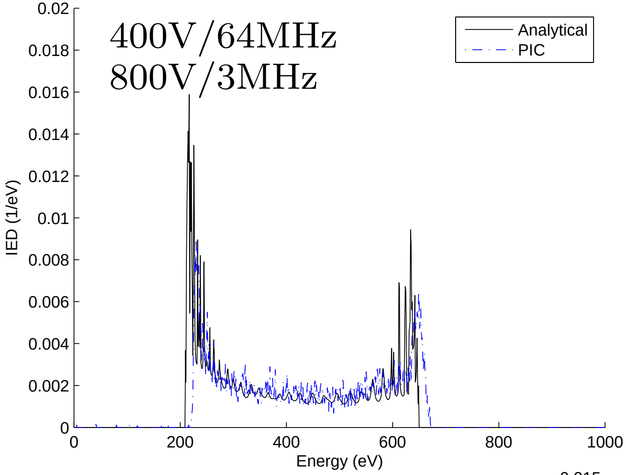
$|dV_i/dt|^{-1}$

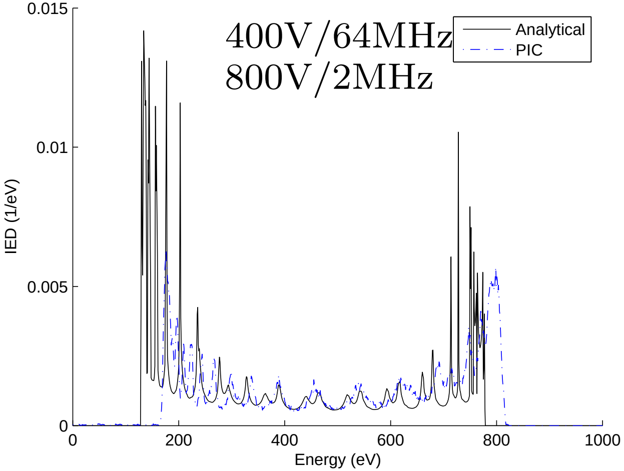
IEDF

- Use filter $\alpha(\omega) = [(c\,\omega\tau_i)^p + 1]^{-1/p}$ with $c = 0.3$, $p = 5$, and $\tau_i =$ ion transit time across the sheath $= 3s_m\,(M/2e\overline{V}_s)^{1/2}$ $s_m =$ maximum sheath width; $\overline{V}_s =$ dc voltage across sheath

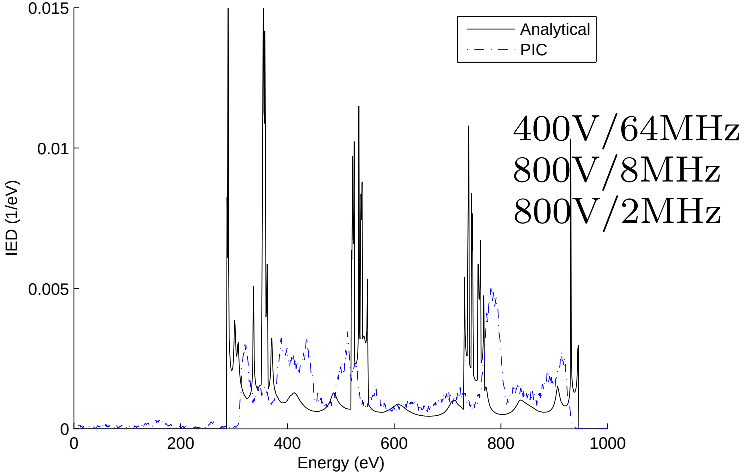
(A. Wu et al, 2007)

DUAL/TRIPLE FREQUENCY PIC SIMULATIONS





Gap=3 cm
p=30 mTorr
Collisionless ions



HIGH FREQUENCY ELECTROMAGNETIC EFFECTS

STANDING WAVES AND SKIN EFFECTS

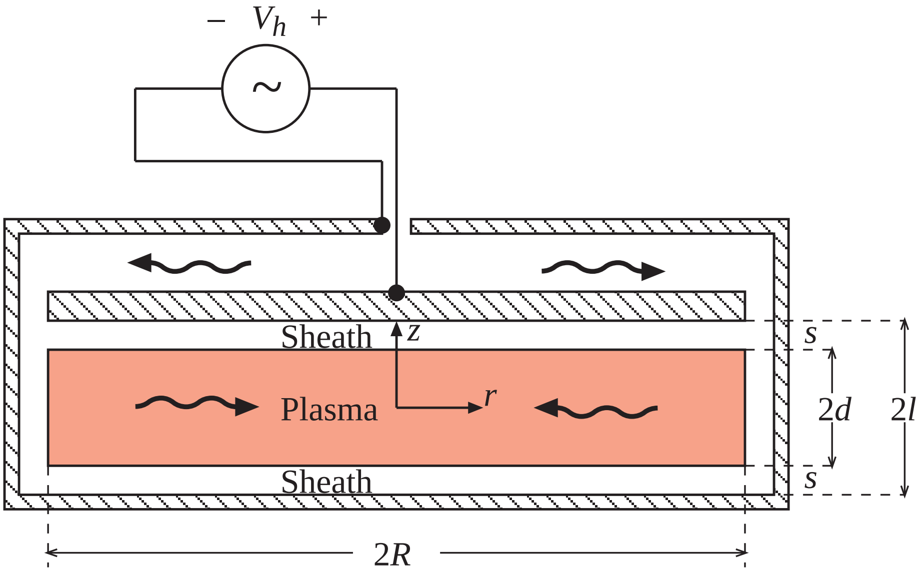
- High frequency and large area ⇒ $\boxed{\text{standing wave effects}}$

- High frequency ⇒ high density ⇒ $\boxed{\text{skin effects}}$

1. M.A. Lieberman, J.P. Booth, P. Chabert, J.M. Rax, and M.M. Turner, *Plasma Sources Sci. Technol.* **11**, 283, 2002
2. P. Chabert, *J. Phys. D: Appl. Phys.* **40**, R63, 2007

CYLINDRICAL CAPACITIVE DISCHARGE

Consider only the high frequency source

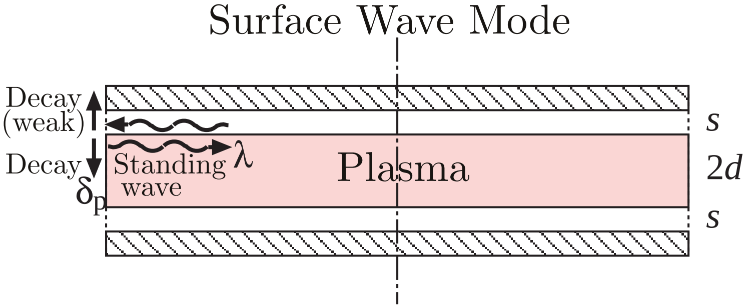


Fields cannot pass through metal plates

(1) V_h excites radially outward wave in top vacuum gap
(2) Outward wave excites radially inward wave in plasma

SURFACE WAVE MODE

- Power enters the plasma via a *surface wave mode*



- Radial wavelength for surface wave (low density limit)

$$\boxed{\lambda \approx \frac{\lambda_0}{\sqrt{1 + d/s}} \sim \frac{\lambda_0}{3}}$$

with $\lambda_0 = c/f$ the free space wavelength

- Axial skin depth for surface wave [p. 99]

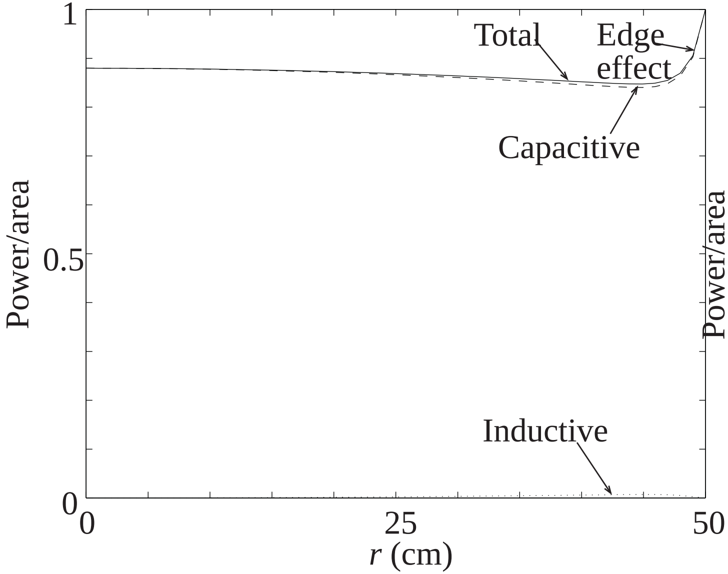
$$\boxed{\delta_p \sim \frac{c}{\omega_p}}$$

- There are also *evanescent modes* leading to edge effects near $r = R$

STANDING WAVE EFFECTS — FIXED DENSITY $\mathbf{n_e}$

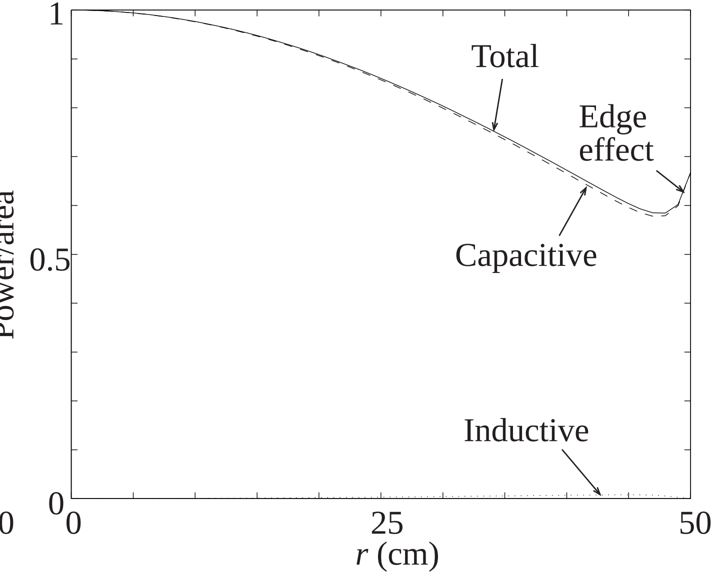
- $R = 50$ cm, $d = 2$ cm, $s = 0.4$ cm, $n_e = 10^9$ cm^{-3} ($\delta_p \approx 16$ cm)
- P_{cap} (dash), P_{ind} (dot) and P_{tot} (solid) as a function of r

13.56 MHz ($\lambda \approx 9$–10 m)



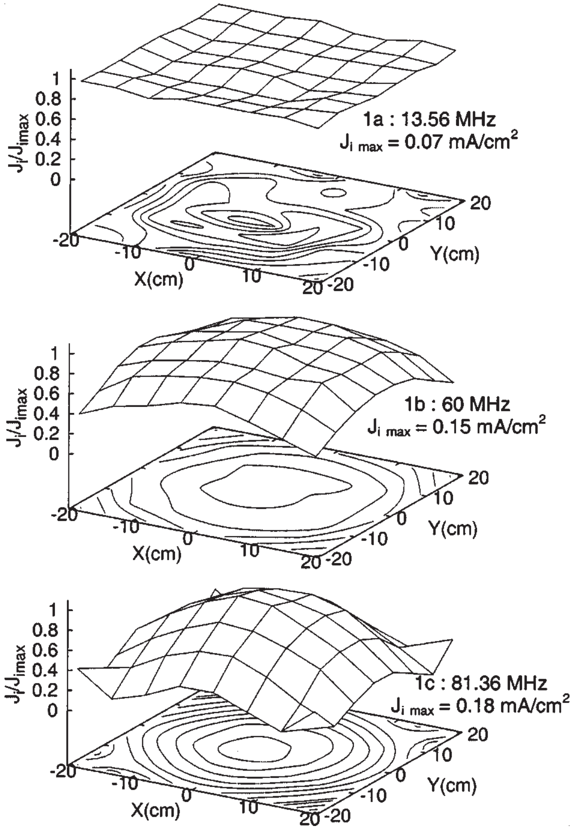
Small standing wave and skin effects

40.7 MHz ($\lambda \approx 3$ m)



Large standing wave effect;
center-high profile

EXPERIMENTAL RESULTS FOR STANDING WAVES



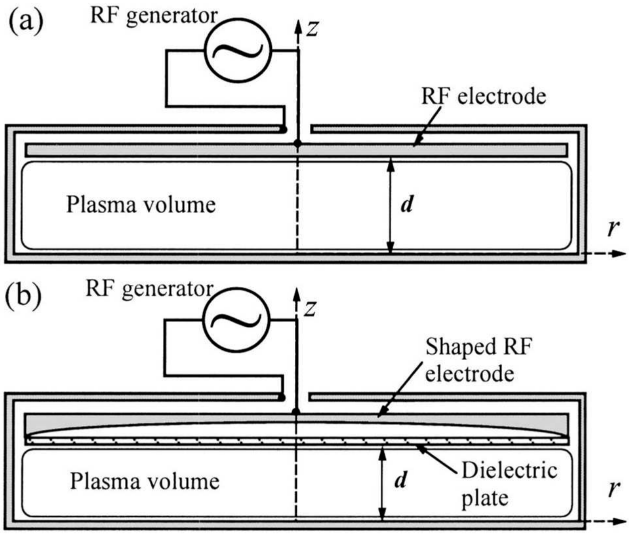
40×40 cm discharge
$p = 150$ mTorr
50 W rf power

The standing wave effect is seen at 60 MHz and is more pronounced at 81.36 MHz

(A. Perret, P. Chabert, J-P Booth, J. Jolly, J. Guillon and Ph. Auvray, *Appl. Phys. Lett.* **83**, 243, 2003)

SUPPRESSION OF STANDING WAVE EFFECTS

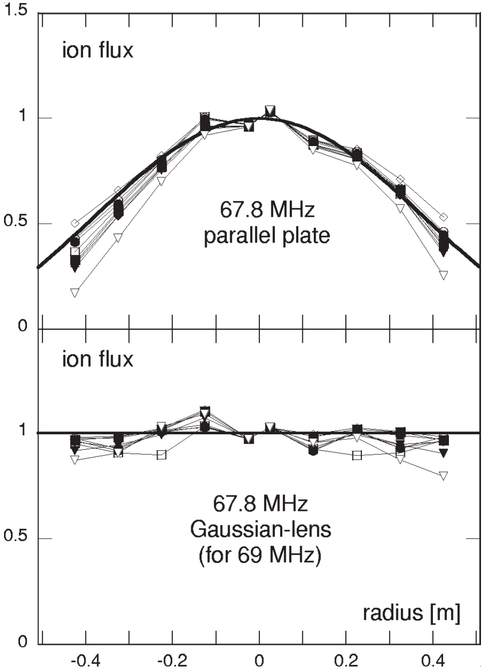
- Shaped electrode with dielectric plate eliminates standing wave effects



- Increased overall thickness in center compared to edge keeps voltage across discharge section constant
- The electrode shape is a Gaussian, independent of the plasma properties

EXPERIMENTAL CONFIRMATION

- Vary pressure and power (5–250 mTorr argon, 50–300 W)

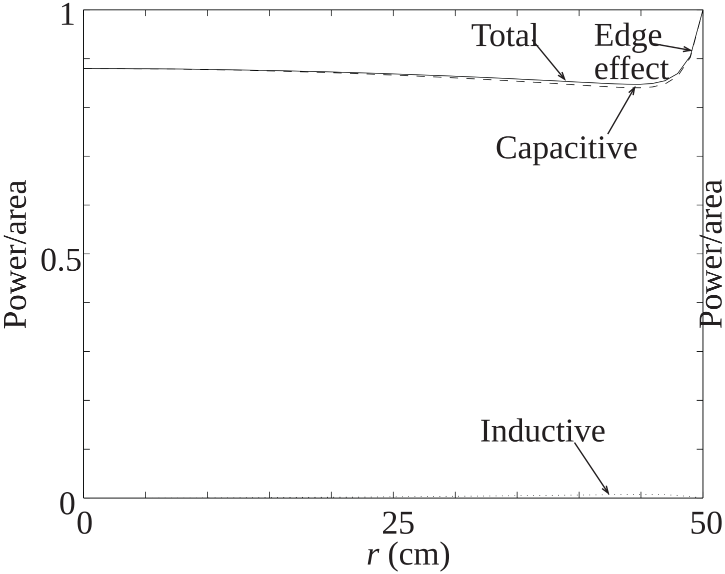


(H. Schmitt, L. Sansonnenns, A.A. Howling, Ch. Hollenstein, M. Elyaakoubi, and J.P.M. Schmitt, *J. Appl. Phys.* **95**, 4559, 2004)

SKIN EFFECTS — FIXED FREQUENCY f

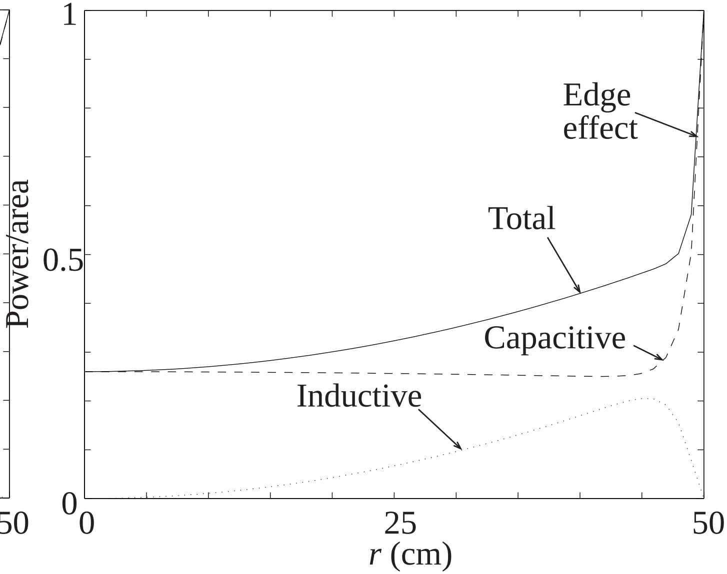
- $R = 50$ cm, $d = 2$ cm, $s = 0.4$ cm, $f = 13.56$ MHz, $\lambda \approx 9$ m
- $P_{\rm cap}$ (dash), $P_{\rm ind}$ (dot) and $P_{\rm tot}$ (solid) as a function of r

$\mathbf{n_e = 10^9\ cm^{-3}}$ ($\delta_p = 17$ cm)



Small standing wave and skin effects

$\mathbf{n_e = 10^{10}\ cm^{-3}}$ ($\delta_p = 5.3$ cm)



Large skin effects; center-low profile

SKIN EFFECTS

- Skin effects $\Longrightarrow$ radial nonuniformities at high densities when

$$\boxed{\delta_p \lesssim 0.45\sqrt{d\,R}}$$

$$\delta_p \propto \frac{1}{\sqrt{n_e}} = \text{collisional or collisionless skin depth [p. 99]}$$

d = bulk plasma half-thickness

R = discharge radius

- Skin effects become important for large radius discharges
- Standing wave and skin effects are an active area of research

THANK YOU FOR ATTENDING THIS COURSE

MIKE LIEBERMAN

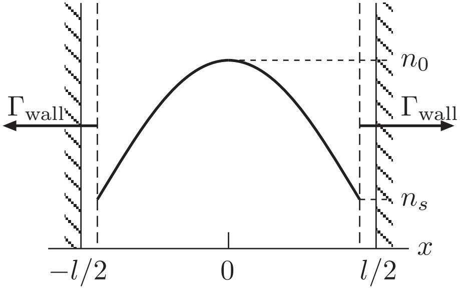
HIGH PRESSURE DISCHARGES

AMBIPOLAR DIFFUSION AT HIGH PRESSURES

- Plasma bulk is quasi-neutral ($n_e \approx n_i = n$) and the electron and ion loss fluxes are equal ($\Gamma_e \approx \Gamma_i \approx \Gamma$)

$$\Longrightarrow \text{Fick's law } \Gamma = -D_a \nabla n \text{ with } D_a = kT_e/M\nu_i$$

- Density profile is sinusoidal with $\bar{n} = 2n_0/\pi$



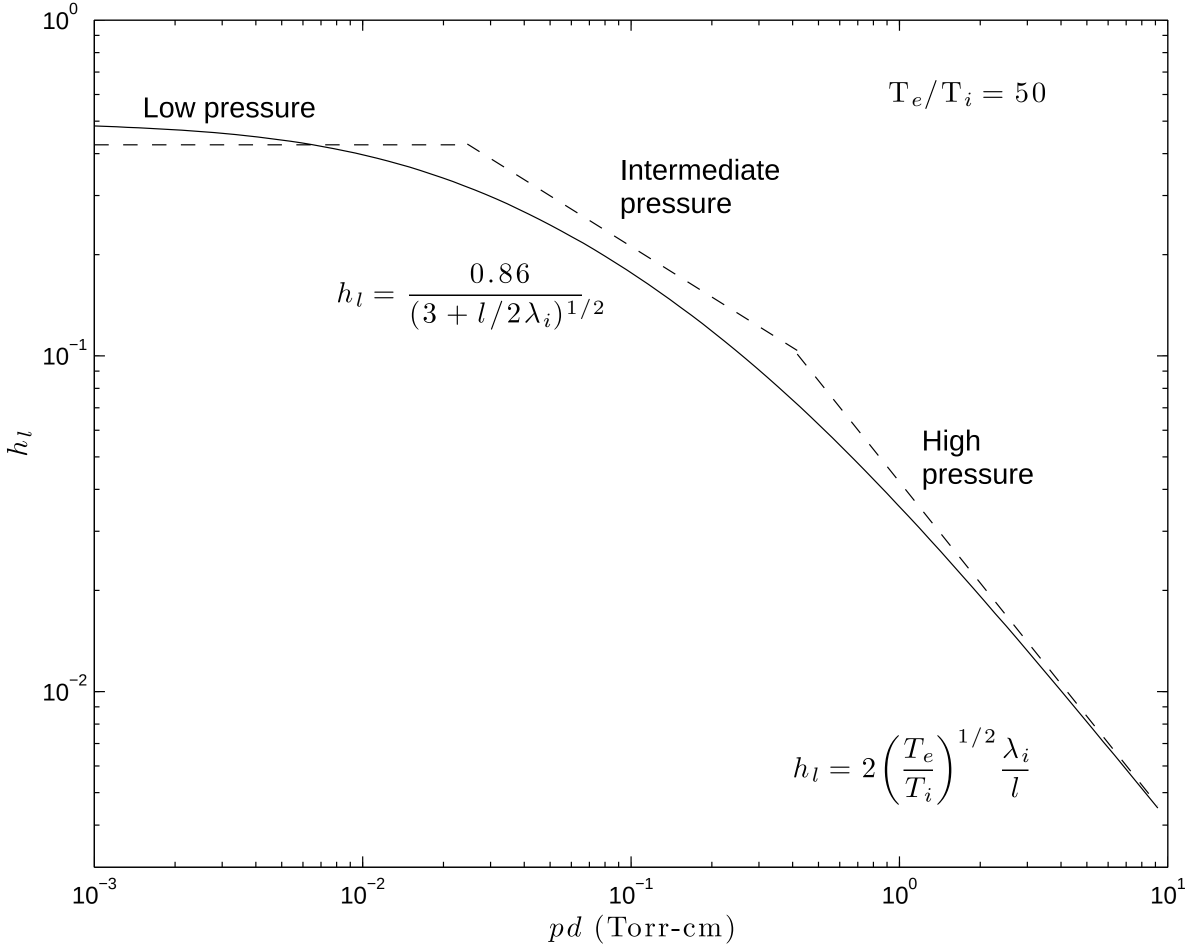
- Loss flux to the wall is

$$\Gamma_{\text{wall}} = n_s u_B \equiv h_l n_0 u_B$$

- From diffusion theory, edge-to-center density ratio is

$$\boxed{h_l \equiv \frac{n_s}{n_0} \approx 2 \left(\frac{\mathrm{T}_e}{\mathrm{T}_i} \right)^{1/2} \frac{\lambda_i}{l}}$$

DIFFUSION REGIMES AND h_l FACTOR



HIGH PRESSURE PARTICLE BALANCE

- Assume electrodes of radius R, with gap $l \ll R$
- Particle balance

Production due to ionization = loss to the two electrodes

$$\boxed{K_{\mathrm{iz}} n_g \left(\frac{2}{\pi}\cancel{n}_0\right)\pi R^2 l = 2\pi R^2 h_l \cancel{n}_0 u_B}$$

- Solve with $h_l \approx 2(\mathrm{T}_e/\mathrm{T}_i)^{1/2}\lambda_i/l$ to obtain

$$\boxed{\frac{K_{\mathrm{iz}}(\mathrm{T}_e)}{\mathrm{T}_e^{1/2} u_B(\mathrm{T}_e)} = \frac{1}{n_g d_{\mathrm{eff}}}}$$

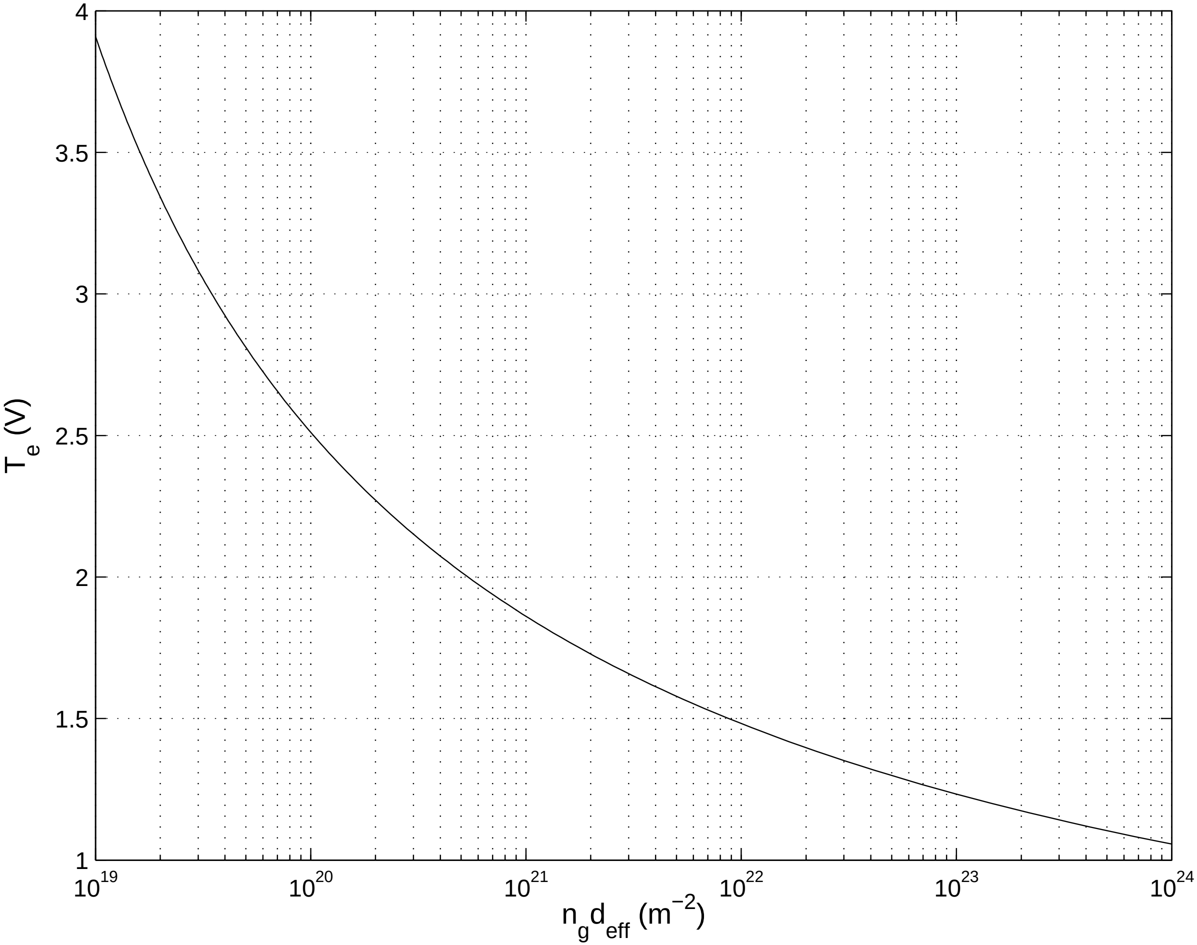
where

$$d_{\mathrm{eff}} = 0.16\,\mathrm{T}_i^{1/2}\frac{l^2}{\lambda_i} \qquad (\mathrm{T}_i \text{ in volts})$$

is an effective plasma size

- Given n_g and $d_{\mathrm{eff}} \Longrightarrow$ electron temperature T_e
- T_e varies over a narrow range of 1–3 volts

HIGH PRESSURE T_e IN ARGON



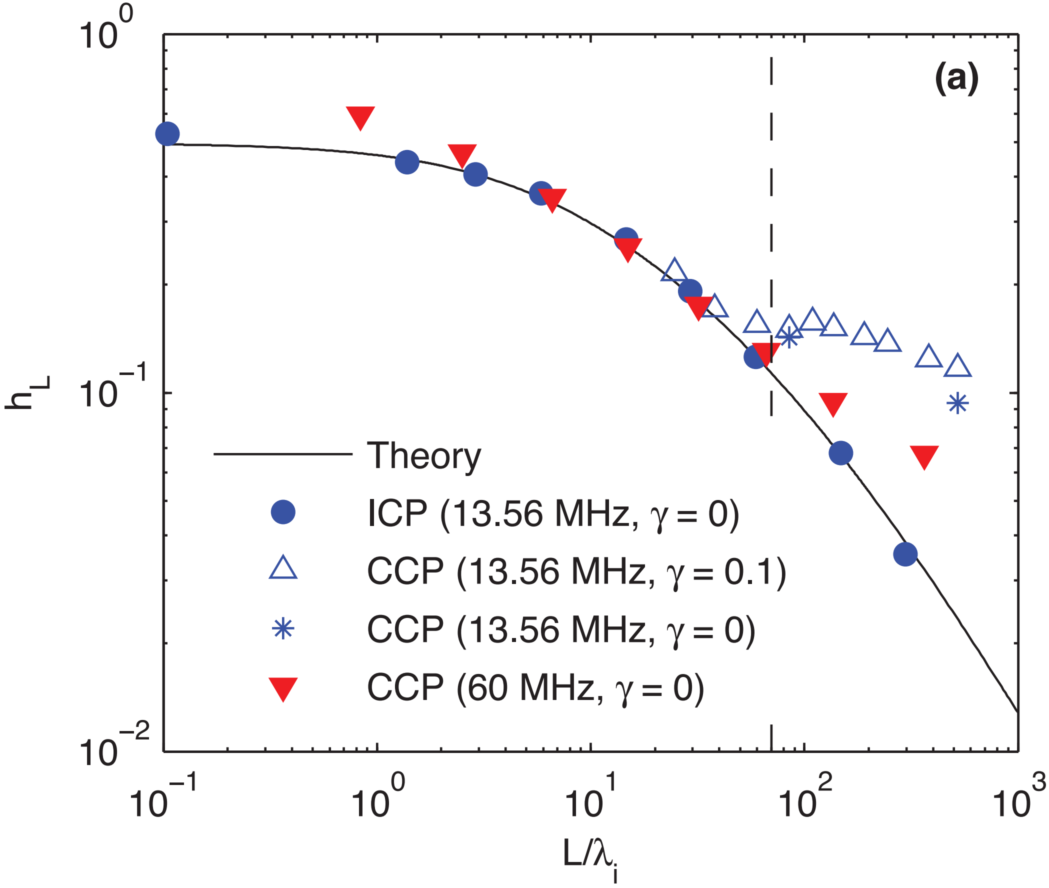
EXAMPLE—HIGH PRESSURE

- Let $R = 0.25$ m, $l = 0.02$ m, $n_g = 3.3 \times 10^{22}$ m^{-3} ($p = 1$ Torr at 300 K), and $P_{\text{abs}} = 800$ W
- Assume axial losses only and low voltage sheaths at electrodes (not a capacitive discharge)
- Find $\lambda_i = 3 \times 10^{-5}$ m [p. 38]. Then $d_{\text{eff}} = 0.34$ m [p. 273] and $n_g d_{\text{eff}} = 1.1 \times 10^{22}$ m^{-2}.
- T_e versus $n_g d_{\text{eff}}$ figure [p. 274] gives $\mathrm{T}_e \approx 1.5$ V . Using this, $h_l = 0.022$ [p. 271].
- $\mathcal{E}_c$ versus T_e figure [p. 40] gives $\mathcal{E}_c \approx 303$ V. Adding $\mathcal{E}_e = 2\mathrm{T}_e \approx 3$ V and $\mathcal{E}_i \approx 5.2\,\mathrm{T}_e \approx 7.8$ V yields $\mathcal{E}_T = 314$ V [p. 39].
- Find $u_B \approx 1.9 \times 10^3$ m/s [p. 41] and find $A_{\text{eff}} \approx 0.0088$ m^2 [p. 50].
- Power balance yields $n_0 \approx 1.5 \times 10^{18}$ m^{-3} [p. 50]
- Ion current density $J_{il} = e h_l n_0 u_B \approx 1.0$ mA/cm^2 [p. 46]
- DC sheath voltage $\overline{V}_s \approx 7.8$ V [p. 48]
- What are T_e and n_0 if there is a dc sheath voltage $\overline{V}_s = 500$ V at each electrode?

HIGH PRESSURE CAPACITIVE DISCHARGES

ACTUAL h_l FACTORS FROM PIC SIMULATIONS

(Lafleur and Chabert, 2014)

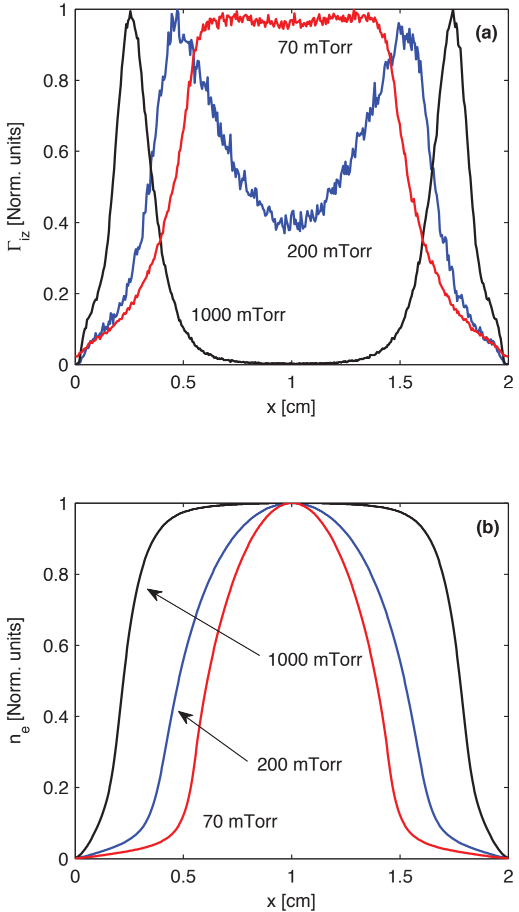


IONIZATION AND DENSITY FROM PIC SIMULATIONS

(Lafleur and Chabert, 2014)

- Example of argon: $J_{\text{rf}} = 2.56\ \text{A/m}^2$ at 13.56 MHz, $\gamma_e = 0.1$
- At high pressure, ionization occurs near plasma-sheath edge; central region is “inactive”
- Flat central density falling sharply near the plasma-sheath edge
- Effective discharge size is $2s_m < l$, so $l/\lambda_i \to 2s_m/\lambda_i$

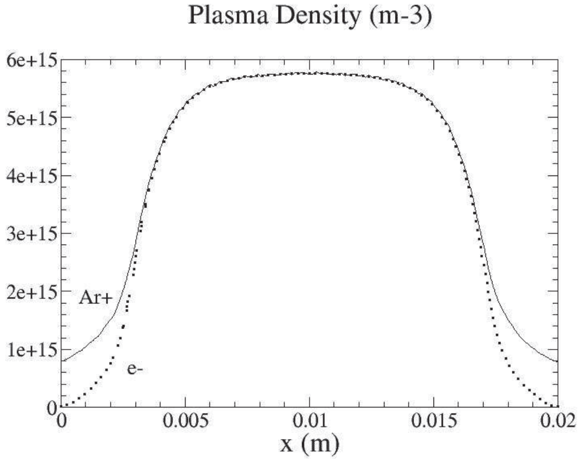
$\Longrightarrow h_l$ is larger



HIGH PRESSURE OHMIC HEATING

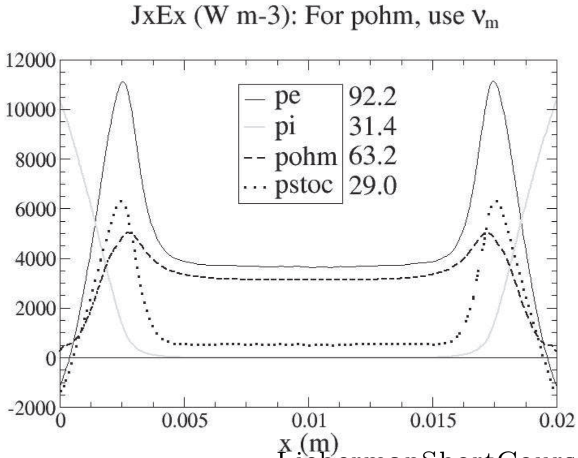
(Kawamura et al, PoP 123505 , 2014)

- Example of 700 mTorr, 2.56 A/m^2, 13.56 MHz, $\gamma_e = 0.1$


Plasma Density (m-3)

$$p_{\rm ohm}(x) = \frac{|\tilde{J}|^2}{2}\,\frac{m\nu_m}{e^2 n_e(x)}$$

- Enhanced bulk ohmic heating near the plasma-sheath edge where n_e is small
- Large ohmic heating inside the sheaths
- Stochastic heating comparable to sheath ohmic heating


JxEx (W m-3): For pohm, use ν_m

HIGH PRESSURE OHMIC HEATING (CONT'D)

- Ohmic heating in the plasma bulk (W/m^2):

$$\boxed{S_{\mathrm{ohm}} = 1.73\,\frac{m}{2e}\epsilon_0\omega^2(\mathrm{T}_e\widetilde{V}_s)^{1/2}\nu_m h_l\left[l + 2\,s_m\left(\frac{1}{\pi}\ln\frac{2}{h_l} - 1\right)\right]}$$

- Ohmic heating in a single sheath (Chabert et al, 2004):

$$\boxed{S_{\mathrm{ohm,sh}} = 0.24\frac{m}{2e}\epsilon_0\omega^2\nu_m s_m\widetilde{V}_s}$$

- Stochastic heating in a single sheath:

$$\boxed{S_{\mathrm{stoc}} = 0.92\frac{m}{2e}\epsilon_0\omega^2\bar{v}_e\widetilde{V}_s}$$

with $v_e = (8e\mathrm{T}_e/\pi m)^{1/2}$ the mean electron speed

COLLISIONAL CHILD LAW

- The collisionless Child law (sheath width s_{m0})

$$\bar{J}_i = e n_s u_B = 0.82\,\epsilon_0 \left(\frac{2e}{m}\right)^{1/2} \frac{\overline{V}_s^{3/2}}{s_{m0}^2}$$

is replaced by the collisional law (sheath width s_m)

$$\boxed{\bar{J}_i = e n_s u_B = 1.68\,\epsilon_0 \left(\frac{2e}{m}\right)^{1/2} \frac{\overline{V}_s^{3/2} \lambda_i^{1/2}}{s_m^{5/2}}}$$

- For the same $\bar{J}_i$ and $\overline{V}_s$

$$s_m = 1.33\,\lambda_i^{1/5} s_{m0}^{4/5}$$

Since $\lambda_i \ll s_{m0}$, the collisional sheath is typically 2–3 × thinner than the collisionless sheath

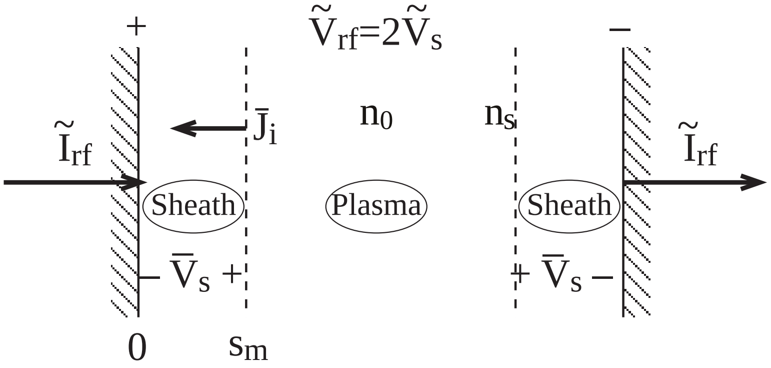
ION BOMBARDING ENERGY

- The average ion bombarding energy is reduced below $\overline{V}_s$ because energy is lost during charge transfer and elastic collisions in the sheath, creating fast neutrals

$$\boxed{\mathcal{E}_i = \frac{1}{2} M_i u_i^2 \approx 0.62 \frac{\lambda_i}{s_m} \overline{V}_s}$$

- However, the total energy (ions + fast neutrals) lost per ion transiting the sheath is still $\overline{V}_s$

SUMMARY — HIGH PRESSURE CAPACITIVE MODEL



$$\overline{V}_s = 0.78\,\widetilde{V}_s, \qquad \mathcal{E}_i = 0.62\,\frac{\lambda_i}{s_m}\overline{V}_s$$

$$\bar{J}_i = e n_s u_B = 1.68\,\epsilon_0 \left(\frac{2e}{M}\right)^{1/2} \frac{\overline{V}_s^{3/2}\lambda_i^{1/2}}{s_m^{5/2}}$$

$$\tilde{I}_{\mathrm{rf}} = 1.52\, j\omega \frac{\epsilon_0 A}{s_m}\widetilde{V}_s$$

$$P_{\mathrm{sh}} = \frac{m}{2e}\epsilon_0\omega^2(0.24\,\nu_m s_m + 0.92\,\bar{v}_e)\widetilde{V}_s A$$

$$P_{\mathrm{ohm}} = 1.73\,\frac{m}{2e}\epsilon_0\omega^2(\mathrm{T}_e\widetilde{V}_s)^{1/2}\nu_m h_l\left[l + 2\,s_m\left(\frac{1}{\pi}\ln\frac{2}{h_l} - 1\right)\right]A$$

EXAMPLE — HIGH P CAPACITIVE DISCHARGE

- Let $p = 1$ Torr argon at 300 K, $l = 2$ cm, $A = 1000$ cm^2, $f = 13.56$ MHz ($\omega = 8.52 \times 10^7$ s^{-1}), and $V_{\text{rf}} = 300$ V
- Start with estimate $s_m \approx 0.5$ cm
- Ion mean free path $\lambda_i = 1/n_g\sigma_i \approx 0.003$ cm [p. 38]
- Then $l/\lambda_i \approx 660$ and from h_l-figure [p. 277], $h_l \approx 0.1$
- With bulk plasma thickness $d = l - 2s_m = 1$ cm, $d_{\text{eff}} = d/2h_l = 5$ cm [p. 46]
- With $n_g d_{\text{eff}} \approx 1.65 \times 10^{21}$ m^{-2}, the T_e versus $n_g d_{\text{eff}}$ figure [p. 47] yields $\mathrm{T}_e \approx 1.7$ V
- Bohm velocity $u_B \approx 2.0 \times 10^3$ m/s [p. 41]
- Mean electron speed $\bar{v}_e \approx 8.8 \times 10^5$ m/s [p. 280]
- $\mathcal{E}_c$ versus T_e figure [p. 40] yields $\mathcal{E}_c \approx 187$ V and $\mathcal{E}_c + 2\mathrm{T}_e \approx 191$ V
- Use the K_{el} versus T_e figure [p. 37] to find $\nu_m \approx K_{\text{el}} n_g \approx 1.23 \times 10^9$ s^{-1}

EXAMPLE (CONT'D)

- Evaluate bulk and sheath electron heating [p. 283]

$$P_{\rm ohm} \approx 0.10\,\widetilde{V}_s^{1/2} \qquad [\rm W]$$
$$P_{\rm sh} \approx 0.042\,\widetilde{V}_s \qquad [\rm W]$$

- Use $\widetilde{V}_s \approx V_{\rm rf}/2 = 150$ V in above to find $P_{\rm ohm} \approx 1.2$ W and $P_{\rm sh} \approx 6.3$ W
- Electron power balance [p. 84] yields $n_s \approx 1.1 \times 10^{15}\ {\rm m}^{-3}$
- Since $h_l = 0.1$, $n_0 \approx 1.1 \times 10^{16}\ {\rm m}^{-3}$
- DC sheath voltage $\overline{V}_s \approx 0.78\,\widetilde{V}_s \approx 117$ V and $\mathcal{E}_i \approx 0.11$ V [p. 283]
- $\bar{J}_i = en_su_B \approx 0.36\ {\rm A/m^2}$ [p. 283]
- $J_{\rm rf} \approx 34\ {\rm A/m^2}$ [p. 283]
- Total power balance [p. 84] gives $P_{\rm abs} \approx 22$ W
- The Child law [p. 283] gives $s_m \approx 0.33$ cm
- s_m reasonably close to the initial estimate
  $\Longrightarrow$ but could iterate using this new value of s_m

ALPHA-TO-GAMMA TRANSITION

1. Y.P. Raizer, M.N. Shneider and N.A. Yatsenko, ”Radio Frequency Capacitive Discharges”, CRC Press, 1995.
2. V.A. Godyak and A.S. Khanneh, IEEE Trans. Plasma Sci. PS-14, 112 (1986)

ALPHA MODE AND GAMMA MODE

(Raizer, Schneider, Yatsenko, 1995)

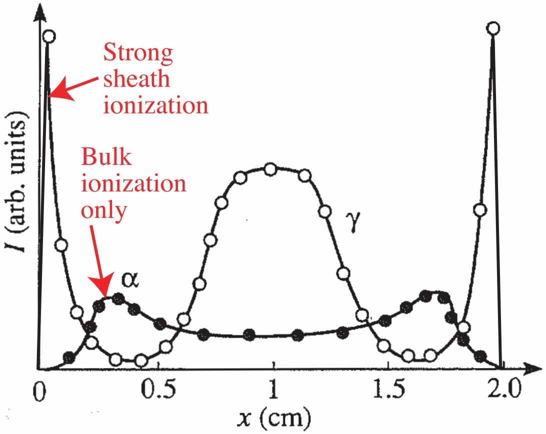
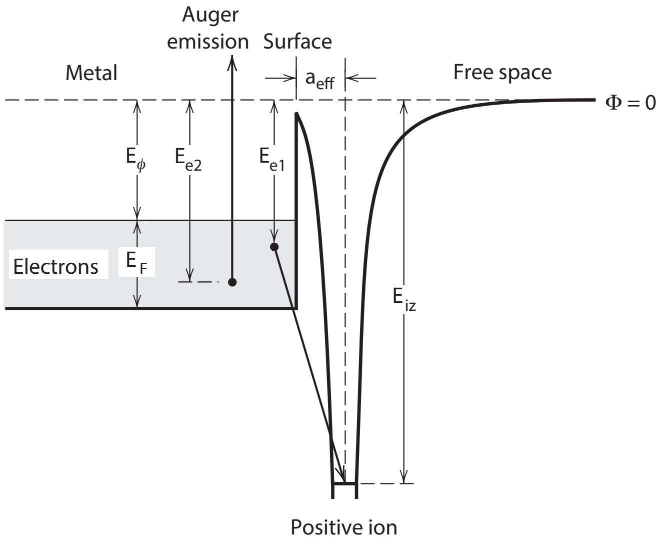


FIGURE 1.12
Glow intensity distribution in the gap of α- and γ-discharges with air, $p = 10$ Torr, $f = 13.56$ MHz, and $L = 2$ cm between brass electrodes. rms voltage is close to 300 V in both modes.

- Alpha mode: low current, ionization in bulk plasma only, displacement current in thick sheaths
- Gamma mode: high current, strong ionization in thin sheaths, conduction current in sheaths, secondary electrons play essential role

SECONDARY ELECTRON EMISSION

- Auger emission for ion bombarding energy $\mathcal{E}_i \lesssim 1$ kV



- Work function $\mathcal{E}_\phi \sim 4$–5 V, ionization energy $\mathcal{E}_{\text{iz}} \sim 10$–$25$ V
- Condition for emission: $\mathcal{E}_{\text{iz}} \geq 2\mathcal{E}_\phi$

$$\boxed{\gamma \approx 0.016(\mathcal{E}_{\text{iz}} - 2\,\mathcal{E}_\phi), \text{ independent of } \mathcal{E}_i}$$

- $\gamma \sim 0.25$ for He^+, 0.1 for Ar^+, 0.03 for O_2^+, N_2^+

FIRST TOWNSEND COEFFICIENT α

- An electron moving in an electric field E in a gas at pressure p creates α e-i pairs/unit length

$$\boxed{\alpha = A p\, \mathrm{e}^{-Bp/E}}$$

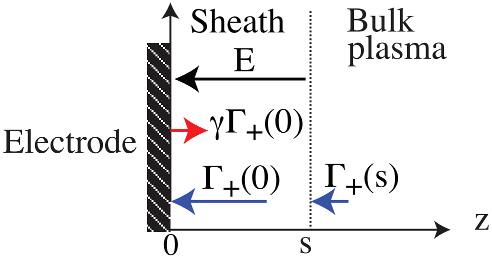
Gas	A (cm^{-1}-Torr^{-1})	B (V-cm^{-1}-Torr^{-1})	Range of E/p (V-cm^{-1}-Torr^{-1})
He	2.8	77	30–250
Ar	11.5	176	100–600
Xe	24	330	200–800
H_2	4.8	136	15–600
N_2	11.8	325	100–600
O_2	6.5	190	50–130
CH_4	17	300	150–1000
CF_4	11	213	25–200

- Hence an initial electron flux grows exponentially in space

$$\frac{\mathrm{d}\Gamma_e}{\mathrm{d}z} = \alpha \Gamma_e \qquad \Longrightarrow \qquad \Gamma_e = \Gamma_{e0}\, \mathrm{e}^{\alpha z}$$

SHEATH BREAKDOWN CONDITION

- Consider the ion balance for a sheath of width s



- Ion flux balance in the sheath

$$\Gamma_+(0) = \Gamma_+(s) + \gamma\Gamma_+(0)\left(\mathrm{e}^{\alpha s} - 1\right)$$

- Townsend condition for sheath breakdown: $\Gamma_+(s) = 0$

$$\gamma\left(\mathrm{e}^{\alpha s} - 1\right) = 1$$

- Substitute for α [p. 289]

$$\boxed{E_b = \frac{Bp}{\ln Aps - \ln[\ln(1 + 1/\gamma)]}}$$

- Breakdown field E_b depends on p, s, and weakly, on γ

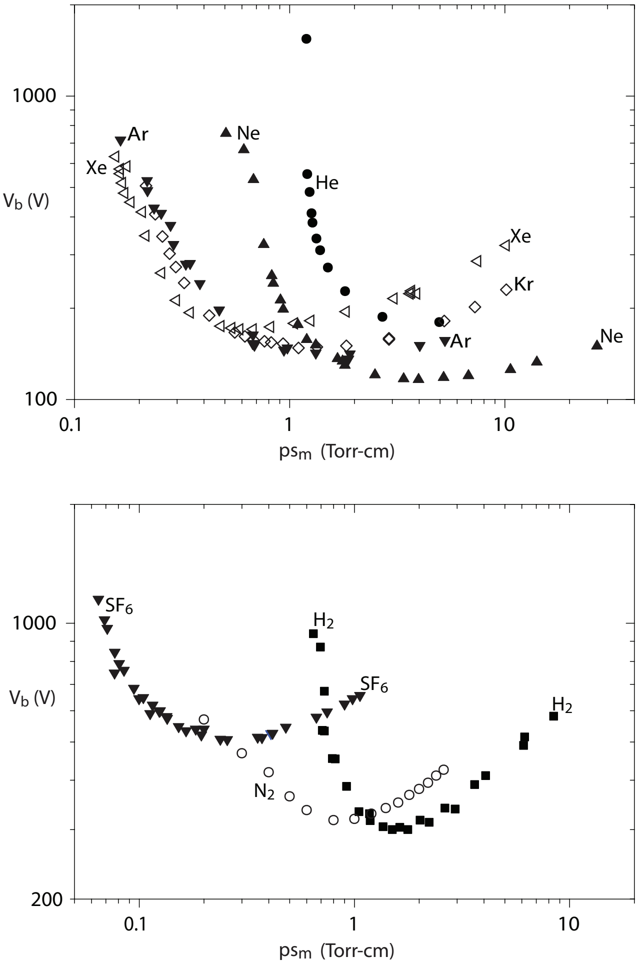
PASCHEN CURVE

- Put $E_b = V_b/s_m$, with V_b the maximum sheath voltage and s_m the maximum sheath width:

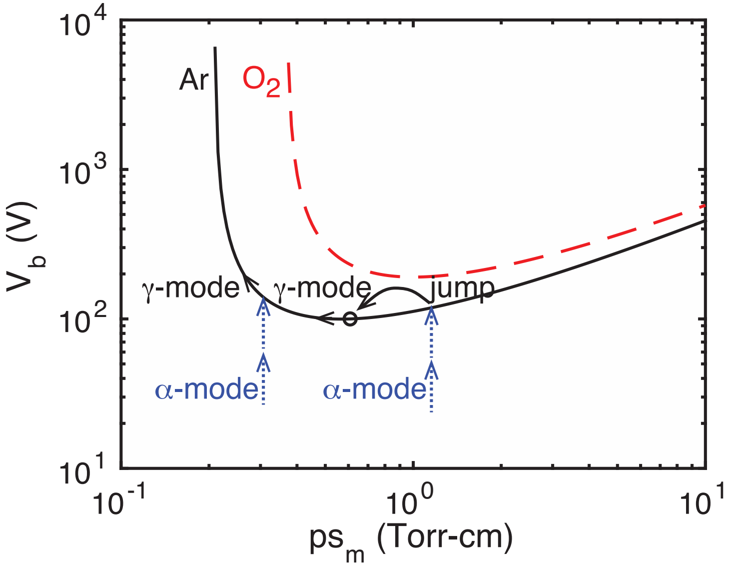
$$\boxed{V_b = \frac{Bps_m}{\ln Aps_m - \ln[\ln(1+1/\gamma)]}}$$

- V_b has a minimum at some value of ps_m
- $V_b \to \infty$ for

$$\boxed{ps_m \to A^{-1}\ln(1+1/\gamma)}$$



ALPHA-GAMMA TRANSITION



- α-mode: $s_m \approx$ const as V_b increases
- γ-mode (high p): s_m suddenly decreases and discharge constricts radially; then s_m slowly decreases following the Paschen curve
- γ-mode (low p): no sudden jump;
  s_m slowly decreases following the Paschen curve
- Molecular or electronegative gases have higher values of $(ps_m)_{\min}$

HIGH P VOLTAGE VS CURRENT MEASUREMENTS

(Raizer, Schneider, Yatsenko, 1995)

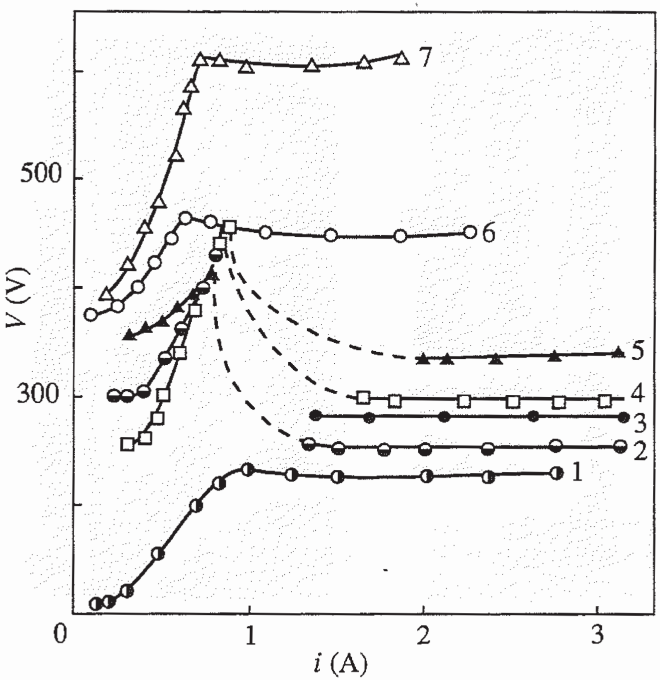
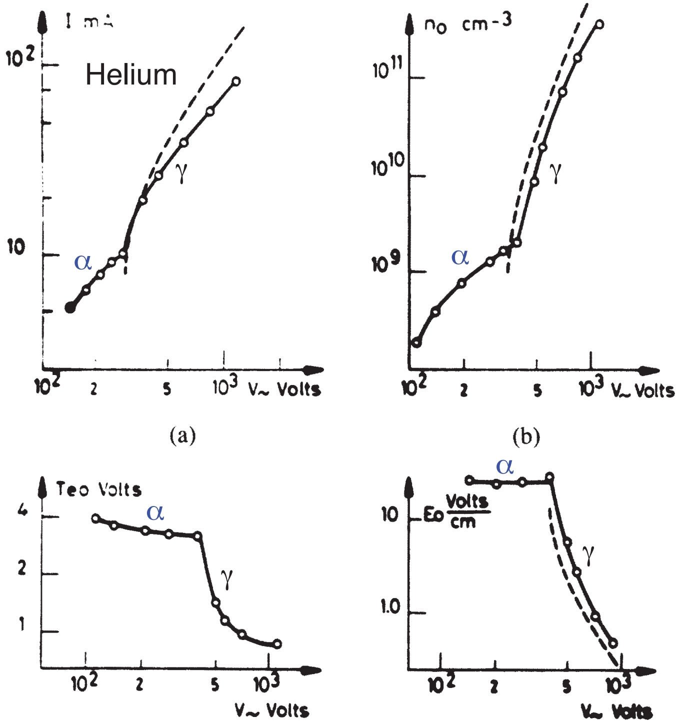


FIGURE 1.13
CVC rms values of RF discharge at 13.6 MHz: 1, helium, $p = 30$ Torr, $L = 0.9$ cm; 2 air $p = 30$ Torr, $L = 0.9$ cm; 3 air, $p = 30$ Torr, $L = 3$ cm; 4, CO_2, $p = 30$ Torr, $L = 0.9$ cm; 5, CO_2, $p = 15$ Torr, $L = 3$ cm; 6, air, $p = 7.5$ Torr, $L = 1$ cm, glass-coated electrodes; 7, air, $p = 7.5$ Torr, $L = 1$ cm, Teflon-coated electrodes [1.9].

LOW P VOLTAGE VS CURRENT MEASUREMENTS

(Godyak and Khanneh, 1986)



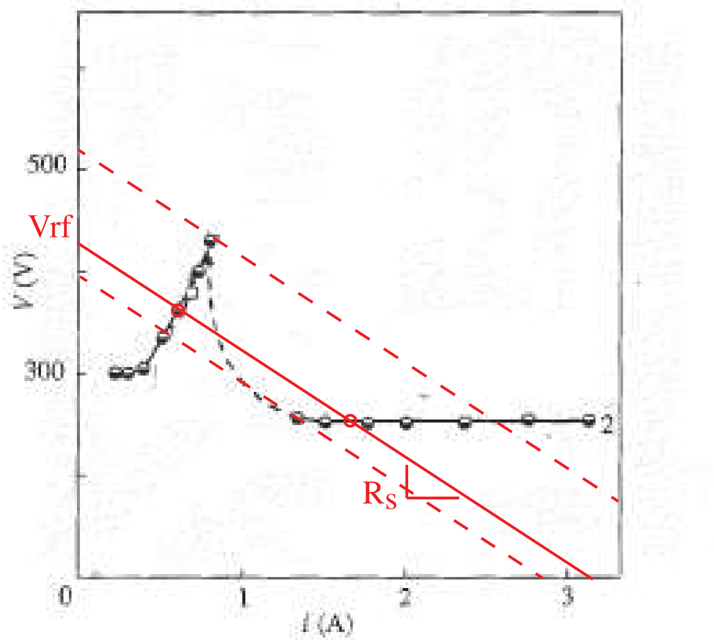
(a) (b)

(c) (d)

Fig. 4. (a)–(d) Evolution of discharge parameters I, T_{eo}, n_o, and E_o during transition of a discharge into γ regime; f = 3.2 MHz, p = 3 torr. Dotted line is theory from (26), (29), and (30) using experimental data of function $F(V_c)$ from Fig. 8(a).

ALPHA-GAMMA TRANSITION HYSTERESIS

Intersection of power supply V versus I (red line) with discharge V versus I (black curve) gives equilibrium (○)



(air, 30 Torr, 0.9 cm gap, from p. 293)

HYSTERESIS MEASUREMENTS

(Raizer, Schneider, Yatsenko, 1995)

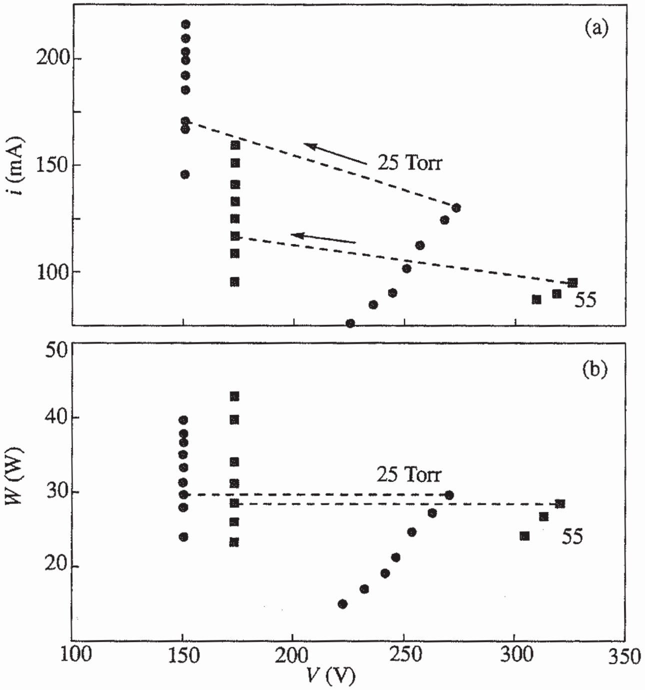


FIGURE 2.7
Root-mean-square values of the (a) current–voltage and (b) power–voltage characteristics for a nitrogen discharge at $L = 0.59$ cm, $f = 29.25$ MHz for two pressure values. Dashed lines with arrows are the $\alpha-\gamma$ transition due to increasing current and voltage. As the current in the γ-mode decreases, the current, prior to the reversal $\gamma-\alpha$, drops below the end points of the dashed lines, producing a hysteresis [2.20].

SIMULTANEOUS ALPHA AND GAMMA MODES

- α and γ modes can co-exist (e.g., dielectric coated electrodes)

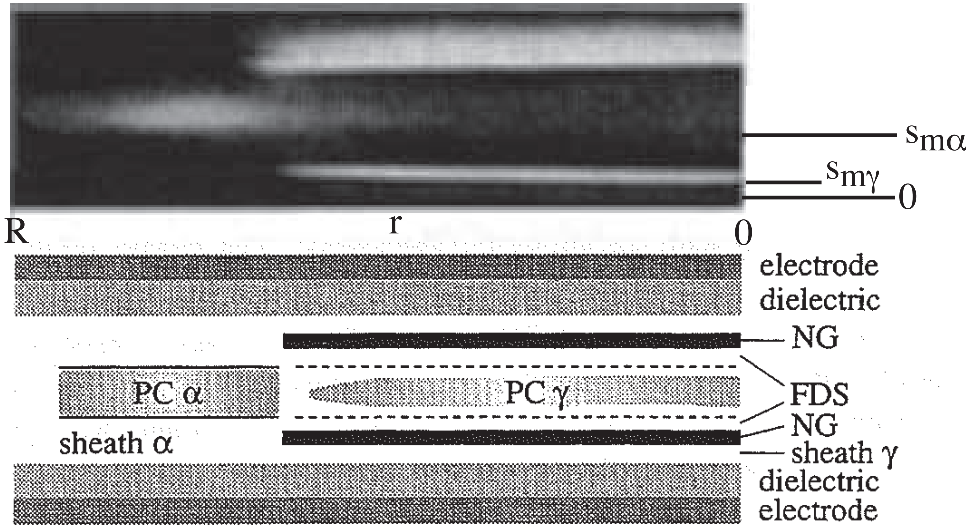


FIGURE 2.30

Coexistence of a ‘subnormal’ γ-mode and an α-mode in a gap with insulated electrodes. The photograph shows the discharge half symmetrical to the right vertical boundary due to the cylindrical symmetry of the discharge. The focal point is on the lower electrode, so the sheaths at the top are slightly shifted and fuse together. Discharge in air, $f = 13.56$ MHz, $p = 7.5$ Torr, $L = 0.7$ cm. Below is a schematic ‘negative film’: bright spots are made dark while dark areas are left white.

(NG=negative glow, FDS=Faraday dark space, PC=positive column)

SUMMARY — ALPHA-GAMMA TRANSITION

- The γ mode is undesirable for processing discharges (radial contraction, hysteresis, dependence on wafer surface conditions, etc)
- For low pressures, $ps_m < A^{-1}\ln(1 + 1/\gamma)$, there is no γ mode limitation (for argon, $ps_m < 0.21$ Torr-cm)
- For higher pressures, the α mode discharge voltages are limited to below the Paschen voltage V_b
- Molecular and electronegative gases have higher V_b's than noble gases

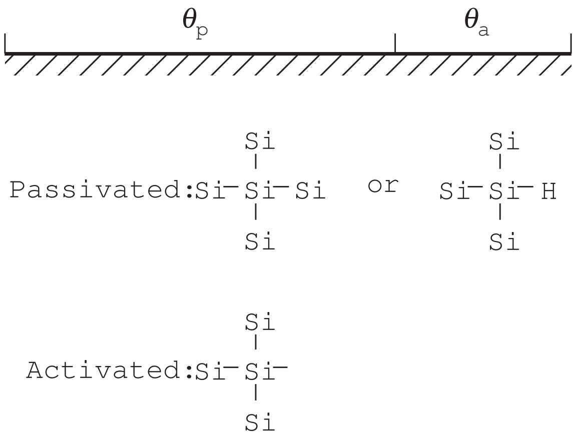
CHEMISTRY IN DISCHARGES

DEPOSITION KINETICS

TWO-SITE MODEL FOR a-Si:H DEPOSITION

(after McCaughey and Kushner, 1989)

- 0.2–2 Torr silane or silane/H_2 capacitive discharges are used
- Active (dangling bond) and passive sites (area density n'_0)



- SiH_2 can insert at active and passive sites (“bad” film)
- SiH_3 diffuses along surface and inserts into active sites (“good” film)
- SiH_3^+ bombardment creates active sites and removes H-atoms
- SiH_4 hydrogenates the surface, creating passive sites

SURFACE REACTIONS AND RATES

$$\mathrm{SiH}_3^+ + \theta_p \xrightarrow{K_i} \theta_a + Y_i\mathrm{H(g)}$$

$$\mathrm{SiH}_2 + \theta_a \xrightarrow{K_2} \theta_a$$

$$\mathrm{SiH}_2 + \theta_p \xrightarrow{K_{2p}} \theta_p$$

$$\mathrm{SiH}_3 + \theta_a \xrightarrow{K_3} \theta_p$$

$$\mathrm{SiH}_4 + \theta_a \xrightarrow{K_4} \theta_p + \mathrm{SiH}_3\mathrm{(g)}$$

- $Y_i \sim 5$–10 is the yield of H atoms removed per incident ion
- $K_i \approx u_B/n_0'$, $K_2 \approx \frac{1}{4}s_2\bar{v}_2/n_0'$, $K_3 \approx \frac{1}{4}\overline{M}s_3\bar{v}_3/n_0'$, $K_4 \approx \frac{1}{4}s_4\bar{v}_4/n_0'$, and $K_{2p} \approx \frac{1}{4}s_{2p}\bar{v}_2/n_0'$ are the rate coefficients
- s_2, s_{2p}, s_3, and s_4 the sticking coefficients (all of order unity)
- $\overline{M} \sim 10$ is the mean number of sites visited by surface-diffusing SiH_3 before desorption

STEADY STATE ACTIVE SITE FRACTION

- Ion bombardment creates active sites
- SiH_3 and SiH_4 adsorption destroy active sites

$$\frac{\mathrm{d}\theta_a}{\mathrm{d}t} = Y_i K_i n_{\mathrm{is}}(1-\theta_a) - K_3 n_{3S}\theta_a - K_4 n_{4S}\theta_a = 0$$

$$\Longrightarrow \qquad \theta_a = \frac{Y_i K_i n_{\mathrm{is}}}{Y_i K_i n_{\mathrm{is}} + K_3 n_{3S} + K_4 n_{4S}}$$

- For $n_{4S} \gg n_{3S},\ n_i$, we find

$$\boxed{\theta_a \approx \frac{Y_i K_i n_{\mathrm{is}}}{K_4 n_{4S}}}$$

- In typical silane deposition discharges $n_{4S}/n_{\mathrm{is}} \sim 10^4$ and $K_i \sim 10\,K_4$

$$\Longrightarrow \theta_a \sim 10^{-2}$$

DEPOSITION RATE

- The deposition rate is due to SiH_3 at the active sites and SiH_2 adsorption at all sites

$$\boxed{D_{\mathrm{Si}} = (K_3 n_{3S} \theta_a + K_2 n_{2S}) \frac{n_0'}{n_{\mathrm{Si}}}}$$

- In typical silane deposition discharges $n_{3S}/n_{2S} \sim 10^2$
- Then for $\theta_a \sim 10^{-2}$ and $K_3 \sim \overline{M} K_2 \sim 10 K_2$, the first term ("good" film deposition) is about 10× the second term ("bad" film deposition)
- The preceding picture is oversimplified; for example

$$\mathrm{H} + \theta_a \longrightarrow \theta_p$$

$$\mathrm{H} + \theta_p \longrightarrow \theta_a + \mathrm{H_2(g)}$$

$\Longrightarrow$ three-site model (McCaughey and Kushner, 1989)

25 November 2007

ERRATA — SECOND EDITION

Principles of Plasma Discharges and Materials Processing
Michael A. Lieberman and Allan J. Lichtenberg
John Wiley and Sons, New York, 2005

p. 19, Fig. 1.14: Add labels (a)–(d).
p. 22, line 4: “$T = 0.026$ V” should be “$\mathrm{T} = 0.026$ V”.
p. 29, line 6: “$a_x v \mathrm{d}v_x/\mathrm{d}t$” should be “$a_x = \mathrm{d}v_x/\mathrm{d}t$”.
p. 32, Eq. (2.3.14): remove “.” (period) from the equation.
p. 37, equation above Eq. (2.4.12): “$4\pi g(W)\,\mathrm{d}W$” should be “$g(W)\,\mathrm{d}W$”.
p. 37, Eq. (2.4.12): “$v(W)$” should be “$4\pi\, v(W)$”.
p. 75, line 3: “(3.4.7)” should be “(3.4.6)”.
p. 143, Eq. (5.2.38): “$\frac{\nu_{\mathrm{iz}}^2}{D^2}$” should be “$\frac{\nu_{\mathrm{iz}}}{D}$”.
p. 144, 2nd line from the last: “to obtain” should be “obtain”.
p. 147, 1st line after *Heuristic Solutions:* “(5.3.23)” should be “(5.3.7)”.
p. 159, line 5: “Fig. 12.10” should be “Fig. 12.12”.
p. 162, Problem 5.7: “(5.2.22)” should be “(5.2.29)”.
p. 170, Eq. (6.2.11): “$\frac{du_i}{dx}$” should be “$n\frac{du_i}{dx}$”.
p. 174, 3rd line from bottom: “5×10^{-8} s” should be “4×10^{-8} s”.
p. 177, line 12: “$E = \mathrm{d}\Phi/\mathrm{d}x$” should be “$E = -\mathrm{d}\Phi/\mathrm{d}x$”.
p. 195, 5th line of 2nd paragraph: “all to easy” should be “all too easy”.
p. 197, Eq. (6.6.36): “$[1 + \frac{(V_{\mathrm{B}} - \Phi_{\mathrm{p}})^{1/2}}{\mathrm{T_e}}]$” should be “$[1 + \frac{(V_{\mathrm{B}} - \Phi_{\mathrm{p}})}{\mathrm{T_e}}]^{1/2}$”.

p. 221, line 4: add a space between "gas," and "to obtain".

p. 221, 3rd line after Eq. (7.3.31): "$\mu_j^\ominus = \mu_j$" should be "$\mu_j = \mu_j^\ominus$".

p. 224, 1st two lines after the table: "(7.4.9)" and "(7.4.10)" should be exchanged.

p. 244, line 11: "atom" should be "molecule".

p. 258, 7th line from the last: "state 2" should be "state 3".

p. 269, 3rd and 4th reactions: "AB*" should be "AB^+".

p. 302, top of the page: add the line "$\sim a_{\mathrm{eff}}$. An electron with energy $\mathcal{E}_{\mathrm{e}}$ can".

p. 314, line after Eq. (9.4.11): "(5.2.10)" should be "the equation after (5.2.10)".

p. 317, unnumbered equation for AS(g) immediately above Eq. (9.4.29): "K_{d}" should be "K_{r}".

p. 346, equation after Eq. (10.3.20): "$\mathrm{T_i} n_{\mathrm{e}} E + \mathrm{T_i} n_- E$" should be "$n_{\mathrm{e}} E/\mathrm{T_i} + n_- E/\mathrm{T_i}$".

p. 346, line 8: "(10.3.14)" should be "(10.3.21)".

p. 350, 4th line after Eq. (10.3.37): "(10.3.26)" should be "(10.3.36)".

p. 361, 4th line from bottom: "43 mTorr" should be "45 mTorr".

p. 380, Eq. (10.6.31): "$K_{\mathrm{diss}} n_{\mathrm{e}} n_{\mathrm{a0}}$" should be "$K_{\mathrm{diss}} n_{\mathrm{e}}$".

p. 382, Problem 10.2(c), 2nd line: "(10.2.9)" should be "(10.2.4)".

p. 384, Problem 10.13, 4th line: "12, and 22" should be "and 12".

p. 408, 2nd line above *Example 1:* "(11.2.38)" should be "(11.2.35)".

p. 412, Eq. (11.2.58): "0.59" should be "0.49".

p. 414, Eq. (11.2.63a): "$2e$" should be "$2\pi e$" (an error in Misium et al, 1989).

p. 426, last line: "(11.5.6)" should be (11.5.20)".

p. 431, line 8: "along" should be "along (in the plane of)".

p. 436, Eq. (11.5.5): "$V_a(t)$" should be "$-V_a(t)$".

p. 436, Eq. (11.5.6): "$V_b(t)$" should be "$-V_b(t)$".
p. 439, line 2: "(10.2.8)" should be "(10.2.4)".
p. 442, 3rd line below Eq. (11.6.3): "(11.5.14)" should be "$V_\mathrm{s} = -V(t)$".
p. 465, 2nd line above Eq. (12.1.8): "(18.5.2)" should be "(18.5.12)".
p. 467, Fig. 12.2: "Z" should be "Z_s".
p. 472, 1st line after Eq. (12.2.6): "cubic" should be "quartic".
p. 472, 8th line of last paragraph: "(12.1.24)" should be "(12.2.5)".
p. 475, 2nd line above Fig. 12.6: "(10.4.24)" should be "(10.4.7b)".
p. 476, 3rd line in 2nd paragraph: "(3.3.7)" should be "from the equation preceding (3.3.7)".
p. 485, 1st line after Eq. (12.4.3): "0.1 rad" should be "0.02 rad".
p. 505, line 11: "(10.2.7)" should be "(10.2.12)".
p. 512, line 3: "(10.2.9)" should be "(10.2.4)".
p. 521, 4th line from the last: "(10.2.8)" should be "(10.2.13)".
p. 521, 2nd line from the last: "(10.2.1)" should be "(10.2.9)".
p. 521, last line: "(10.2.15)" should be "(10.2.11)", and "(10.2.14)" should be "(10.2.15)".
pp. 523–24: "$K_\perp$, $K_\times$, K_r, K_l, and $K_\|$" should be "$\kappa_\perp$, $\kappa_\times$, κ_r, κ_l, and $\kappa_\|$" wherever they appear in the text and equations.
p. 529, Figure 13.22: "$_z c/\omega_\mathrm{pe}$" should be "$k_z c/\omega_\mathrm{pe}$".
p. 555, line 6: "(14.4.5)" should be "(14.4.4)".
p. 557, 1st line of 2nd paragraph: "(14.4.10)" should be "(14.4.13)".
p. 564, 8th and 10th line from bottom: "target" should be "substrate".
p. 565, line just above Eq. (14.6.2): "substrate" should be "target".
p. 566: Equation number "(4.6.10)" should be "(14.6.10)".

p. 572: “300 nm” in the equation should be “500 nm”.

p. 575, 5th line below Eq. (15.1.13): delete “(dashed curve)”.

p. 591, line 7: “(15.3.7)” should be “(15.3.6)”.

p. 593, Table 15.2, reaction 4: “CF_3^-” should be “CF_3^+”.

p. 603, line 7: “copper chloride (CuCl_3) is” should be “the copper chlorides are”.

pp. 630–33: The equations in Sec. 16.3 were not sequentially numbered; equation number (16.3.2) was inadvertently omitted.

p. 680, line 10: “Kortshagen et al. (1997)” should be “Aliev et al. (1997)”.

p. 689, 1st line after Eq. (18.2.1): “$\bar{\mathbf{E}}_\mathrm{a} + \mathbf{E}_\mathrm{h}$” should be “$\bar{\mathbf{E}} = \bar{\mathbf{E}}_\mathrm{a} + \bar{\mathbf{E}}_\mathrm{h}$”.

p. 689, Eq. (18.2.3): “Re” should be “$\frac{1}{2}\mathrm{Re}$”.

p. 689, last line: “due the the” should be “due to the”.

p. 690, line 4: “that” should be “than”.

p. 700, line 15: “localized rf” should be “localized time-varying”.

p. 702, Eq. (18.4.17): “$(1 - \mathbf{k}\cdot\mathbf{v})/\omega$” should be “$(1 - \mathbf{k}\cdot\mathbf{v}/\omega)$”.

p. 709, 1st line after Eq. (18.5.12): “collisionless” should be “collisional”.

p. 712, 7th line after Eq. (18.6.4): “versus” should be “various”.

p. 712, 5th line of the last paragraph: delete the words “and axial”.

p. 714, 3rd line after Eq. (18.6.6): “(18.3.26)” should be “(18.6.5)”.

p. 718, line 1: “the figure”, should be “Fig. 11.6”.

p. 718, line 1 of the last paragraph: “(18.6.8)” should be “(18.6.12)”.

p. 719, line 4: “(18.6.8)” should be “(18.6.12)”.

p. 719, line 8: “Φ_0” should be “$\mathcal{E} = \Phi_0 \approx 3$ V”.

p. 734, Eq. (C18): The last “+” sign should be an “=” sign.

p. 751, second line from last: “Thompson ionization” should be “Thomson ionization”.

ABOUT THE INSTRUCTOR

Michael A. Lieberman is Professor in the Graduate School in the Department of Electrical Enginering and Computer Sciences at the University of California, Berkeley. He is a co-author of the widely used text, *Principles of Plasma Discharges and Materials Processing*, and he has published over 180 journal articles on the topics of plasmas, plasma processing, and nonlinear dynamics. He is a Fellow of the American Association for the Advancement of Science, the American Physical Society (APS), the American Vacuum Society, the Institute of Electrical and Electronics Engineers (IEEE), and the Institute of Physics (Great Britain). He received the IEEE Plasma Science and Applications Award in 1995, the Hans von Engel Award from the International Union of Pure and Applied Physics in 2005, and the Will Allis Prize for the Study of Ionized Gases from the APS in 2006. He holds the Distinguished Teaching Award of the Berkeley Campus.

SELF-STUDY PROBLEMS

SUGGESTED PROCEDURE:
Work the problems by yourself and then discuss with a colleague.

DAY 1:
Problem 2.2. Homogeneous Discharge Model
Problem 4.6 . Ohmic Heating Power in a Nonuniform RF Discharge
Problem 10.1(a). Low-Pressure Equilibrium
Problem 11.5. Low-Pressure RF Discharge Equilibrium with Power Specified
Problem 12.4. Inductive Discharge Equilibrium
Problem 12.8(a). Discharge Equilibrium and Matching Network

DAY 2:
Problem 8.2. Metastable Molecular States
Problem 9.2(a). Reaction Rate Calculations
Problem 9.11. Normal and Dissociative Adsorption
Problem 15.3. Surface Model for Silicon Etching in a CF_4 Discharge

All problems are taken from M.A. Lieberman and A.J. Lichtenberg, *Principles of Plasma Discharges and Materials Processing*, Second Edition, John Wiley & Sons, New York, 2005.